

UNIVERSIDAD DE OVIEDO

Programa de Doctorado en Ciencia y Tecnología de Materiales

**“Síntesis y caracterización de nuevos materiales
híbridos luminiscentes”**

**“Synthesis and characterization of novel luminescent
hybrid materials”**

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Índices de calidad

Los índices de calidad de las revistas en las que se han publicado o están en trámite de publicación los artículos que se recogen la presente memoria, se presentan en la siguiente tabla:

Revista	Año	Índice de Impacto	Área	nº de orden/ nº total	Cuartil
<i>Journal of Solid State Chemistry</i>	2009	2.340	Chemistry, Inorganic & Nuclear	15/44	Q2
			Chemistry, Physical	49/121	Q2
<i>Inorganic Chemistry</i>	2010	4.326	Chemistry, Inorganic & Nuclear	5/49	Q1
<i>Zeitschrift fur Kristallographie</i>	2011	1.155	Crystallography	15/25	Q3
<i>Crystal Growth & Design</i>	2011	4.390	Chemistry, Multi disciplinary	23/147	Q1
			Crystallography	4/25	Q1
			Materials Science, Multi disciplinary	24/225	Q1
<i>Inorganic Chemistry</i>	2011	4.326	Chemistry, Inorganic & Nuclear	5/49	Q1
<i>Journal of Alloys and Compounds</i>	2011	2.138	Chemistry, Physical	63/127	Q2
			Materials Science, Multi disciplinary	50/225	Q1
			Metallurgy, Metallurgical Engineering	5/76	Q1

Resumen

En condiciones hidrotermales, se sintetizaron dos nuevos succinatos de itrio, $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ (**2**) y $Y_2(C_4H_4O_4)_3(H_2O)_2$ (**3**). Sus estructuras cristalinas, resueltas a partir de datos de difracción de rayos X de monocristal se discutieron a la luz de la del $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$ (**1**). El estudio del comportamiento térmico de los tres compuestos fue posible como consecuencia de su obtención como fases individuales de elevada pureza. El sistema presenta gran diversidad estructural, consecuencia de los diferentes modos de coordinación y la flexibilidad conformacional del ligando succinato que, condicionada por la composición del medio de reacción, dirige la síntesis hacia el producto deseado.

La síntesis de nuevos polímeros de coordinación quirales de itrio(III), $[NaY(Tart)(BDC)(H_2O)_2]$ (**1**) y $[NaY(Tart)(biBDC)(H_2O)_2]$ (**2**) (H_2Tart = ácido tartárico; H_2BDC = ácido tereftálico; H_2biBDC = ácido bifenil-4,4'-dicarboxílico), con la participación de ligandos quirales flexibles y aquirales rígidos, también se efectuó en condiciones hidrotermales. **1** y **2** son compuestos quirales de simetría ortorrómbica, que cristalizan en idéntico grupo espacial ($C222_1$): $a = 6.8854(2) \text{ \AA}$, $b = 30.3859(7) \text{ \AA}$, $c = 7.4741(2) \text{ \AA}$ para **1**, y $a = 6.8531(2) \text{ \AA}$, $b = 39.0426(8) \text{ \AA}$, $c = 7.4976(2) \text{ \AA}$ para **2**. Sus estructuras han sido resueltas utilizando la difracción de rayos X de monocristal, asistida por datos de resonancia magnética nuclear en estado sólido (^{13}C CPMAS-NMR), análisis térmico (TG-MS y DSC) y análisis elemental. Ambos materiales poseen hábito laminar, alcanzando la estabilidad tridimensional mediante enlaces de hidrógeno interlaminares. Los estudios de termodifracción de rayos X de polvo cristalino (HT-pXRD) desvelaron el mecanismo del proceso de deshidratación/rehidratación, siendo modelizadas la estructura de las fases anhidras.

La sustitución de itrio por lantánidos trivalentes permitió la síntesis de dos nuevas series de compuestos: $[NaLn(Tart)(BDC)(H_2O)_2]$ y $[NaLn(Tart)(biBDC)(H_2O)_2]$ ($Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb$). Estos materiales se caracterizaron mediante difracción de rayos X de monocristal y de polvo cristalino, análisis térmico (TG-MS y

DSC), espectroscopia vibracional (FTIR), microscopia electrónica de barrido (SEM-EDX), análisis elemental, y termodifracción de rayos X de polvo cristalino (HT-pXRD). Además de su actividad catalítica, es destacable el comportamiento fotoluminiscente de estos materiales, que presentan emisión sintonizable de luz UV-VIS-IR mediante una efectiva sensibilización de los cationes lantánidos trivalentes a través de los ligandos BDC²⁻ y biBDC²⁻.

Finalmente, el 1,4-fenilbis(fosfonato), usando tanto calefacción convencional como irradiación por microondas, se utilizó como precursor en la síntesis hidrotermal de nuevos materiales híbridos organo-inorgánicos basados en metales lantánidos trivalentes (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Se obtuvieron materiales monofásicos de composición Ln[O₃P(C₆H₄)PO₃H] (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho), aunque sólo en el caso del compuesto de praseodimio (**Za1**) ha sido posible aislar monocristales de calidad suficiente para su determinación estructural mediante difracción de rayos X de cristal único. **Za1** tiene simetría monoclinica (grupo espacial C2/c), con $a = 5.6060(4) \text{ \AA}$, $b = 20.251(7) \text{ \AA}$, $c = 8.2740(6) \text{ \AA}$, $\beta = 108.52(1)^\circ$. Los demás compuestos anhidros de la serie son isoestructurales con **Za1**, y su estructura se refinó a partir de datos de difracción de rayos X de polvo cristalino. Sin embargo, los compuestos basados en Y, Er, Tm, Yb, y Lu cristalizan como fases hidratadas de estructura desconocida. Ambas series de compuestos se caracterizaron mediante análisis térmico (TG-MS, SDTA, y DSC), análisis elemental, espectroscopia infrarroja, termodifracción de rayos X de polvo cristalino (HT-pXRD), microscopia electrónica de transmisión (TEM) y de barrido (SEM-EDX). Estos materiales, que presentan tamaños de partícula variables (> 20 nm), exhiben una inusualmente alta estabilidad térmica. Todos ellos son paramagnéticos, con momentos magnéticos efectivos acordes con los esperados para cationes lantánidos en estado trivalente, mostrando fotoluminiscencia en la región visible del espectro electromagnético, con fuerte luminiscencia roja y verde, respectivamente, para los compuestos basados en europio y terbio.

Abstract

Two new members in the yttrium-succinates family have been reported. These yttrium-succinates coordination polymers, formulated as $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ (**2**) and $Y_2(C_4H_4O_4)_3(H_2O)_2$ (**3**), have been synthesized under hydrothermal conditions. Their structures solved by single crystal X-ray diffraction, are compared with that of $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$ (**1**). The three compounds were obtained as single phases, and their thermal behaviour is described. The results suggest that the structural diversity obtained in this system is related to the coordination diversity and the conformational flexibility of the succinate ligand, which in turn depend on the synthesis conditions that play an important role in directing to one compound or another.

New chiral metal organic frameworks, assembled from Y(III), Na(I) and chiral flexible-achiral rigid dicarboxylate ligands, formulated as $[NaY(Tart)(BDC)(H_2O)_2]$ (**1**) and $[NaY(Tart)(biBDC)(H_2O)_2]$ (**2**) (H_2Tart = Tartaric acid; H_2BDC = Terephthalic acid; H_2biBDC = Biphenyl-4,4'-dicarboxylic acid), were obtained as single phases under hydrothermal conditions. Their structures were solved by single-crystal X-ray diffraction, and characterized by ^{13}C CPMAS NMR, thermal analyses (TG-MS and DSC), elemental analysis, and X-ray powder diffraction. Both compounds crystallize in the orthorhombic chiral space group $C222_1$ with $a = 6.8854(2)$ Å, $b = 30.3859(7)$ Å, $c = 7.4741(2)$ Å for **1**, and $a = 6.8531(2)$ Å, $b = 39.0426(8)$ Å, $c = 7.4976(2)$ Å for **2**. **1** and **2** are layered structures whose three-dimensional stability is ensured by strong hydrogen bond interactions. The X-ray powder thermodiffraction study was performed, and reveals that the dehydration of both compounds is accompanied by phase transformation, while the spontaneous rehydration process is characterized by different kinetics. The crystal structures of anhydrous compounds have been modeled.

Two series of isorecticular chiral metal-organic frameworks assembled from Ln(III) (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), Na(I), and chiral flexible-achiral rigid dicarboxylate ligands, formulated as $[NaLn(Tart)(BDC)(H_2O)_2]$ and $[NaLn(Tart)(biBDC)(H_2O)_2]$ (H_2Tart = Tartaric acid; H_2BDC = Terephthalic acid;

H₂biBDC = Biphenyl-4,4'-dicarboxylic acid), were obtained as single phases under hydrothermal conditions. The compounds have been studied by single-crystal and powder X-ray diffraction, thermal analyses (TG-MS and DSC), vibrational spectroscopy (FTIR), scanning electron microscopy (SEM-EDX), elemental analysis, and X-ray powder thermodiffraction. The activity catalytic has been also investigated. Photoluminescence studies of the investigated materials show room temperature tunable UV-VIS-IR light emission through an effective Ln³⁺ sensitization via BDC²⁻ and biBDC²⁻ ligands.

Series of novel organic-inorganic hybrids materials based on trivalent lanthanide (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and 1,4-phenylbis(phosphonate) has been obtained under hydrothermal conditions either by oven heat or microwave irradiation. Compounds based on La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, formulated as Ln[O₃P(C₆H₄)PO₃H], has been obtained as single phases under hydrothermal conditions. In the praseodymium compound (Za1) single crystals have been obtained and the crystal structure determined. Za1 crystallizes in the monoclinic space group, C2/c, with $a = 5.6060(4) \text{ \AA}$, $b = 20.251(7) \text{ \AA}$, $c = 8.2740(6) \text{ \AA}$, $\beta = 108.52(1)^\circ$. The compounds containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, are anhydrous and isostructural to Za1 as confirmed by Rietveld refinement using X-ray powder diffraction data. However, the compounds based on Y, Er, Tm, Yb, and Lu are hydrated and their structures have not yet been solved. The series of compounds are characterized by thermal analyses (TG-MS, SDTA, and DSC), elemental analysis, IR spectra, X-ray powder diffraction, X-ray powder thermodiffraction, transmission electron microscopy (TEM) and scanning electron microscopy (SEM-EDX). TEM study show a variable particles size with a minimum size of *ca.* 20 nm. These compounds exhibit unusual very high thermal stability. The size of particles and the thermal stability are depending on metal(III) cation features. All the investigated materials show paramagnetic behaviour. The magnetic susceptibility data follow a Curie-Weiss laws with paramagnetic effective moments in good agreement with those expected for Ln³⁺ free ions. The visible photoluminescence properties are also discussed. Eu- and Tb-based compounds exhibit strong red and green luminescence, respectively.

Capítulo 1

Introducción

1. Introducción

Los materiales híbridos organo-inorgánicos constituyen un campo emergente en la interfase entre los materiales clásicos inorgánicos y los orgánicos. Estos sistemas son sólidos cristalinos en el que tanto los elementos estructurales de carácter orgánico como inorgánico coexisten, alternados entre sí, en una única fase. En los últimos años, una buena parte del interés en este área se ha dirigido hacia armazones híbridos porosos, como consecuencia de sus posibles aplicaciones en catálisis, adsorción y separación de gases, además de su interesante comportamiento en campos como el magnetismo y la óptica, incluyendo propiedades electrónicas y dieléctricas. En general, estos materiales presentan una gran diversidad de comportamientos en todas estas áreas, proporcionando interesantes oportunidades de desarrollo para la comunidad científica.

Es bien conocida la existencia de extensas familias de materiales basados en armazones puramente inorgánicos que forman redes extendidas, definiendo cadenas, láminas, o estructuras tridimensionales. Los minerales tipo silicato y aluminosilicato, clasificados ya por Pauling hace más de 80 años [1-3], constituyen el grupo estructuralmente más versátil. Su dimensionalidad puede variar desde cero, como en silicatos simples tales como el circón, basado en unidades ortosilicato SiO_4^{4-} aisladas, hasta redes tridimensionales (por ejemplo, el cuarzo), pasando por estructuras monodimensionales (por ejemplo, los piroxenos) o bidimensionales (por ejemplo, las micas) que originan, respectivamente, cadenas o láminas de complejidad variada. Las zeolitas [4-6] representan una subclase particularmente interesante de estos armazones aluminosilicatos, ya que su estructura tridimensional abierta presenta una intrincada porosidad intracristalina, estando ocupados tanto los poros como los canales que los conectan por moléculas de agua y los cationes alcalinos y alcalinotérreos necesarios para equilibrar la carga negativa inherente al esqueleto estructural, que pueden ser removidos sin colapso de la estructura, lo que hace que estos materiales sean

extraordinariamente útiles en aplicaciones industriales, especialmente en operaciones de intercambio iónico, separación, catálisis y adsorción [7-11]. Más reciente, se ha mostrado que otras familias de compuestos clásicos inorgánicos, especialmente los fosfatos, son capaces de originar fases de topología muy variada, proporcionando una gran diversidad estructural, que incluye armazones de diferente dimensionalidad. Este es el caso, por ejemplo, de los fosfatos de aluminio, de estaño (II), o de zinc [12-15], y también, aunque en menor medida, de los sulfatos metálicos, que en su mayoría son estructuralmente análogos a los fosfatos [16].

En el campo de los sólidos orgánicos clásicos, por el contrario, la diversidad estructural no es tan abundante. La mayor parte de ellos se corresponde con compuestos moleculares (es decir, cero-dimensionales), seguidos por sólidos que forman cadenas mono-dimensionales, entre los que caben citar los sistemas poliméricos que van desde las poliolefinas hasta los copolímeros de bloque y las proteínas. Sin embargo, las redes orgánicas extendidas a más de una dimensión, con la excepción de los armazones orgánicos covalentes (COF) que contienen borato [17], son prácticamente desconocidas, sin olvidar los interesantes polímeros entrecruzados y los sistemas basados en unidades moleculares que ensamblan en redes a través de enlaces de hidrógeno [18].

El conocimiento de diferencias básicas entre las características estructurales de las redes inorgánicas y las redes orgánicas, permite examinar y comprender más fácilmente la diversidad estructural que presentan los híbridos organo-inorgánicos.

El desarrollo en el campo de los materiales híbridos organo-inorgánicos se remonta a los tiempos en que algunas moléculas orgánicas se incluyeron en la estrategia sintética que pretendía aumentar el espacio interlaminar de algunos compuestos laminares, con el objeto de diseñar materiales con porosidad bidimensional controlada. En este campo, merece citarse el gran esfuerzo realizado en la síntesis y caracterización de fosfonatos de zirconio [19,20]. Sin embargo, el interés despertado por los materiales híbridos fue escaso hasta que, en la década de los años 1990, varios grupos de investigación, particularmente los de Yaghi y Robson, reconocieron que las moléculas orgánicas rígidas polifuncionales podían ser utilizadas para enlazar cationes metálicos o clústers, dando lugar a redes extendidas. Así, en 1990, Robson *et al.* publicaron un artículo [21] que a la postre sentó las bases para el desarrollo del campo de la ingeniería de cristales, que puede definirse como la ciencia capaz de predecir la existencia de unidades básicas, con características potencialmente útiles que, mediante el uso de

bloques de construcción molecular adecuados, permita su síntesis en sistemas extendidos donde sean accesibles [22-24]. Yaghi *et al.* han tomado la iniciativa en la aplicación de esta metodología a sistemas basados en carboxilatos. A posteriori, en el año 2003, el grupo de Yaghi introdujo la noción de *síntesis reticular*, como una estrategia para abordar la preparación de nuevos materiales cristalinos híbridos organo-inorgánicos, denominados Metal-Organic Frameworks (MOFs), con geometría, composición, y propiedades predeterminadas, a partir del uso de unidades de construcción secundarias, cuyo ensamblaje conduce a armazones ordenados [25]. Es especialmente interesante la síntesis de MOFs con armazones porosos donde moléculas orgánicas rígidas y átomos metálicos (o clusters) reproducen las posiciones reticulares de los átomos en algunas de las estructuras inorgánicas más clásicas [26]. En esta dirección, son varios los grupos de investigación que se han centrado en la síntesis y caracterización de nuevos híbridos organo-inorgánicos, principalmente basados en óxidos y carboxilatos metálicos [27-33].

De una manera general, los materiales híbridos organo-inorgánicos se definen como compuestos que contienen fracciones inorgánicas y orgánicas, originando enlaces -M-L-M-L- (M = metal, L = ligando orgánico), que se extienden hasta el infinito al menos en una dimensión. Por tanto, esta definición excluye a los sistemas moleculares (oligómeros). La mayor parte de los armazones híbridos conocidos, denominados polímeros de coordinación o MOFs (esta última denominación se utiliza sobre todo cuando son porosos), se pueden dividir en dos categorías. En la primera se engloban las redes extendidas de átomos metálicos aislados (o clusters) vinculados por ligandos orgánicos multifuncionales, basados en la conectividad -M-L-M-. La segunda incluye a los sistemas que contienen redes extendidas de conectividad inorgánica, por lo que habitualmente se habla de híbridos inorgánicos extendidos. Actualmente, la gran mayoría de los híbridos inorgánicos extendidos son óxidos metálicos híbridos, que presentan conectividad infinita metal-oxígeno-metal (-M-O-M-) como parte fundamental de su estructura, representando un subgrupo de una clase de materiales más amplia, que incluye también la existencia de enlaces -M-X-M- (X = Cl, N, S).

Rao *et al.* [34] han establecido una clasificación de los compuestos híbridos organo-inorgánicos en términos de la conectividad -M-L-M- y de la dimensionalidad de la extensión de las fracciones inorgánicas. Así, la notación $I^n O^m$ representa la dimensión global de la estructura, donde m da cuenta de la dimensionalidad del ligando puente y n

de la dimensión de la conectividad de la fracción inorgánica (la Tabla 1.1 muestra toda la gama de posibilidades). Actualmente, la literatura científica recoge una verdadera pléyade de ejemplos para cada una de las clases de materiales híbridos que se citan en dicha Tabla. Sin embargo, aún no han sido sintetizados ejemplos de las cajas que permanecen vacías en su parte inferior derecha.

Tabla 1.1. Clasificación de los sólidos híbridos organo-inorgánicos.

		Dimensionalidad de la conectividad inorgánica, I^n ($n = 0 - 3$)			
		0	1	2	3
Conectividad -M-L-M-, O^m ($m = 0-3$)	0	Complejos moleculares I^0O^0	Híbridos con cadenas inorgánicas I^1O^0	Híbridos con láminas inorgánicas I^2O^0	Híbridos con armazones tridimensionales inorgánicos I^3O^0
	1	Polímeros de coordinación en cadenas I^0O^1	Láminas mixtas organo-inorgánicas I^1O^1	Armazones tridimensionales mixtos organo-inorgánicos I^2O^1	—
	2	Polímeros de coordinación laminares I^0O^2	Armazones tridimensionales mixtos organo-inorgánicos I^1O^2	—	—
	3	Polímeros de coordinación tridimensionales I^0O^3	—	—	—

Aunque los materiales que presentan armazones híbridos involucran una amplia gama de metales, hasta ahora, la mayor parte de los trabajos científicos publicados incluye el uso de metales de transición (zinc, cobre, níquel, cobalto, hierro, manganeso, etc.), siendo notable un interés más reciente hacia sistemas basados en metales lantánidos (principalmente por la gran potencialidad de sus propiedades ópticas), además de un cierto esfuerzo hacia la síntesis de sistemas con elementos del bloque *p* (sobre todo, aluminio, galio y estaño), y el reciente desarrollo de sólidos basados en magnesio, impulsado por la búsqueda de materiales ligeros para el almacenamiento de hidrógeno [35].

En cuanto a los ligandos orgánicos, gran parte de los esfuerzos en este campo se han dirigido hacia la obtención de conectividad a través de átomos de oxígeno,

utilizando fundamentalmente grupos carboxilato y fosfonato, como se recoge en algunas revisiones bibliográficas recientes [27-32,37,38]. En ellas, puede verse que muchos ácidos dicarboxílicos rígidos, tales como el ácido benceno-1,4-dicarboxílico (el miembro más simple de esta familia, el ácido oxálico, también se ha utilizado ampliamente [30]), han mostrado una gran versatilidad, también característica de sistemas alifáticos simples pero más flexibles, como los ácidos succínico y glutámico. La Figura 1.1 muestra los diferentes modos de coordinación de los aniones oxalato y succinato, ilustrando la gran versatilidad de la química de coordinación de estos ácidos dicarboxílicos simples.

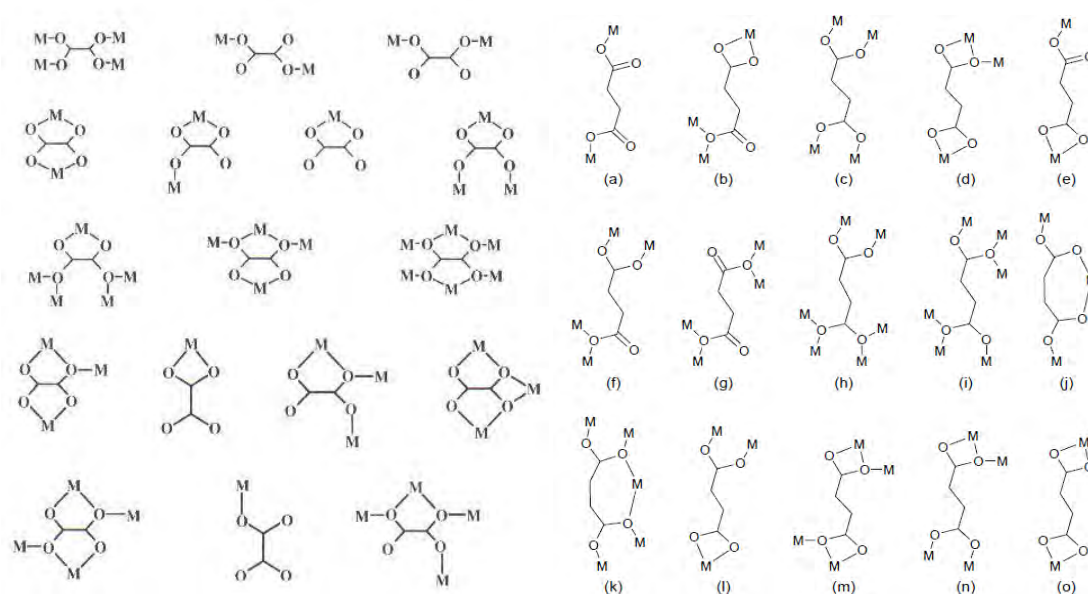


Figura 1.1. Posibles modos de coordinación de los ligandos oxalato [16] y succinato [24].

Los ácidos monocarboxílicos también puede formar estructuras híbridas organo-inorgánicas, siendo destacables algunos materiales basados en los ácidos fórmico y acético [39-42]. Además de los ácidos carboxílicos, los ácidos fosfónicos y fenólicos también han sido utilizados con un propósito similar [37,44-51]. Incluso, más allá de la formación de redes con enlaces M-O, se ha producido una cantidad razonable de informes científicos con otros tipos de ligandos, tales como piridilos e imidazoles [52-55], así como con ligandos mixtos que ofrecen la posibilidad de establecer más de un tipo de conexión, por ejemplo, M-N o M-S en adición a M-O. La principal conclusión

que se extrae de estos trabajos es que aún queda mucho por explorar en el área de trabajo que incluye estos vínculos más complejos.

Algunos de los ejemplos más notables en la literatura de polímeros de coordinación porosos tridimensionales se muestran en un excelente trabajo de Yaghi *et al.*, donde se han explotado los sencillos grupos Zn_4O para, conectados a través de ligandos aromáticos rígidos tipo dicarboxilato (por ejemplo, el ácido benceno-1,4-dicarboxílico), construir redes con muy baja densidad y alta porosidad, tales como el muy conocido MOF-5 [56], demostrando también que se pueden crear familias de numerosos miembros, donde compuestos basados en la misma arquitectura alcanzan su singularidad mediante la alteración de la longitud y otros detalles estructurales del ligando [57,58]. Como puede verse en la Figura 1.2, en el caso de la familia basada en MOF-5, hasta ahora, ha sido posible la síntesis de 16 derivados con la misma arquitectura básica.

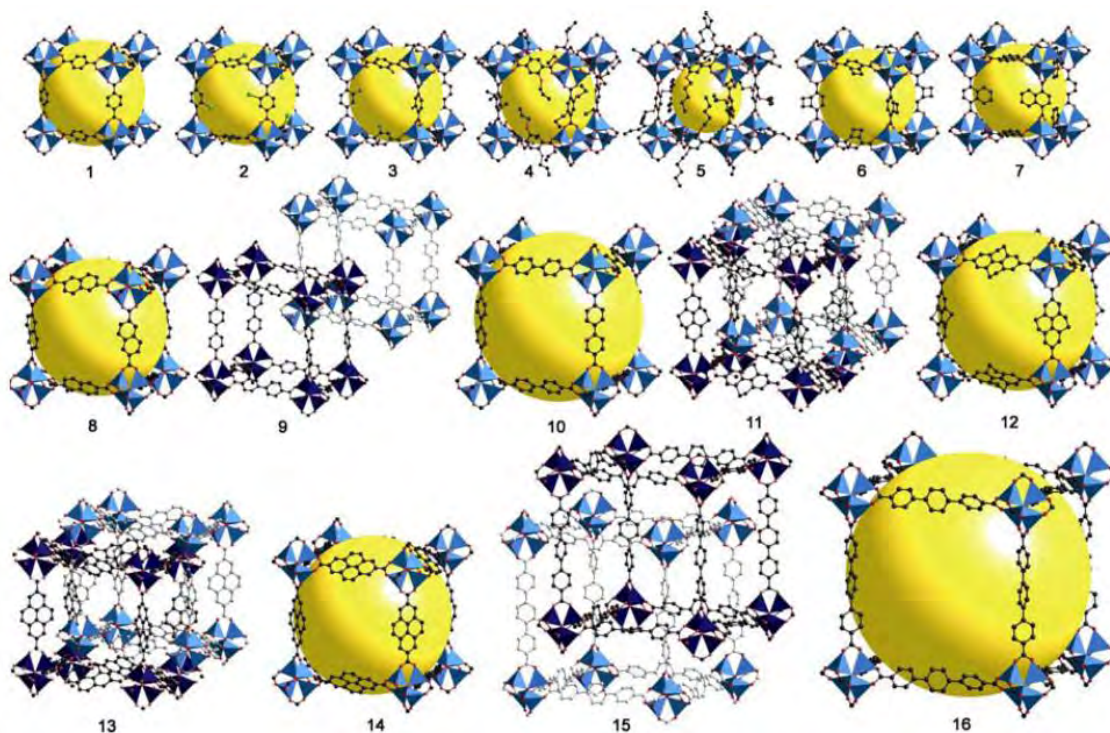


Figura 1.2. Serie de *Metal-Organic Frameworks* isoreticulares (IRMOFs), donde todos los miembros de la familia comparten la misma topología cúbica. Cada compuesto de esta familia se ha sintetizado mediante el uso del ligando correspondiente en las condiciones solvotermiales establecidas para la formación de la unidad de construcción secundaria (SBU) octaédrica. Los ligandos se diferencian tanto en sus grupos

funcionales (IRMOF-1 a -7) como en su longitud (IRMOF-8 a -16). Es reseñable que la elongación de los ligandos aumenta el espacio vacío interno (representado por las esferas amarillas), al tiempo que provoca la formación de fases concatenadas (IRMOF-9, -11, -13 y 15) [57,58].

Unas de las complicaciones que pueden surgir cuando las estructuras son muy abiertas es que las redes pueden interpenetrarse, reduciendo o eliminando la porosidad. Existen algunos ejemplos notables de tal comportamiento, incluidos los casos en los que se ha observado concatenación múltiple [27]. Paradójicamente, Yaghi *et al.* han demostrado que la interpenetración puede ser atractiva para ciertas aplicaciones de almacenamiento de gases, ya que puede originar un aumento de la capacidad real de adsorción por unidad de volumen [59]. Por ejemplo, el MOF-5 es un material de muy baja densidad y, por tanto, *a priori*, un buen candidato para ser usado en el almacenamiento de gases como hidrógeno o metano [60, 61]. Sin embargo, su capacidad real de adsorción de hidrógeno es mucho más baja de lo esperado como consecuencia de que sus poros, excesivamente grandes para este propósito, no llegan a saturarse de gas, reduciéndose el fenómeno de adsorción a la superficie interna de los poros [62, 63]. Este problema puede ser aliviado mediante el uso de materiales con redes interpenetradas, que provocan el aumento de la capacidad de adsorción específica [59].

También debe señalarse que, además de las arquitecturas basadas en las topologías de estructuras inorgánicas simples, también se han obtenido éxitos en la creación de híbridos porosos basados en estructuras de zeolitas conocidas, que adoptan topologías similares a las de sus plantillas [52,64-66]. Los ligandos basados en imidazol son particularmente eficaces para este propósito, ya que pueden imitar los ángulos Si-O-Si que se encuentran en zeolitas naturales [52-54].

En la lucha por obtener materiales con porosidad intracristalina cada vez mayor, el MIL-101 es un ejemplo reciente del gran trabajo realizado por el grupo de Férey [67,68]. Se trata de un polímero de coordinación tridimensional, construido por el uso de clusters de cromo trinucleares en combinación con ácido benceno-1,4-dicarboxílico. La celda unidad de este compuesto tiene un volumen cercano a los 700000 \AA^3 (es decir, similar al de una proteína pequeña), mientras su área superficial específica ronda los $6000 \text{ m}^2/\text{g}$. Aunque el trabajo adquiere aún más valor si se menciona que, en ausencia

de monocristales, la determinación estructural se realizó mediante el uso ingenioso de métodos de simulación tipo *Montecarlo*, Yaghi *et al.* han superado los registros del MIL-101, al sintetizar el MOF-200, que basado en grupos Zn_4O y el ligando aromático rígido tricarboxilato (4,4',4''-(benceno-1,3,5-triyl-tris(benceno-4,1-diyl))tribenzoato), con un volumen de celda unidad de aproximadamente 100000 \AA^3 y un área superficial específica de casi $10000 \text{ m}^2/\text{g}$ [33].

Los polímeros de coordinación de metales de transición han recibido una enorme atención en las últimas dos décadas ya que, debido a las geometrías regulares y predecibles del entorno de coordinación de los metales de transición, su estudio ha tenido gran influencia en el desarrollo de las pautas de diseño de redes periódicas. Sin embargo, los polímeros de coordinación que contienen metales lantánidos (que junto con itrio, escandio y lantano constituyen las denominadas tierras raras) han recibido mucha menor atención en la literatura científica más reciente. Quizás la causa de esta realidad deba buscarse en el hecho de que, como consecuencia de la variedad de geometrías de coordinación que pueden adoptar, las peculiaridades de los metales de tierras raras hacen difícil prever el resultado de una síntesis predeterminada. Es bien conocido que, mientras los metales del bloque *d* originan un número muy limitado de poliedros de coordinación relativamente rígidos, los elementos de bloque *f* dan lugar a geometrías de coordinación difícilmente predecibles (que son una respuesta más a las demandas estéricas de los ligandos que a los efectos electrónicos de los cationes lantánidos), siendo infrecuentes los ejemplos de entornos regulares (cúbicos, octaédricos, tetraédricos). A la ausencia de geometrías de coordinación rígidas, se suma el hecho de que su tamaño, relativamente elevado, hace que los lantánidos presenten números de coordinación usualmente superiores a seis. Por lo general, las tierras raras presentan índices de coordinación que varían en el rango 7-10 (2-12 en el caso de los complejos moleculares). Los números de coordinación muy bajos sólo se observan en los complejos que contienen ligandos extremadamente voluminosos y, por el contrario, los que tienen números de coordinación muy altos son característicos de complejos con ligandos estéricamente poco exigentes. La contracción de los lantánidos también tiene su efecto sobre la capacidad de prevenir las estructuras de sus compuestos (el tamaño de los cationes lantánidos disminuye al avanzar en el período, lo que provoca un aumento en la tendencia hacia la disminución en su número de coordinación). Así, las estructuras obtenidas utilizando un catión lantánido pueden ser no reproducibles con un elemento

diferente (el gadolinio a menudo actúa como cuenca divisoria entre las diferentes estructuras de los elementos lantánidos pesados y ligeros). Además, cuando se trabaja con metales de tierras raras, una complicación adicional es su naturaleza oxofílica que, muchas veces, hace de la síntesis en medio acuoso un reto difícil de superar debido a su afinidad hacia el agua como ligando. Del mismo modo, también presentan una fuerte tendencia a ser coordinados por oxoaniones (por ejemplo, el anión nitrato). Aunque la mayor parte de las veces es un problema, la naturaleza oxofílica de los cationes lantánidos puede ser ventajosa en la síntesis de complejos heterometálicos que incorporen metales del bloque *d*. Otra consecuencia de la naturaleza oxofílica de los metales de tierras raras es que, para evitar la incorporación de ligandos oxo o hidroxilo a sus complejos, una parte importante del trabajo de síntesis debe realizarse bajo atmósfera inerte y, en muchos casos, los productos finales también muestran sensibilidad al oxígeno y/o al agua.

A pesar de los desafíos inherentes al diseño y la síntesis de polímeros de coordinación basados en elementos lantánidos, hay recompensas importantes de la construcción de tales sistemas. Muchos de los metales de tierras raras tienen propiedades únicas, especialmente en términos de actividad luminiscente, que hacen que la síntesis de sus compuestos, a veces exóticos, sea un objetivo muy atractivo. En particular, los complejos de europio, terbio y erbio muestran características luminiscentes que pueden ser explotadas en materiales prediseñados. Además, es creciente el interés en el conocimiento de las propiedades magnéticas de los metales de tierras raras, particularmente en aquellos con gran número de electrones no apareados, como gadolinio y samario. Los polímeros de coordinación de tierras raras también han mostrado resultados alentadores en la construcción de materiales ópticos no lineales (NLO) y redes porosas [69-72]. Además, es reseñable que existe la posibilidad de diseñar redes funcionales usando diferentes estados de oxidación de metales de tierras raras, cuyo cambio no afecta drásticamente a su geometría de coordinación, a diferencia de lo que sucede habitualmente en los compuestos de metales de transición. Finalmente, por razones puramente estéticas, los polímeros de coordinación basados en las tierras raras son altamente atractivos como consecuencia de sus poco comunes geometrías de coordinación. Nuevamente, debido a su naturaleza oxofílica, la mayor parte de los trabajos científicos publicados sobre polímeros de coordinación basados en tierras raras se han centrado en el uso de ligandos derivados de los ácidos carboxílicos, aunque

existe un número significativo de sistemas interesantes que utilizan compuestos nitrogenados [73-77].

El autoensamblaje puede definirse como el proceso por el que una especie supramolecular se forma espontáneamente a partir de sus componentes. Particularmente, el autoensamblaje entre iones metálicos y ligandos orgánicos es uno de los procedimientos más eficaces y actualmente más utilizados en el diseño y la construcción de arquitecturas novedosas de polímeros de coordinación, ya que: *i)* puede originarse una amplia variedad de armazones a partir de bloques de construcción formados por los iones metálicos y ligandos orgánicos de vinculación, *ii)* es posible la modificación racional de los ligandos orgánicos de vinculación, *iii)* pueden existir varios tipos de interacción, tales como enlaces metal-ligando, enlaces metal-metal, enlaces de hidrógeno, apilamientos de anillos aromáticos, o las omnipresentes fuerzas de Van der Waals, y *iv)* la reacción puede ser controlada por la temperatura, la presión, el pH, o la adición de disolventes, entre otros factores.

Uno de los retos de la investigación en este campo es la obtención de monocristales adecuados para su determinación estructural mediante técnicas de difracción. A diferencia de las especies moleculares, la mayoría de los polímeros de coordinación son insolubles una vez sintetizados y esta propiedad, que puede ser ventajosa para otros aspectos de su química, hace que las operaciones de recristalización no sean una opción cuando se pretenden obtener compuestos de gran pureza o monocristales de gran tamaño. Como consecuencia, tratando de solventar el problema, han sido numerosas las aproximaciones sintéticas que se han desarrollado.

Los primeros ejemplos de monocristales de polímeros de coordinación fueron obtenidos bajo métodos sintéticos tradicionales de la química de coordinación [21], obteniéndose a temperatura ambiente o temperaturas moderadas, y usando sistemas abiertos. Dichos métodos incluyen la evaporación lenta de una disolución de precursores [78-81], disoluciones en capas [82-84], o la difusión lenta de una disolución de un solo componente en otra a través de una membrana o un gel de inmovilización [85,86]. Para este último propósito, se han diseñado tubos de cristalización de formas variadas y, a veces, visualmente muy atractivas.

Posteriormente, el método hidrotérmal, que es un procedimiento bien establecido para la síntesis de materiales inorgánicos porosos, tal como zeolitas y AIOs (aluminofosfatos), se convirtió en la técnica más extendida para la preparación

de polímeros de coordinación. Con el nombre general de síntesis solvotermal se agrupan una serie de técnicas en las que un líquido, en un recipiente cerrado, es calentado por encima de su punto de ebullición, lo que genera una presión superior a la atmosférica (normalmente moderada). El líquido que se usa habitualmente es el agua, y de ahí el nombre de síntesis hidrotermal. Sin embargo, cada vez se utilizan con mayor frecuencia otros medios líquidos, fundamentalmente disolventes orgánicos (por ejemplo, la dimetilformamida), y de ahí el nombre genérico de síntesis solvotermal. Esta reacción heterogénea, por lo general lleva a cabo en un rango de temperaturas moderado (100-250 °C) y presión autógena. Una característica distintiva de la síntesis solvotermal es que los reactivos poco solubles en condiciones ambientales, en medios solvotermales pasan fácilmente a la disolución por la propia acción del disolvente o mediante el concurso de agentes externos, conocidos con el nombre de mineralizadores. El hecho de que se encuentren en disolución especies muy poco solubles en condiciones ordinarias, favorece el autoensamblaje de especies muy diversas hasta originar nuevos productos difíciles de imaginar en recipientes abiertos. Además, como consecuencia de que las diferencias de solubilidad entre los diferentes reactivos se reducen enormemente, pueden introducirse en el medio de reacción una gran variedad de precursores que, en ausencia de equilibrio de cristalización, mediante control cinético, favorecen la aparición de fases metaestables, muchas veces de estructura desconocida.

Aunque la variedad de métodos de síntesis relacionados con los métodos solvotermales es grande, es destacable que la síntesis de polímeros de coordinación es cada vez más frecuente el uso de la radiación microondas como fuente de calefacción de la mezcla de síntesis bajo condiciones solvotermal [87-91], habiéndose mostrado como una manera eficaz para la síntesis de nuevos materiales en tiempos de cristalización cortos, como consecuencia de una rápida cinética de nucleación y crecimiento cristalino, proporcionando materiales con una distribución estrecha de tamaños de partículas, usualmente de dimensiones nanométricas, con morfologías definidas, altos rendimientos de los productos deseados, escasos productos secundarios, y control eficiente de los parámetros del proceso [89-92]. En esta misma dirección, la síntesis asistida mediante ultrasonidos también parece prometedora, aunque el número de ejemplos descritos hasta la actualidad es escaso [88,93,94]. Finalmente, en la síntesis ionotermal [95-98] se utilizan líquidos iónicos como medio de reacción,

proporcionando productos habitualmente diferentes a los que se alcanzan en presencia de disolventes convencionales.

Capítulo 2

Objetivos

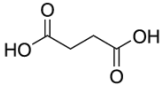
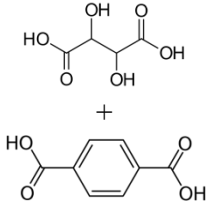
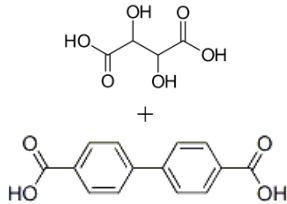
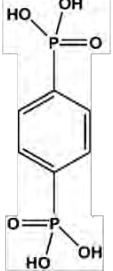
2. Objetivos

Este trabajo se enmarca en el campo de la síntesis y caracterización estructural de nuevos materiales híbridos organo-inorgánicos, MOFs o polímeros de coordinación, basados en elementos lantánidos que presenten propiedades luminiscentes. Este objetivo general se concreta en los siguientes objetivos específicos:

- i)* Establecer las condiciones de síntesis de nuevos materiales híbridos organo-inorgánicos (MOFs) basados en elementos lantánidos, usando ligandos de vinculación bidentados de tipo carboxílico ($O_2C-R-CO_2$) flexibles, rígidos, o mezclas rígido-flexible, además de ligandos bidentados rígidos tipo fosfonato ($O_3P-R-PO_3$).
- ii)* Completar la caracterización y evaluación mediante diversas técnicas de caracterización estructural (difracción de rayos-X de monocristal y de polvo cristalino, termodifracción de rayos-X) y con otras técnicas complementarias de análisis, que permitan la caracterización completa de estos materiales, tales como los métodos de análisis térmico (TG/SDTA/DSC), análisis elemental, microanálisis mediante microscopía electrónica de barrido (SEM/EDX) y transmisión (TEM), y técnicas espectroscópicas como la resonancia magnética nuclear de estado sólido (SS-NMR) y el infra-rojo (IR).
- iii)* Evaluación de los nuevos materiales como catalizadores heterogéneos, y en procesos de adsorción de gases, realizándose además la determinación de sus propiedades magnéticas y luminiscentes.

Para ejecutar el presente trabajo (véase la Tabla 2), se seleccionaron y usaron diversos ligandos orgánicos de vinculación bidentados: *i*) tipo carboxílico ($O_2C-R-CO_2$), o *ii*) tipo fosfonato ($O_3P-R-PO_3$). Entre los ligandos de vinculación dicarboxílicos, se utilizaron ligandos flexibles, como el ácido succínico ($HO_2C-CH_2-CH_2-CO_2H$) y el ácido tartárico ($HO_2C-CHOH-CHOH-CO_2H$), y rígidos como el ácido tereftálico ($HO_2C-C_6H_4-CO_2H$) y el ácido bifenil-4,4'-dicarboxílico ($HO_2C-C_6H_4-C_6H_4-CO_2H$). Entre los ligandos de vinculación difosfonatos, se seleccionó un ligando rígido, el ácido-1,4-benzenodifosfonico ($HO_3P-C_6H_4-PO_3H$).

Tabla 2.1. Metales y ligandos, clasificados en función de sus características, utilizados como precursores de los materiales sintetizados experimentalmente.

	Ligando flexible	Ligando flexible + rígido	Ligando flexible + rígido	Ligando rígido
	Ácido succínico (S)	Ácido tartárico (Tart) + Ácido tereftálico (BDC)	Ácido tartárico (Tart) + Ácido bifenil-4,4'-dicarboxílico (biBDC)	Ácido-1,4-benzenodifosfonico (BDP)
				
Y^{3+}	SY2 , SY3	BDCTartNaY	biBDCTartNaY	BDPY
La^{3+}				BDPLa
Ce^{3+}				BDPCe
Pr^{3+}				BDPPr
Nd^{3+}				BDPNd
Sm^{3+}		BDCTartNaSm	biBDCTartNaSm	BDPSm
Eu^{3+}		BDCTartNaEu	biBDCTartNaEu	BDPEu
Gd^{3+}		BDCTartNaGd	biBDCTartNaGd	BDPGd
Tb^{3+}		BDCTartNaTb	biBDCTartNaTb	BDPTb
Dy^{3+}		BDCTartNaDy	biBDCTartNaDy	BDPDy
Ho^{3+}		BDCTartNaHo	biBDCTartNaHo	BDPHo
Er^{3+}		BDCTartNaEr	biBDCTartNaEr	BDPEr
Tm^{3+}				BDPTm
Yb^{3+}		BDCTartNaYb	biBDCTartNaYb	BDPYb
Lu^{3+}				BDPLu

La posterior caracterización y evaluación de los materiales obtenidos se completó mediante diversas técnicas de caracterización estructural (difracción de rayos X de monocristal y de polvo cristalino, termodifracción de rayos-X) y con otras técnicas complementarias de análisis, que permitieron su caracterización completa, tales como las técnicas de análisis térmico (TG/DTA/DSC), análisis elemental, microscopia electrónica de barrido (SEM/EDX) y transmisión (TEM), y técnicas espectroscópicas como la resonancia magnética nuclear de estado sólido (SS-NMR) y el infrarrojo (IR). Por último, se procedió a la evaluación de algunos de los nuevos materiales como catalizadores heterogéneos, en procesos de adsorción de gases, y se realizó la determinación de sus propiedades magnéticas y luminiscentes.

Como consecuencia de la experiencia acumulada por nuestro grupo de trabajo en la síntesis y caracterización de materiales con base fosfato, nos fue encargada la elaboración del capítulo "*Les Phosphates hybrides organique-inorganique*" como una parte del libro titulado "*Les Phosphates à l'aube du XXIème siècle*" que, editado por el Prof. Gille Le Flem (*Université de Bordeaux*, Francia), sirvió para que el autor de esta tesis realizase un intenso trabajo de recopilación bibliográfica y síntesis de resultados de otros autores que es de esperar se haya traducido en un mejor conocimiento del estado del arte en este dominio científico.

En cuanto a los resultados de investigación originales, esta tesis se iniciará con la presentación de la síntesis y caracterización de dos nuevos polímeros de coordinación, uno de ellos laminar, $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$, y el otro tridimensional, $Y_2(C_4H_4O_4)_3(H_2O)_2$, basados en itrio y un ligando de vinculación bidentado tipo carboxílico flexible, el ácido succínico. Se describirá la estructura cristalina de ambos materiales, elucidada mediante difracción de rayos-X de monocristal, y se analizará su comportamiento térmico mediante técnicas termoanalíticas (TG-MS/SDTA y DSC).

Posteriormente, se presentará la síntesis y caracterización de dos nuevos polímeros de coordinación bidimensionales, basados en itrio y ligandos de vinculación mixtos bidentados tipo carboxílico rígido-flexible (ácido tartárico - ácido tereftálico / ácido bifenil-4,4'-dicarboxílico) de fórmulas $NaY(C_4H_4O_6)(C_8H_4O_4)(H_2O)_2$ y $NaY(C_4H_4O_6)(C_{14}H_8O_4)(H_2O)_2$. Se describirá la estructura cristalina de ambos materiales, obtenida también por difracción de rayos-X de monocristal, y su caracterización mediante diferentes técnicas: análisis elemental, microanálisis acoplado a microscopia electrónica de barrido (SEM/EDX), análisis térmico (TG-MS/SDTA y

DSC), difracción de rayos-X de polvo cristalino, termodifracción de rayos-X, y resonancia magnética nuclear de estado sólido (SS-NMR).

En el ámbito de la serie de compuestos comentados en el párrafo anterior, se abordará la modelización estructural de sus fases anhidras, $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)$ y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)$, reveladas mediante estudios de termodifracción de rayos-X, donde se observó que la deshidratación es un proceso complejo acompañado de cambios de fase.

La optimización del proceso de síntesis de los compuestos de itrio permitirá abrir el camino hacia la preparación y caracterización estructural de toda la familia de compuestos basados en elementos lantánidos de composición análoga, $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ y $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$). Se describirá la estructura cristalina de cada miembro de estas series, utilizando para ello datos de difracción de rayos-X de monocristal, y se caracterizará mediante diferentes técnicas: análisis elemental, microanálisis acoplado a microscopía electrónica de barrido (SEM/EDX), análisis térmico (TG-MS/SDTA y DSC), difracción de rayos-X de polvo cristalino y termodifracción de rayos-X, previamente a la descripción de su actividad catalítica y sus propiedades fotoluminiscentes.

Utilizando el ligando de vinculación bidentado rígido 1,4-fenilbis(fosfonato), se abordará la síntesis y caracterización estructural de nueva familia de híbridos isoestructurales órgano-inorgánicos tridimensionales basados en elementos lantánidos, $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$). Sus estructuras cristalinas se determinarán a partir de datos difracción de rayos-X de monocristal del compuesto de praseodimio y refinamiento Rietveld de los datos de difracción de rayos X de polvo cristalino del resto de los miembros de la serie. La caracterización mediante análisis elemental, microanálisis asociado a microscopía electrónica de barrido (SEM/EDX), espectroscopía de infrarroja (IR), análisis térmico (TG-MS/SDTA) y termodifracción de rayos-X, precederá al estudio de sus propiedades fotoluminiscentes.

Finalmente, también con el uso del ligando de vinculación bidentado rígido 1,4-fenilbis(fosfonato), se presentará la síntesis y caracterización estructural de los compuestos basados en itrio, erbio, tulio, iterbio, y lutecio. Su caracterización mediante difracción de rayos-X de polvo cristalino, microscopía electrónica de transmisión (TEM) y barrido (SEM/EDX), espectroscopía infrarroja y análisis térmico (TG-

MS/SDTA y DSC) se completará con el estudio de las propiedades magnéticas de los compuestos basados en gadolinio, disprosio, holmio, erbio, tulio, e iterbio.

Capítulo 3

Resultados y discusión

3.1. Fosfatos híbridos organo-inorgánicos.

Capítulo de libro

Capítulo en trámite de publicación, con el título “Les Phosphates hybrides organique-inorganique”, como una parte del libro titulado “Les Phosphates à l’aube du XXIème siècle” editado por el Prof. Gille Le Flem (Université de Bordeaux, Francia).

Resumen

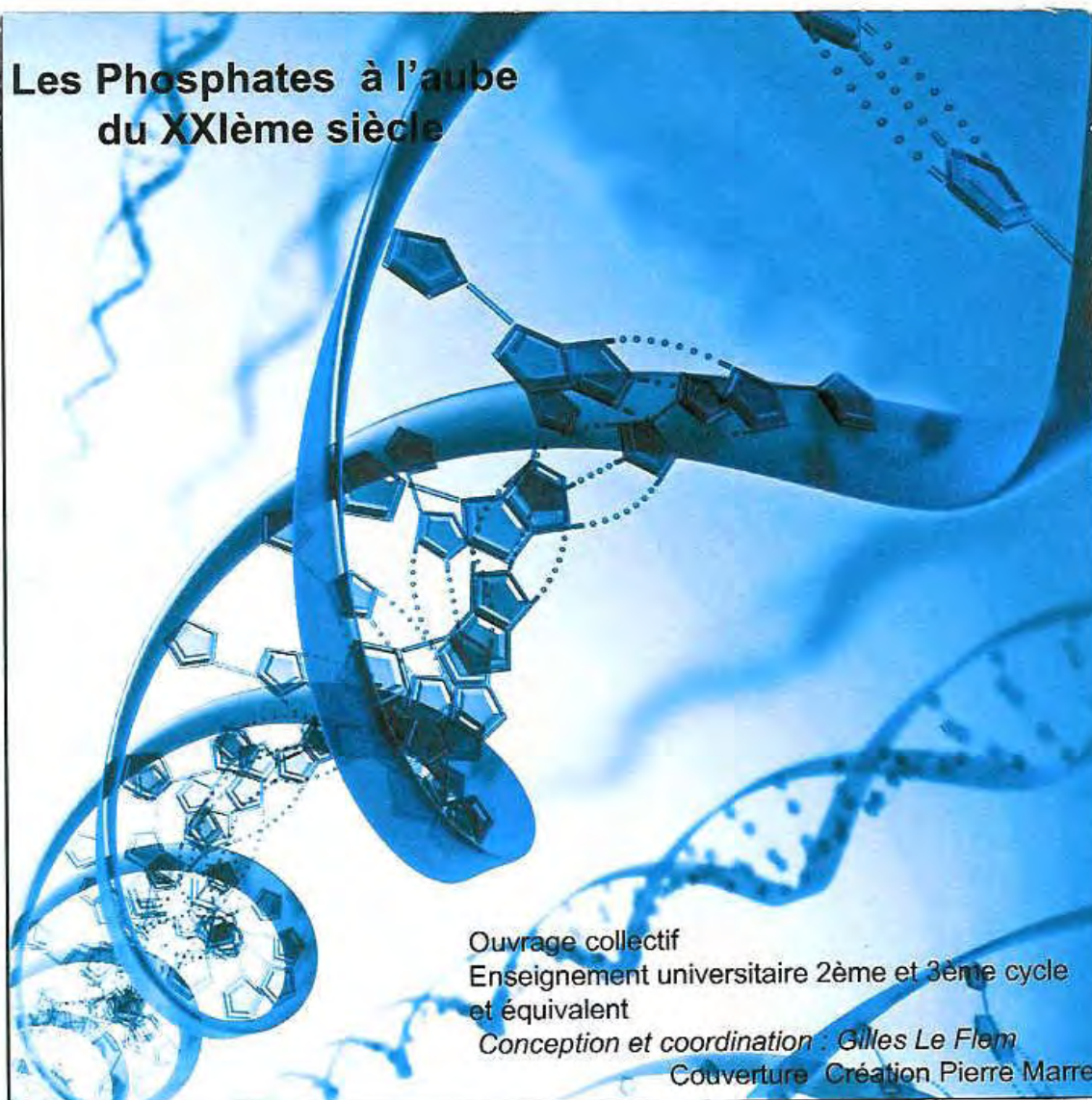
En este capítulo de libro se describen, de manera breve y general, los conocimientos relevantes más recientes en el campo de los fosfatos metálicos con estructuras abiertas, destacando los métodos utilizados para su síntesis y caracterización, con especial atención hacia las técnicas de resonancia magnética nuclear en estado sólido. El resultado alcanzado es consecuencia de un gran esfuerzo de sistematización de la enorme cantidad de datos experimentales publicados en los últimos años, que esperamos contribuya a mejorar el conocimiento del estado del arte en este dominio científico.

El trabajo se divide en dos partes. La primera recoge los diversos tipos de precursores utilizados con mayor asiduidad en la preparación de fosfatos híbridos organo-inorgánicos (sales metálicas, fuentes de fosfato, especies orgánicas) para luego pasar a describir los métodos utilizados más habitualmente en la síntesis de estos

materiales, destacando entre ellos los procedimientos hidrotermales. A continuación, se ilustra el procedimiento de síntesis y caracterización estructural de un fosfato metálico, para continuar discutiendo la influencia que, sobre el producto final, tienen las especies orgánicas, el tipo del disolvente, y el agente mineralizador adicionados al medio de la reacción, en adición de otros factores que juegan un papel crucial en la naturaleza del material obtenido: pH, temperatura y tiempo de síntesis. Finalmente, se ilustra la diversidad estructural de los fosfatos híbridos órgano-inorgánicos mediante la exposición de algunos ejemplos seleccionados de la bibliografía, incluyendo compuestos con estructuras abiertas de diferentes dimensionalidades (cero-, mono-, bi-, y tri-dimensionales), originadas por la combinación de poliedros compartiendo vértices, que pueden ser tetraédricos, como $[\text{PO}_4]$ y $[\text{MO}_4]$ ($M = \text{Zn, Co, Al}$), tetraédricos $[\text{PO}_4]$ y octaédricos, como $[\text{MO}_4\text{F}_2]$ ($M = \text{Fe}$) o $[\text{MO}_5\text{N}]$ ($M = \text{V}$), tetraédricos $[\text{PO}_4]$ y una combinación de tetra-, penta-, y octaédricos, como $[\text{MO}_4] - [\text{MO}_4\text{F}] - [\text{MO}_4\text{F}_2]$ ($M = \text{Ga}$), o tetraédricos $[\text{PO}_4]$ y octacoordinados tipo $[\text{MO}_3\text{F}_5]$ ($M = \text{Ce}$), generando unidades de construcción secundarias (SBU) muy variadas, que a su vez forman redes extendidas, definiendo cadenas, láminas o sistemas tridimensionales (incluso, en algunos casos particulares, estructuras adimensionales) que incluyen diferentes tipos de moléculas orgánicas.

Como consecuencia de los recientes avances obtenidos en la aplicación de la resonancia magnética nuclear en estado sólido (SS-NMR) a la caracterización de los materiales descritos en esta recopilación, que proporciona valiosa información, estructural y dinámica, en sólidos cristalinos y amorfos, complementando eficazmente los datos obtenidos mediante técnicas de difracción, se abordan algunos ejemplos particulares de experimentos de SS-NMR, detallando los datos que pueden ser extraídos de ellos. Así, la segunda parte de esta recopilación recoge algunos resultados de la investigación realizada en nuestros laboratorios de las Universidades de Oviedo y Aveiro, donde los datos de SS-NMR han contribuido, en combinación con técnicas de difracción de rayos X de polvo cristalino, a la elucidación de las complejas estructuras cristalinas de algunos nuevos compuestos.

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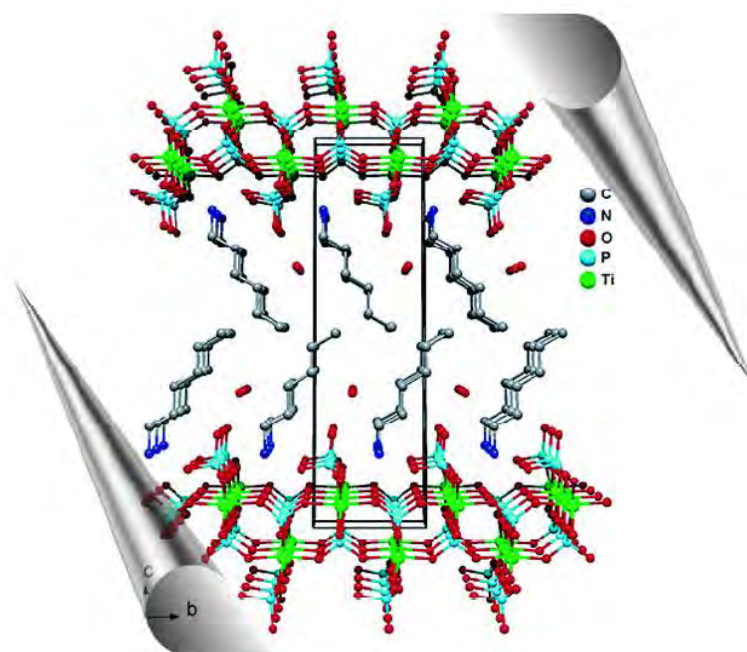


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1. Introduction générale.

Le phosphore est un élément vital se trouvant à la fois dans la matière vivante et dans la croûte terrestre. Le corps humain contient environ 1% en poids de l'élément phosphore, et environ 4/5 se trouve sous forme d'hydroxyapatite dans les os et les dents et le reste de phosphore se trouve sous forme de phosphates organiques, qui existent sous des formes diverses telles que les mono et diesters phosphoriques [1] et l'ADN. D'autre part, un grand nombre de phosphates métalliques sont également présents dans la nature comme minéraux. Le terme «phosphate» désigne les oxyanions de phosphore pentavalent, qui vont de l'entité PO_4 isolée jusqu'à des assemblages plus complexes en anneaux et chaînes d'anions de longueurs variables et pouvant être infinies [2,3].

La diversité de phosphates métalliques résulte donc de la variété de ces assemblages, du grand nombre de cations auxquels peuvent se coordonner ces groupements phosphates et de la présence des autres anions ou molécules dans leur voisinage [3]. De ce fait les matériaux phosphates peuvent avoir des utilisations très diverses par exemple comme échangeurs d'ions [4], conducteurs ioniques [5], et catalyseurs [6]. En outre, puisque les anions phosphates n'absorbent pas dans la région UV-visible, les phosphates métalliques trouvent également leur utilisation comme composants optiques, par exemple, comme luminophores [7], matériaux pour l'optique non linéaire [8] et matériaux laser [9]. Les dépôts de phosphorite amorphes sont importants comme engrais phosphatés [10]. La chimie des phosphates inorganiques a été dominée traditionnellement par l'étude des espèces minérales. Mais la découverte récente de phosphates analogues aux zéolithes de type aluminosilicate avec des structures à charpente ouverte, a donné une nouvelle orientation, très riche, à l'étude des structures de phosphate métalliques.

Le domaine des matériaux inorganiques à structure ouverte se nourrit de la variété d'architectures qui peuvent être obtenus par des nouvelles approches expérimentales. Au cours des deux dernières décennies les activités de recherche dans ce domaine ont été très importantes en termes de découverte de nouvelles charpentes à base d'oxydes, de chalcogénures, d'halogénures et de nitrures, ainsi que par la découverte des composés de type MOFs (Metal-Organic Frameworks) aussi connues sous le nom de polymères de coordination, en particulier ceux incorporant des ligands carboxyliques. Parmi les matériaux à charpente ouverte qui sont donc chimiquement très variés on trouve les solides comportant des polyèdres oxygénés tels que les zéolithes aluminosilicates et les phosphates métalliques.

Avant la découverte des phosphates d'aluminium à charpente ouverte (AIPO's) par Flanigen et *al.* en 1982 [11], seules les zéolithes aluminosilicates de structures tridimensionnelles avaient été étudiées. Cependant, les deux dernières décennies ont été le témoin de la croissance rapide de matériaux à charpente ouverte à base des phosphates métalliques. Ainsi pas moins de 20 éléments du tableau périodique sont capables de former des telles charpentes. Les solides à charpente ouverte à base de phosphate, sont très diversifiés et complexes, ils possèdent une grande variété de structures et de propriétés. Les premiers phosphates d'aluminium (AIPO's), étaient construits à partir de tétraèdres (AlO_4 , SiO_4 , PO_4 , etc...), liées par leurs sommets mais de nouvelles charpentes ont été découvertes impliquant des polyèdres octaédriques XO_6 (exemple : FeO_6 , TiO_6), pentacoordinés XO_5 (exemple : CrO_5), pyramidales XO_4

(exemple: ZnO_4 , CoO_4 , AlO_4) trigonales-pyramidales XO_3 (exemple : SnO_3), octa-coordinés (exemple : CeO_3F_5)

Finalement, sur le plan des applications des matériaux à charpente ouverte, les zéolithes aluminosilicates restent en position dominante en raison de leur remarquable stabilité mais les phosphates commencent à se développer en catalyse et pour le stockage de l'hydrogène.

L'objectif de ce chapitre est de donner un aperçu bref et général dans le domaine des phosphates métalliques à charpente ouverte. Il est divisé en deux parties : la première partie est fondée sur la bibliographie, elle illustre la diversité structurale de ces matériaux, la deuxième partie découle des résultats de travaux de recherche réalisés par nos groupes de recherche de l'université d'Oviedo et l'université d'Aveiro : elle témoigne de notre expérience dans la synthèse et la caractérisation de tels composés, qui sera illustrée par deux exemples de synthèse et caractérisation de deux nouveaux phosphates de titane à charpente ouverte, résumant des travaux publiés récemment [12,13].

2. Source de métal.

Les sources du métal utilisé sont très variables. Elles peuvent être des sels solubles simples, comme les chlorures, les nitrates ou les sulfates ou d'espèces moins solubles comme les fluorures, les oxydes, les alcoolates, les complexes de coordination ou même le métal pur.

3. Source de phosphate.

Contrairement au choix du métal, le choix de la source de phosphate est très limité : la plus utilisée est l'acide phosphorique (H_3PO_4), et la moins utilisée est l'oxyde de phosphore (P_2O_5) ou bien l'anion pyrophosphate ($P_2O_7^{4-}$). Récemment, d'autres sources ont été utilisées, comme :

1. les esters de l'acide phosphorique $[O=P(OR)_3]$, tel que le tributylphosphate, [14]
2. les phosphates de type organoammonium (les phosphates d'amine), qui fournissent à la fois l'amine et le phosphate au milieu réactionnel, [15]
3. les amides phosphoriques (les phosphates d'amide) $[O=P(NR_2)_3]$ qui à l'hydrolyse libèrent l'acide phosphorique et l'amine. [16]

Généralement, les sources décrites dans les points 1 et 2 permettent essentiellement de réaliser des réactions dans un milieu non aqueux, ce qui favorise la formation des matériaux avec des structures de faible dimension ou basse dimensionnalité.

4. Source d'amine.

Une grande variété d'amines organiques et de cations ammonium a été utilisée comme agent structurant (ADS) ou comme templates (voir paragraphe 8 : Rôle des molécules organiques où sont définies les notions d'« agents structurant » et de « templates »). Il s'agit notamment des amines aliphatiques, monoamines, diamines, triamines, et tétramines linéaires, leur amino alkyle ou dérivés d'alkyl, monoamines et diamines cyclique aliphatiques et leurs dérivés. Les amines aromatiques comme la pyridine et leurs substituants,...etc. Divers cations ammonium quaternaire sont également impliqués dans ces études. La Figure 1 énumère plus de 100 amines présentes dans diverses synthèses de phosphate métallique templétés.

5. Synthèse hydrothermale.

La technique de synthèse hydrothermale très utilisée ces quinze dernières années, a été développée initialement pour comprendre la formation des minéraux dans la nature sous pression et température élevées en présence d'eau. En fait, ce terme a été d'abord utilisé pour décrire l'action de l'eau dans les conditions qui provoquent des changements dans la croûte terrestre menant à la formation de diverses roches et minéraux. La technique hydrothermale a été adoptée par Schafthaul en 1845 pour obtenir des cristaux de quartz par la transformation de l'acide silicique fraîchement précipité dans la marmite de Papin. Plus de 130 espèces minérales ont été ensuite synthétisées à la fin du 19ème siècle. Mais sa première application commerciale réussie a commencé avec l'extraction des minéraux ou l'enrichissement du minerai au cours du siècle précédent.

La technique de synthèse hydrothermale des composés inorganiques au niveau commercial, a pris une importance accrue au milieu du XXe siècle, juste après la synthèse des gros monocristaux de quartz par Nacken. La première élaboration des zéolites par Barrer qui n'avait pas d'équivalent dans la nature, est à l'origine d'une nouvelle branche de la science: la technologie des tamis moléculaire. De nos jours, la technique hydrothermale s'est développée dans plusieurs domaines de la science et technologie, avec la mise au point de plusieurs techniques dérivées de la méthode originale.

Cette évolution découle des progrès rapides des équipements impliqués dans la recherche hydrothermale et aussi des travaux d'un grand nombre de chimistes et de physiciens visant à comprendre la chimie hydrothermale. En outre, la sensibilisation croissante à la sécurité environnementale et à la nécessité de l'utilisation optimale de l'énergie, a permis à la technique hydrothermale d'occuper une place unique dans les développements technologiques modernes.

Même s'il n'y a pas de consensus concernant la définition du terme hydrothermal, ce vocable fait référence généralement à toute réaction hétérogène en présence de solvants aqueux ou minéralisants sous pression et température élevées pour dissoudre et recristalliser les matériaux qui sont relativement insolubles dans les conditions ordinaires. Toutefois, en raison de la faible solubilité de certains composés

dans l'eau, la recherche de minéralisant approprié a été mise au point en envisageant une variété de solutions aqueuses et non aqueuses testées pour convenir à la préparation

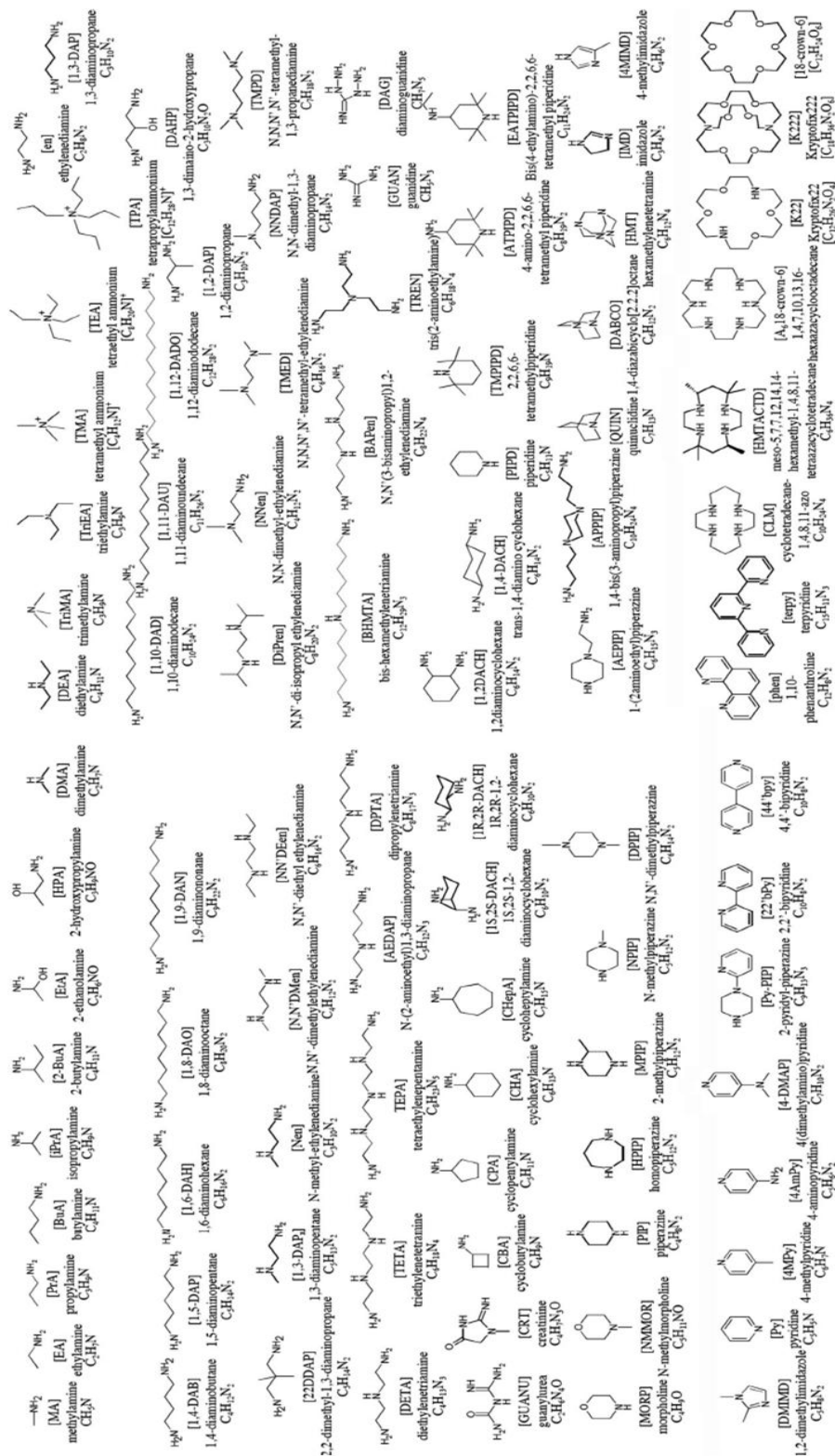


Figure 1. Exemples de différents types d'amines utilisés comme templates dans la formation de phosphates métalliques à structure ouverte. [17]

d'un composé particulier. En fait, des cristaux de grande taille peuvent souvent être obtenus par des procédés de synthèse non aqueux en employant généralement des alcools. Quelle que soit la nature du solvant le terme solvothérmal est souvent utilisé pour définir toute réaction chimique se déroulant en présence du solvant soumis à un état des conditions supercritiques ou proche de celles-ci.

La synthèse hydrothermale suit la loi d'Ostwald* qui dit: la phase formée n'est pas généralement la plus stable, bien que cela soit accessible par moyens de contrôle thermodynamique. En conséquence, la phase métastable formée est d'abord dissoute, puis remplacée par une seconde phase plus stable, ce processus se poursuit par étapes successives jusqu'à ce que la phase la plus stable soit enfin atteinte. Pour une certaine composition les phases thermodynamiquement stables sont celles de densité la plus élevée et leur synthèse est généralement aussi accessible par des techniques à haute température en partant des précurseurs appropriés. Dans un système donné, où plusieurs phases métastables coexistent, la phase qui cristallise à plus basse température et dans le temps le plus court possible, sera celle qui a une structure plus ouverte et une plus faible stabilité thermodynamique. Puisque il y a des barrières cinétiques entre les phases métastables successives, il est possible d'arrêter la réaction à un moment donné en choisissant les conditions expérimentales appropriées, de manière à obtenir le produit métastable désiré. Par conséquent, le temps de réaction est une variable importante dans la préparation de ces matériaux.

En plus de la simplicité de la méthode de synthèse hydrothermale, son grand avantage sur les méthodes synthétiques conventionnelles, réside dans la possibilité de formation des phases à basse température et /ou métastables. Mais cette méthode nécessite le contrôle de plusieurs paramètres: température, temps de réaction, le rapport et les concentrations des réactifs, les valeurs de pH, ...etc.

**Loi d'Ostwald [18-21] : aussi dite loi de réactions successives, prévoit que dans tous les processus, ce n'est pas l'état le plus stable avec le minimum d'énergie libre qui est initialement obtenu, mais l'état le moins stable situé plus proche de l'état initial en terme d'énergie libre.*

6. Synthèse de phosphates métalliques à structure ouverte.

Les phosphates métalliques à structure ouverte, peuvent être également obtenus à partir d'un mélange de réactionnel ou d'un gel formé par le tétraéthylorthosilicate - Si(OEt)₄-(TEOS) laissé à température et pression ambiante pendant de longues périodes (souvent plusieurs jours). Parfois, les tensioactifs, les micelles inverses, ou microémulsions sont utilisés pour obtenir ce type de phosphates dans des conditions hydrothermales et non hydrothermales. Cette méthode permet aussi de modifier ou de maîtriser la morphologie du matériau.

Traditionnellement les solides à structure ouverte sont synthétisés par voie hydrothermale ou solvothérmale en présence d'une amine organique. Cette méthode est encore considérée comme un procédé chimique doux. Cependant, il existe des exemples où les phosphates à structure ouverte stables tels que A₂Cu₃(P₂O₇) (A= K, Rb) et Na₂Cs₂Cu₃(P₂O₇)Cl₂ qui ont été préparés dans des conditions plus agressives par

exemple par la méthode du sel fondu ou dans un flux de chlorure de métal alcalin à des températures élevées (500-800°C).

Enfin l'utilisation des méthodes combinatoires pour la synthèse de matériaux phosphatés permet d'explorer les nombreuses conditions de réaction et la caractérisation des nouveaux matériaux.

7. Elaboration d'un phosphate métallique et caractérisation structurale.

Pour illustrer la procédure de synthèse d'un phosphate métallique, on va considérer l'exemple d'une réaction typique :

- dans une première étape, le sel métallique est dissous ou dispersé dans l'eau sous agitation.
- dans la deuxième étape, la source de phosphate (comme l'acide phosphorique H_3PO_4) est ajoutée à la solution en obtenant un mélange de réaction très acide.
- ensuite l'amine (ou le sel d'ammonium) est ajoutée à ce mélange ce qui réduit l'acidité du milieu.
- le mélange réactionnel est transféré dans un bécher en téflon (le facteur de remplissage ~ 40-50%), puis scellé dans un autoclave en acier. L'autoclave est chauffé à 125-180 °C pendant environ 18-72 h. Dans ces conditions, la pression typique atteint environ 30-910 bar.
- à l'issue de la réaction, l'autoclave est retiré du four, refroidi à l'air jusqu'à la température ambiante, puis ouvert. Le produit solide obtenu est filtré et lavé avec de l'eau.

En nombreuses occasions, le produit de réaction est un mélange de phases, mais dans certains cas, il est possible d'obtenir une phase unique en faisant varier des paramètres tels que : la température, le temps, la composition, et le rapport des réactifs dans le mélange réactionnel.

En général, le produit obtenu est caractérisé à l'aide de :

- la diffraction des rayons X sur poudre (DRXP) : un diagramme de diffraction des rayons X en poudre, révèle immédiatement si le composé obtenu est une phase connue ou inconnue,
- la spectroscopie infrarouge : les spectres IR sont utilisés pour savoir si les amines ou les ions ammonium sont présents dans le matériau,
- l'analyse par dispersion d'énergie aux rayons X (ADEX) : elle permet de déterminer la proportion (ratio) métal / phosphore,

- l'analyse thermo-gravimétrique (ATG) : elle permet de déterminer la teneur totale des amines et de l'eau,
- la spectroscopie de Résonance Magnétique Nucléaire (RMN) à l'état solide : c'est une technique de caractérisation structurale extrêmement puissante, qui permet d'extraire des informations structurales très locales sur les matériaux étudiés. L'apport de cette technique à l'étude et à la caractérisation des matériaux, sera illustré dans ce chapitre, en soulignant son potentiel pour l'étude de ce type de matériaux.

Toutes ces informations, permettent de savoir si l'on est en face d'un matériau à structure ouverte ou seulement d'une phase condensée. Au cas où le produit obtenu est une nouvelle phase, sa structure peut être résolue soit par des méthodes *ab-initio* dans le cas d'un échantillon pulvérulent ou par des méthodes de diffraction pour un monocristal.

8. Rôle des molécules organiques.

L'utilisation du seul phosphate dans la conception de matériaux à charpente ouverte impose certaines restrictions en raison de la nature et la taille de l'ion phosphate PO_4^{3-} (et plus généralement de polyanions tétraédriques) qui sont les facteurs limitatifs, car ils doivent partager leurs oxygènes avec au moins trois autres cations pour assurer une structure tridimensionnelle. Cependant, la richesse des ligands organiques et la stabilité thermique du groupement phosphate peuvent être combinés pour créer de nouveaux matériaux à charpente ouverte. Les amines sont parmi les ligands organiques qui jouent un rôle important dans la formation des phosphates métallique à structure ouverte, mais leur rôle exact n'est pas encore clair. En plus de leurs fonctions en tant que cations nécessaires à l'équilibre des charges, ces molécules, dont le rôle fait appel à la notion de « template » (dont la meilleur traduction en français est « gabarit ») peuvent agir de trois manières distinctes

- comme espèces remplissant l'espace :

si la structure est souple, le template agit seulement comme un agent de remplissage.

- comme des agents structurants (ADS) :

lorsque, les formes du template et du cadre dans lequel il est introduit, sont liées, le template (amine) est appelé un agent structurant. (ADS). Au contraire du cas précédent le template est partie prenante dans la formation de la charpente.

- comme des véritables templates :

C'est l'extrapolation de la situation précédente. Le template, situé dans une cage à l'intérieur de la structure, garde sa conformation d'énergie le plus basse et une symétrie correspondant à celle de la cage où il n'est plus en mesure de tourner librement.

Cependant, les exemples de templates au vrai sens du terme sont rares et le terme de templates organiques est utilisé sans trop de rigueur pour décrire tous les cas où l'amine est présente dans la structure d'un phosphate métallique indépendamment de sa dimensionnalité.

9. Rôle du solvant.

Le solvant joue aussi un rôle important dans la synthèse des phosphates à structure ouverte. La synthèse hydrothermale, comme son nom l'indique, doit être effectuée en utilisant l'eau, mais l'utilisation des solvants non aqueux ou un mélange de solvants aqueux et non aqueux peut être efficace pour la synthèse des matériaux connus et/ou des nouveaux matériaux de structure ouverte car le transport des espèces chimiques et des ions dépend largement de leur interaction avec le solvant utilisé. Sachant que les solvants organiques possèdent des propriétés physiques tout à fait différentes (viscosité, constantes diélectriques,...etc.) de celles de l'eau, l'utilisation de solvants non aqueux ou mixtes conduit à des mobilités différentes de molécules et des ions. Ces différences de mobilité peuvent conduire à des nouveaux matériaux à structure ouverte puisque la cinétique joue un rôle majeur dans la formation de solides métastables.

Actuellement, les solvants non aqueux sont très fréquemment utilisés, et les plus couramment sont :

- les alcools : les monoalcools comme l'éthanol, le butanol...etc., et les polyalcools comme l'éthylène glycol,
- le tétrahydrofurane (THF),
- le diméthylsulfoxyde (DMSO),
- les dialkylformamides comme le diméthylformamide (DMF) et le diéthylformamide (DEF). Elles se décomposent souvent en diméthylamine et diéthylamine, qui à leur tour agissent en tant que templates.
- des autres solvants qui jouent ce double rôle de remplir l'espace tout en se décomposant. Ce sont les aminoalcools, comme le 2-hydroxy-propylamine.

10. Rôle du minéralisant.

Le minéralisant aide à solubiliser une substance insoluble ou peu soluble. Dans le domaine des phosphates à structure ouverte, l'ion F^- a été largement utilisé comme un minéralisant, et très souvent, les ions F^- sont alors intégrés dans le squelette en assemblant deux métaux grâce à des liaisons M-F-M. Ils peuvent être également observés comme groupement terminal -F, ou occlus dans la cage, donnant ainsi naissance à des charpentes oxyfluorées avec de nouvelles architectures.

L'utilisation de l'ion fluorure a permis d'obtenir de nombreux phosphates à structure ouverte qui possèdent des grands pores. Aujourd'hui, ce mode de formation n'est pas limité seulement aux phosphates de gallium (GaPO) ou d'aluminium (AlPO) mais inclut les phosphates de V, Fe, Zr, Ti, Ni, In, et Sb.

L'ion Cl^- a été beaucoup utilisé dans la synthèse des phosphates de zinc, mais il est rarement incorporé dans la charpente. Les ions chlorures peuvent se trouver en position terminale dans la charpente ou comme liens entre deux atomes de zinc dans le cas de phosphates de zinc de structure bidimensionnelle et tridimensionnelle.

En dehors des ions F^- et Cl^- , le tétraéthylorthosilicate $\text{Si}(\text{OEt})_4$, a été utilisé dans la synthèse des phosphates de gallium où il améliore la cristallinité tout en agissant comme minéralisant.

11. Effet de pH, pression, température et temps de réaction.

Le pH joue un rôle important et complexe dans la formation des phosphates à structure ouverte, il influe sur:

- la nature des produits formés,
- l'hydratation de l'amine,
- la nature et le type de connectivité de l'atome métallique avec les polyèdres voisins.

Par exemple, les zéolithes aluminosilicates, qui sont toujours synthétisées en milieu basique, sont composées de tétraèdres unis entre eux par des sommets en communs, alors que les phosphates métalliques, qui sont préparés en milieu acide, semblent former des bipyramides et des octaèdres à des valeurs moyennes du pH, et des octaèdres avec sommets et arêtes communs à des valeurs du pH basses (en milieu fluorure). Il est également constaté que la taille de la SBU (*Secondary Building Unit* ou unités de construction secondaires. Elles sont à distinguer des unités de construction primaires par exemple les tétraèdres PO_4 .) dont le rôle sera précisé au paragraphe suivant augmente avec l'abaissement du pH. Ces observations sont, en grande partie, spécifiques aux phosphates de gallium et ne peuvent être étendues aux phosphates de zinc. Néanmoins, elles suggèrent que le pH du milieu joue un rôle important.

La plupart des réactions hydrothermales sont effectuées pendant environ 18-72 h, et en principe, seul le produit final est examiné. Il résulte probablement de la transformation de plusieurs intermédiaires et il est donc important d'examiner l'évolution des phases avec le temps afin de comprendre le mécanisme de formation de ces solides. Toutefois, comme les réactions hydrothermales se déroulent dans des récipients fermés sous pression autogène, des techniques spéciales sont donc nécessaires pour la réalisation des études *in situ*, qui restent encore limités.

À des pressions et températures élevées, les propriétés physiques du solvant, telles que la viscosité et la constante diélectrique, changent ce qui peut à son tour influencer la nature des composés formés. Bien que ces données soient bien étudiées dans le cas de l'eau, les études sur la nature des phases en fonction de la pression n'ont pas été encore réalisées.

12. Les différentes dimensionnalités des phosphates à structure ouverte.

12. 1. Définitions.

Un cristal se définit comme un assemblage périodique en trois dimensions d'unités structurales identiques se répétant à l'infini. Ces unités structurales peuvent être constituées par des atomes, des ions ou des groupes d'atomes reliés entre eux par des liaisons covalentes, des molécules. Ces unités peuvent être une molécule, une partie d'une molécule ou une partie d'une structure étendue. C'est cette dernière catégorie qui est impliquée dans la suite de notre discussion.

L'unité asymétrique des phosphates métalliques à charpente ouverte est constituée de deux entités distinctes :

1. des atomes reliés par des liaisons covalentes en formant le réseau inorganique (M, P, O, F / Cl),
2. de la totalité ou d'une partie de l'amine organique (souvent protonée).

12. 2. Les structures zéro-dimensionnelles.

Si dans une structure cristalline, les liaisons covalentes ne s'étendent pas à l'infini dans aucune direction de l'espace, elle est nommée comme une structure « zéro-dimensionnelle ». Ce type structural peut être un cluster moléculaire simple ou un complexe (par exemple un anneau isolé à quatre chaînons formé par deux atomes métalliques et deux atomes de phosphore reliés entre eux par des atomes d'oxygène), ou bien une structure plus complexe conduisant à un cluster plus étendu.

12. 2. 1. Exemple 1.

La structure zéro-dimensionnelle possède souvent un anneau à quatre chaînons formé par deux atomes métalliques et deux atomes de phosphore reliés par des atomes d'oxygène. En outre, il peut y avoir des groupes $\text{HPO}_4/\text{H}_2\text{PO}_4$ pendentifs au centre métallique pour compléter la coordination du métal. C'est le cas de la structure de phosphate de zinc de formule $[\text{C}_6\text{H}_{18}\text{N}_2][\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$ [22], qui est construite par des tétraèdres de H_2PO_4 et ZnO_4 , liés entre eux alternativement pour former l'anneau à quatre chaînons. On trouve aussi les groupes HPO_4 et H_2PO_4 coordonnés à l'atome de Zn (Figure 2). Ces anneaux isolés à quatre chaînons forment des liaisons hydrogène avec l'amine en figeant ainsi l'assemblée cristalline tridimensionnelle. L'anneau de quatre chaînons est une SBU, qui est la plus souvent rencontrée dans les zéolites et les phosphates à charpente ouverte.

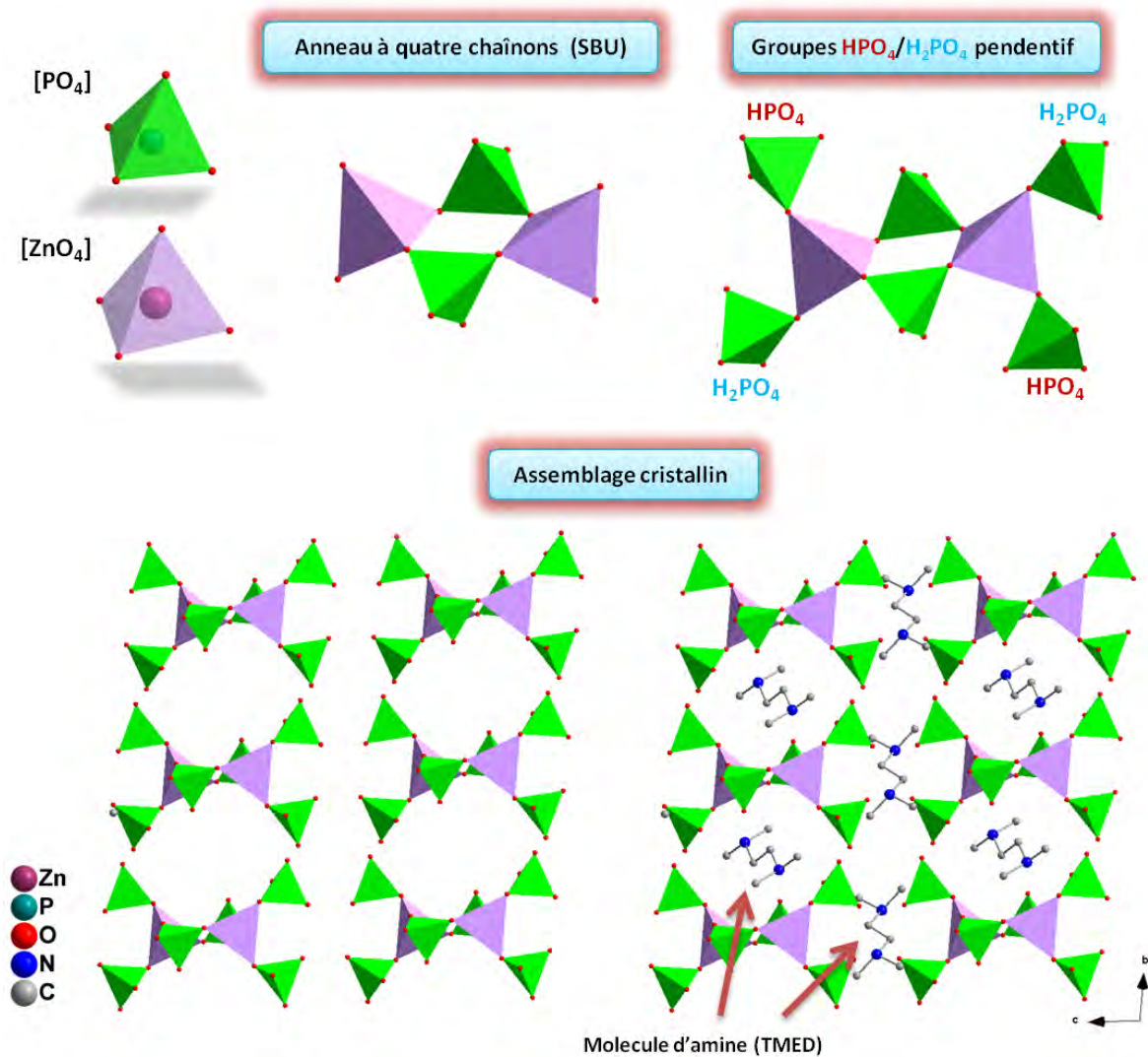


Figure 2. Structure zérodimensionnelle de phosphate de zinc de formule $[C_6H_{18}N_2][Zn(HPO_4)(H_2PO_4)_2]$.

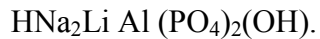
12. 3. Les structures monodimensionnelles.

Une structure cristalline est dite monodimensionnelle, lorsque la charpente covalente s'étend dans une seule direction de l'espace. Les structures monodimensionnelles des phosphates métalliques templétés présentent une grande variété. Cette charpente peut être constituée par une seule chaîne formée alternativement de polyèdres oxygénés entourant le métal et le phosphore ou bien par une chaîne limitée de polyèdres oxygénés métalliques qui peut être reliée à une chaîne similaire par des groupements phosphates. Se rencontrent également des anneaux (comme exemple l'anneau à quatre chaînons) qui sont regroupés pour former une chaîne et finalement des structures complexes impliquant simultanément certains motifs précédents. Beaucoup de structures monodimensionnelles sont isostructurales de certains minéraux.

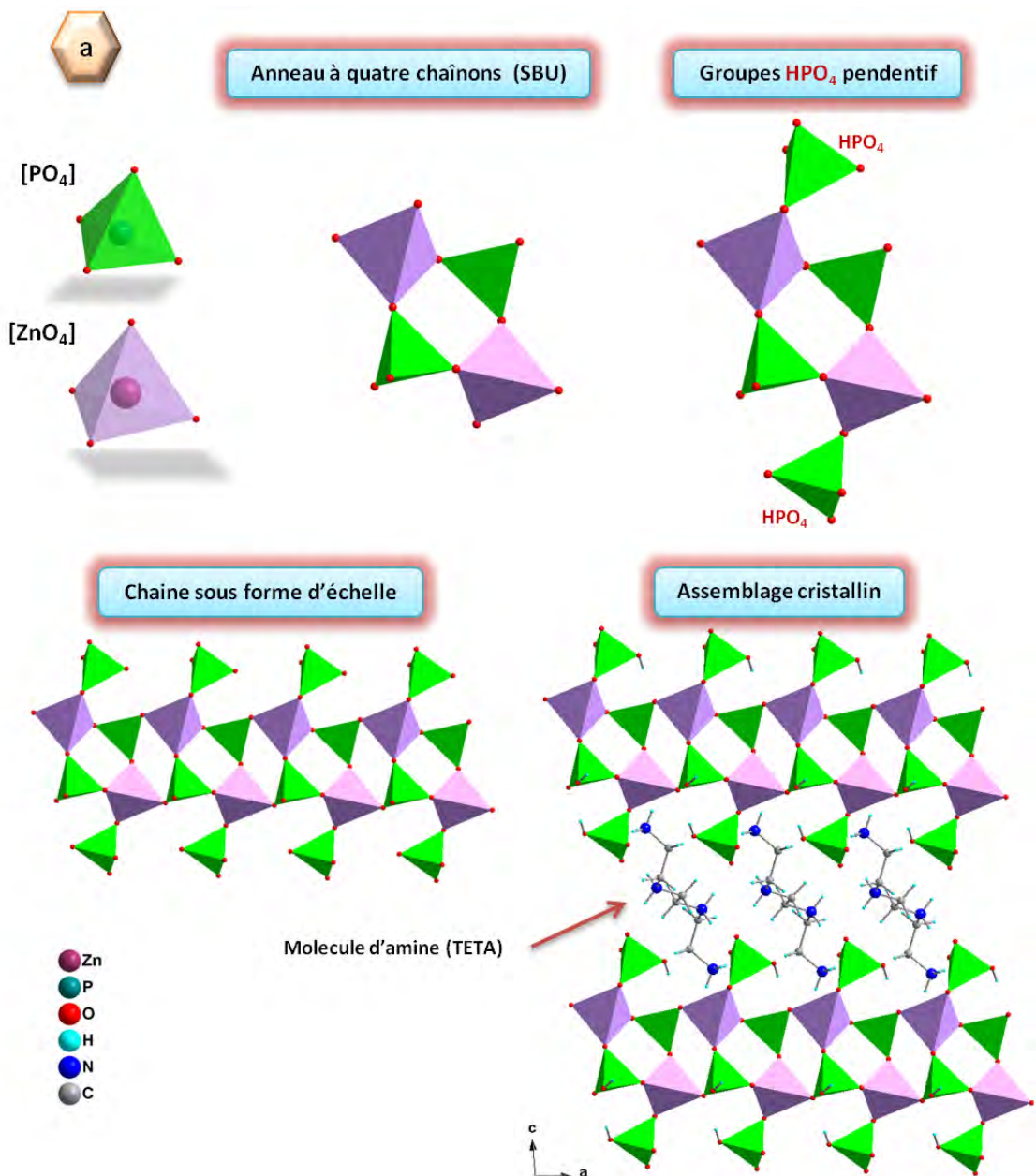
Dans le cas d'une géométrie de coordination tétraédrique du métal : la chaîne est formée d'anneaux à quatre chaînons partageant soit :

- des arêtes ; dans ce cas la chaîne est connue sous le nom « échelle ».
- des sommets.

Dans le cas d'une géométrie de coordination octaédrique du métal, la structure la plus rencontrée est celle de chaînes de sommet commun d'octaèdres doublement reliés par des groupes phosphates, comme dans le cas du minéral « *Tancoite* » de formule



Prenons comme exemple quelques-unes de structures monodimensionnelles rencontrées dans la littérature.



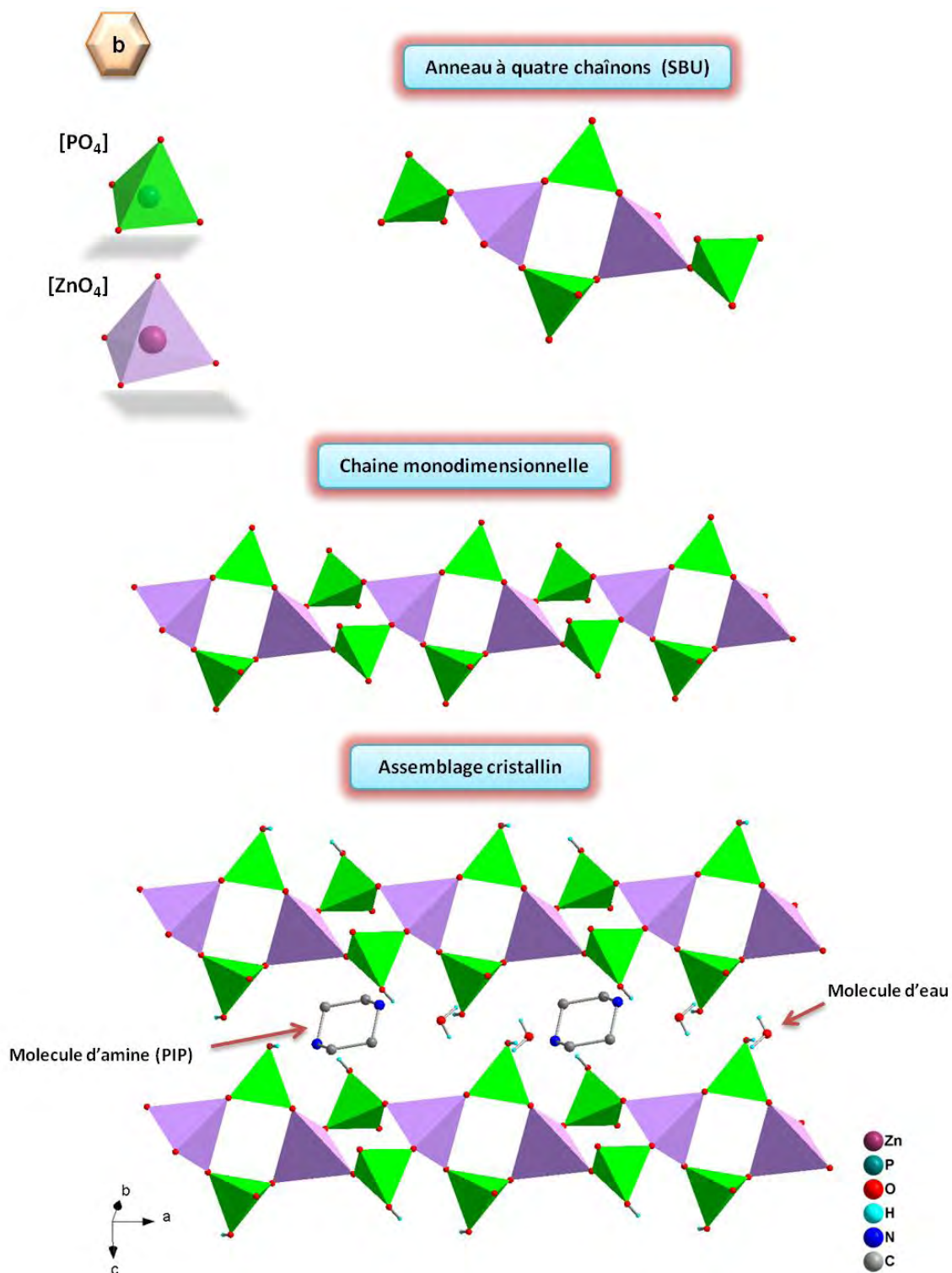


Figure 3. Structure monodimensionnelle des phosphates de zinc templatés : (a) le cas de $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ où les anneaux à quatre chaînons partagent les arêtes. (b) le cas de $[C_4N_2H_{12}][Zn(HPO_4)_2] \cdot H_2O$ où les anneaux à quatre chaînons partagent les sommets.

12. 3. 1. Exemple 1.

Les structures de type « échelle » comme le cas de phosphate de zinc de formule $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ [23] (Figure 3a) où les groupes ZnO_4 et HPO_4 sont connectés alternativement, pour former des anneaux à quatre chaînons. Ceux-ci partagent des arêtes pour créer une chaîne sous forme d'échelle avec des tétraèdres de HPO_4 greffés sur cette chaîne, qui agissent comme pendentifs à la chaîne anioniques monodimensionnelle. Entre les deux chaînes se trouvent des molécules protonées de triéthylentetramine (TETA) qui équilibrent la charge et stabilisent l'assemblage cristallin à travers des liaisons hydrogène fortes avec les oxygènes de la fraction inorganique.

En revanche, les anneaux à quatre chaînons formés par les groupes ZnO_4 et HPO_4 , dans le cas de phosphate de zinc de formule $[C_4N_2H_{12}][Zn(HPO_4)_2] \cdot H_2O$ [15], ont des sommets communs en formant la chaîne monodimensionnelle (Figure 3b). Il faut signaler que dans ce cas, il n'existe pas des groupes HPO_4 en pendentifs associés à l'atome de Zn parce que tous les atomes d'oxygènes coordonnés au Zn proviennent de groupes ponts HPO_4 .

11. 3. 2. Exemple 2.

Dans le cas du phosphate de fer(III) de formule $[C_4N_2H_{12}]_{0.5}[FeF(HPO_4)(H_2PO_4)]$ [24], le métal adopte une coordination octaédrique, la charpente inorganique anionique se compose de polyèdres FeF_2O_4 , $PO_3(OH)$, et $PO_2(OH)_2$ qui partagent les sommets, formant ainsi des chaînes infinies qui se prolongent le long de l'axe a . Les molécules de pipérazine sont insérées entre ces chaînes comme le montre la Figure 4. Dans ces chaînes anioniques, les octaèdres FeF_2O_4 partagent leurs sommets F en position trans, en créant une épine dorsale linéaire infinie $\{-Fe-\mu F-Fe-\mu F-Fe-\}$. Les tétraèdres $PO_3(OH)$ et le $PO_2(OH)_2$ sont greffés sur la chaîne en pontant les octaèdres FeF_2O_4 de façon symétrique .

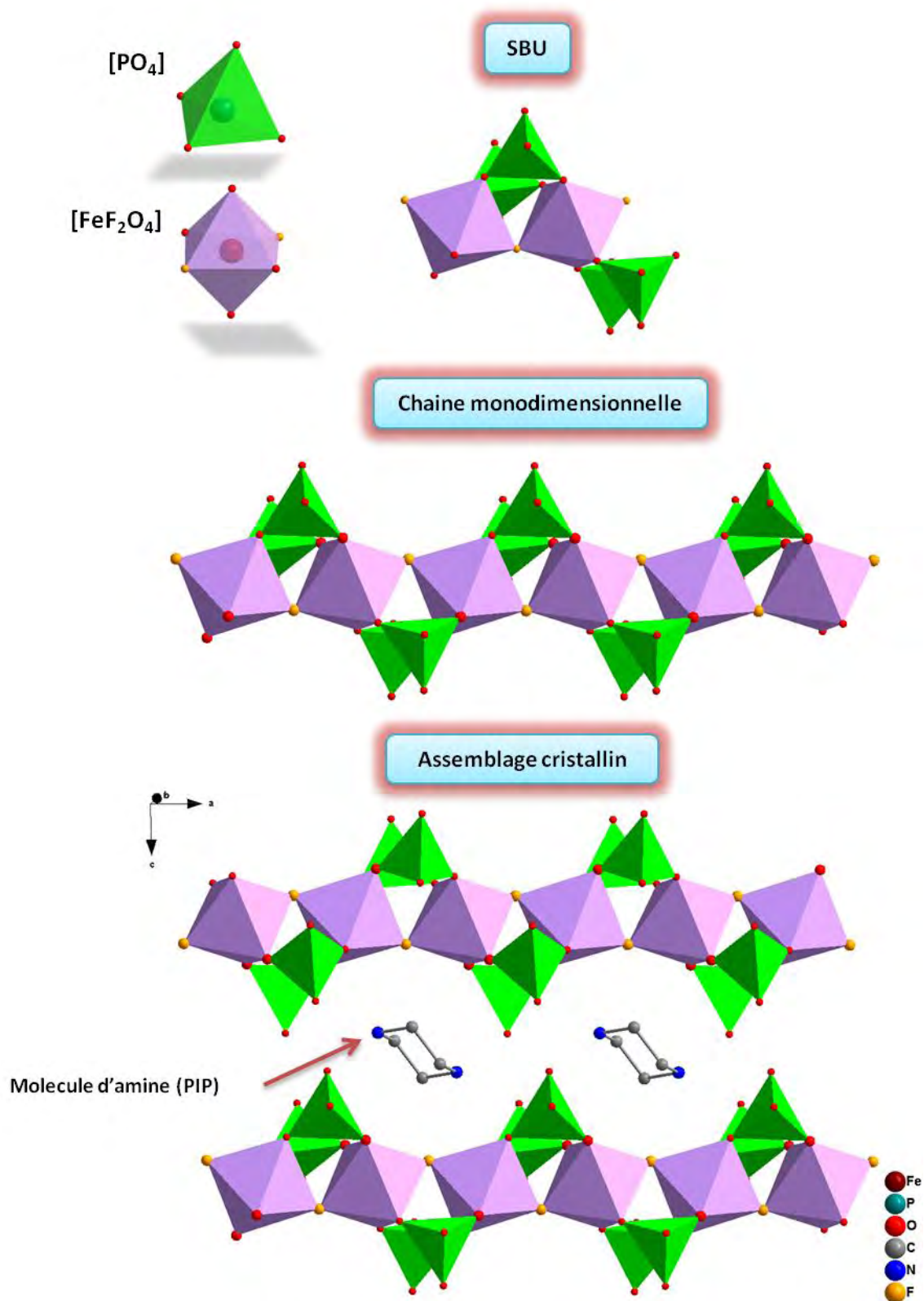


Figure 4 : Structure monodimensionnelle d'un phosphate de fer(III) templaté par pipérazine.

12. 3. 3. Exemple 3.

Un autre exemple intéressant d'une structure monodimensionnelle est illustré dans le cas d'un phosphate de cobalt (III) templaté par la pipérazine, de formule $[C_4H_{12}N_2]_{1.5}[Co(HPO_4)(PO_4)] \cdot H_2O$ [15] : on observe deux chaînes à quatre chaînons partageant un sommet. Ces chaînes sont reliés entre eux par un atome d'oxygène dont le nombre de coordination égale trois (Figure 5).

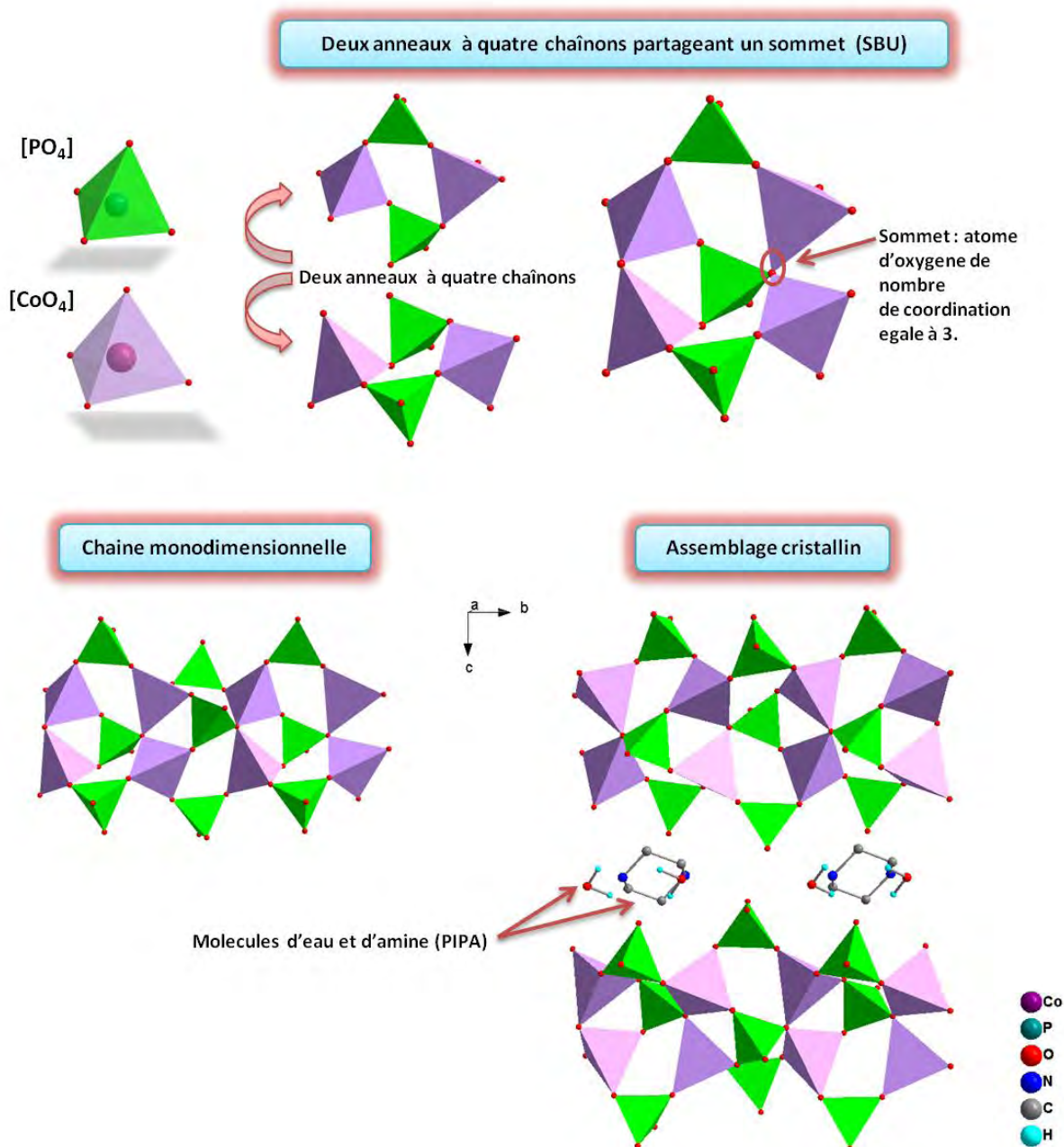


Figure 5. Structure monodimensionnelle d'un phosphate de cobalt(III) templaté par la pipérazine.

12. 4. Les structures bidimensionnelles.

Les structures bidimensionnelles (ou lamellaires) de phosphates métalliques templétés sont très diverses, soit en terme de stœchiométrie ce qui se reflète par la proportion variable du rapport M / P , soit en terme de variété structurale où, pour une même stœchiométrie, des topologies très diverses sont observées. Les structures lamellaires peuvent être construites par le partage des sommets des polyèdres métallique et des tétraèdres PO_4 d'une manière strictement alternative conduisant à de nombreuses ouvertures dans la couche. Elles peuvent également résulter de la condensation de certaines chaînes ou de certaines « SBUs » particulièrement fréquentes. Il est donc difficile de trouver des points communs entre les structures lamellaires.

Prenons l'exemple des trois structures lamellaires différentes les plus fréquemment rencontrées dans la littérature :

12. 4. 1. Exemple 1 :

l'aluminophosphate de formule chimique $[C_5H_{12}N][C_5H_{16}N_2][Al_3(PO_4)_4]$ [25] a une structure lamellaire avec une proportion Al / P de 3:4. La stœchiométrie $Al_3P_4O_{16}^{3-}$ se retrouve dans de nombreux composés 2D qui possèdent des topologies différentes. Elle est typique de cette famille de phosphate. La structure est construite à partir de l'enchaînement alternatif de tétraèdres AlO_4 et PO_4 dans lequel tous les sommets de AlO_4 et trois quarts des sommets des groupements PO_4 sont liés entre eux. Cet enchaînement de groupements AlO_4 et PO_4 forme une couche (Figure 6). Ces couches sont empilées selon une séquence *AAAA*, c'est-à-dire sans décalage d'une couche à l'autre. Cependant, la séquence d'empilement pourrait être différente (*ABAB* par exemple, c'est à-dire un décalage d'une chaîne par rapport à l'autre) pour la même stœchiométrie avec amine différente au sein du réseau.

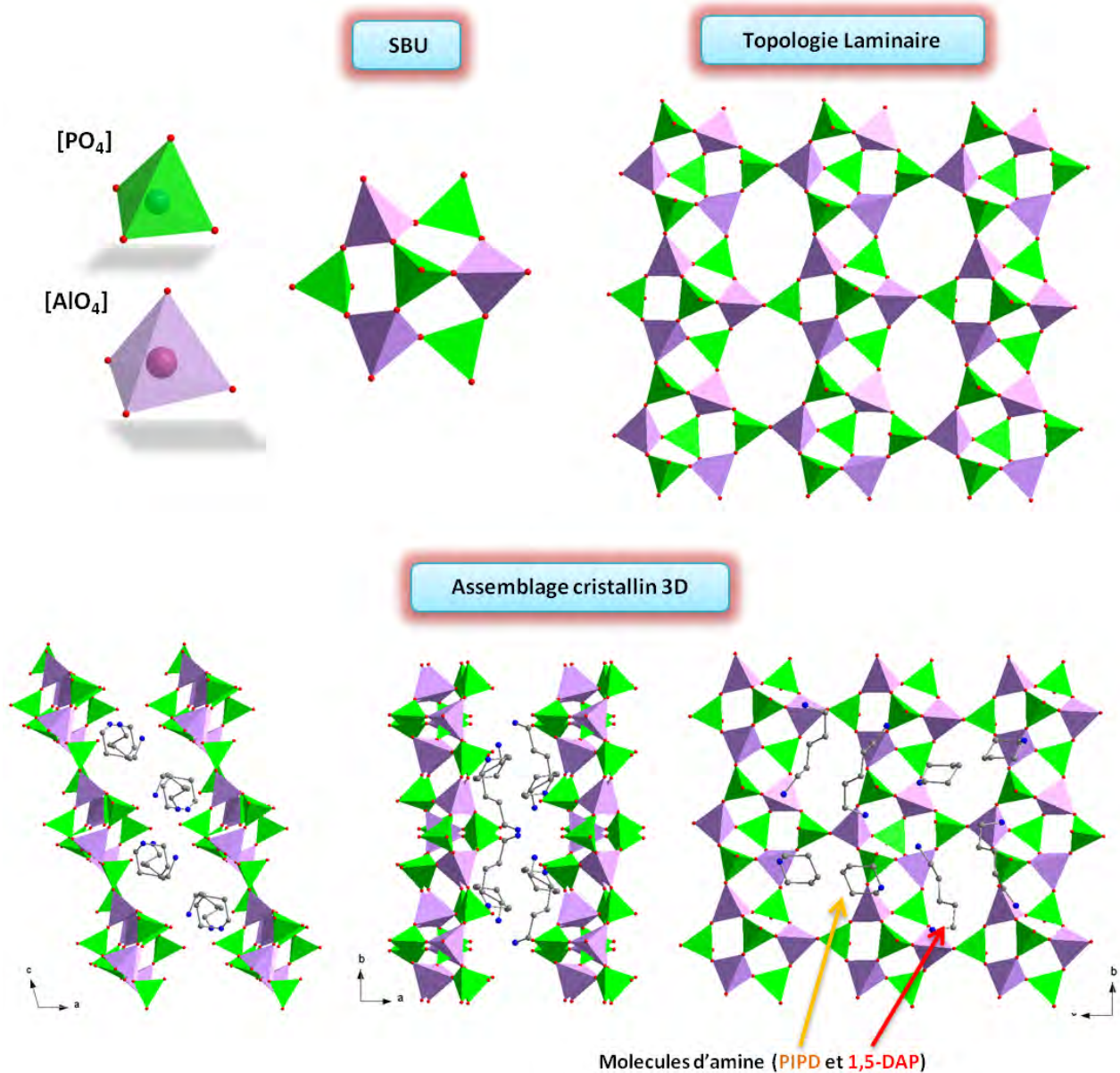


Figure 6. Structure bidimensionnelle d'un aluminophosphate templaté par la pipéridine et 1.5-diaminopentane.

12. 4. 2. Exemple 2.

Un autre exemple d'une topologie lamellaire usuelle est illustré par le phosphate de cobalt(II) de composition $[C_4H_{12}N_2]_{1.5}[Co(HPO_4)(PO_4)] \cdot H_2O$ [15], qui appartient à d'autres familles de phosphates métalliques. La connectivité des tétraèdres CoO_4 et HPO_4 donne naissance à des anneaux à quatre chaînons, qui sont liés par les arêtes formant des chaînes monodimensionnelles sous forme d'une échelle en zigzag. Ces chaînes sont reliées par un groupement phosphate comme le montre la Figure 7, résultant en la formation d'une ouverture à douze chaînons.

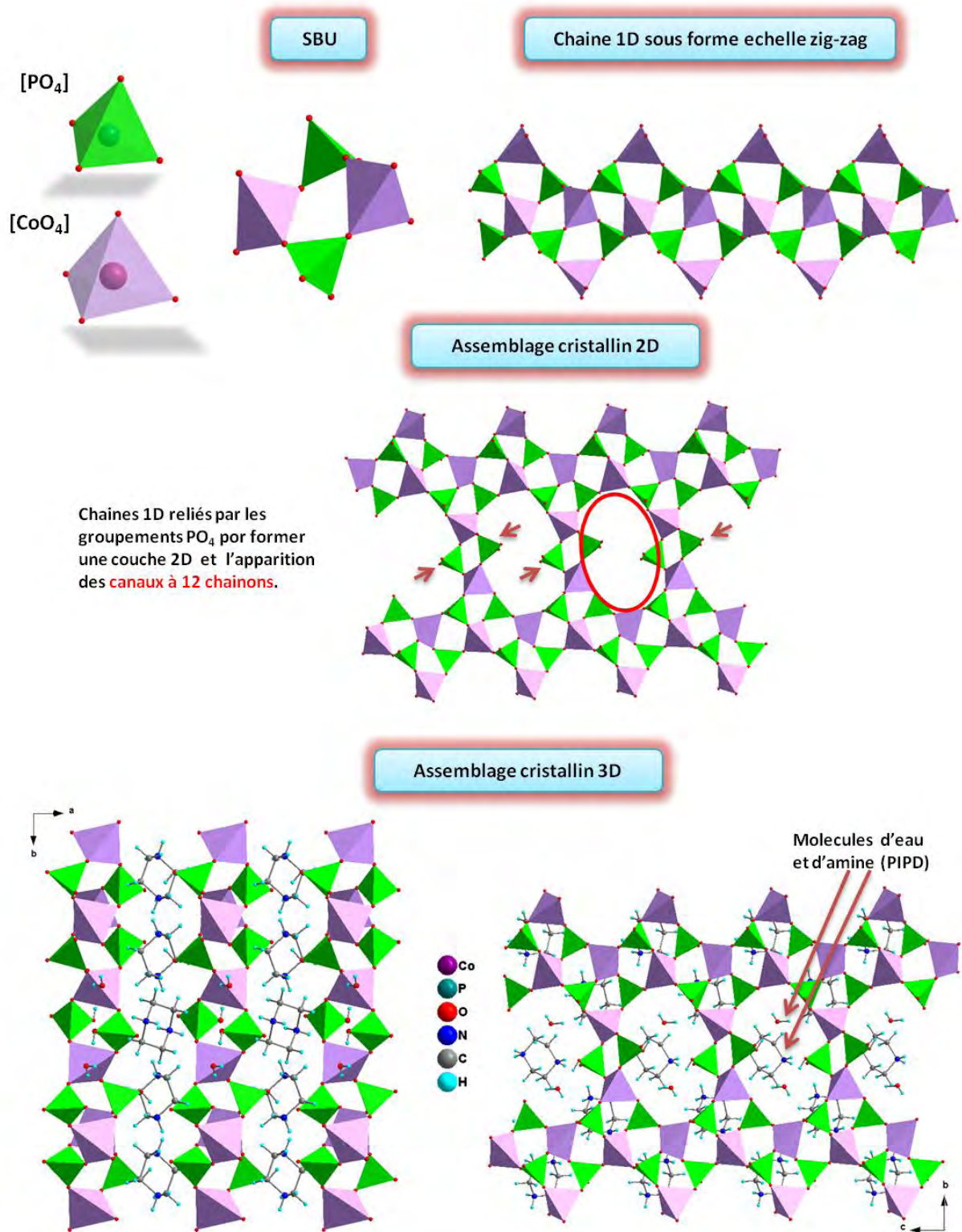


Figure 7. Structure bidimensionnelle d'un phosphate de cobalt(II) templaté par la pipéridine.

12. 4. 3. Exemple 3.

La structure lamellaire de phosphate de vanadium de composition chimique $(C_2H_9N_2)VOPO_4$ [26], est constituée par l'enchaînement linéaire des octaèdres VO_5N associés par leurs sommets en position trans. Ces chaînes sont reliées transversalement entre elles par les tétraèdres PO_4 , formant la structure lamellaire (Figure 8).

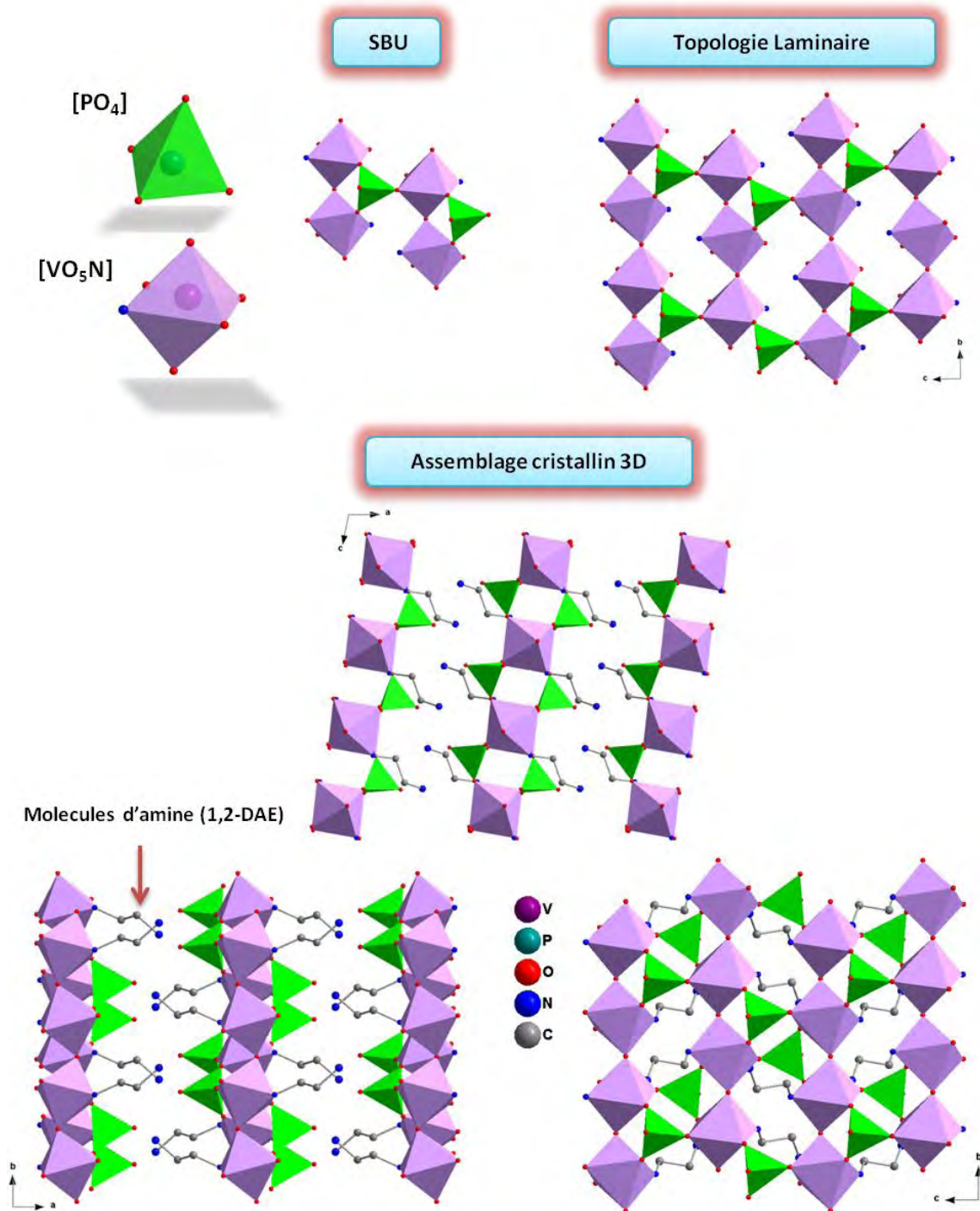


Figure 8. Structure bidimensionnelle d'un phosphate de vanadium templaté par le 1,2-diaminoethane.

Une autre caractéristique intéressante de cette structure est que l'atome d'azote du groupement éthylènediamine est lié au vanadium pour compléter sa coordination octaédrique. Ce rôle supplémentaire de l'amine est aussi observé dans d'autres phosphates métalliques.

12. 4. 4. Exemple 4.

Les lanthanides sont caractérisés par un degré d'oxydation +3 en général, un numéro de coordination élevé, et une géométrie de coordination variable, donc il était évident de supposer qu'on retrouvera une grande diversité structurale en type de charpente pour cette famille des éléments. Mais étonnamment, il n'y a que quelques exemples trouvés dans la littérature des structures connues de phosphate des lanthanides templatés à charpente ouverte.

Un exemple d'une topologie lamellaire non-usuelle, caractérisée par un numéro de coordination élevée (8) est illustré par le phosphate de cerium (IV) templaté de composition chimique $[(\text{CH}_2)_2(\text{NH}_3)_2]_{0.5}[\text{CeF}_3(\text{HPO}_4)]$ [27]. La structure est constituée par l'enchaînement zig-zag des polyèdres octa-coordonnés CeO_3F_5 associés par leurs arrêts F-F. Ces chaînes sont reliées transversalement entre elles par les tétraèdres PO_4 , formant la structure lamellaire (Figure 9).

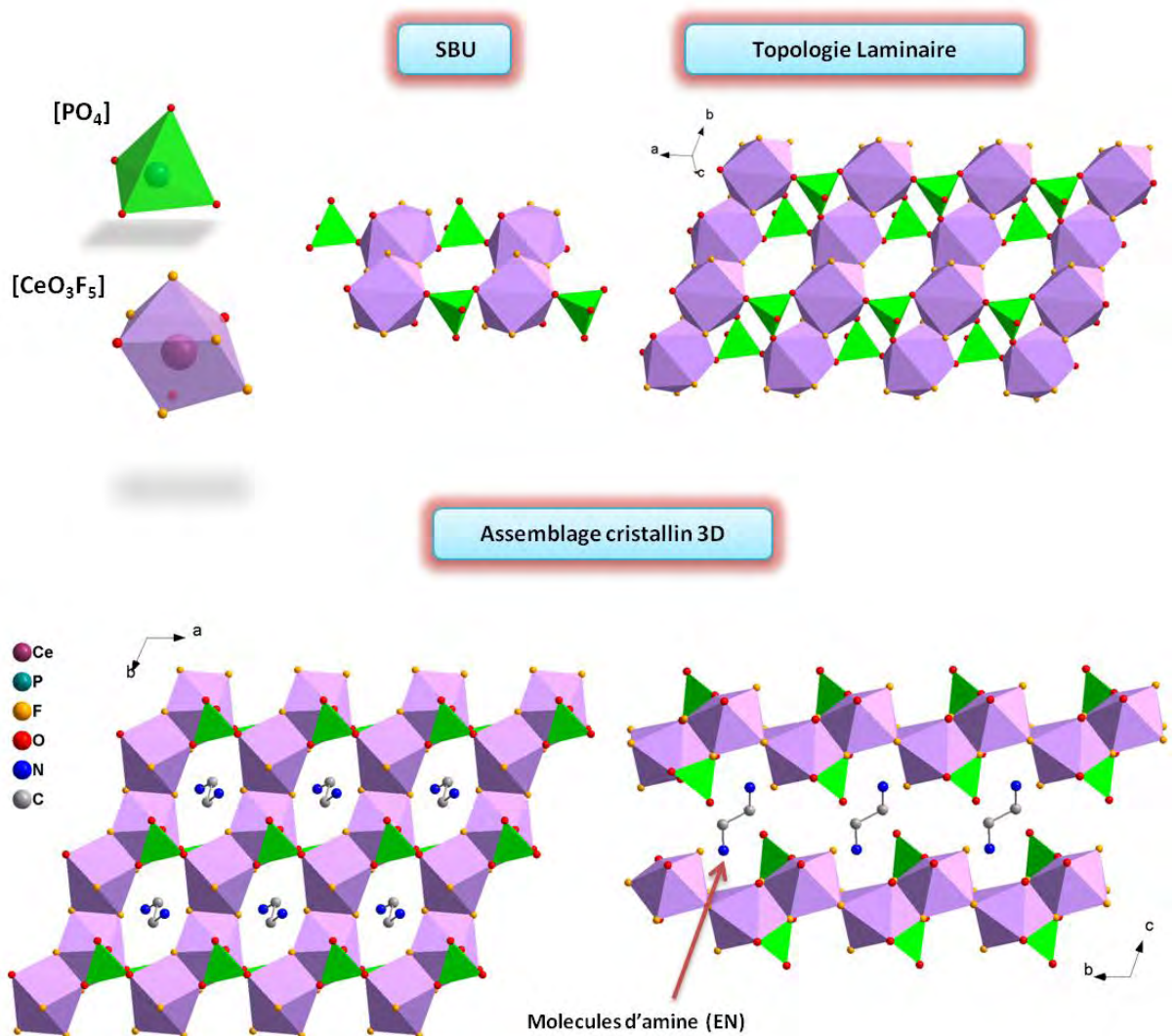


Figure 9. Structure bidimensionnelle d'un phosphate de cerium(IV) templaté par le 1,2-diaminoéthane.

12. 5. Les structures tridimensionnelles.

Une structure est dite tridimensionnelle lorsque la connectivité des liaisons fortes s'effectue dans les trois directions de l'espace.

Les phosphates métalliques tridimensionnels à charpente ouverte sont parfois totalement réticulés (similaire aux zéolites) lorsque tous les atomes d'oxygène des tétraèdres PO_4 sont connectés au métal. La charpente peut être interrompue par un ou deux groupes terminaux HPO_4 ou H_2PO_4 . Dans ces deux cas, la structure peut avoir ou non des canaux croisés dans une, deux ou trois directions de l'espace et dans la plupart des cas :

- la charpente est chargée négativement (sauf dans certains de premiers aluminophosphates (AlPO) où elle était neutre, l'amine organique – par exemple tetraalkylammoniumhydroxide étant également neutre),
- l'amine organique (sous forme protonée) ou le cation alcalin, résident dans les canaux et équilibrent la charge de la charpente. L'amine peut également interagir par des liaisons hydrogène avec la charpente.

Dans beaucoup de phosphates métalliques, la coordination du métal est supérieure à 4, avec :

- une bipyramide trigonale ou pyramidale à base carrée, de coordination cinq,
- un octaèdre de coordination six

Si le nombre de coordination cinq ou six n'est pas satisfait par les oxygènes du groupe PO_4 , les coupures au sein de la charpente peuvent survenir par des groupes terminaux $-\text{H}_2\text{O}$, $-\text{OH}$, ou par des atomes de fluor.

Dans le cas des systèmes de coordination cinq et six, on trouve fréquemment un enchaînement M-X-M ($\text{X} = \text{O}$, OH , ou F) fini ou infini, alors que dans le cas des systèmes de coordination tétraédriques ces enchaînements sont interdits par la règle de Lowenstein, qui est strictement suivie dans le cas de l'aluminium. Dans le cas des phosphates de zinc, par exemple $[\text{C}_6\text{H}_{22}\text{N}_4]_{0.5}[\text{Zn}_3(\text{HPO}_4)(\text{PO}_4)_2]$, les enchaînements Zn-O-Zn dans lesquels l'oxygène du groupe phosphate devient tricoordonné ont été observés.

Quelle que soit la dimensionnalité des phosphates métallique templétés, il y a toujours un cation organo-ammonium qui interagit avec le réseau inorganique anionique par des liaisons hydrogène ou des forces de van der Waals pour rigidifier la charpente cristalline en trois dimensions. Pour cette raison, de nombreux auteurs préfèrent ajouter l'adjectif «prépondérant» quant à la dimensionnalité : la structure est prépondérante—monodimensionnelle et ainsi de suite. Dans le cas de structures « tridimensionnelles », il n'y a aucune ambiguïté. Lorsque la densité de charpente* (DC) est inférieure ou proche de la limite supérieure ($\text{DC} = 21$), comme dans le cas des zéolites réticulées, elle porte le nom de structure à charpente ouverte. On peut étendre cette notion aux phosphates pour les distinguer des structures condensés tridimensionnelles.

Prenons trois exemples de prototypes pour comprendre la description structurale.

* *Densité de Charpente (DC) est définie comme le numéro des atomes T (atomes en positions tétraédriques) par 1000 \AA^3 de volume, cette définition a été introduite pour les zéolithes et à la suite elle a été extrapolée à d'autres types de composés, tels que les phosphates, pour distinguer si la structure est à charpente ouverte.*

12. 5. 1. Exemple 1.

Soit le phosphate de cobalt(II) de composition $[\text{C}_2\text{N}_2\text{H}_{10}]_2[\text{Co}_4(\text{PO}_4)_4]\cdot\text{H}_2\text{O}$ [28], où le rapport Co/P est de 1/1. La connectivité alternative stricte des tétraèdres CoO_4 et PO_4 conduit au réseau à charpente ouverte comme le montre la Figure 10. La structure est construite à partir d'anneaux qui réunissent deux entités de deux groupements CoO_4 et PO_4 liés entre eux par leurs sommets (1^{ère} SBU et 2^{ème} SBU de la figure 9). Ces nouvelles entités à huit tétraèdres (*D4R pour Double Four Rings*) sont reliées les unes aux autres *via* des atomes d'oxygène à huit autres unités identiques, à travers des liaisons Co-O-P, en formant des canaux à huit chaînons dans les trois directions cristallographiques. Les molécules d'eau et les molécules d'éthylènediamine protonées se placent à l'intérieur de ces canaux. Ce type de topologie a été prévu théoriquement il y a 40 ans. (Le code de cette charpente dans les publications sur les zéolithes est ACO : *schématiquement il correspond à une structure ayant la symétrie ou presque la symétrie d'un cubane soit un cube environné par 8 autres cubes*).

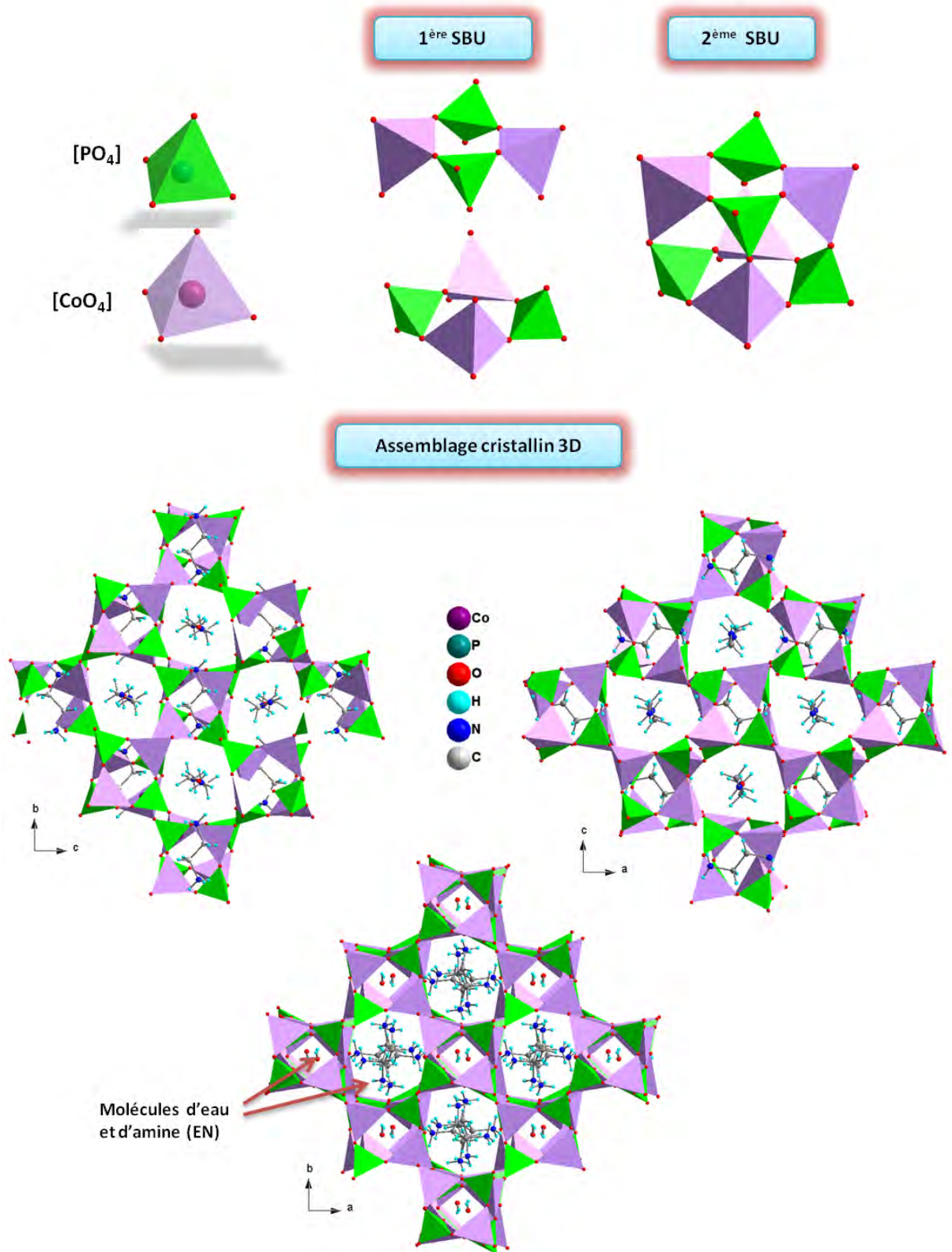


Figure 10. Structure d'un phosphate de cobalt (III) tridimensionnel à charpente ouverte.

12. 5. 2. Exemple 2.

Prenons un autre exemple d'une structure complexe, illustrée dans le cas de d'un phosphate de gallium MIL-31 (Figure 11), de formule $[C_{20}H_{52}N_4][H_3O][Ga_9(PO_4)_9F_3(OH)_2(H_2O)] \cdot 2H_2O$ [29]. La structure de MIL-31 est construite à partir de deux types d'unités de construction hexamériques Ga_3P_3 (SBU-6 *unité de construction secondaire à six unités de construction primaires*) différentes, où les polyèdres de gallium possèdent trois modes de coordinations différentes: tétraédrique, bipyramide trigonale, et octaédrique. La connectivité entre les unités SBU-6 conduit à une structure tridimensionnelle avec des canaux à 18 chaînons.

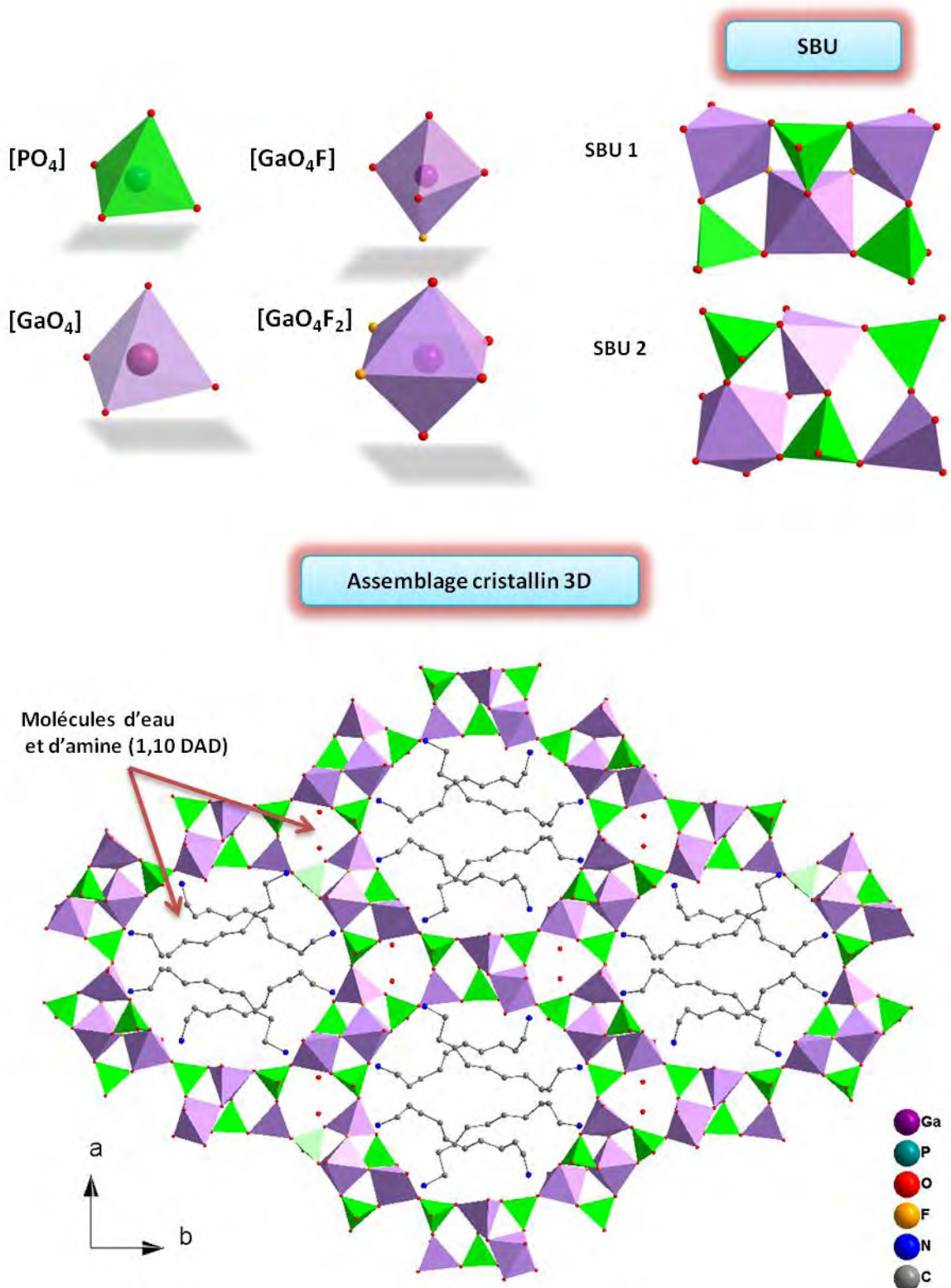


Figure 11. Structure d'un phosphate de gallium MIL-31 tridimensionnel à charpente ouverte et les deux unités de construction hexamérique impliquées SBU (1 et 2).

12. 5. 3. Exemple 3.

Prenons le cas d'un exemple complexe où l'unité de construction secondaire SBU n'est pas reconnaissable, comme dans le cas du phosphate de fer(III) de formule $[C_4N_3H_{16}]_2[Fe_5F_4(H_2PO_4)(HPO_4)_2(PO_4)_4] \cdot 0.5H_2O$ [30], de structure tridimensionnelle avec des canaux à 18 chaînons. Le réseau complexe dans cette structure est construit à partir de polyèdres FeO_4F_2 , FeO_5F , FeO_6 , PO_4 , PO_3OH , et le $PO_2(OH)_2$, ayant une connectivité Fe-X-Fe infinie ($X = O, F$), avec la présence d'un dimère inhabituel de groupements FeO_6 et PO_4 partageant une arête. Sans entrer dans les détails des connectivités de polyèdres, on peut discerner les couches de cette structure 3D dans l'encadré de la Figure 12. Elles sont reliées par les tétraèdres PO_4 le long de l'axe c (en formant un anneau à quatre chaînons) pour constituer la structure 3D. Un tel mécanisme de liaison entre ces couches, induit la formation des canaux elliptiques à 18 chaînons le long de l'axe a (voir figure 11) et des canaux à 10 chaînons le long de l'axe b. L'empilement ABAB des couches parallèles au plan *ab* rend les ouvertures à sept chaînons inaccessibles.

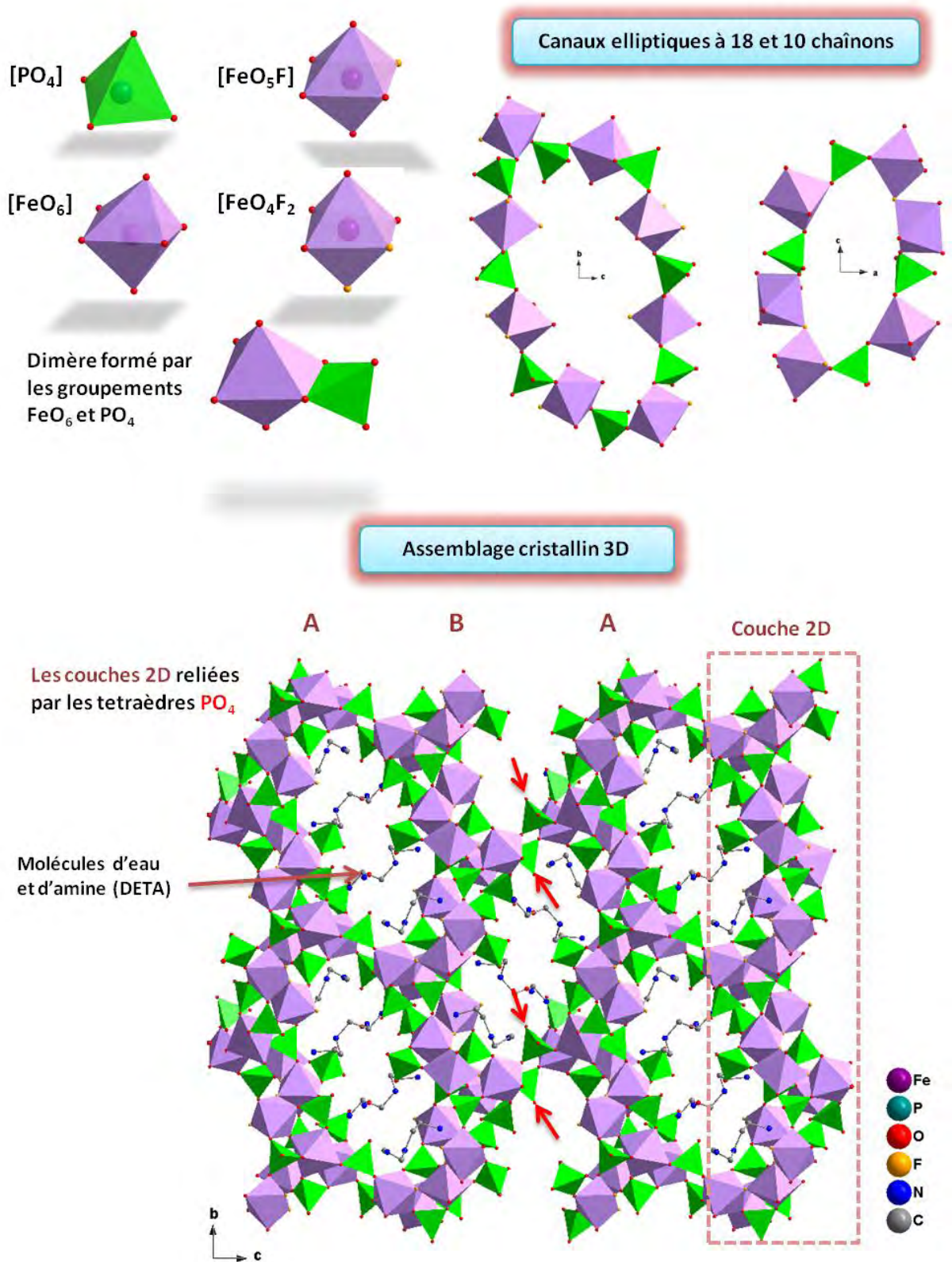


Figure 12. Structure d'un phosphate de fer(III) tridimensionnel à charpente ouverte.

13. Introduction à la Résonance Magnétique Nucléaire à l'État Solide (RMNES)

13.1. Description de la technique

La spectroscopie de Résonance Magnétique Nucléaire à l'État Solide (RMNES) est une technique d'analyse utilisée pour étudier la structure et la dynamique des solides cristallins, amorphes ou désordonnés organiques, inorganiques ou hybrides. La source du signal de RMN est le noyau atomique avec un moment cinétique intrinsèque (ou spin), et par conséquent avec un moment magnétique. Lorsque l'échantillon est placé dans un champ magnétique externe B_0 (Figure 13), une différence d'énergie ΔE est créée entre les états nucléaires magnétiques. L'excitation du système des spins nucléaires est réalisée avec des impulsions radiofréquences résonantes de fréquence $\nu = \gamma B_0 / 2\pi$, où γ est le rapport gyromagnétique du noyau. Cette fréquence relativement faible (quelques centaines de MHz) indique que la séparation de l'énergie des états de spin est assez faible. Puisque les noyaux dans chacun des états sont en équilibre, leurs nombres dans les différents états de spin seront semblables (en fait, parce qu'il y a une distribution de Boltzmann parmi les états de spin, quelques noyaux de plus résident dans les états de plus basse énergie). Parce que le rayonnement incident est également susceptible de provoquer une émission stimulée (passage du haut état vers le bas état) comme absorption, l'effet RMN dépend d'un petit excès de noyaux dans les états les plus bas. Cela fait de la RMN une technique intrinsèquement insensible (d'autant plus que, par exemple, les spectroscopies vibrationnelles et électroniques). Les informations fournies par la RMN ne dépend pas seulement du type de noyaux, mais aussi informations sur les caractéristiques de l'environnement électronique dans lequel les noyaux sont immergés et les positions des noyaux dans les molécules. Ainsi, en RMN, les noyaux magnétiques sondent la structure moléculaire, ils sondent aussi le mouvement moléculaire interne (si ce n'est pas plus rapide que l'échelle de temps de RMN) et la mobilité des molécules. Un exemple de la façon dont RMNES peut sonder la dynamique moléculaire est illustré dans la Figure 14. Les lignes spectrales de la RMN des échantillons liquides sont beaucoup plus étroites que celles des solides (Figure 15). Cette différence s'explique par les interactions anisotropes statiques auxquelles les noyaux sont soumis à l'état solide. Dans les liquides, les mouvements rapides isotropes des noyaux moyennent les interactions anisotropes. Les principales interactions anisotropes nucléaires qui sont de grand intérêt à l'état solide (et peuvent être la source de l'élargissement des raies) sont les suivantes: l'interaction Zeeman avec le champ magnétique externe, interaction magnétique dipolaire directe; interaction des électrons couplés indirectement (couplage J); interaction quadripolaire électrique (uniquement pour les noyaux ayant un spin supérieur à $1/2$); blindage électronique (déplacement chimique pour les non-métaux et déplacement de Knight pour les métaux). Ces interactions anisotropes, ne sont pas disponibles dans les liquides isotropes, et nous donnent des informations géométriques locales et des informations de distance entre les noyaux interagant. Un autre avantage de la RMN des solides sur RMN en solution est le fait que, dans les solides le nombre de résonances observées dans le spectre est directement lié au nombre de molécules distinctes cristallographiquement existant dans l'unité asymétrique d'un groupe d'espace donné (Figure 16). Cette caractéristique rend la spectroscopie RMNES un très bon complément à la diffraction des rayons X. Des techniques spéciales ont été développées afin de moyennner (réduire) les interactions d'élargissement de raies. Dans le cas de la technique de rotation à l'angle magique de (MAS), un échantillon en poudre est placé dans un rotor cylindrique dont l'axe est

incliné à $54,7^\circ$ par rapport au champ magnétique externe B_0 , et qui est mis en rotation à une fréquence jusqu'à 70 kHz. La technique CRAMPS (combinaison de rotation et de la spectroscopie de impulsions multiples) est une technique particulièrement utile pour l'enregistrement des spectres RMN de ^1H , où MAS est combiné avec un train d'impulsions radiofréquences soigneusement conçu (Figures 17 et 18). Les techniques dédiées, telles que les méthodes d'excitation quantiques multiples (MQ) (par exemple, la spectroscopie de corrélation double-quantum single-quantum (Figure 18), MQMAS RMN et transitions satellites (ST) MAS RMN), ont été développées pour les noyaux quadropolaires demi-entier (spin supérieur à $1/2$), qui posent des problèmes particuliers (Figures 19-21). Les spectres des noyaux de faible abondance naturelle tels que ^{13}C , ^{15}N ou ^{29}Si , sont en général enregistrés avec une technique connue sous le nom de polarisation croisée, ce qui améliore la sensibilité (en combinaison avec MAS).

Pour plus de détails sur la technique de RMN à l'état solide (théorie et applications) le lecteur peut consulter les excellents articles suivants:

- Laws et al. Solid-state NMR spectroscopic methods in chemistry. *Angew Chem Int Edit* (2002) vol. 41 (17) pp. 3096-3129
- Dybowski and Bai. Solid state nuclear magnetic resonance. *Anal Chem* (2000) vol. 72 (12) pp. 1R-7R
- Eckert. Solid state NMR as a tool of structure and dynamics in solid state chemistry and materials science: Recent progress and challenges. *Curr Opin Solid St M* (1996) vol. 1 (4) pp. 465-476
- Andrew and Szczesniak. A historical account of NMR in the solid state. *Prog Nucl Mag Res Sp* (1995) vol. 28 pp. 11-36
- Hodgkinson. Chapter 5 - High-Resolution ^1H NMR Spectroscopy of Solids . *Annual Reports on NMR Spectroscopy* (2011) vol. 72 pp. 185-223
- Kolodziejcki and Klinowski. Kinetics of cross-polarization in solid-state NMR: A guide for chemists. *Chem Rev* (2002) vol. 102 (3) pp. 613-628
- Tycko. Applications of solid state NMR to the structural characterization of amyloid fibrils: methods and results. *Prog Nucl Mag Res Sp* (2003) vol. 42 (1-2) pp. 53-68
- Kovacs et al. A practical guide for solid-state NMR distance measurements in proteins. *Concept Magn Reson A* (2007) vol. 30A (1) pp. 21-39
- Freude. Quadrupolar Nuclei in Solid-state Nuclear Magnetic Resonance. *Encyclopedia of Analytical Chemistry* (2000) pp. 12188–12224



Figure 13. Spectromètre RMN à l'état solide. L'aimant supra-conducteur est indiqué sur la droite. La flèche représente la direction z du champ magnétique statique B_0 .

13.2. Exemples d'applications typiques

RMNES est maintenant utilisée pour étudier presque tous les types de matériaux, les céramiques, les verres et les minéraux, les catalyseurs, produits pharmaceutiques, les polymères et divers autres composés inorganiques, organiques et hybrides. Elle est particulièrement utile lorsque les échantillons ne sont pas cristallins, mal cristallisés ou microcristallins, parce que ces systèmes sont difficilement étudiables par la diffraction des rayons X. En outre les échantillons mous qui sont intermédiaires entre un liquide et un 'vrai' solide (par exemple les molécules de gaz adsorbé sur une surface du catalyseur) sont également mieux étudiés par des techniques RMNES. Les échantillons et les métaux paramagnétiques ne sont pas en général faciles à étudier. En outre, la RMN est une technique non destructive et l'échantillon est disponible à la fin de l'étude (bien que d'une poudre qui est normalement requis parce que l'échantillon doit être soumis à la rotation). Par exemple, la nature de l'espèce Al (aluminium) dans les zéolithes catalyseurs ou la quantification des domaines amorphe/cristallin dans les polymères ont été étudiés par RMNES.

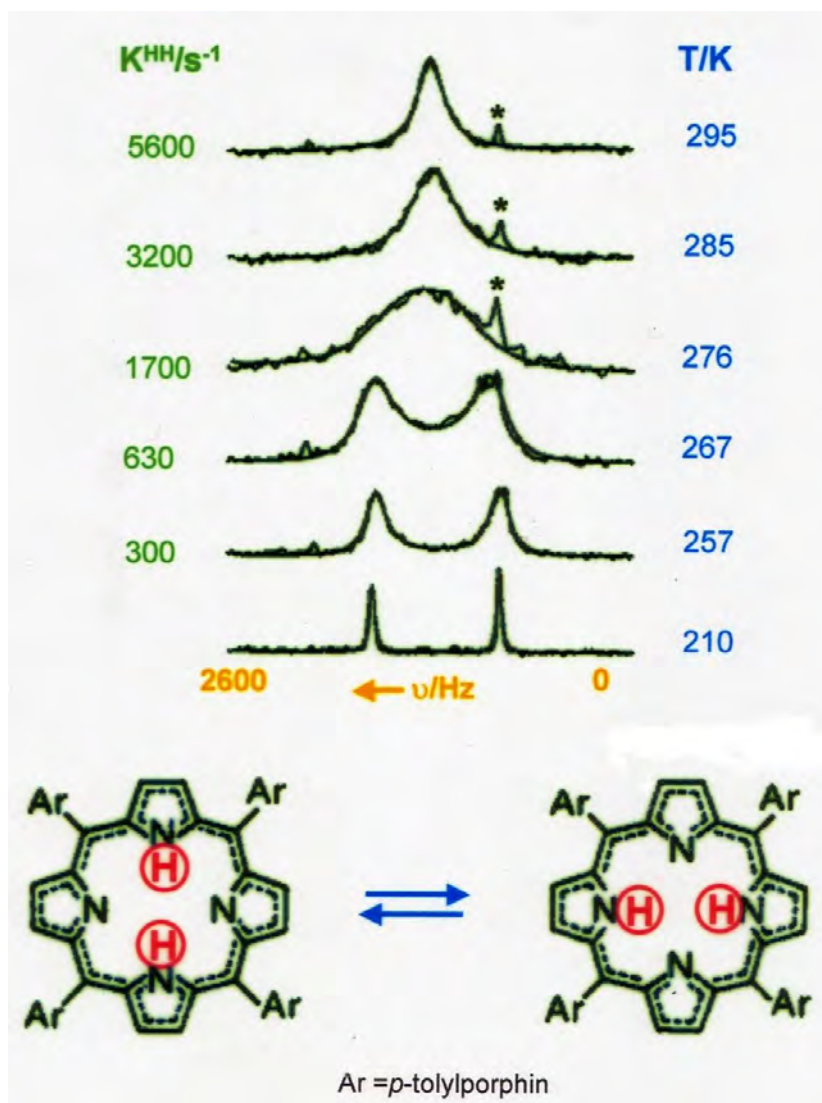


Figure 14. Étude de tautomérie par ^{15}N CPMAS RMN (astérisque représente une impureté). Les changements observés dans les spectres en fonction de la température fournissent des indices sur la dynamique moléculaire du système. La largeur de ligne en absence d'échange a été prise à partir du spectre à 210 K. La valeur de la constante d'équilibre de la tautomérie était supposée d'être l'unité. K^{HH} est la constante de taux de migration HH. (Basé sur la référence [31])

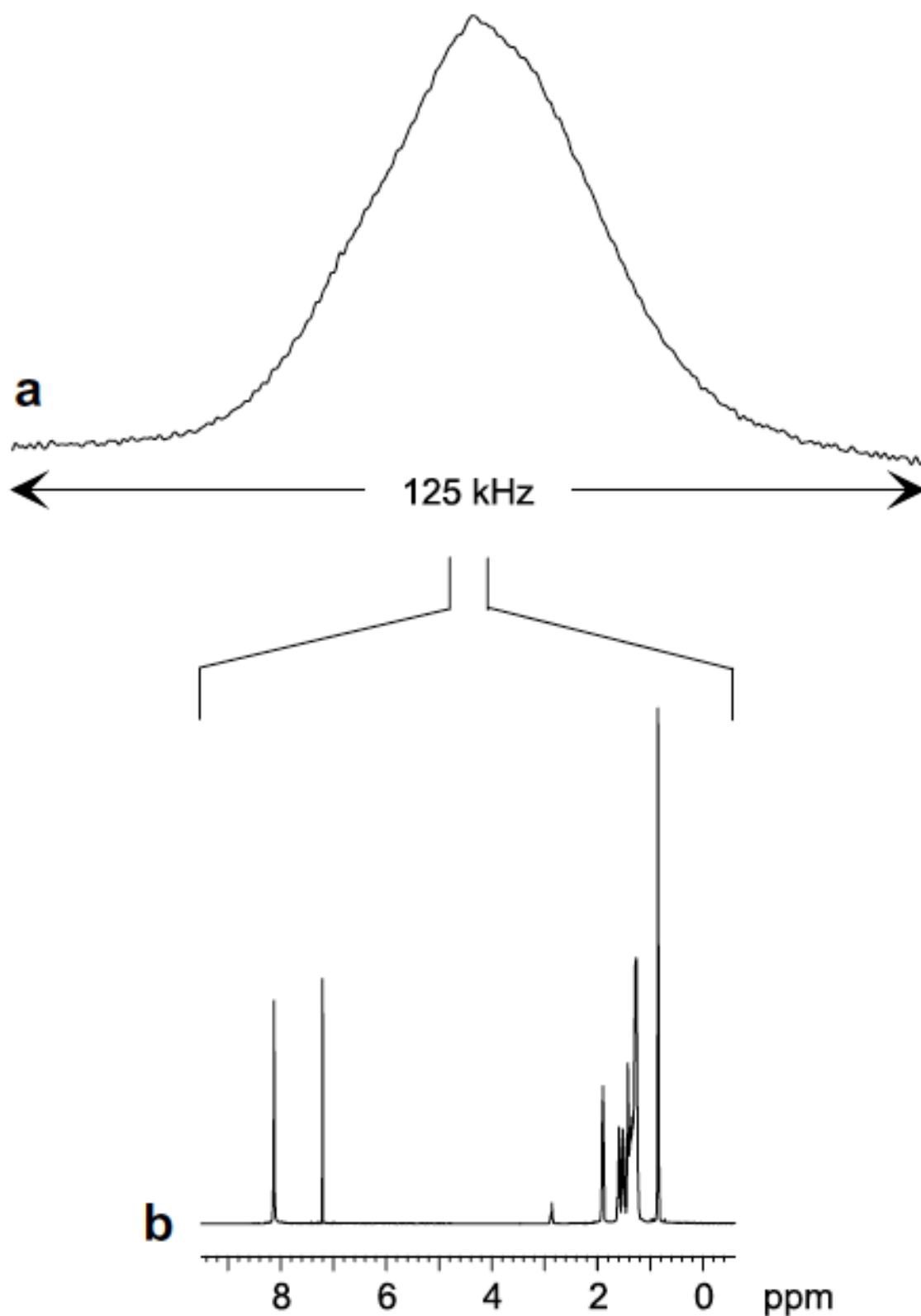


Figure 15. Spectres RMN ^1H : (a) statique à l'état solide (sans utilisation des techniques qui améliorent la résolution des spectres de l'état solide), et (b) à l'état liquide d'un composé organique typique. Image prise de la référence [32]

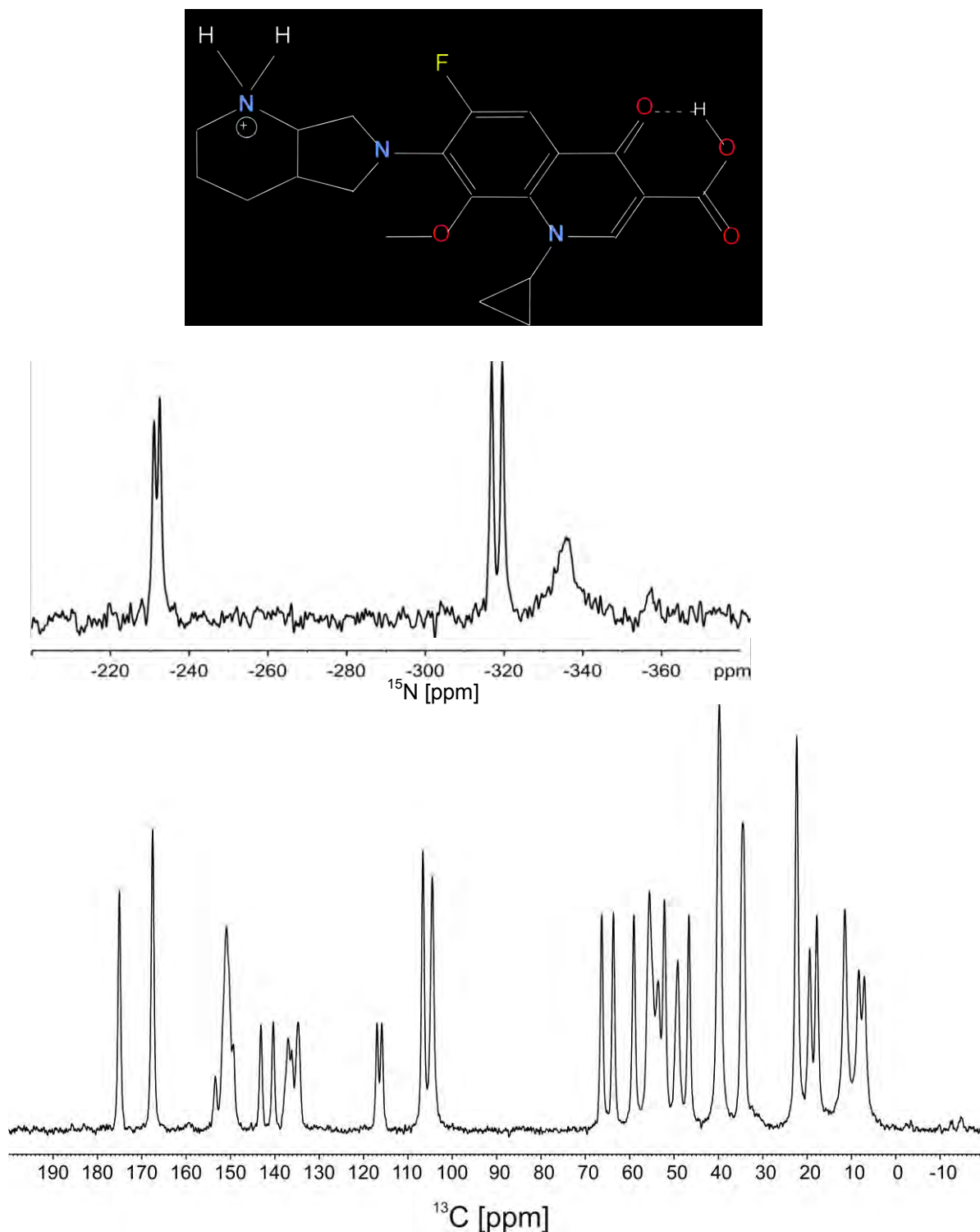


Figure 16. Spectres RMN de polarisation croisée (CP)MAS ^1H - ^{15}N (en haut) et CPMAS ^1H - ^{13}C du solide antibiotiques moxifloxacin, enregistré à 9,4 T (400 MHz). Comme il ya deux molécules non-équivalentes par maille plusieurs signaux sont observés que ceux prévus. Par exemple, il existe trois types d'atomes N dans la molécule, mais six résonances sont effectivement observées (bien que deux se chevauchent dans le pic à environ -335 ppm). (Résultats non publiés)

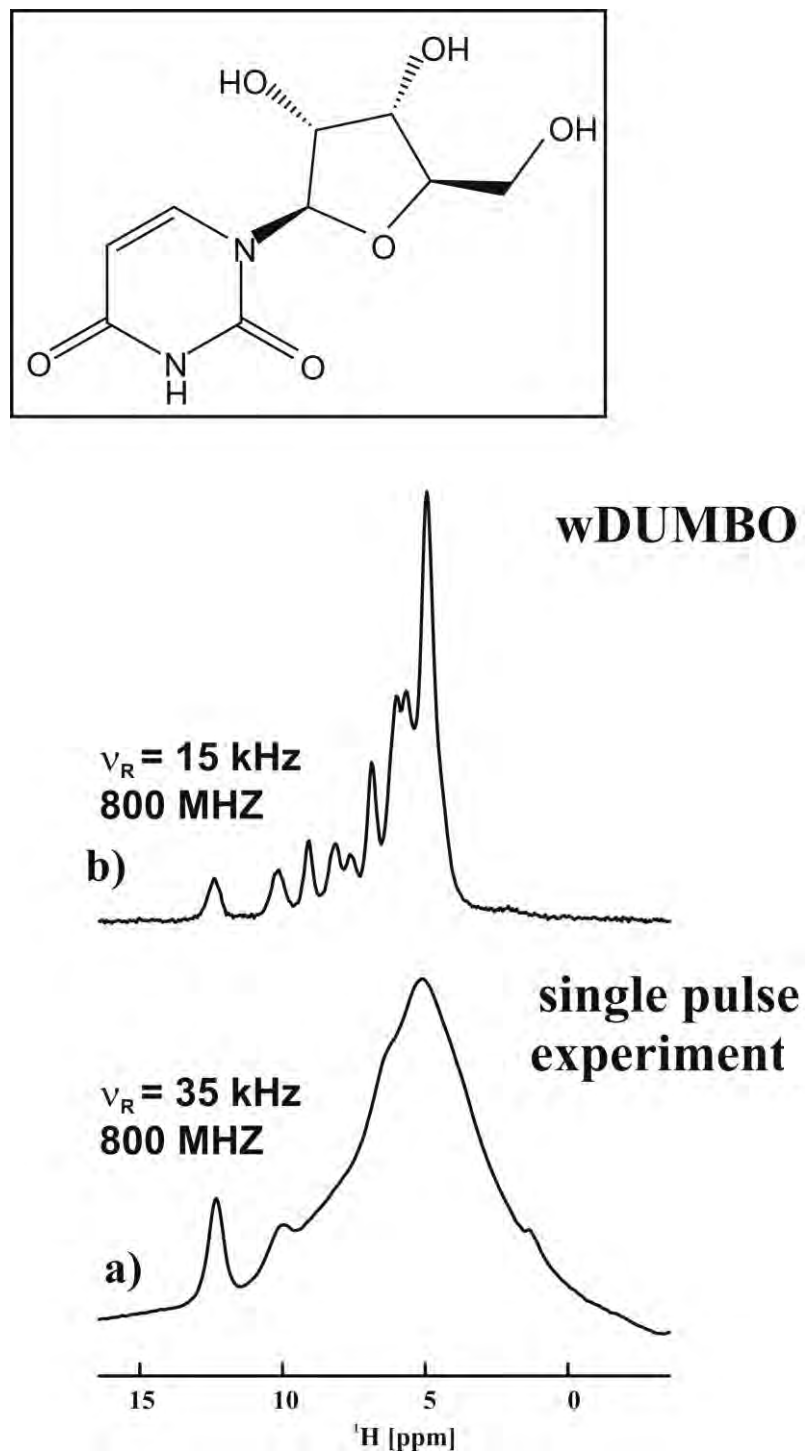


Figure 17. Spectres de l'uridine : (a) 'normal' ^1H MAS (mono-impulsion), et (b) CRAMPES ^1H (wDUMBO séquence d'impulsions). L'amélioration de la résolution obtenue avec CRAMPS est considérablement notable, même à un taux de rotation beaucoup plus faible. [33]

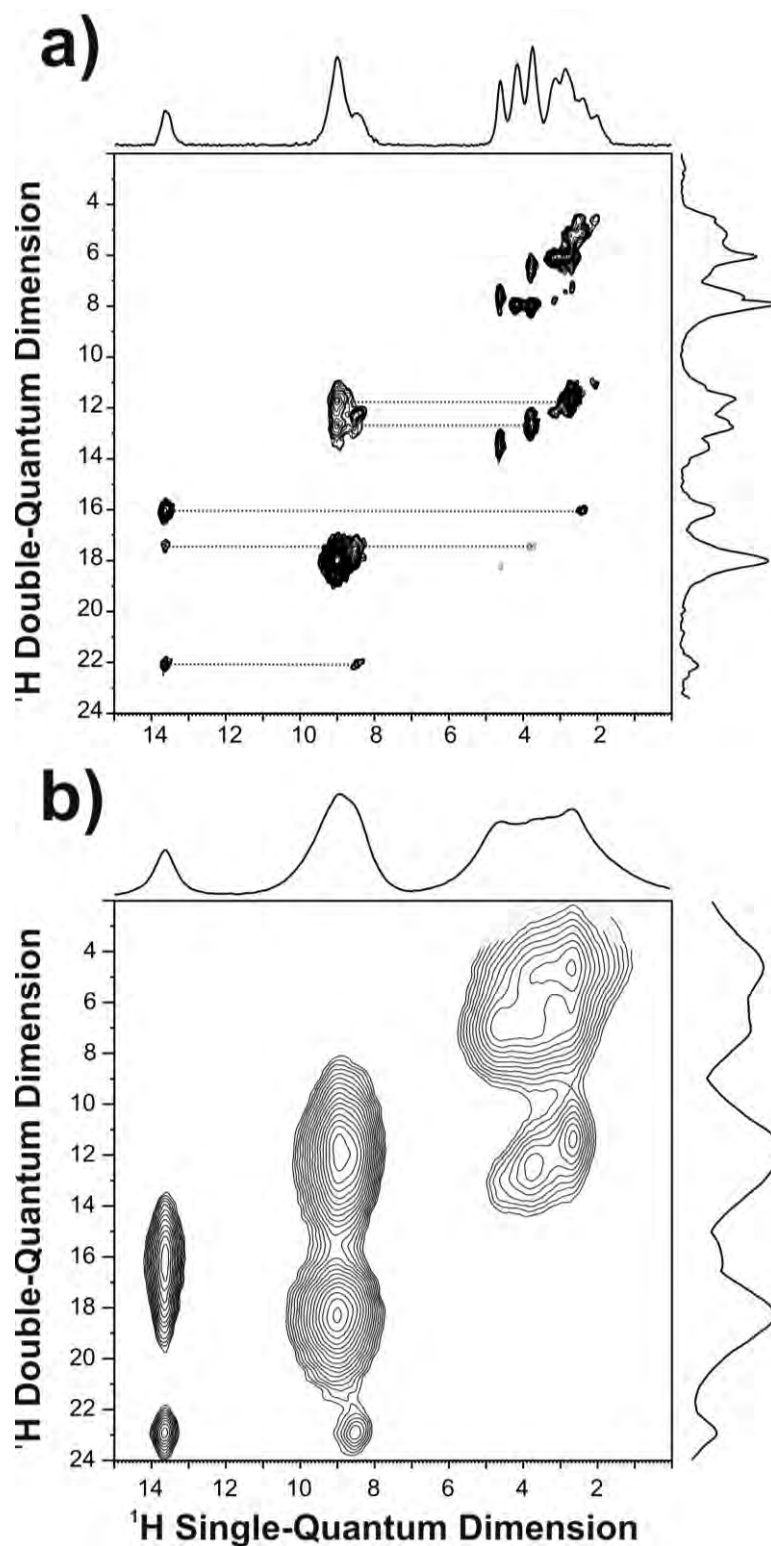


Figure 18. Spectre RMN ^1H - ^1H double quantum-single quantum enregistré à 18,8 T (800 MHz) avec une vitesse de rotation de 30 kHz; (a) avec, et (b) sans découplage ^1H CRAMPS. Les lignes horizontales en pointillés représentent certaines résonances ^1H qui sont «couplées», c'est-à-dire, de proximité spatiale étroite. [34]

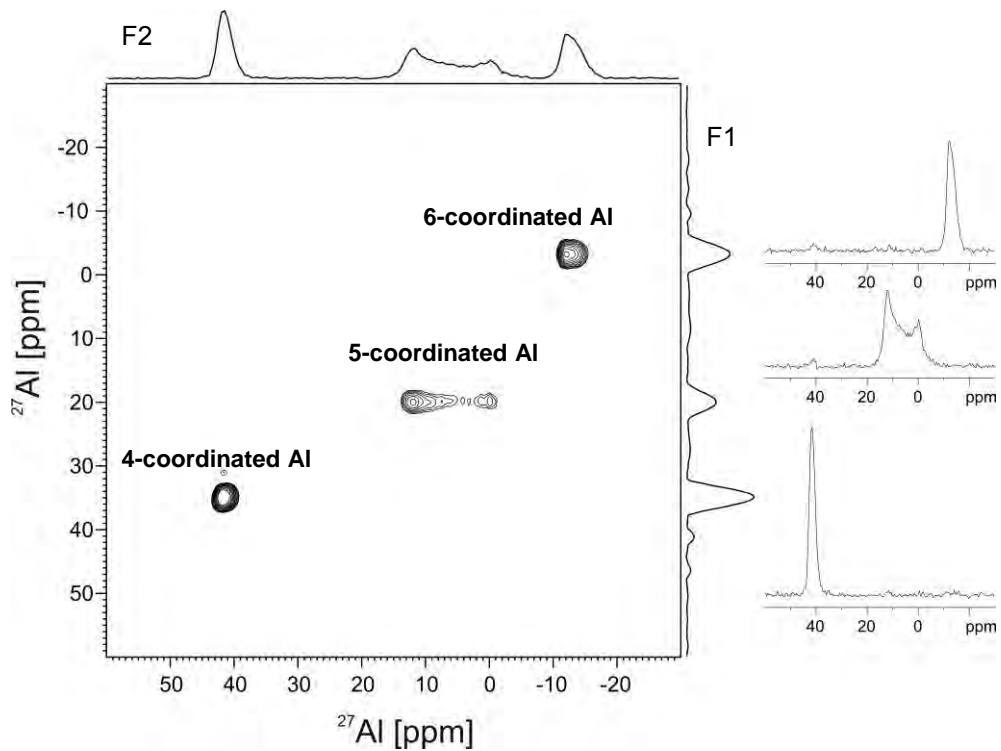


Figure 19. Spectre RMN ^{27}Al triple-quantum MAS d'aluminophosphate IST-1 microporeux, enregistré à 9,4 T et une vitesse de rotation de 15 kHz. La projection F2 est essentiellement le spectre «normal» de résonance à l'angle magique, tandis que la projection F1 est un spectre à haute résolution (isotrope). Les spectres sur la droite sont des coupes prises à travers les 3 résonances et parallèlement à l'axe F2, montrant pour la Al de coordination égale à 5 un diagramme de poudre typique du à l'interaction quadripolaire de second ordre.

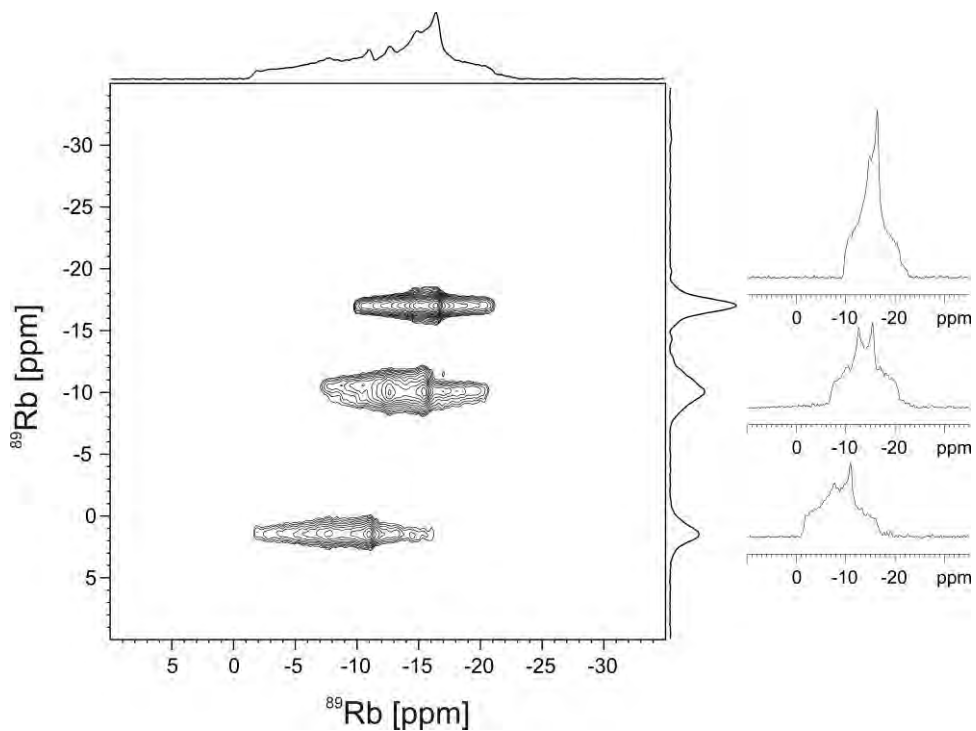


Figure 20. Spectre RMN ST MAS ^{89}Rb de RbNO_3 , enregistré à 9,4 T et MAS de 15 kHz. Comparaison du spectre RMN MAS «normal» (projection F2) et du spectre isotrope (projection F1).

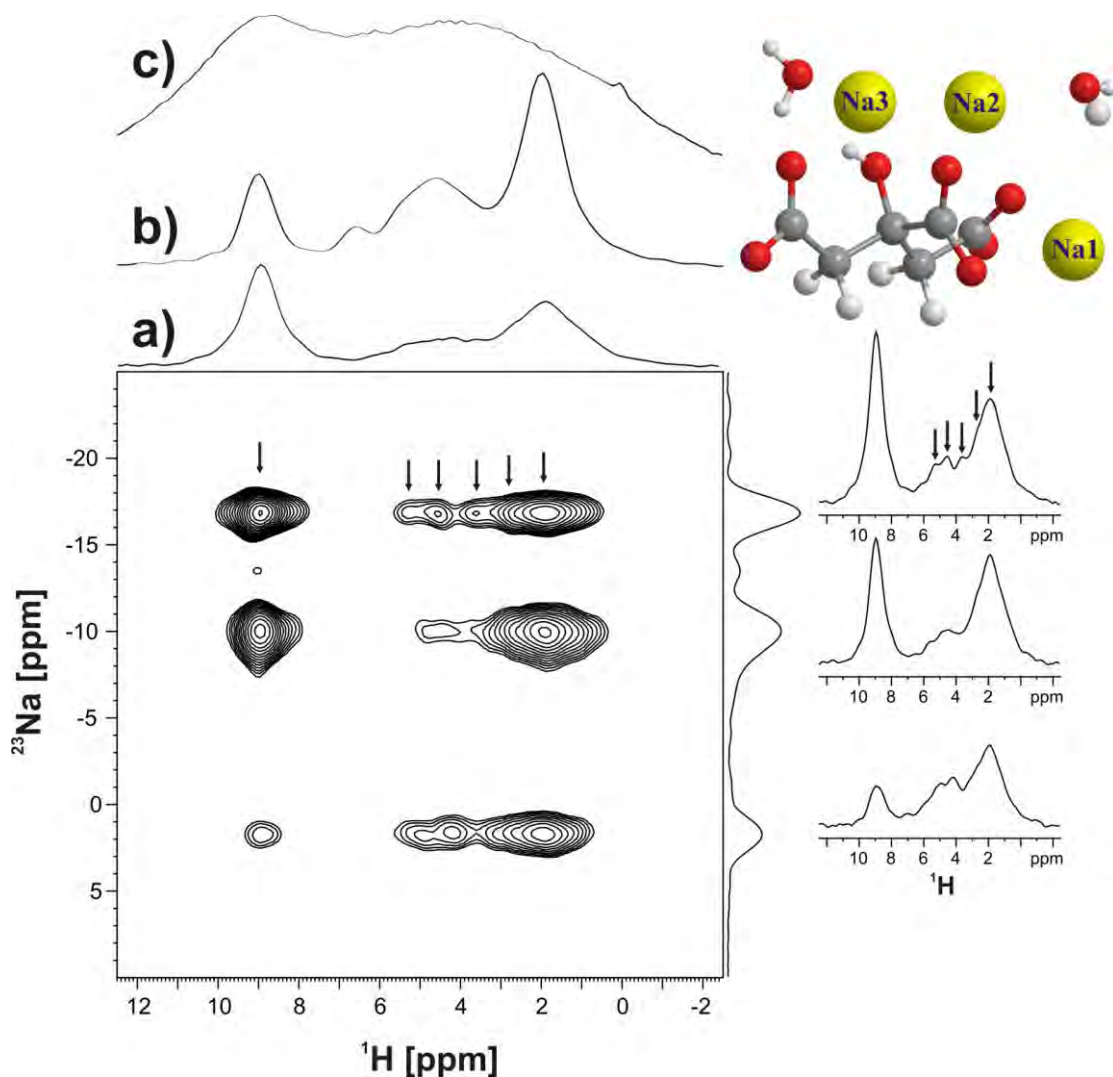


Figure 21. Spectre RMN CPMAS ^{23}Na - ^1H de corrélation hétéronucléaire de citrate de sodium dihydraté, enregistré avec STMAS (pour une haute résolution dans la dimension de ^{23}Na) et CRAMPS (séquence d'impulsions wPMLG, pour une haute résolution dans la dimension de ^1H). 9,4 T (400 MHz) et vitesse de rotation de 15 kHz. (a) projection F2, (b) spectre ^1H wPMLG3, (c) Spectre «normal» RMN MAS ^1H . Les spectres sur la droite sont des coupes transversales prises par les résonances et parallèle à l'axe F2. Image prise de la référence [35]

13.3. Autres exemples d'applications

Nous présentons ci-dessous, une liste de publications (classés par date) illustrant l'application de la RMN à l'étude des solides. Les titres des publications donnent une indication des types de systèmes étudiés.

- 1) Rocha, J., Duer, M. J. and Klinowski, J., "Solid-state NMR studies of the molecular motion in the kaolinite:DMSO intercalate", *J. Am. Chem. Soc.*, **114**: 6867 (1992).
- 2) Anderson, M. W., Philippou, A., Ferreira, A., Lin, Z. and Rocha, J., "Al, Ti, avoidance in the microporous titano-aluminosilicate ETAS-10", *Angew. Chem., Int. Ed. Engl.*, **34**: 1003 (1995).
- 3) Rocha, J., Esculcas, A. P., Fernandez, C. and Amoureux, J. P., "Two-dimensional triple-quantum ^{27}Al MAS NMR spectroscopic study of the high-temperature phase transformation of microporous VPI-5", *J. Phys. Chem.*, **100**: 17889 (1996).
- 4) Rocha, J., Orion, I., Nahring, J., Heaton, B. T., Fernandez, C. and Amoureux, J. P., "Solid-state NMR studies of interstitial P atoms within rhodium carbonyl clusters", *Solid State NMR*, **8**: 195 (1997).
- 5) Orion, I., Rocha, J., Jobic, S., Abadie, V., Brec, R., Fernandez, C. and Amoureux, J. P., " ^{125}Te solid-state NMR studies of transition metal ditellurides", *J. Chem. Soc. Dalton Trans.*, **20**: 3741 (1997).
- 6) Cruz, L. P., Rocha, J., Pedrosa de Jesus, J. D., Savariault, J. M. and Galy, J., "Solid-state single and triple-quantum ^{93}Nb MAS NMR studies of ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and a related pyrochlore", *Solid State NMR*, **15**: 153 (1999).
- 7) Nunes, C. D., Valente, A., Pillinger, M., Fernandes, A. C., Romão, C. C., Rocha, J., Gonçalves, I. S., "MCM-41 functionalised with bipyridyl groups and its use as a support for oxomolybdenum(VI) catalysts", *J. Mater. Chem.*, **12**, 1735-1742 (2002).
- 8) Nunes, C. D., Valente, A. A., Pillinger, M., Rocha, J. and Gonçalves, I. I., "Molecular structure-activity relationship for the oxidation of organic compounds using mesoporous silica catalysts derivatised with bis(halogeno)dioxomolibdenum(VI) complexes", *Chem. Eur. J.*, **9**: 4380-4390 (2003).
- 9) Mafra, L., Almeida Paz, F. A., Shi, F.N., Rocha, J., Trindade, T., Fernandez, C., Makal, A., Wozniak, K., Klinowski, J., "Hydrothermal synthesis and structural characterization of a Ge-pmida binuclear complex: X-ray diffraction and HETCOR MAS NMR with FS-LG decoupling", *Chem. Eur. J.*, **12**: 363-375 (2006).
- 10) Mafra, L., Rocha, J., Fernandez, C. and Paz, F. A. A., "Characterisation of microporous aluminophosphate IST-1 using ^1H Lee-Goldburg techniques", *J. Magn. Reson.*, **180**: 235-243 (2006).
- 11) Mafra, L., Rocha, J., Fernandez, C. and Paz, F. A. A., "Characterisation of microporous aluminophosphate IST-1 using ^1H Lee-Goldburg techniques", *J. Magn. Reson.*, **180**: 235-243 (2006).
- 12) Carlos, L. D., de Zea Bermudez, Amaral, V. S., Nunes, S. C., Silva, N. J. O., Ferreira, R. A. S., ; Rocha, J., Santilli, C. V. and Ostrovskii, D., "Nanosopic photoluminescence memory as a fingerprint of complexity in hierarchically-structured self-assembled alkylene/siloxane hybrids", *Adv. Mater.*, **19**: 341-348 (2007).
- 13) Smirnova, O. A., Rocha, J., Nalbandyan, V. B., Kharton, V. V. and Marques, F. M. B., "Crystal structure, local sodium environments and ion dynamics in $\text{Na}_{0.9}\text{Ni}_{0.6}\text{Sb}_{0.4}\text{O}_2$, a new mixed antimonate", *Solid State Ion.*, **178**: 1360-1365 (2007).
- 14) Coelho C., Rocha, J., Madhu, P. K. and Mafra L., "Practical aspects of Lee-Goldburg based CRAMPS techniques for high-resolution ^1H NMR spectroscopy in solids: implementation and applications", *J. Mag. Reson.*, **194**: 264-282 (2008).
- 15) Mafra, L., Gomes J. R. B., Trébosc, J, Rocha, J, and Amoureux J. P., " ^1H - ^1H double-quantum CRAMPS NMR at very-fast MAS (vR = 35 kHz): A resolution enhancement method to probe ^1H - ^1H proximities in solids" *J. Mag Reson.*, **196** : 88-91 (2009).
- 16) Coelho, C., Siegel, R., Rocha, J, Mafra, L. "Assessing the performance of windowed ^1H CRAMPS methods, on biological solids, at high-field and MAS up to 35 kHz" *J. Mag Reson.*, **197** : 20-27 (2009).
- 17) Siegel, R., Rocha, J. and Mafra, L., Combining STMAS and CRAMPS NMR spectroscopy: high-resolution HETCOR NMR spectra of quadrupolar and ^1H nuclei in solids, *Chem. Phys. Lett.*, **470**: 337-341 (2009).
- 18) Mafra, L., Siegel, R., Fernandez, C., Schneider, D., Aussenac, F., and Rocha, J., High-resolution ^1H homonuclear dipolar recoupling NMR spectra of biological solids at MAS rates up to 67 kHz, *J. Magn. Reson.*, **199**: 111-114 (2009).
- 19) Rocha, J., Shi, F-N., Paz, F. A. A., Mafra, L., Sardo, M., Cunha-Silva, L. Chisholm, J., Ribeiro-Claro, P. and Trindade, T., 3D-2D-0D stepwise deconstruction of a water framework templated by a nanoporous organic-inorganic hybrid host, *Chem-Eur J.*, **26**: 7741-7749 (2010).
- 20) Garcia-Granda, S., Khainakov, S. A., Espina, A., Garcia, J. R., Castro, G. R., Rocha, J. and Mafra, L., Revisiting the Thermal Decomposition of Layered γ -Titanium Phosphate and Structural Elucidation of Its Intermediate Phases, *Inorg. Chem.*, **49**: 2630-2638 (2010).
- 21) Pinto, M., Mafra, L., Guil, J., Pires, J., and Rocha, J., Adsorption and activation of CO_2 by amine-modified nanoporous materials studied by solid-state NMR and $^{13}\text{CO}_2$ adsorption, *Chem. Mater.*, (2011) in press.

14. Exemple d'étude expérimentale. Synthèse hydrothermale et caractérisation structurale de deux nouveaux phosphates de titane (IV) bidimensionnels à charpente ouverte de formule $(C_6H_{13}NH_3)[Ti(HPO_4)(PO_4)] \cdot H_2O$ (1) et $(C_2H_5NH_3)[Ti(H_{1.5}PO_4)(PO_4)]_2 \cdot H_2O$ (2).

Ces dernières années, l'une des activités importantes de notre laboratoire, a été l'étude des composés lamellaires de phosphates de titane (IV). Elle s'est concrétisée par l'obtention de deux de nouveaux phosphates organiquement templétés qui s'ajoutent à la famille des structures lamellaires du phosphates de titane, dans laquelle les composés les plus connues sont les phosphates de formules α - $Ti(HPO_4)_2 \cdot H_2O$ et γ - $Ti(H_2PO_4)(PO_4) \cdot 2H_2O$ qui étaient connues depuis les années 1960-70.

14. 1. La synthèse hydrothermale.

La synthèse hydrothermale du composé lamellaire de phosphates de titane (IV), de composition $(C_6H_{13}NH_3)[Ti(HPO_4)(PO_4)] \cdot H_2O$ (1), obtenu avec un rendement supérieur de 90%, a été réalisée dans un réacteur de 120 ml en téflon scellé dans un autoclave en acier inoxydable sous pression autogène (Figure 22), en mélangeant du n-hexylamine, de l'acide phosphorique (H_3PO_4) à 85% et du chlorure de titane ($TiCl_4$) avec un rapport molaire 1:10:10 ($TiCl_4$: H_3PO_4 : $C_6H_{13}NH_2$). Le volume total est environ 40 ml. Le réacteur a été scellé et chauffé à 185 °C pendant 10 jours. Le solide obtenu est filtré, lavé avec un excès d'eau distillée et séché à l'air à température ambiante. La même procédure de synthèse a été suivie dans le cas de $(C_2H_5NH_3)[Ti(H_{1.5}PO_4)(PO_4)]_2 \cdot H_2O$ (2) (rendement > 90%), en remplaçant seulement l'hexylamine par l'éthylamine ($C_2H_5NH_2$).



Figure 22. Image de l'autoclave en acier inoxydable et de son réacteur de 120 ml en téflon utilisés pour la synthèse hydrothermale dans notre laboratoire de l'université d'Oviedo.

14. 2. Techniques de caractérisations structurales utilisées:

La structure de composés **1** et **2** a été caractérisée par plusieurs techniques :

- la spectrométrie de masse à plasma à couplage inductif (ICP-MS) pour déterminer les teneurs en phosphore et titane, après qu'une masse connue l'échantillon ait été dissoute dans l'acide fluorhydrique aqueux (HF).
- l'analyse élémentaire : les teneurs en carbone (C) et azote (N) ont été déterminées au moyen d'un analyseur élémentaire.
- les analyses thermiques : les courbes d'analyse thermogravimétrique (ATG) et de calorimétrie différentielle à balayage (CDB) ont été réalisées sous atmosphère d'azote, avec une vitesse de chauffage de 10°C/min dans l'intervalle 30-900 °C.
- la spectroscopie infrarouge : les spectres IR ont été enregistrés par un spectrophotomètre à transformée de Fourier dans l'intervalle 4000-400 cm⁻¹ en utilisant des pastilles de KBr.
- la microscopie électronique : les images sont prises à l'aide d'un microscope électronique à balayage (MEB) dans le cas du composé **1** (Figure 23a) et d'un microscope électronique en transmission (MET) dans le cas du composé **2** (Figure 23b).
- la diffraction des rayons X sur poudre : Le diagramme de diffraction des rayons X sur poudre dans le cas de composé **1** (Figure 23c₍₁₎), a été collecté sur un diffractomètre de laboratoire, opérant avec la radiation monochromatique CuK α 1 (longueur d'onde $\lambda = 1,5418 \text{ \AA}$). Dans le cas du composé **2** un diagramme de diffraction en poudre de haute résolution a été collecté à l'aide de la radiation synchrotron (Figure 23d_{points noirs}) utilisant la ligne de lumière BM25A de l'ESRF (European Synchrotron Radiation Facility) à Grenoble (France), avec une longueur d'onde incidente $\lambda = 0.82648(6) \text{ \AA}$.
- La spectroscopie RMN à l'état solide : Les mesures de RMN à l'état solide ont été réalisées à 9,4 T (Tesla) sur un spectromètre *Bruker Avance 400 WB* (modèle *DSX*) fonctionnant à des fréquences de Larmor de 400.1, 100.6, 161.9 et 40.5 MHz pour les noyaux ¹H, ¹³C, ³¹P et ¹⁵N, respectivement. Les échantillons ont été emballés dans des rotors de ZrO₂ o.d., de 2mm seulement pour le noyau ¹H, de 4mm pour ¹H, ¹³C et ³¹P, et de 7 mm seulement pour ¹⁵N, en utilisant des sondes à double résonance.

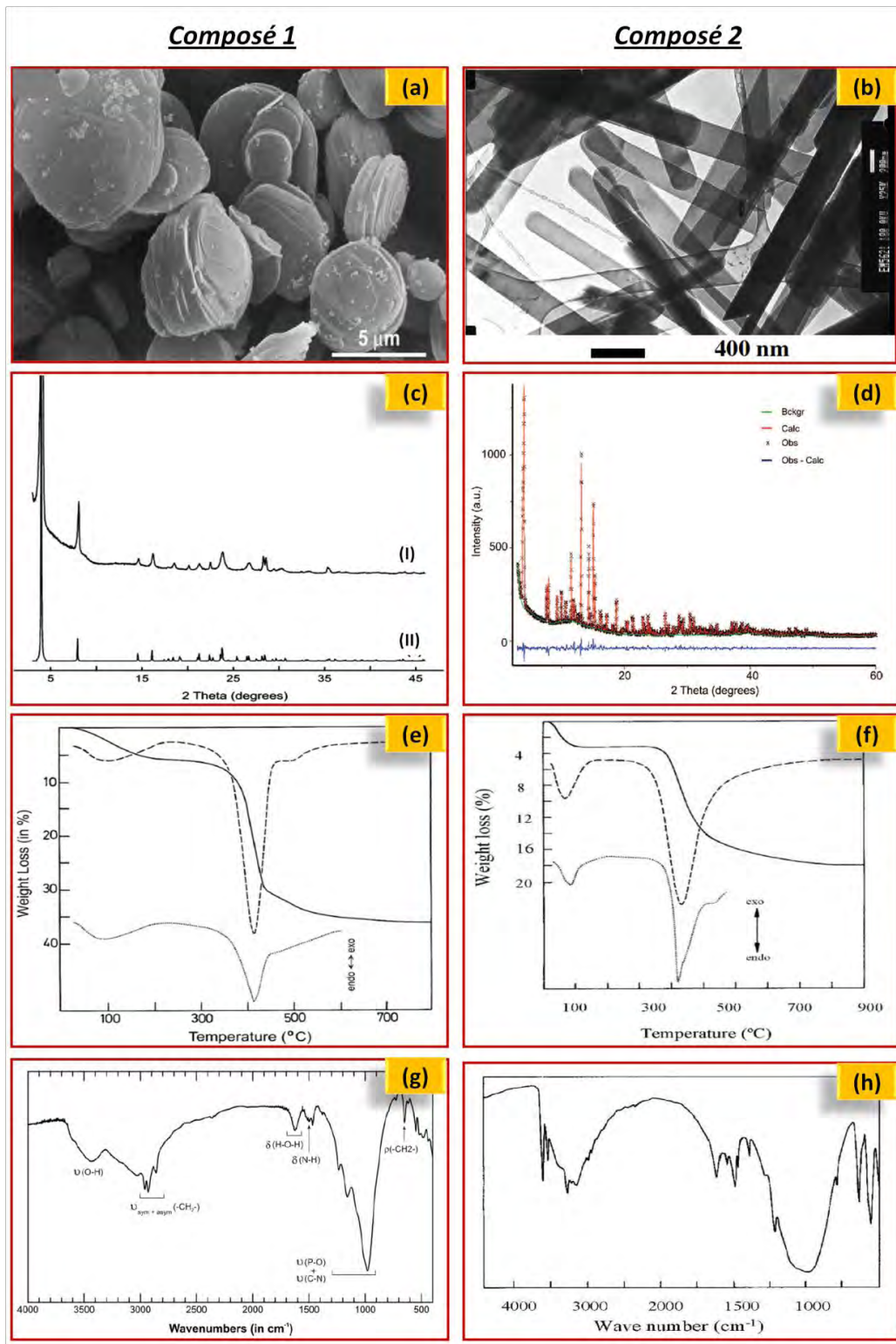


Figure 23. Images obtenues par MEB (a) et MET (b), (c, d) Diagrammes de diffraction des rayons X sur poudre, expérimentaux (c_I) et d_{points noirs} et calculés c_{II}) et d_{rouge}). (e, f) Courbes ATG (—), ATD (- - -) et DSC (•••), (g, h) Spectres infrarouges.

14. 3. Interprétation et discussions des résultats.

14. 3. 1. Description de structures.

Les structures lamellaires des composés **1** et **2** de phosphates de titane(IV) sont comparées dans les Figures 24a et 24b. Elles sont formées de feuillets anioniques à deux dimensions $[\text{Ti}(\text{HPO}_4)(\text{PO}_4)]^-$ qui sont construits à partir d'anneaux, formés par les tétraèdres PO_4 et octaèdres TiO_6 partageant des sommets communs. Les longueurs (Ti-O, P-O) et les angles de liaison (O-Ti-O, O-P-O) trouvées sont typiques et en bon accord avec les valeurs rapportés pour les autres phosphates de titane.

Ces structures comportent deux sortes de groupements phosphates: le groupe PO_4^{3-} qui partage leurs atomes d'oxygène avec les atomes de titane, et le groupes HPO_4^{2-} qui a deux atomes d'oxygène reliés aux groupements TiO_6 et les deux autres terminaux. Ces groupes terminaux HPO_4^{2-} sont dirigés vers la région intercalaire, en interagissant directement avec les groupements amines protonés voisins des cations n-hexylammonium (dans le cas de **1**) ou n-éthylammonium (dans le cas de **2**) à travers des liaisons hydrogène.

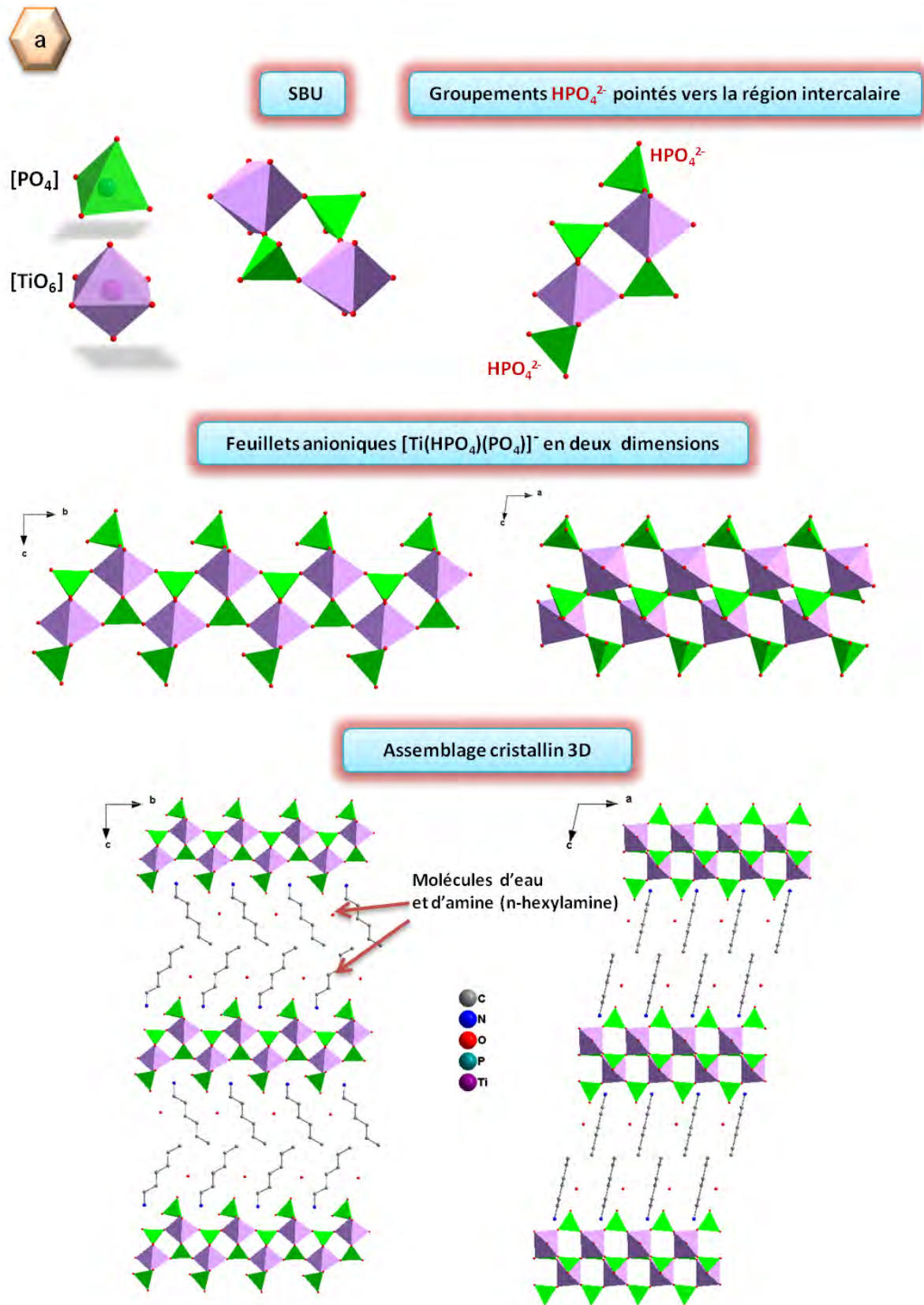


Figure 24(a). Structure du composé 1.

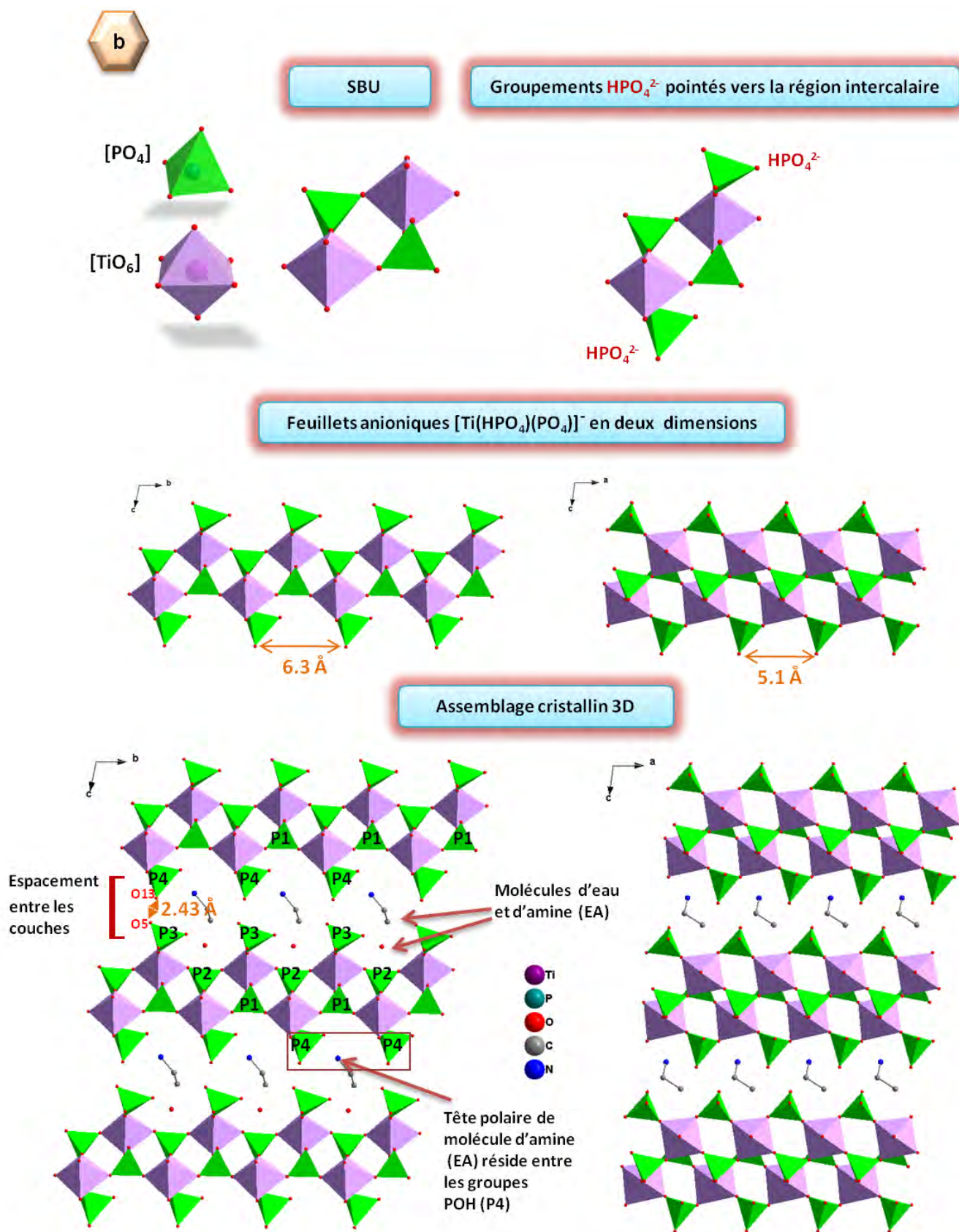


Figure 24(b). Structure du composé 2.

14. 3. 1. 1. Étude structurale par diffraction des rayons X.

Les structures cristallines des composés **1** et **2**, ont été résolues et analysées à partir de la combinaison de deux techniques : la diffraction des rayons X sur poudre et la RMN à l'état solide. Le composé **1** cristallise dans le système monoclinique, de groupe d'espace $P2_1$, avec les paramètres de maille suivants : $a = 5.089(2) \text{ \AA}$, $b = 6.335(2) \text{ \AA}$, $c = 22.792(5) \text{ \AA}$, $\beta = 102.48(2)^\circ$ et le composé **2** cristallise dans le système triclinique de groupe d'espace $P1$, avec $a = 5.1126(1) \text{ \AA}$, $b = 6.31892) \text{ \AA}$, $c = 12.0396(5) \text{ \AA}$, $\alpha = 100.93(2)^\circ$, $\beta = 102.48(2)^\circ$, $\gamma = 90.683(3)^\circ$.

Les inclusions de l'hexylamine dans le cas du composé **1** ou de l'éthylamine dans le cas du composé **2**, provoquent un transfert du proton de groupes hydrogénophosphates (appartenant aux couches de phosphate de titane) au groupe amine, conduisant ainsi à la présence des cations hexylammonium ($C_6H_{13}NH_3^+$) et éthylammonium ($C_2H_5NH_3^+$) dans les espaces intercalaires ce qui est illustré par des études par spectroscopie RMN à l'état solide.

Puisque ces structures sont topologiquement semblables, elles diffèrent principalement par la taille de l'amine intercalée. L'utilisation d'une amine à chaîne aliphatique plus longue dans le composé **1** conduit à une structure avec un espace intercalaire plus grand (manifesté par un axe cristallographique $c = 22.792(5) \text{ \AA}$). Dans le cas du composé **2** l'amine possède une chaîne aliphatique courte, ce qui induit un petit espace intercalaire (manifesté par un axe cristallographique plus petit $c = 12.0396(5) \text{ \AA}$) et par conséquent à une forte interaction entre les couches inorganiques adjacentes.

14. 3. 1. 2. Étude structurale par spectroscopie RMN à l'état solide.

L'outil le plus complet pour l'analyse structurale des solides cristallins est la diffraction des rayons X. Cependant, comme des nombreux auteurs l'ont montré, [36] tous les solides ne peuvent pas être obtenus sous forme de monocristaux de bonne qualité. Une autre limitation importante c'est qu'avec la DRX les atomes lourds ont tendance à dominer et, par conséquent, les atomes de faible numéro atomique, tels que 1H sont difficiles à détecter. [37] Ainsi, les études par RMN de 1H à l'état solide jouent un rôle important dans la chimie des matériaux. Les liaisons hydrogène et d'autres groupes fonctionnels acides sont, en général, facilement détectés par RMN à l'état solide en raison de leur déplacements chimiques typiquement élevés, et parce que les résonances sont généralement séparées de la région spectrale plus entravée (en général, environ 1-8 ppm). Ainsi, l'étude de tels environnements de 1H peut être facilement réalisée sans le besoin de techniques RMN sophistiquées [38, 39] D'autres groupes de recherche ont exploré, ils ont exploré l'utilisation de techniques de recouplage homonucléaires, comme la spectroscopie DQ, pour détecter les liaisons hydrogène dans les molécules organiques. [40-42]

Les matériaux hybrides inorganiques-organiques ont été également étudiés par RMN à l'état solide, en particulier, les matériaux hybrides à base de organosilice et de siloxane ont été largement étudiés par les techniques de routine RMN ^{29}Si et ^{13}C , et sporadiquement, par RMN de 1H , lorsque la résolution suffisante est atteinte. En outre, les matériaux hybrides inorganiques-organiques contenant de phosphates / phosphonate

métalliques ont été étudiés par spectroscopie RMN à l'état solide. En particulier, les études par RMN de ^{27}Al , ^{31}P et ^{19}F des composés à charpente ouverte contenant des amines comme des agents structurants (ADS), [43, 44] et de ^{17}O sur des composés hybrides à base de titane. [45]

L'utilisation de la RMN à l'état solide a été plus largement exploitée en tirant pleinement parti des expériences sophistiquées, telles que la RMN de corrélation 2D. Cependant, les études RMN ^1H à haute résolution des matériaux hybrides complexes et relativement riches en protons sont relativement rares. L'observation de ^1H souffre, dans la plupart des cas, d'un élargissement homogène des résonances du ^1H , en raison des forts couplages dipolaires homonucléaires entre voisins noyaux ^1H . Avec les développements récents de l'électronique, l'étude du noyau les plus disponibles dans les matériaux hybrides, ^1H , peut être effectuée à l'aide des techniques CRAMPS [46] pour obtenir des spectres ^1H de haute résolution.

Des exemples de techniques à base de ^1H CRAMPS appliquée à l'étude des matériaux hybrides ayant des groupes phosphate [12, 13, 46-49] ou non sont encore rares. Et parmi celles-ci les expériences ^1H CRAMPS qui s'appliquent à des systèmes relativement simples. Cette section illustre comment les expériences ^1H CRAMPS en 2D, en particulier en utilisant le régime de découplage FSLG, peuvent être utilisées pour l'étude des composés **1** et **2**. Ces deux études de cas, déjà publiées ailleurs [12, 13], montrent des aspects particuliers sur la façon dont la spectroscopie RMN peut donner lieu à une connaissance approfondie de structure et d'être combinée avec la diffraction des rayons X pour aider à l'obtention de la meilleure structure cristalline possible.

La RMN des solides confirme et éclaire encore les détails du modèle de structures cristallines proposées, déjà décrits précédemment (voir paragraphe 13. 3. 1 et 13. 1. 1. 1.), Ci-dessous nous détaillons deux études de cas (pour le composé **1** et **2**) en démontrant, pour chacun, des aspects particuliers sur la façon dont la spectroscopie RMN à l'état solide peut donner un aperçu de la structure cristalline et d'être combinée avec la diffraction des rayons X pour aider à obtenir la structure cristalline.

A) Étude RMN du composé **1**.

A1) Relation entre le spectre RMN 1D et la structure cristalline.

Le spectre RMN CPMAS ^{13}C (Figure 25a) montre six résonances à des déplacements chimiques (δ) d'environ 13.4, 22.1, 26.0, 26.7, 31.0, et 39.6 ppm attribués aux C-6, C-5, C-3, C-4, C-2, et C-1, respectivement. Ce résultat est en accord avec la structure cristalline proposée, car elle indique que l'intercalé n-hexylamine est protoné et qu'il existe un seul type de cation n-hexylammonium dans la maille. Les résultats montrent que le nombre de résonances RMN individuelles observées dans le spectre correspond au nombre de carbones figurant dans l'unité asymétrique cristallographique. En d'autres termes, le nombre de pics apparaissant dans le spectre RMN nous donne directement une idée de l'unité asymétrique, aidant ainsi dans le choix du groupe d'espace cristallographique approprié

Le spectre RMN MAS ^{31}P présente deux résonances à $\delta \sim -13.5$ and -26.5 ppm avec une relation d'intensité 1:1 (aire) (Figure 25b), en accord avec la structure

crystalline proposée, qui implique la présence de deux types de ^{31}P d'environnements locaux différents. Le pic à -13,5 ppm est augmenté beaucoup par l'utilisation de la technique ^{31}P CP en comparaison à la technique ^{31}P MAS, et par conséquent il est attribué aux sites HPO_4^{2-} (Figure 25b).

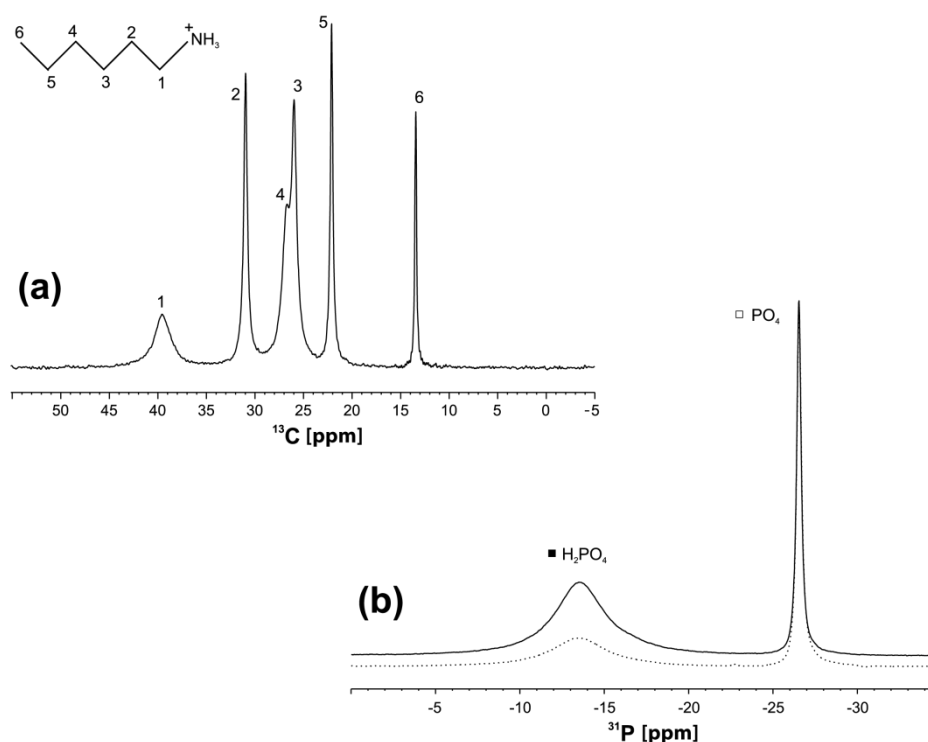


Figure 25. (a) Spectres RMN CPMAS 1 de ^{13}C (CT=500 μs) et (b) de ^{31}P (CT=1500 μs) [ligne continue], spectre RMN MAS de ^{31}P (CT=1500 μs) [ligne pointillé] du composé **1**.

A2) Obtention des renseignements quantitatifs et le sondage des interactions hôte-invité.

Le spectre RMN MAS ^1H (Figure 26a) et le spectre RMN 2D ^1H (FS-LG)- ^1H de corrélation homonucléaire (HOMCOR) (Figure 26c) du composé **1** présentent cinq résonances. La déconvolution du premier spectre nécessite un total de sept pics ^1H (Figure 26b), dont cinq sont attribués à l'ion n-hexylammonium (surface relative entre parenthèses): 0,8 ppm (1,5), H-6; 1,3 ppm (3), H-3-5; 1,7 ppm (1), H-2; 3,1 ppm (1), H-1; et 7,6 ppm (1,5), N-H. Les résonances restantes, ont été déconvoluées avec deux pics, à 5,7 ppm (0,9), attribué à des molécules d'eau, et à 5,8 ppm (1), attribué à des groupes P-OH. En effet, lors de la déshydratation de l'échantillon (environ 150 $^\circ\text{C}$, 24 h), l'intensité de la première résonance baisse considérablement (non représentée). Il faut noter que les informations obtenues par les spectres 15a et 15c sont les mêmes. Le premier spectre RMN 1D ^1H à haute résolution est obtenu en utilisant une vitesse de rotation rapide ($v_R = 30$ kHz) de l'échantillon, tandis que le deuxième spectre RMN 2D

^1H CRAMPS est obtenu à une vitesse de rotation modérée ($\nu_R = 12$ kHz). Les deux méthodes améliorent considérablement la résolution spectrale, ce qui est essentiel dans la tâche d'affectation de résonance ^1H .

Les spectres 2D ^1H DQ - SQ BABA (Figure 26d) confirment l'intégrité du cation n-hexylammonium dans l'espace intercalaire. Fait important, c'est que le pic de croisement de H_2O et P-OH à $\delta_{\text{SQ}} \sim 5,7$ ppm pratiquement disparaît de la diagonale du spectre, ce qui peut être attribué probablement à l'échange rapide de ^1H impliquant les molécules d'eau ou les groupes NH des cations n-hexylammonium et les groupes P-OH voisins.

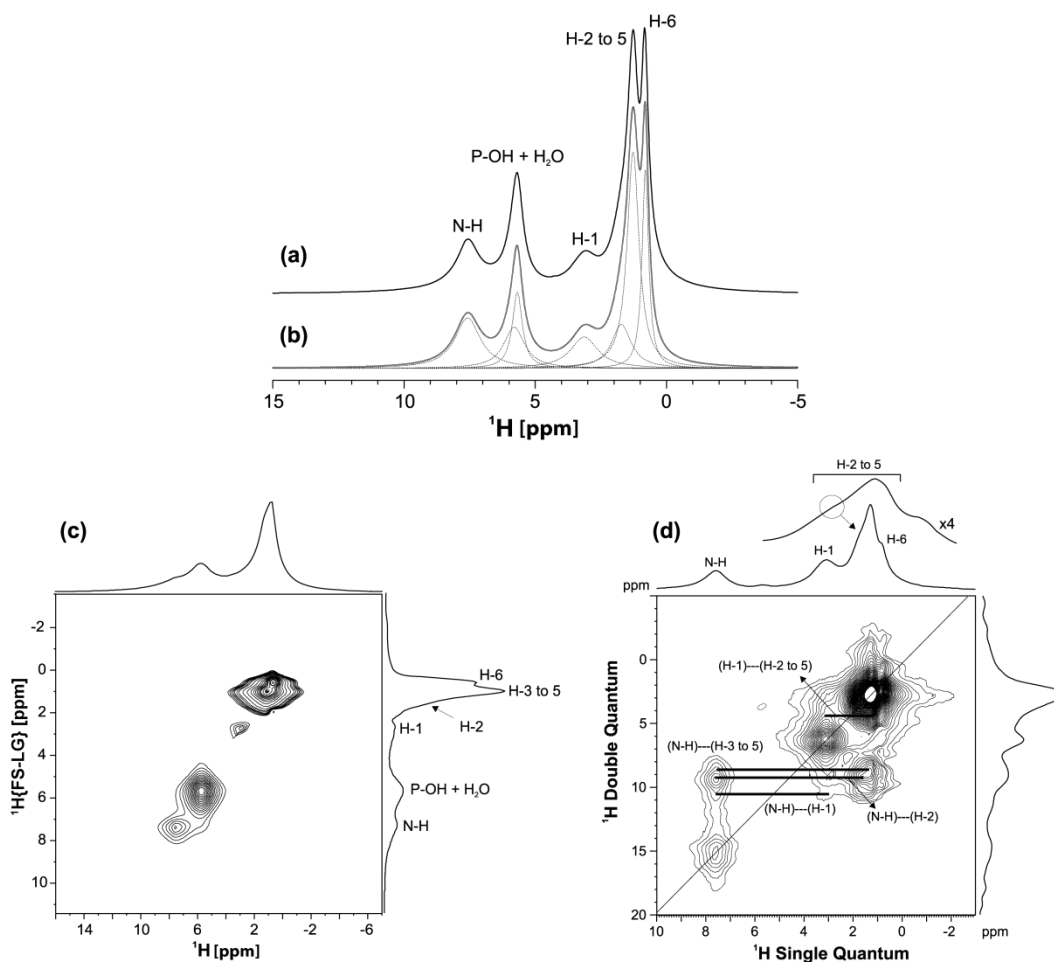


Figure 26. Spectre RMN ^1H du composé **1**. (a) Spectre RMN MAS ^1H enregistrés avec une vitesse de rotation de 30 kHz et (b) le spectre simulé correspondant représenté avec les composants individuels de Lorentz. (C) spectre RMN 2D $^1\text{H}(\text{FS-LG})\text{-}^1\text{H}$ HOMCOR. (D) spectre RMN 2D ^1H DQ-SQ BABA acquis à $\nu_R=30$ kHz. Les temps d'excitation et de reconversion DQ ont été réglé à 66 μs .

Pour le cas du spectre RMN 2D $^1\text{H}\text{-}^{31}\text{P}$ HETCOR (Figure 27) et ses tranches en F1 (Figure 28), utilisant un temps de contact relativement court ($\text{CT} = 100$ μs) les résonances des protons H_2O , P-OH, et N-H dominant le spectre, cependant, aux longs temps de contact ($\text{CT} = 3$ ms) l'intensité des pics de protons H-1-6 est considérablement améliorée. Encore une fois, ces observations confirment la structure cristalline

proposée, car elles indiquent que les groupes H₂O, P-OH, et NH de n-hexylammonium sont plus proches des deux sites de phosphore que les protons de la chaîne d'alkyle.

Une deuxième observation importante c'est que, a CT = 100 μ s, la tranche F1 prise à travers de pic ³¹P (HPO₄²⁻) à environ -13,5 ppm, montre un pic ¹H attribué aux H₂O/P-OH aussi intense que celui de NH. En revanche, la tranche F1 prise à travers de pic de ³¹P à environ -26,5 ppm, présente une résonance plus forte de proton N-H. Par conséquent, la preuve de RMN ¹H-³¹P HETCOR indique que l'environnement de HPO₄²⁻ est plus proche que celui de PO₄³⁻ aux molécules d'eau et des cations n-hexylammonium, comme prévu.

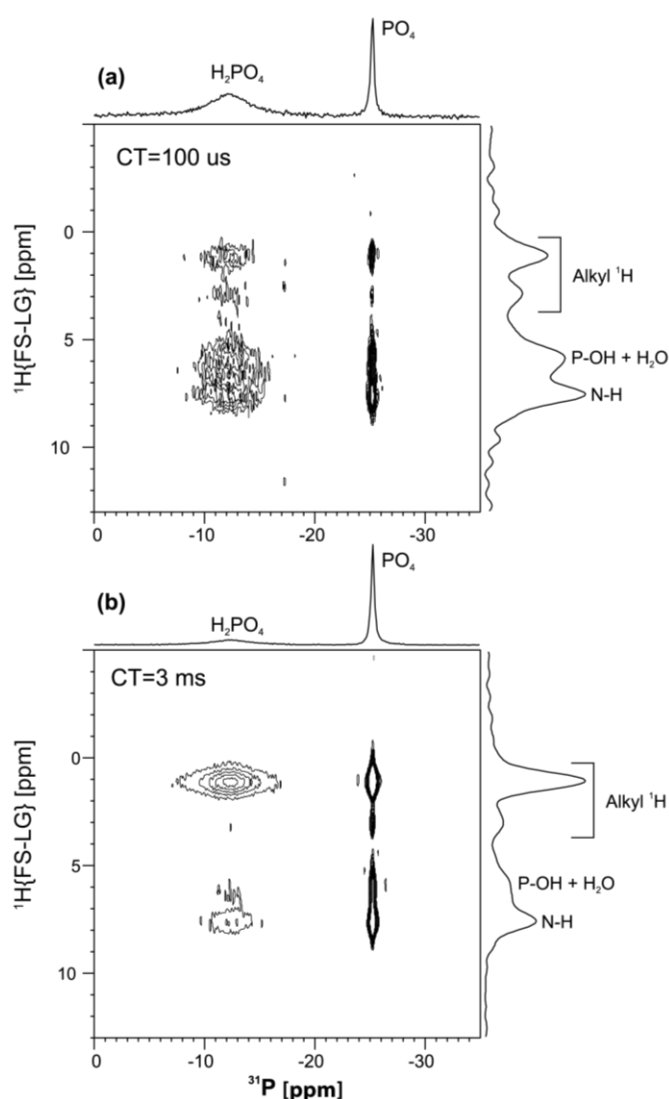


Figure 27. Spectre RMN 2D ¹H{FS-LG}-³¹P CP HETCOR du composé **1**, enregistré avec CT de (a) 100 μ s et (b) 3000 μ s.

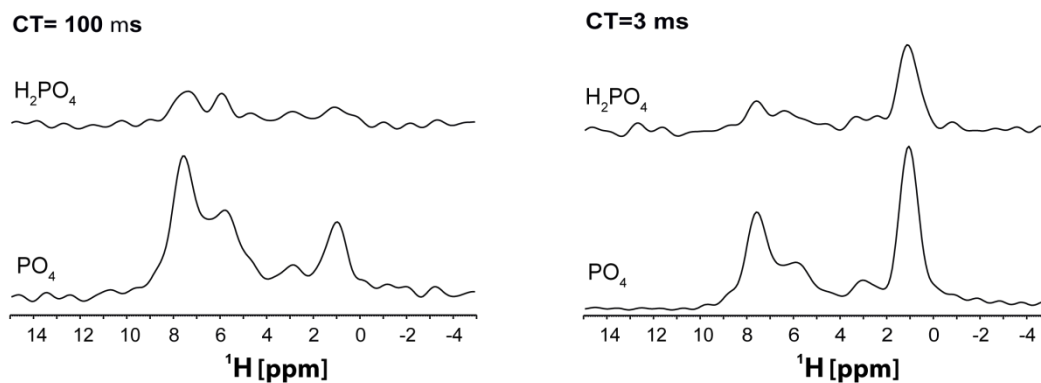


Figure 28. Tranche F1 du spectre RMN 2D $^1\text{H}\{\text{FSLG}\}-^{31}\text{P}$ CP HETCOR NMR du composé **1**.

B) Etude RMN du composé **2**.

B1) Identification de l'unité asymétrique et la corrélation entre l'espace intercalaire de différents composés de phosphate de titane intercalés et les interactions des protons.

Le spectre RMN CPMAS ^{13}C (Figure 29a) présente des pics à $\delta \sim 38,6$ et $15,2$ ppm attribué, respectivement, à des groupes N-CH₂ et CH₃, alors que le spectre CPMAS ^{15}N (Figure 29b) montre un seul pic à environ -343 ppm, typique des amines protonées. [38] Par conséquent, les spectres RMN CPMAS ^{13}C et ^{15}N du composé **2** confirment la présence d'une seule molécule-hôte d'éthylamine cristallographique dans l'unité asymétrique.

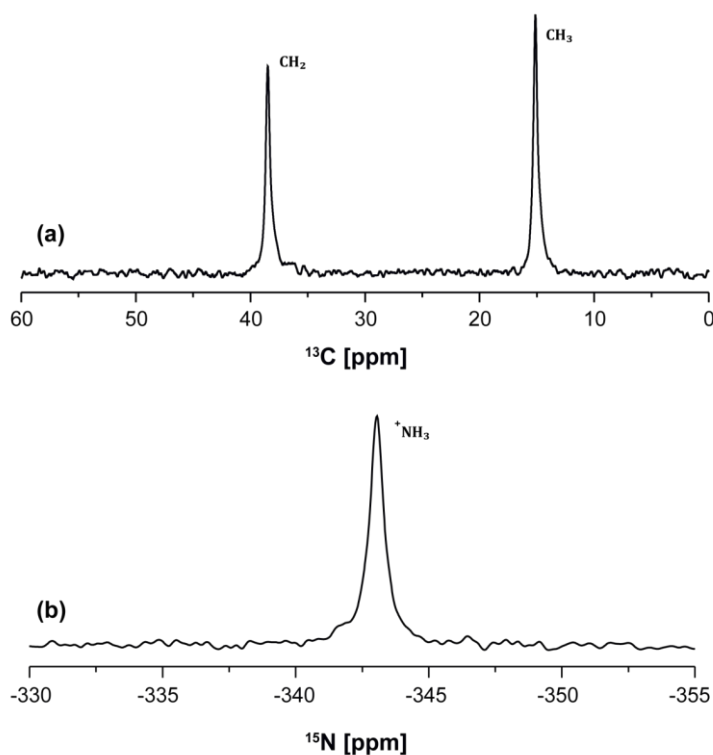


Figure 29. Spectres RMN CPMAS de ^{13}C (a) et ^{15}N (b) du composé **2**.

Le spectre RMN MAS ^1H du composé **2** (Figure 30a) présente entre 0-10 ppm, plusieurs pics et épaulements. La résonance ^1H inattendue à environ 16,2 ppm est probablement due à des atomes d'hydrogène impliqués dans une liaison hydrogène forte ou dans un environnement ^1H très acide. Les spectres RMN MAS ^1H de différents composés d'intercalation de phosphate de titane (Figure 30b-f) ne présentent pas le pic à 16,2 ppm. Puisque tous ces trois matériaux contiennent également des groupes amine près de groupes POH, cette résonance qui n'est vraisemblablement pas due à la formation des liaisons hydrogène forte entre l'amine et les groupes hydrogénophosphate. La considération de l'espace intercalaire, montré dans la Figure 30, suggère que seul l'espacement basal de composé **2** (Figure 30a) est compatible avec une distance de liaison hydrogène, à travers l'espace, entre les groupes POH des feuillets de phosphate de titane ($d_{05-013} = 2,43 \text{ \AA}$, voir Figure 24b). Ainsi, les couches inorganiques peuvent être connectées à travers des liaisons hydrogène $\text{PO} \cdots \text{H} \cdots \text{OP}$ intercalaires. Cependant, le composé $\text{Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$, qui a un espacement basal similaire (11,6 \AA , Figure 30e), ne montre pas le pic à 16,2 ppm, donc, des études de RMN additionnelles sont nécessaires pour comprendre leur attribution comme démontré dans la section B2.

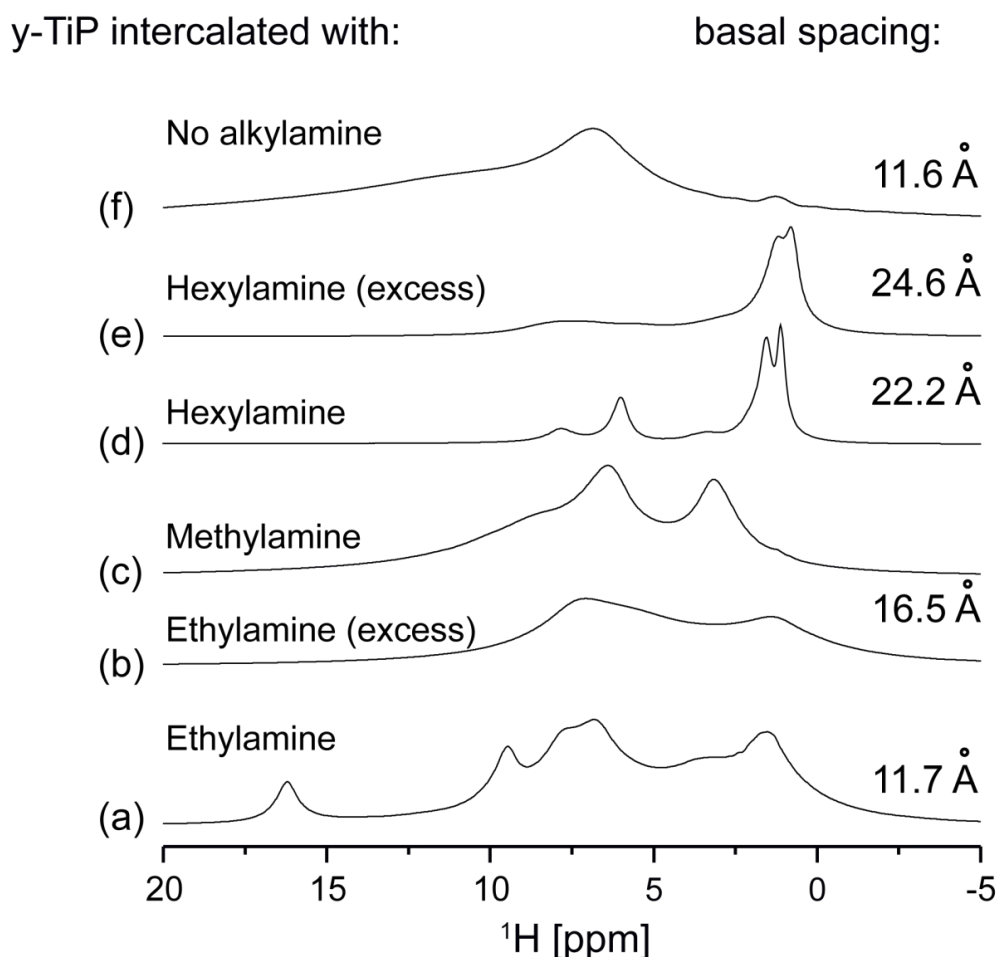


Figure 30. Spectres RMN MAS ^1H des composés de phosphate de titane intercalés par différents n-alkylamine.

B2) Étude des liaisons hydrogène dans le composé 2 en employant RMN 2D ^1H haute résolution.

Pour améliorer la résolution des résonances ^1H dans la région 0 - 10 ppm du spectre ^1H MAS, (Figure 30a), l'expérience RMN 2D $^1\text{H}\{\text{FSLG}\}$ - ^1H HOMCOR a été réalisée (Figure 31a). Le spectre MAS ^1H enregistré à $\nu_R = 30$ kHz (Figure 31b) est également présenté pour comparaison. La Figure 31 révèle la présence de six résonances de ^1H . Les pics qui apparaissent à $\delta \sim 1,6$ (H^{F}) et 3.2 (H^{E}) ppm sont assignés respectivement aux groupes CH_3 et CH_2 des molécules éthylamine. Les pics de résonance ^1H restants à $\delta \sim 16,2$, 9.4, 7.6 et 6.8 ppm ($\text{H}^{\text{A-D}}$) doivent être assignés aux groupes NH et OH (-POH ou H_2O), car aucun des autres groupes fonctionnels contenant hydrogène n'est présent. Ces résonances apparaissant à plus de 6 ppm suggèrent la présence de réseaux de liaisons hydrogène ou des espèces protonés. En effet, selon Ratcliffé *et al.* [50], les liaisons hydrogène de l'eau protonée (H_3O^+ , H_5O_2^+) peuvent résonner de 10,4 à 18,1 ppm. En outre, des groupes P-OH et NH avec différentes forces de liaison hydrogène peuvent se chevaucher dans cette région, ce qui complique l'interprétation spectrale.

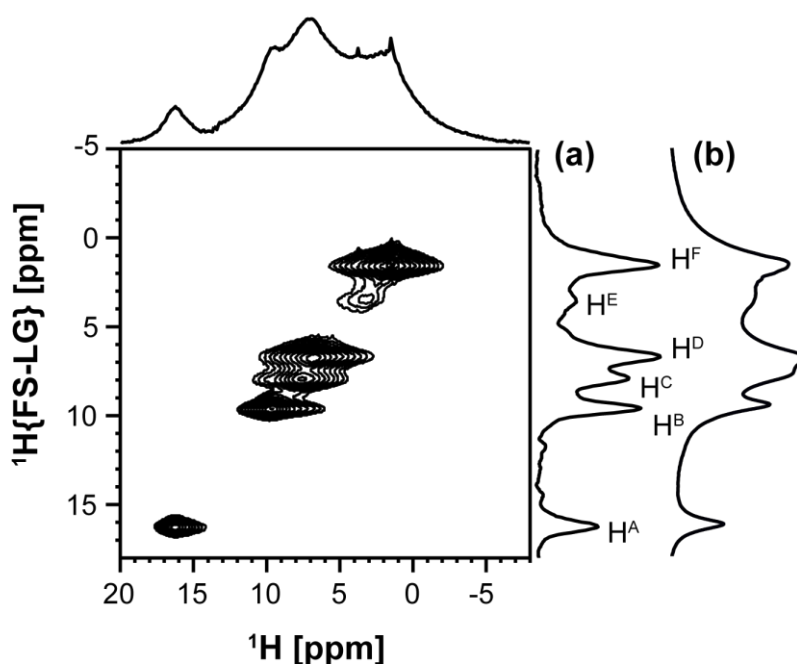


Figure 31. Spectres RMN (a) 2D $^1\text{H}\{\text{FSLG}\}$ - ^1H HOMCOR et (b) MAS ^1H rapide du composé 2.

L'expérience RMN 2D $^1\text{H}\{\text{FSLG}\}$ - ^{31}P HETCOR (Figure 32) montre clairement que la résonance de ^1H à 16,2 ppm (H^{A}) est corrélée à la fois aux pics de hydrogénophosphate (sites P3 et P4). Nous écartons, en principe, la possible affectation de ce pic à la liaison hydrogène entre le groupe NH d'éthylamine et les groupes POH de la couche de phosphate de titane pour les raisons suivantes:

- 1) Selon la Figure 32, les deux sites cristallographiquement distincts POH (P3 et P4) se trouvent sur des côtés opposés des couches de phosphate de titane (Schéma 1);
- 2) Si les molécules d'éthylamine sont alignées perpendiculairement, et de façon non alternée (exemple, les molécules éthylamine sont toutes orientées dans la même direction), par rapport aux couches de phosphate de titane, avec la tête polaire pointant vers une de ces couches, seulement un site ^{31}P (P3 ou P4) devrait avoir un pic de croisement important avec H^{A} dans le spectre HETCOR. En outre, si les molécules d'éthylamine ont été alternées entre un arrangement en haut et en bas, tous les sites hydrogénophosphate (P3 et P4) ^{31}P seraient cristallographiquement équivalents. La même situation se produit si les molécules d'alkylamine intercalées adoptent un arrangement bicouche. En plus, les pics de croisement entre H^{A} et P3 et P4 sont très intenses, ce qui indique que les distances entre ces protons et les atomes de phosphore sont similaires.

En résumé, le spectre $^1\text{H}\{\text{FSLG}\}-^{31}\text{P}$ HETCOR indique la présence d'une liaison hydrogène forte $(\text{P3})\text{O} \cdots \text{H}^{\text{A}} \cdots \text{O}(\text{P4})$ (Schéma 1). D'autres travaux montrent que les déplacements chimiques des protons impliqués dans des liaisons hydrogène $\text{PO} \cdots \text{H} \cdots \text{OP}$ peuvent se trouver au dessus de 16 ppm, ce qui inclut la valeur de 16.2 ppm trouvée dans notre travail [51]. Pour confirmer l'attribution des spectres RMN ^1H , les déplacements chimiques ont été calculés par DFT en utilisant la méthode GIPAW en employant différentes espèces moléculaires comme modèles [13]. Par exemple, les déplacements chimiques calculés des environnements H^{A} sont de $\delta = 18,2$ et $15,3$ ppm, qui sont en bon accord avec la valeur expérimentale. Les déplacements chimiques calculés et expérimentaux des protons $\text{H}^{\text{B-D}}$ ont également été conformément équitables [13].

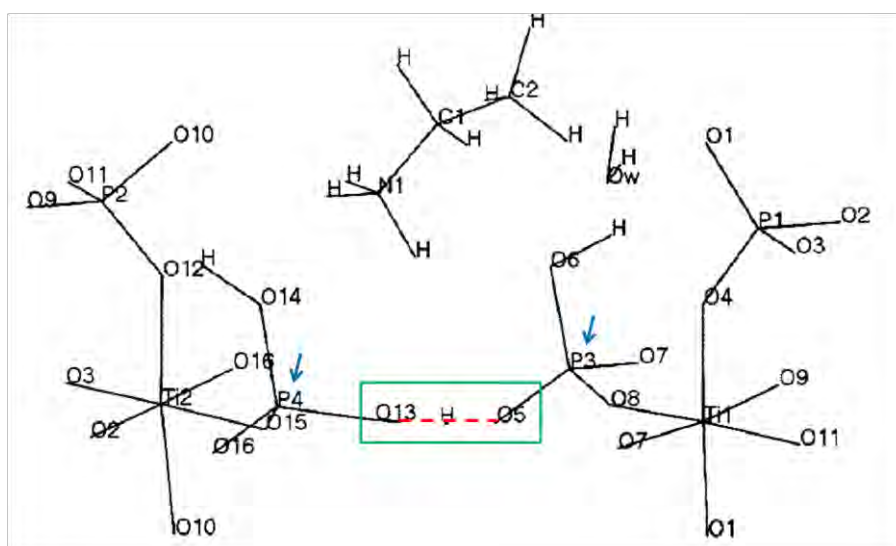


Schéma 1. Fragment de la structure cristalline du composé **1**, montrant que les deux sites cristallographiquement distincts POH (P3 et P4) se trouvent sur des côtés opposés des couches de phosphate de titane, et la présence d'une liaison hydrogène forte $(\text{P3})\text{O} \cdots \text{H}^{\text{A}} \cdots \text{O}(\text{P4})$

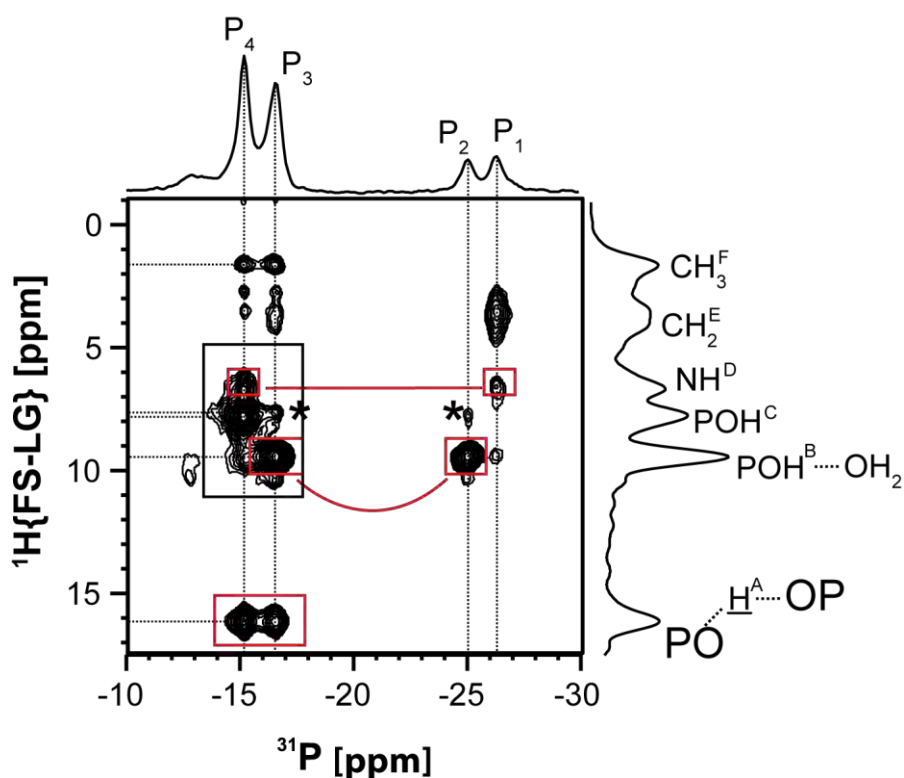


Figure 32. Spectre RMN 2D $^1\text{H}\{\text{FSLG}\}-^{31}\text{P}$ HETCOR du composé **2** employant CTs de (a) 0,1 ms et (b) 1 ms.

Les protons H^{B} et H^{D} ont des forts pics de croisement uniquement avec les phosphores P2 et P3, P1 et P4 respectivement. Par conséquent, puisque P3 et P4 sont des groupes POH résidant sur les côtés opposés de la couche inorganique, H^{B} et H^{D} doivent être également situés dans les côtés opposés de la couche inorganique, en accord avec les contacts $^1\text{H}-^{31}\text{P}$ observé sur le spectre 2D (Figure 32). Ainsi, H^{D} est attribué aux protons NH avec la tête polaire d'éthylamine situés entre les groupes POH (P4) (voir partie encadrée de la Figure 24b). En outre, le déplacement chimique du proton H^{D} ($\delta \sim 6,8$ ppm) est caractéristique des groupes NH protonés. Cette assignation est également soutenue par la présence d'un seul pic de croisement entre les protons N- CH_2 (H^{E}) et P1 (PO₄ groupes), en soutenant que la partie polaire des molécules d'éthylamine est interpénétrée dans les couches inorganiques de phosphate de titane. La résonance H^{C} est probablement la plus difficile à assigner: elle peut être donnée par les molécules d'eau et / ou les groupes P4-OH. Suite de la discussion sur l'attribution des protons H^{C} ne sera pas fait ici.

B3) Sondage des distances $^1\text{H}-^1\text{H}$.

Le spectre ^1H DQ-SQ du composé **2** (Figure 33) montre tous les pics présents dans le spectre ^1H MAS (Figure 30a). Cela indique que le réseau ^1H est relativement rigide et par conséquent, l'intensité des pics de croisement de ^1H est principalement affectée par la distance $^1\text{H}-^1\text{H}$ et pas par la mobilité. Les pics le long de la diagonale sont observés pour les protons qui appartiennent aux mêmes environnements chimiques,

CH_3 ($\text{H}^{\text{F}} \cdots \text{H}^{\text{F}}$) et CH_2 ($\text{H}^{\text{E}} \cdots \text{H}^{\text{E}}$), en raison de la présence de protons géminés sur tels atomes de carbone. En outre, H^{D} présente également un pic DQ ($\text{H}^{\text{D}} \cdots \text{H}^{\text{D}}$) à environ 13.6 ppm, ce qui soutient leur assignation à des protons NH, comme indiqué précédemment, parce qu'il y a plus d'un atome d'hydrogène lié à l'atome d'azote qui peuvent provenir des transitions DQ. En revanche, et en accord avec le modèle de la structure cristalline proposée, les protons H^{A} ne présentent pas de pics sur la diagonale, ce qui montre que dans une couche donnée de phosphate de titane, la plus courte distance $\text{P} \cdots \text{P}$ entre les groupes P-OH adjacents est de 5.1 – 6.3 Å (Figure 24b). Ce comportement est normal car l'expérience DQ-SQ détecte de manière sélective les distances $^1\text{H}\text{-}^1\text{H}$ plus courte que d'environ 3.5 Å. Pour des distances $^1\text{H}\text{-}^1\text{H}$ supérieures les corrélations disparaissent du spectre. H^{B} a également un pic DQ hors diagonale ($\text{H}^{\text{B}} \cdots \text{H}^{\text{F}}$) à $\delta \sim 11$ ppm, ce qui indique sa proximité aux protons CH_3 , comme le montrent les données de diffraction des rayons X.

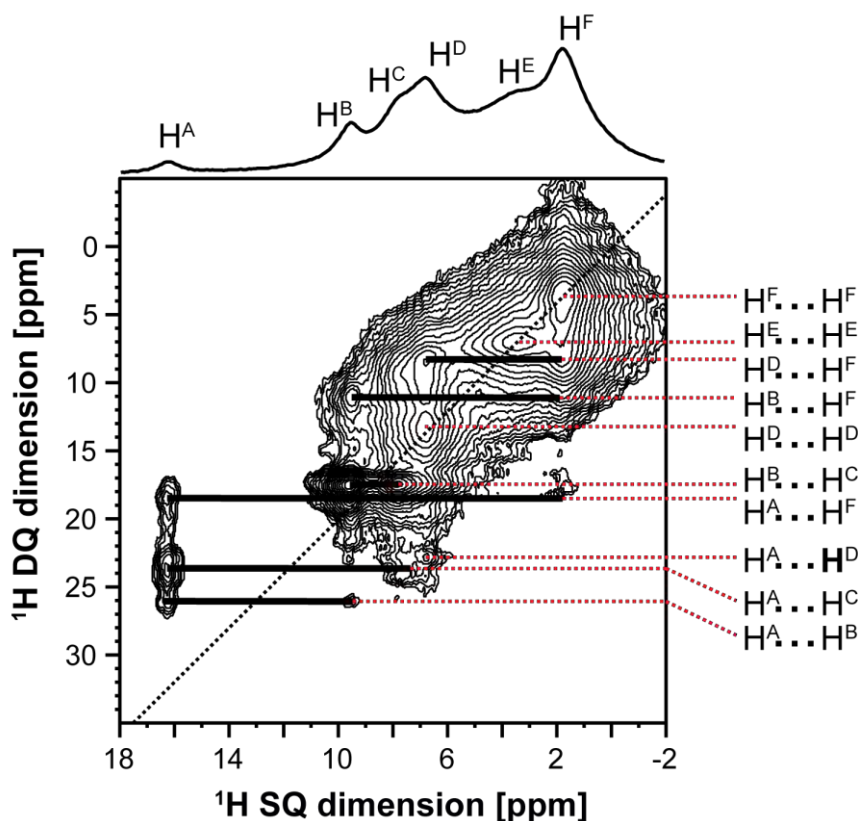


Figure 33. Spectre RMN 2D $^1\text{H}\text{-}^1\text{H}$ DQ-SQ MAS du composé 2.

B4) Suivi de l'effet de la déshydratation et de la réhydratation du composé 2 par RMN et ATG.

Les expériences de déshydratation et de réhydratation (Figure 34) ont montré que dans le composé 2, la perte d'eau est un processus réversible. Lors de la déshydratation, le pic de ^1H à $\delta \sim 9.4$ ppm (H^{B}) disparaît, tandis que les autres résonances sont pas affectée (Figure 34a). Cette résonance peut être attribuée soit à des groupes POH reliés par des liaisons hydrogène aux molécules d'eau, ou plus

probablement, aux protons de cation hydronium (qui peuvent être présents en principe) [50]. Bien que la déshydratation ne change pas beaucoup les résonances RMN du ^{31}P des groupes orthophosphate (sites P1 et P2), il ya un décalage considérable à haute fréquence de pics hydrogène-phosphate (sites P3 et P4) (Figure 34b).

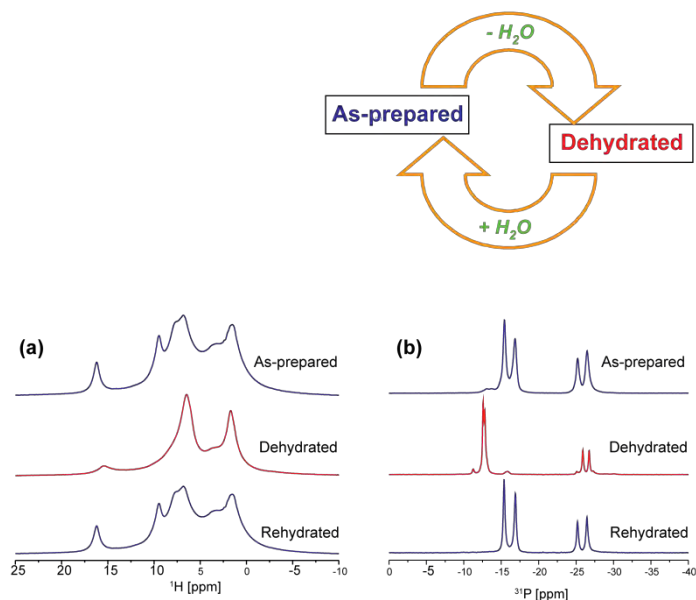


Figure 34. Spectres RMN (a) ^1H MAS, (b) ^{31}P CP/MAS, du processus de déshydratation-hydratation du composé **2**.

B5) Mesures RMN à température variable.

Nous avons suivi l'effet de la température sur la résonance à $\delta \sim 16,2$ ppm par RMN MAS du ^1H (Figure 35, gauche). À 350 K ce pic n'est plus observé, indiquant que le fort réseau de liaisons hydrogène a été détruit. Simultanément, les spectres RMN CPMAS ^{31}P changent de quatre à deux sites ^{31}P cristallographiquement distincts (Figure 35, droite). Ce gain de symétrie, qui rend les sites P3 et P4 équivalents est probablement provoqué par la grande mobilité moléculaire des molécules invitées à température plus élevée.

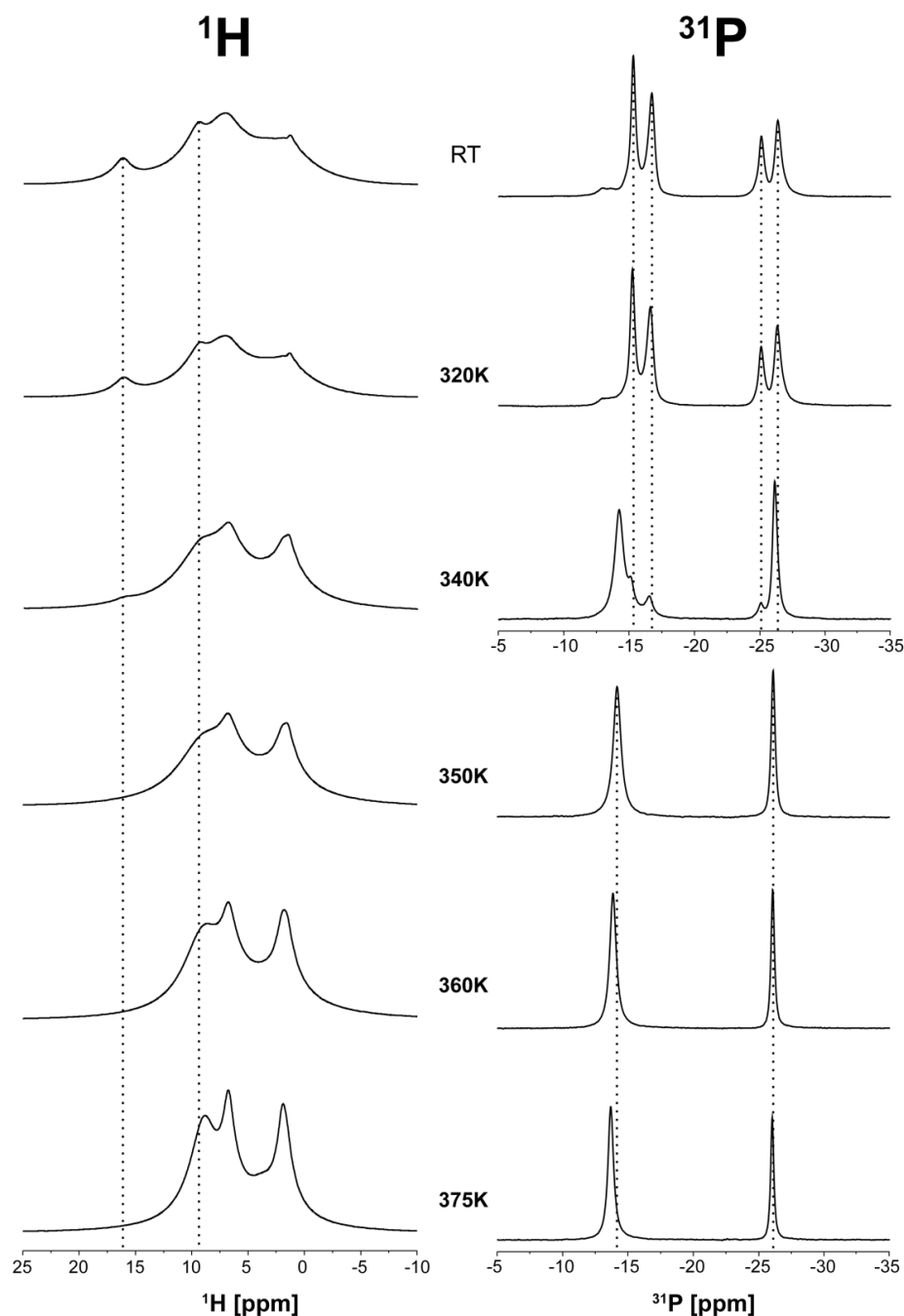
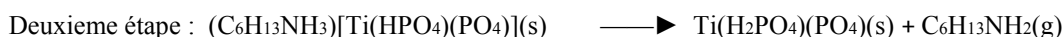
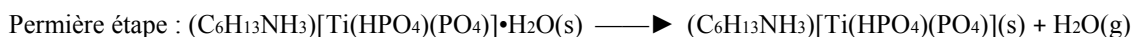


Figure 35. Mesures RMN à température variable du composé **2**. Spectres RMN (a) ^1H MAS et (b) ^{31}P CPMAS.

14. 3. 2. Étude par analyses thermiques.

Dans le cas de composé **1**, l'analyse thermogravimétrique (ATG) (Figure 23e) montre une perte de masse totale entre 30°C et 800°C de 36,0% ce qui correspond au résidu TiP_2O_7 (perte de masse calculée 38,2%). Les courbes d'analyse thermique différentielle (ATD) et d'analyse calorimétrique différentielle à balayage (CDB) montrent un processus complexe de décomposition thermique en trois étapes qui se chevauchent partiellement. La première étape, entre 50-200°C correspond à la libération

d'une molécule d'eau par unité formulaire (valeur observée 5,9%, et calculée 5,0%). La deuxième et la troisième étape (entre 200-490°C et 490-700°C) correspondent respectivement à l'élimination de l'hexylamine (valeur observée 25,2%, calculée 28,1%) et à la libération d'eau provenant de la condensation des groupes hydrogénophosphate HPO_4 (valeur observée 4,9%, calculée à 5,0%). La décomposition thermique s'explique par les trois équations suivantes :

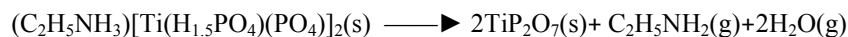


Dans le cas du composé **2**, l'ATG (Figure 23f) montre une perte de masse totale de 18,0%, entre 30°C et 1000°C ce qui correspond au résidu TiP_2O_7 (perte de masse calculée 18,2%). Les courbes d'ATD et DSC montrent un processus de décomposition thermique en deux étapes. La première étape, entre 40-150°C correspond à la libération d'une molécule d'eau par unité formulaire (valeur observée 3.3%, et calculée 3.3%). La deuxième étape, qui commence à une température de plus de 300°C correspond à l'élimination séquentielle de l'éthylamine et de l'eau provenant de la condensation des groupes hydrogénophosphate HPO_4 (valeur observée 14.7%, calculée à 14.9%). Le processus de décomposition s'explique par les deux équations suivantes :

Première étape :



Deuxième étape :



14. 3. 3. Étude par spectroscopie Infrarouge.

Le spectre infrarouge du composé **1** (Figure 23g) montre une forte bande centrée à 982cm^{-1} avec deux épaulements à 1236 et 1155cm^{-1} , attribués aux différents modes vibrationnels d'élongation P-O (symétrique et asymétrique) des groupes phosphate, ainsi que la présence des vibrations d'élongation C-N. La présence de molécules d'eau de cristallisation impliquée dans des liaisons hydrogène avec les fragments voisins, est confirmée par les modes vibrationnels d'élongation O-H vers 3414cm^{-1} et de déformation dans le plan H-O-H vers 1622cm^{-1} . Les cations hexylammonium donnent deux bandes d'élongation symétrique (2859cm^{-1}) et asymétrique ($2957, 2930\text{cm}^{-1}$) correspondant aux chaînes alkyle $-\text{CH}_2-$. Les bandes à 1520cm^{-1} et 2450cm^{-1} sont attribuées respectivement à la déformation dans le plan et à l'élongation de la liaison N-H de l'amine protonée. La vibration de balancement, typique du groupe méthylène, dans laquelle tous les groupes méthylène vibrent en phase, apparaît comme une bande d'intensité moyenne à 700cm^{-1} . En outre, les groupes $-\text{CH}_2-$ montrent une bande de cisaillement forte vers 1400cm^{-1} .

Dans le cas du composé **2**, le spectre infrarouge (Figure 23h) montre les vibrations d'élongation O-H et de déformation H-O-H. Les bandes fortes à 3611cm^{-1} et 3546cm^{-1} sont associées aux vibrations d'élongation O-H et P-O-H, alors que la bande à 1617cm^{-1} correspond aux modes vibrationnels de déformation dans le plan H-O-H. En

outre, les bandes intenses vers 1220 cm^{-1} sont attribuées au mode d'élongation dans le plan de P-O-H ou à la présence de molécules d'eau adsorbées sur les couches de phosphates. Les cations éthylammonium donnent les bandes qui correspondent aux modes d'élongation symétrique (vers 3009 cm^{-1}) et antisymétrique (vers 2987 et 2944 cm^{-1}) de chaînes alkyle $-\text{CH}_2-$, ainsi que les bandes vers 1560 cm^{-1} qui sont attribuées à la déformation planaire N-H, tandis que les bandes à 3284 cm^{-1} et 3144 cm^{-1} sont attribuées respectivement aux vibrations d'élongation N-H symétrique et asymétrique de la fonction amine protonée. Les groupes $-\text{CH}_2-$ montrent aussi une bande de cisaillement aiguë vers 1400 cm^{-1} . Une bande large à $900\text{-}1200\text{ cm}^{-1}$ correspond aux vibrations d'élongation et de déformation des liaisons

15. Applications.

Les applications potentielles des phosphates métalliques à charpente ouverte sont multiples : catalyse, séparation des gaz, échange d'ions [11, 52] etc. Les activités catalytiques restent actuellement limitées aux groupes des aluminophosphates et des matériaux dérivés en raison de leur stabilité thermique. Les tamis moléculaires de ce type contenant un autre métal, offrent un potentiel énorme en tant que catalyseurs hétérogènes pour des réactions d'oxydation en phase liquide dans la production de produits chimiques fins [53].

En revanche les applications des phosphates à charpente ouverte sont très limitées, à cause de la faible stabilité thermique des charpentes lors de l'élimination des templates par calcination. Certains matériaux, comme les phosphates de nickel (nommés VSB-1 et VSB-5) [54, 55] où il n'y a pas de matière organique dans les canaux, sont suffisamment stables et possèdent une très grande surface B.E.T : ils possèdent des propriétés d'échange d'ions, de catalyse sélective, et d'adsorption de l'hydrogène [55-58]. Les matériaux à charpente ouverte semblent être des candidats potentiels pour le stockage de l'hydrogène.

Sur un plan plus fondamental les solides à charpente ouverte, contenant un métal de transition, possèdent des propriétés magnétiques remarquables. Cette catégorie de matériaux montre différents types d'ordre magnétique (du ferromagnétisme à l'antiferromagnétisme). Ainsi, les charpentes de type phosphate-oxalate possèdent un ordre antiferromagnétique, comme cela est observé dans les cas de phosphates-oxalates de fer [59-63], de manganèse [64-66] et de cobalt [67].

16. Bibliographie générale :

- (1) H. Goldwhite, *Introduction to Phosphorus Chemistry*, Cambridge University Press: Cambridge, U.K. (1981).
- (2) M. T. Averbuch-Pouchot et A. Durif, *Topics in Phosphate Chemistry*, World Scientific, Singapore (1994).
- (3) A. Durif, *Crystal chemistry of Condensed Phosphates*, Plenum Press. New York (1995).
- (4) C. Alvarez, R. Llavona, J. R. García, M. Suárez, J. Rodríguez, *Lamellar inorganic ion exchangers. H⁺/Ca²⁺ ion exchange in γ -titanium phosphate*. *Inorg. Chem.* 1987, **26**, 1045–1049.
- (5) S. W. Martin, *Ionic Conduction in Phosphate Glasses*. *J. Am. Ceram. Soc.* 1991, **74**, 1767–1784.
- (6) L. Monceaux, P. Courtine, *Phosphorus in mild oxidation catalysts*, *Eur. J. Solid State Inorg. Chem.* 1991, **28**, 233–251.
- (7) D. Bartolo, *Luminescence of Inorganic Solids*, Ed. Plenum, New York (1978).
- (8) S. B. Ungashe, W. L. Wilson, H. E. Katz, G. R. Scheller, T. M. Putvinski, *Synthesis, self-assembly, and photophysical dynamics of stacked layers of porphyrin and viologen phosphonates*. *J. Am. Chem. Soc.* 1992, **114**, 8717–8719.
- (9) J. E. Marion, M. J. Weber, *Phosphate laser glasses*. *Eur. J. Solid State Inorg. Chem.* 1991, **28**, 271–287.
- (10) J. J. Videau, V. Dupuis, *Phosphates and biomaterials*. *Eur. J. Solid State Inorg. Chem.* 1991, **28**, 303–343.
- (11) S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, E. M. Flanigen, *Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids*. *J. Am. Chem. Soc.* 1982, **104**, 1146–1147.
- (12) L. Mafra, F. A. Almeida Paz, J. Rocha, A. Espina, S. A. Khainakov, J. R. García, C. Fernandez. *Structural Characterization of Layered γ -Titanium Phosphate (C₆H₁₃NH₃)[Ti(HPO₄)(PO₄)] · H₂O*. *Chem. Mater.* 2005, **17**, 6287–6294.
- (13) L. Mafra, J. Rocha, C. Fernandez, G. R. Castro, S. García-Granda, A. Espina, S. A. Khainakov, J. R. García. *Characterization of Layered γ -Titanium Phosphate (C₂H₅NH₃)[Ti(H_{1.5}PO₄)(PO₄)₂ · H₂O Intercalate: A Combined NMR, Synchrotron XRD, and DFT Calculations Study*. *Chem. Mater.* 2008, **20**, 3944–3953.
- (14) S. Neeraj, P. M. Forster, C. N. R. Rao, A. K. Cheetham, *A new route for the synthesis of open-framework metal phosphates using organophosphates*. *Chem. Commun.* 2001, **24**, 2716–2717.
- (15) C. N. R. Rao, S. Natarajan, S. Neeraj, *Exploration of a Simple Universal Route to the Myriad of Open-Framework Metal Phosphates*. *J. Am. Chem. Soc.* 2000, **122**, 2810–2817.
- (16) S. Neeraj, A. K. Cheetham, *Synthesis of open-framework zinc phosphates from organophosphorus amides*. *Chem. Commun.* 2002, **16**, 1738–1739.
- (17) R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja, C. N. R. Rao, *Metal Complexes of Organophosphate Esters and Open-Framework Metal Phosphates: Synthesis, Structure, Transformations, and Applications*. *Chem. Rev.* 2008, **108**, 3549–3655.

- (18) L. Rocés, J. R. García, *Novel polyvalent metal phosphates. Hydrothermal synthesis and characterization*. Recent Res. Dev. Inorg. Chem. 2003, **3**, 1–18.
- (19) D. Turnbull, *Metastable Structures in Metallurgy*. Metall. Trans. 1981, **124**, 695–708.
- (20) A. Smits, *The Theory of Allotropy*. BiblioLife, LLC (2009) (page 98).
- (21) H. H. Tung, E. L. Paul, M. Midler. *Crystallization of organic compounds: an industrial perspective*. John Wiley & Sons, New York (2009) (page 50).
- (22) S. Neeraj, S. Natarajan, C. N. R. Rao, *Isolation of a Zinc Phosphate Primary Building Unit, $[C_6N_2H_{18}]^{2+}[Zn(HPO_4)(H_2PO_4)_2]^{2-}$, and Its Transformation to an Open-Framework Phosphate, $[C_6N_2H_{18}]^{2+}[Zn_3(H_2O)_4(HPO_4)_4]^{2-}$* , J. Solid State Chem. 2000, **150**, 417–422.
- (23) A. Choudhury, S. Natarajan, C. N. R. Rao, *Formation of One-, Two-, and Three-Dimensional Open-Framework Zinc Phosphates in the Presence of a Tetramine*. Inorg. Chem. 2000, **39**, 4295–4304.
- (24) A. Choudhury, C. N. R. Rao, *Hydrothermal Synthesis and Structure of Organically Templated One-Dimensional and Three-Dimensional Iron Fluorophosphate*. J. Struct. Chem. 2002, **43**, 632–642.
- (25) A. M. Chippindale, S. Natarajan, J. M. Thomas, R. H. Jones, *An Example of a Reactive Template in the Synthesis of a Novel Layered Aluminum Phosphate, $(Al_3P_4O_{16})^{3-}(NH^3(CH^2)^5NH^3)^{2+}(C_5H_{10}NH_2)^+$* , J. Solid State Chem. 1994, **111**, 18–25.
- (26) D. Zhang, Z. Shi, S.-H. Feng, *Hydrothermal synthesis and crystal structure of inorganic-organic hybrid compound $[H_3NC_2H_4NH_2]VOPO_4$* . Chem. Res. Chin. Univ. 2001, **17**, 249.
- (27) R. Yu, D. Wang, S. Ishiwata, T. Saito, M. Azuma, M. Takano, Y. Chen, J. Li. *Synthesis and Characterization of the First Organically Templated Layered Cerium Phosphate Fluoride: $[(CH_2)_2(NH_3)_2]_{0.5}[Ce^{IV}F_3(HPO_4)]$* , J. Chem. Lett. 2004, **33**, 458.
- (28) S. Natarajan, S. Neeraj, A. Choudhury, C. N. R. Rao, *Three-Dimensional Open-Framework Cobalt(II) Phosphates by Novel Routes*. Inorg. Chem. 2000, **39**, 1426–1433.
- (29) C. Sassoey, T. Loiseau, F. Taulelle, G. Férey, *A new open-framework fluorinated gallium phosphate with large 18-ring channels (MIL-31)*, Chem. Commun. 2000, **11**, 943–944.
- (30) A. Choudhury, S. Natarajan, C. N. R. Rao, *An open-framework iron phosphate with large voids, exhibiting spin-crossover*. Chem. Commun. 1999, **14**, 1305–1306.
- (31) H. H. Limbach, J. Hennig, R. Kendrick, C. S. Yannoni, *Proton-transfer kinetics in solids: tautomerism in free base porphines by nitrogen-15 CPDAS NMR*. J. Am. Chem. Soc. 1984, **106**, 4059–4060.
- (32) S. P. Brown, H. W. Spiess, *Advanced Solid-State NMR Methods for the Elucidation of Structure and Dynamics of Molecular, Macromolecular, and Supramolecular Systems*. Chem. Rev. **101**, 2001, 4125.
- (33) L. Mafra, C. Coelho, R. Siegel, J. Rocha, *Assessing the performance of windowed 1H CRAMPS methods, on biological solids, at high-field and MAS up to 35 kHz*. J. Magn. Reson. 2009, **197**, 20–27.
- (34) L. Mafra, R. Siegel, C. Fernandez, D. Schneider, F. Aussenac, J. Rocha, *High-resolution 1H homonuclear dipolar recoupling NMR spectra of*

- biological solids at MAS rates up to 67 kHz*. J. Magn. Reson. 2009, **199**, 111-114.
- (35) R. Siegela, J. Rocha, L. Mafra, *Combining STMAS and CRAMPS NMR spectroscopy: High-resolution HETCOR NMR spectra of quadrupolar and ^1H nuclei in solids*. Chem. Phys. Lett. 2009, **470**, 337-341.
- (36) D.M. Poojary, and A. Clearfield, *Application of X-ray Powder Diffraction Techniques to the Solution of Unknown Crystal Structures*. Accounts of Chemical Research **30** (1997) 414 - 422.
- (37) R.K. Harris, *NMR Crystallography*. Solid State Sciences The Use of Chemical Shifts (2004)
- (38) R.K. Harris, P. Jackson, L.H. Merwin, B.J. Say, and G. Hagele, *Perspectives in High-Resolution Solid-State Nuclear Magnetic-Resonance, with Emphasis on Combined Rotation and Multiple-Pulse Spectroscopy*. Journal of the Chemical Society-Faraday Transactions I **84** (1988) 3649 - 3672.
- (39) E. Brunner, and U. Sternberg, *Solid-State NMR Investigations on the Nature of Hydrogen Bonds*. Progress in Nuclear Magnetic Resonance Spectroscopy **32** (1998) 21 - 57.
- (40) I. Schnell, *Dipolar Recoupling in Fast-MAS Solid-State NMR Spectroscopy*. Progress in Nuclear Magnetic Resonance Spectroscopy **45** (2004) 145 - 207.
- (41) S. Pawsey, M. McCormick, S.D. Paul, R. Graf, Y.S. Lee, L. Reven, and H.W. Spiess, *H-1 Fast MAS NMR Studies of Hydrogen-Bonding Interactions in Self-Assembled Monolayers*. Journal of the American Chemical Society **125** (2003) 4174 - 4184.
- (42) A.E. Aliev, and K.D.M. Harris, *Probing Hydrogen Bonding in Solids Using Solid State NMR Spectroscopy*, Springer-Verlag, Berlin, 2004.
- (43) T. Loiseau, G. Ferey, M. Haouas, and F. Taulelle, *Structural Analysis of F/OH Distribution in a Hybrid Open-Framework Fluorinated Gallium Oxalate-Phosphate Templated by 1,3-Diaminopropane (MIL-90)*. Chemistry of Materials **16** (2004) 5318 - 5326.
- (44) G. Mali, N. Rajic, N.Z. Logar, and V. Kaucic, *Solid-State NMR Study of an Open-Framework Aluminophosphate-Oxalate Hybrid*. Journal of Physical Chemistry B **107** (2003) 1286 - 1292.
- (45) V. Lafond, C. Gervais, J. Maquet, D. Prochnow, F. Babonneau, and P.H. Mutin, *O-17 MAS NMR Study of the Bonding Mode of Phosphonate Coupling Molecules in a Titanium Oxo-Alkoxo-Phosphonate and in Titania-Based Hybrid Materials*. Chemistry of Materials **15** (2003) 4098 - 4103.
- (46) C. Coelho, J. Rocha, P.K. Madhu, and L. Mafra, *Practical aspects of Lee-Goldburg based CRAMPS techniques for high-resolution H-1 NMR spectroscopy in solids: Implementation and applications*, J Magn Reson, 2008, pp. 264-282.
- (47) L. Cunha-Silva, L. Mafra, D. Ananias, L.D. Carlos, J. Rocha, and F.A. Almeida Paz, *Photoluminescent lanthanide-organic 2D networks: A combined synchrotron powder X-ray diffraction and solid-state NMR study*, Chem Mater, 2007, pp. 3527-3538.
- (48) L. Liu, S. Ferdov, C. Coelho, Y. Kong, L. Mafra, J.P. Li, J.X. Dong, U. Kolitsch, R.A.S. Ferreira, E. Tillmanns, J. Rocha, and Z. Lin, *New Crystalline Layered Zinc Phosphate with 10-Membered-Ring Channels Perpendicular to Layers*, Inorg Chem, 2009, pp. 4598-4600.
- (49) -, G. Castro, J. Rocha, and L. Mafra, *Revisiting the Thermal Decomposition of Layered γ -Titanium*

- Phosphate and Structural Elucidation of Its Intermediate Phases*. Inorg. Chem, 2010, **49**, pp. 2630–2638.
- (50) C.I. Ratcliffe, J.A. Ripmeester, and J.S. Tse, *NMR chemical shifts of dilute 1H in inorganic solids*. Chemical Physics Letters **120** (1985) 427.
- (51) M.J. Potrzebowski, X. Assfeld, K. Ganicz, S. Olejniczak, A. Cartier, C. Gardiennet, and P. Tekely, *An experimental and theoretical study of the ^{13}C and ^{31}P chemical shielding tensors in solid *o*-phosphorinated amino acids*. Journal of the American Chemical Society **125** (2003) 4223 - 4232.
- (52) M.E. Davis. *Ordered porous materials for emerging applications*. Nature, 2002, **417**, 813–821.
- (53) M. Hartmann, L. Kevan, *Transition-Metal Ions in Aluminophosphate and Silicoaluminophosphate Molecular Sieves: Location, Interaction with Adsorbates and Catalytic Properties*. Chem. Rev. 1999, **99**, 635–664.
- (54) N. Guillou, Q. Gao, M. Nogues, R. E. Morris, M. Hervieu, G. Férey, A. K. Cheetham, *Zeolitic and magnetic properties of a 24-membered ring porous nickel(II) phosphate, VSB-1*. C. R. Acad. Sci Paris 1999, **2**, 387–392.
- (55) N. Guillou, Q. Gao, P. M. Forster, J.-S. Chang, M. Nogues, S. E. Park, G. Férey, A. K. Cheetham, *Nickel(II) Phosphate VSB-5: A Magnetic Nanoporous Hydrogenation Catalyst with 24-Ring Tunnels*. Angew. Chem., Int. Ed. 2001, **40**, 2831–2834.
- (56) J.-S. Chang, S.-E. Park, Q. Gao, G. Férey, A. K. Cheetham, *Catalytic conversion of butadiene to ethylbenzene over the nanoporous nickel(II) phosphate, VSB-1*. Chem. Commun. 2001, **9**, 859–860.
- (57) J.-S. Chang, J.-S. Hwang, S. H. Jung, S. E. Park, G. Férey, A. K. Cheetham, *Nanoporous Metal-Containing Nickel Phosphates: A Class of Shape-Selective Catalyst*. Angew. Chem., Int. Ed. 2004, **43**, 2819–2822.
- (58) P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Férey, A.K. Cheetham, *Hydrogen Adsorption in Nanoporous Nickel(II) Phosphates*. J. Am. Chem. Soc. 2003, **125**, 1309–1312.
- (59) A. Choudhury, S. Natarajan, *A hybrid open-framework structure: synthesis and structure of an iron phosphate oxalate, $[C_{10}N_4H_{28}][Fe_2(HPO_4)_3(C_2O_4)]_2$* . J. Mater. Chem. 1999, **9**, 3113–3117.
- (60) A. Choudhury, S. Natarajan, C. N. R. Rao, *A Hybrid Open-Framework Iron Phosphate–Oxalate with a Large Unidimensional Channel, Showing Reversible Hydration*. Chem. Mater. 1999, **11**, 2316–2318.
- (61) A. Choudhury, S. Natarajan, C. N. R. Rao, *Hybrid Open-Framework Iron Phosphate-Oxalates Demonstrating a Dual Role of the Oxalate Unit*. Chem. Eur. J. 2000, **6**, 1168–1175.
- (62) Y. C. Jiang, S. L. Wang, S. F. Lee, K. H. Lii, *Novel Transition Metal Oxalatophosphates with a Two-Dimensional Honeycomb Structure: $(H_3TREN)[M_2(HPO_4)(C_2O_4)_{2.5}] \cdot 3H_2O$ ($M = Mn^{II}$ and Fe^{II} , TREN = Tris(2-aminoethyl)amine)*. Inorg. Chem. 2003, **42**, 6154–6156.
- (63) Y. C. Jiang, S. L. Wang, K. H. Lii, *Synthesis, Crystal Structure, Magnetic Susceptibility, and Mössbauer Spectroscopy of a Mixed-Valence Organic–Inorganic Hybrid Compound: $(H_3DETA)[Fe_3(C_2O_4)_2(HPO_4)_2(PO_4)]$ (DETA = Diethylenetriamine)*. Chem. Mater. 2003, **15**, 1633–1638.

- (64) Z. A. D. Lethbridge, A. D. Hillier, R. Cywinski, P. Lightfoot, *Mixed inorganic–organic anion frameworks: synthesis and characterisation of $[Mn_4(PO_4)_2(C_2O_4)(H_2O)_2]$ and $[H_3N(CH_2)_3NH_3][Mn_2(HPO_4)_2(C_2O_4)(H_2O)_2]$* . J. Chem. Soc., Dalton Trans. 2000, **10**, 1595–1599.
- (65) Z. A. D. Lethbridge, S. K. Tiwary, A. Harrison, P. Lightfoot, *Synthesis, structural relationships and magnetic properties of new amine-templated manganese(II) phosphate oxalate framework materials*. J. Chem. Soc., Dalton Trans. 2001, **12**, 1904–1910.
- (66) Z. A. D. Lethbridge, M. J. Smith, S. K. Tiwary, A. Harrison, P. Lightfoot, *Synthesis of Hybrid Framework Materials under “Dry” Hydrothermal Conditions: Crystal Structure and Magnetic Properties of $Mn_2(H_2PO_4)_2(C_2O_4)$* . Inorg. Chem. 2004, **43**, 11–13.
- (67) A. Choudhury, S. Natarajan, *Inorganic hybrid open-framework structures: synthesis and structure of a cobalt phosphate-oxalate, $[C_4N_2H_{12}]_{0.5}[Co_2(HPO_4)(C_2O_4)_{1.5}]$* . Solid State Sci. 2000, **2**, 365–372.

3.2. Polímeros de coordinación basados en succinatos de itrio.

Artículo I

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Resumen

Este trabajo recoge la síntesis de nuevos polímeros de coordinación basados en itrio y un ligando de vinculación bidentado flexible de tipo carboxílico, el ácido succínico.

Se describe la síntesis hidrotérmica de dos nuevos polímeros de coordinación, uno de ellos laminar, $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$, y otro tridimensional, $Y_2(C_4H_4O_4)_3(H_2O)_2$. Las estructuras cristalinas de ambos materiales se determinan mediante difracción de rayos X de monocristal, describiéndose comparativamente con la de un compuesto tridimensional, $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$, caracterizado previamente [99]. Los tres compuestos han podido ser obtenidos como fases de elevada pureza, analizándose su comportamiento térmico mediante técnicas termoanalíticas (TG-MS/SDTA y DSC).

Los ligandos flexibles de tipo dicarboxilato son muy utilizados en la síntesis de polímeros de coordinación con estructuras bi- y tri-dimensionales, ya que presentan una gran versatilidad, que deriva en propiedades interesantes, consecuencia de la diversidad

de sus diferentes modos de coordinación con los elementos metálicos, que pueden coexistir en una misma estructura, así como de su flexibilidad conformacional, en adición a su capacidad para actuar como donantes y receptores de puentes de hidrógeno. Entre ellos, encontramos el ácido succínico, cuya capacidad para adoptar diferentes conformaciones (eclipsada, oblicua, opuesta, anti) facilita la formación de estructuras que involucran iones metálicos de muy distintos tamaños.

Se han realizado numerosos esfuerzos en la síntesis hidrotermal de polímeros de coordinación basados en elementos lantánidos y ácido succínico, algunos de ellos con interesantes propiedades luminiscentes, magnéticas, y catalíticas. Sin embargo, solamente hemos accedido a escasos estudios detallados sobre polimorfos de polímeros de coordinación basados en succinatos de lantánidos. Así, Ruiz-Valero *et al.* [99] son los únicos que, previamente a nuestra investigación, habían reportado la síntesis y caracterización estructural de un succinato de itrio: $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$. Su actividad como catalizador heterogéneo hizo que considerásemos potencialmente interesante la síntesis de otros miembros de esta familia, llevándonos a explorar el autoensamblaje de especies succinato y cationes itrio(III) mediante dos aproximaciones sintéticas diferentes: *i*) la variación de las concentraciones y la relación molar succinato-itrio, y *ii*) el uso de ligandos adicionales, como los derivados del ácido tereftálico o del ácido trimelítico.

Los tres polímeros de coordinación basados en succinatos de itrio, $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$ (**1**) [99], $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ (**2**), y $Y_2(C_4H_4O_4)_3(H_2O)_2$ (**3**), se han obtenido mediante síntesis hidrotermal, partiendo de $YCl_3 \cdot 6H_2O$, ácido succínico, H_2O , NaOH, y ligandos adicionales (ácido tereftálico en el caso de **2**, y ácido trimelítico en el caso de **3**). La mezcla de reacción se agitó en un recipiente de teflón (volumen interno de 40 mL) a temperatura ambiente hasta su homogenización y luego se introdujo en un autoclave de acero inoxidable que se mantuvo durante 78 horas en estufa a la temperatura de 180 °C. Después de su optimización, las condiciones de síntesis, que conducen a la obtención de sólidos monofásicos, se resumen en la siguiente Tabla:

Compuesto	YCl ₃ ·6H ₂ O	Ácido succínico	Ligando adicional	NaOH	H ₂ O
1	1 mmol (0.31 g)	1.5 mmol (0.17g)	—	1.5 mmol (0.06g)	15 mL
2	1 mmol (0.31 g)	0.5 mmol (0.06g)	Ácido tereftálico 0.08 g (0.5 mmol)	2 mmol (0.08g)	10 mL
3	1 mmol (0.31 g)	0.5 mmol (0.06g)	Ácido trimelítico 0.08 g (0.5 mmol)	2 mmol (0.08g)	10 mL

Las estructuras cristalinas de los compuestos **2** y **3** fueron determinadas por difracción de rayos X de monocristal y comparadas con la del compuesto **1**. La siguiente Tabla muestra los parámetros cristalográficos de estos compuestos:

Compuesto	1	2	3
<i>Sistema cristalino</i>	Monoclínico	Triclínico	Triclínico
<i>Grupo espacial</i>	<i>C2/c</i>	<i>P -1</i>	<i>P -1</i>
<i>Dimensiones de la celda unidad</i>			
<i>a (Å)</i>	19.937(2)	6.5328(2)	7.5909(1)
<i>b (Å)</i>	7.6855(7)	9.7828(4)	8.4348(2)
<i>c (Å)</i>	13.811(1)	10.4889(3)	13.8238(3)
<i>α (°)</i>	-	80.211(1)	97.104(2)
<i>β (°)</i>	121.652(1)	89.831(2)	98.377(2)
<i>γ (°)</i>	-	71.378(2)	98.696(2)
<i>Volumen de celda (Å³)</i>	1801.4(3)	625.05(4)	855.94(3)

El compuesto **1** [99] presenta una estructura tridimensional con canales vacíos (sección transversal de aproximadamente 7x3 Å²) extendidos a lo largo del eje cristalográfico *c* y cavidades, de aproximadamente 7x5 Å², alineadas en la dirección del eje *b*, que albergan las moléculas de agua estructural (Figura 3.2.1a). Cada catión itrio está coordinado por nueve átomos de oxígeno (Figura 3.2.1b), adoptando una geometría de prisma trigonal tricofiado (Figura 3.2.1c) que, compartiendo aristas, originan cadenas de poliedros paralelas al eje *b*, con una distancia entre cationes itrio adyacentes de 4.0088(3) Å. Estas cadenas, a su vez, están vinculadas a través de aniones succinato en las direcciones cristalográficas [001] y [101], constituyendo la estructura tridimensional característica del compuesto. De los nueve átomos de oxígeno que rodean cada catión itrio, ocho pertenecen a tres grupos carboxílicos cristalográficamente independientes, que a su vez proceden de dos aniones succinato, también cristalográficamente diferentes, mientras que el último átomo de oxígeno pertenece a la molécula de agua coordinada.

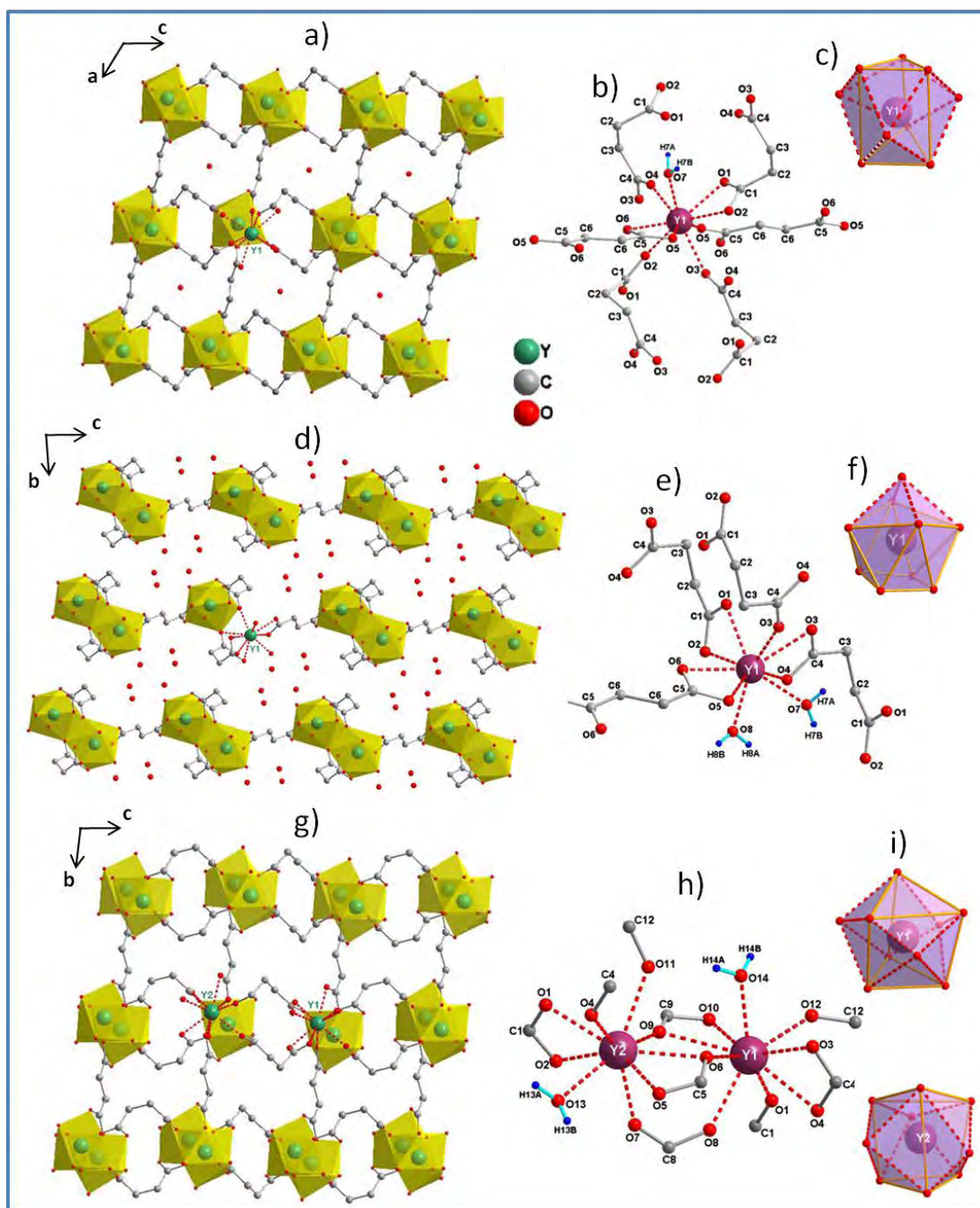
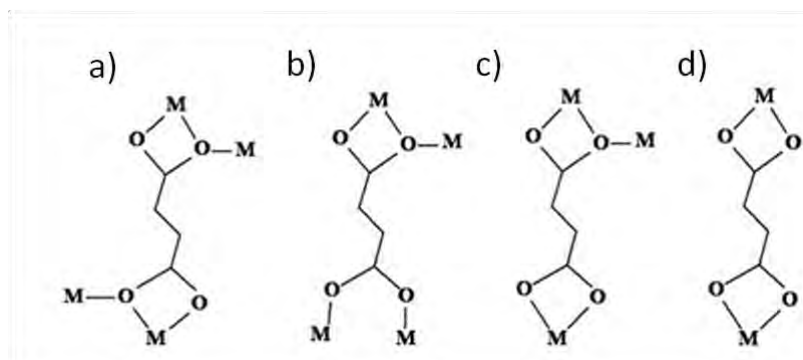


Figura 3.2.1. Proyección de la estructura de **1** (a) a lo largo del eje *b*, y de **2** (d) y **3** (g) a lo largo del eje *a*. Entorno de coordinación local del cation itrio en **1** (b,c), **2** (e,f), y **3** (h,i).

La estructura laminar del compuesto **2** está construida a partir de la vinculación bidimensional de cationes itrio y ligandos succinato, situándose las moléculas de agua no coordinadas en el espacio interlaminar (Figura 3.2.1d). Cada catión itrio está coordinado por nueve átomos de oxígeno (Figura 3.2.1e), siete de ellos pertenecientes a dos ligandos succinato cristalográficamente independientes, mientras que los otros dos provienen de las dos moléculas de agua coordinadas, definiendo un poliedro de coordinación tipo antiprisma cuadrado monocofiado (Figura 3.2.1f). Poliedros adyacentes, compartiendo una arista, generan dímeros Y_2O_{16} centrosimétricos (distancia itrio-itrio: 4.114(2) Å) que se unen mediante ligandos succinato en las direcciones cristalográficas [100] y [101]. Adicionalmente, existen enlaces de hidrógeno interlaminares que involucran tanto a moléculas de agua coordinadas como no coordinadas y a átomos de oxígeno de los grupos carboxílicos, proporcionando la estabilidad 3D de la estructura.

La estructura del compuesto **3** es tridimensional (Figura 3.2.1g), con dos cationes itrio cristalográficamente independientes, ambos nonacoordinados (Figura 3.2.1h) en una geometría de prisma trigonal tricofiado (Figura 3.2.1i), definida por ocho átomos de oxígeno asociados a seis grupos carboxílicos, que pertenecen a tres aniones succinatos diferentes, y un noveno procedente de una molécula de agua coordinada. Estos poliedros de coordinación, compartiendo aristas, forman cadenas a lo largo del eje *a*, vinculadas a través de puentes succinato a lo largo de los ejes *b* y *c*, formando el marco 3D. La distancia entre cationes itrio adyacentes en la cadena es de 4.0001(2) Å.

Al contrario que en el compuesto **2**, en las estructuras **1** y **3** el ligando succinato adopta modos de coordinación idénticos (ver Esquema 3.2.1). A pesar de ello, ambos compuestos tridimensionales presentan diferencias topológicas debidas a las distintas conformaciones adoptadas por el ligando succinato en cada estructura. La formación del compuesto **3**, está favorecida por la presencia del ácido trimelítico como ligando adicional en el medio de reacción, lo que deriva en la adopción de un número más elevado de conformaciones diferentes del ligando succinato que el manifestado en los compuestos **1** y **2**. Por otro lado, la presencia del ácido tereftálico como ligando adicional conduce a la formación de **2**, con una disminución en el número de grupos carboxílicos coordinados y, consecuentemente, con un aumento en el número de moléculas de agua en la primera esfera de coordinación del itrio, que a su vez induce la presencia de agua no coordinada.



Esquema 3.2.1. Modos de coordinación de ligandos succinato en 1 y 3 (a,b), y en 2 (c,d).

Se ha investigado la estabilidad térmica de los compuestos sintetizados (**1**, **2** y **3**). La Figura 3.2.2 recoge los resultados obtenidos, en atmósfera dinámica de oxígeno, mediante calorimetría diferencial de barrido (DSC) y termogravimetría asociada al análisis por espectrometría de masas de los gases evacuados (TG-MS) y al análisis térmico diferencial (SDTA). Las curvas TG desde temperatura ambiente hasta 1000 °C de **1**, **2** y **3** muestran, respectivamente, las siguientes pérdidas de masa total (el producto final, confirmado por difracción de rayos X del polvo cristalino residual, es Y_2O_3): 60.6% (cal. 61.05%), 69.3% (cal. 68.01%), y 58.6% (cal.59.78%).

Los compuestos **1** y **3** poseen secuencias de descomposición térmica similares, esperables en función de sus semejanzas en composición química, modo de coordinación de los ligandos y dimensionalidad estructural. Sin embargo, la cuantificación de las temperaturas tanto de deshidratación como de descomposición traslucen que el compuesto **3** es el térmicamente más estable del conjunto, seguido por el **1**, siendo el **2** el que presenta una menor resistencia a la descomposición. La secuencia es lógica al considerar que solamente los compuestos **1** y **2** poseen agua no coordinada y, de ellos, el compuesto que posee estructura tridimensional (**1**) debe ser más estable que el que presenta hábito laminar (**2**). Después de la deshidratación, los compuestos resultantes de la deshidratación de **1** y **3** son estables, respectivamente, hasta 370 °C y 400 °C, presentando variaciones de entalpía de descomposición térmica oxidativa comparables entre sí, -2888 y -2710 kJ/mol respectivamente, pero inferiores en valor absoluto a la del compuesto **2** (-3601 kJ/mol), como consecuencia de la diferencia en composición y estructura de los compuestos intermedios.

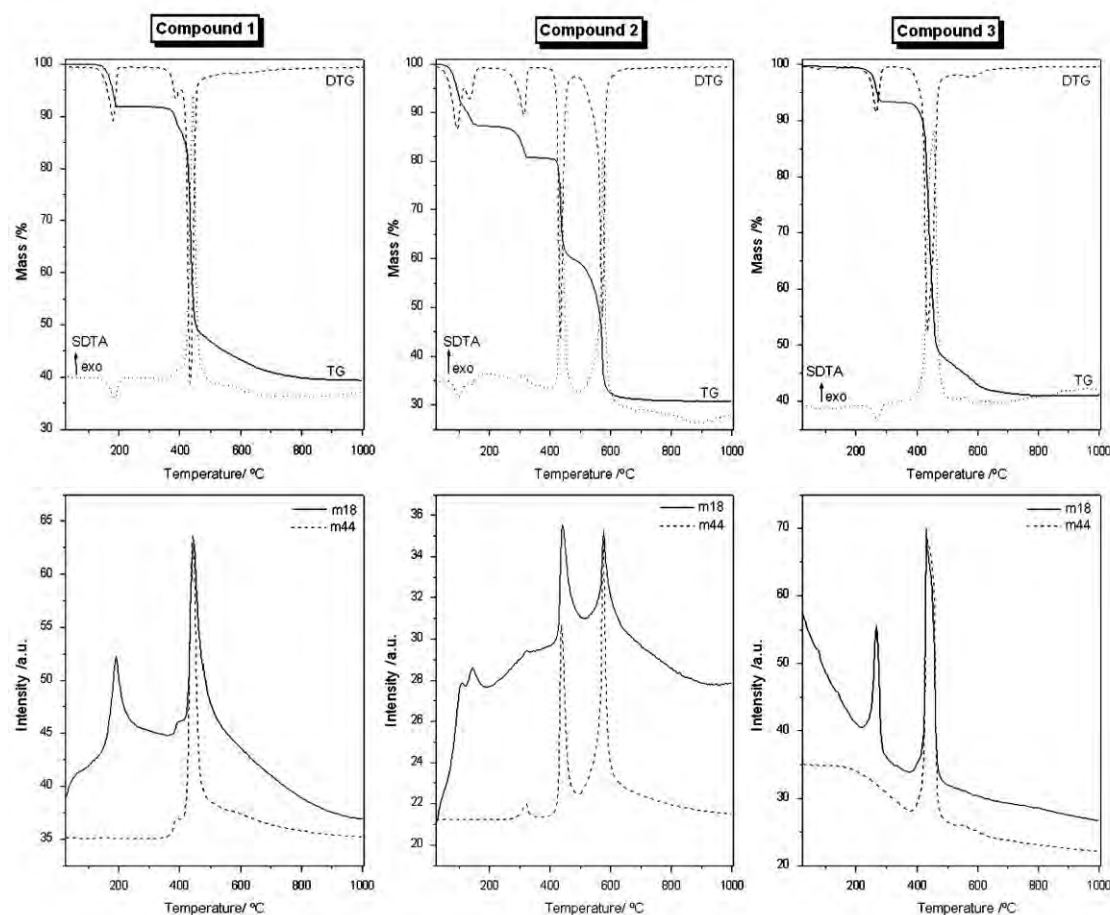


Figura 3.2.2. Curvas TG-DTG-SDTA y monitorización de los vapores evacuados por espectrometría de masas, m/z 18 (H_2O) y m/z 44 (CO_2).

El conocimiento de las peculiaridades estructurales de estos compuestos permite comprender los factores causantes del grado de estabilidad térmica de los compuestos sintetizados, entre los que deben mencionarse: *i*) el gran número de moléculas de agua (coordinadas y no coordinadas) en el caso de **2**, *ii*) las moléculas de agua no coordinadas que residen en los canales de **1**, *iii*) las distancias Y-O más cortas en **3** que en **1** y en **2**, y *iv*) la conectividad Y-O-Y doble e infinita en **1** y en **3**, pero ausente en **2**.

Artículo I



Yttrium-succinates coordination polymers: Hydrothermal synthesis, crystal structure and thermal decomposition

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ABSTRACT

New polymeric yttrium-succinates, $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ and $Y_2(C_4H_4O_4)_3(H_2O)_2$, have been synthesized, and their structures (solved by single crystal XRD) are compared with that of $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$. Three compounds were obtained as single phases, and their thermal behaviour is described.

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1. Introduction

The materials known as coordination polymers or MOF's, built from organic and inorganic units, represent one of the most active and attractive research fields in materials science, that has known a considerable development in the last decade, because of their structural diversity, and interesting properties, which lead to applications in areas such as gas (especially hydrogen) storage [1–9] and separation [10–13], catalysis [14–19], ion-exchange [20,21], magnetism [22,23], luminescence [24–27], or non-linear optics [28], and therefore open up the possibility of creating novel multifunctional devices.

The flexible dicarboxylates ligands are much used in the synthesis of 2D and 3D coordination polymers, and present interesting properties, owing to both their diversity of coordination modes with metals, which may coexist in a given material, and to their conformational flexibility and ability to act as hydrogen-bond donors and acceptors. Among them, succinic acid adopts eclipsed, skew, opposed, and anti conformations, and possesses the ability to form frameworks with metal ions of different size [29,30]. The synthesis of such systems has been,

mainly, focused on the use of transition metals. However, lanthanides (Ln) have received significant attention in the last years, because of their wide range of properties such as magnetism and photoluminescence. Ln^{3+} cations exhibit high affinity for oxygen [31], diverse coordination modes and variable coordination numbers [31,32]. Numerous works have been carried out using the hydrothermal synthesis route to prepare lanthanide coordination polymers of succinic acid [33–38], and some of them have investigated their luminescence [29,39,40], magnetic [30], and catalytic properties [41,42]. Nevertheless, to the best of our knowledge, there are only a few detailed studies reporting polymorphs of Ln(III)-succinic acid, either by using different synthetic methods, or by changing the reaction conditions [29,43].

Ruiz-Valero et al. [41] have reported the synthesis and structural characterization of the unique yttrium-succinate described up to now, $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$. Its activity as heterogeneous catalyst makes the synthesis of other members in this family potentially interesting. These observations have prompted us to explore self-assembly in Y(III)-succinate systems. Here, we wish to report the hydrothermal synthesis and structural characterization of two novel yttrium-succinates coordination polymers, layered $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ and framework $Y_2(C_4H_4O_4)_3(H_2O)_2$. Two synthetic approaches were used: (i) changing the concentrations and succinate/yttrium ratios and

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(ii) using additive ligands, such as terephthalic acid and trimellitic acid.

2. Experimental section

2.1. Synthesis

The yttrium-succinates, $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$ (**1**), $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ (**2**) and $Y_2(C_4H_4O_4)_3(H_2O)_2$ (**3**) were synthesized under hydrothermal conditions.

For the preparation of **1**, 0.31 g (1 mmol) of $YCl_3 \cdot 6H_2O$, 0.17 g (1.5 mmol) of succinic acid was mixed in 15 mL of distilled water. After adjusting the pH value to 5 by addition of NaOH 1M (ca. 1.5 mL) the reaction mixture was stirred at room temperature to homogeneity and then placed in a Teflon-lined stainless vessel (40 mL) and heated to 180 °C for 78 h under autogenous pressure and afterwards cooled to room temperature.

Compounds **2** and **3** were obtained in presence of terephthalic acid or trimellitic acid, respectively, with a synthesis procedure analogous to the preparation of **1**. Compound **2**: 0.31 g of $YCl_3 \cdot 6H_2O$ (1 mmol), 0.06 g of succinic acid (0.5 mmol), 0.08 g of terephthalic acid (benzene-1,4-dicarboxylic acid) (0.5 mmol) and 0.08 g of NaOH (2 mmol) in 10 mL of distilled water. Compound **3**: $YCl_3 \cdot 6H_2O$ (1 mmol), 0.06 g of succinic acid (0.5 mmol), 0.07 g of trimellitic acid (benzene-1,2,4-tricarboxylic acid) (0.33 mmol) and 0.08 g of NaOH (2 mmol) in 10 mL of distilled water.

In all cases, the resulting products were obtained as a single phase of colourless crystals. The solids were filtered off, washed thoroughly with distilled water, and finally air-dried at room temperature. The yield of such phase (based on Y) was of about 10% (**1** and **2**) or 15% (**3**).

We are still investigating this system, however, we have to admit that this system is very complicated to study. By using BDC and BTC, we have obtained pure phases with poor yield

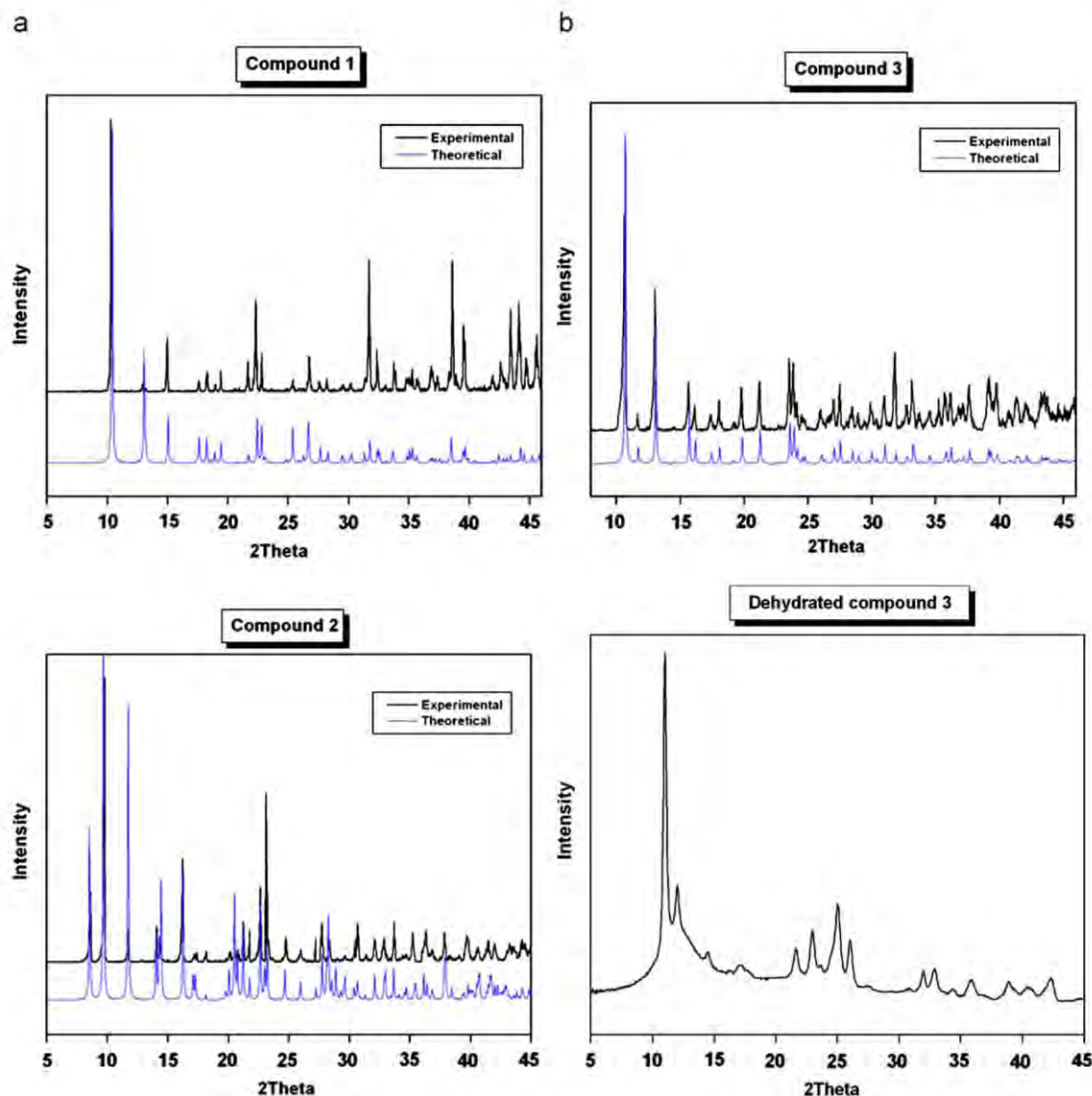


Fig. 1. XRD patterns of **1**, **2**, **3** compared with the theoretical ones (a) and dehydrated compound **3** (b).

(mentioned above), in most cases, by changing Y-succinic acid ratio/concentration, we obtain mixture of two phases belonging to the compounds **1** and **3**. The reaction yields are low, the optimisation of the synthesis conditions are needed. The use of the pH in the range of 5–6 is sufficient to deprotonate the carboxylate ligands used. At low pH value no phase has been formed. In the case of Y-BDC system, BDC crystalline was obtained, in the case of Y-BTC system no phase has been formed.

The X-ray powder diffraction patterns of the three compounds were performed and compared with the theoretical ones (Fig. 1a). The powder XRD pattern of dehydrated **3** showed a poor crystallinity for this material (Fig. 1b). **1** shows a similar behaviour. For **2**, both dehydration and decomposition steps are overlapped.

2.2. Single-crystal X-ray diffraction studies

Data collection was performed at 293 K on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using CuK α radiation ($\lambda=1.54180\text{ \AA}$). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image. The crystal structure was solved by direct methods. The refinement was performed using full-matrix least squares on F 2 . All non-H atoms were anisotropically refined. All H atoms were either geometrically placed riding on their parent atoms or obtained from the difference Fourier map, with isotropic displacement parameters set to 1.2 times the U $_{eq}$ of the atoms to which they are attached. Crystallographic calculations were carried out using the following

Table 2

Selected bond lengths (Å) and bond angles ($^\circ$) for compounds **2** and **3**.

Compound 2			
Y(1)–O(8)	2.318(2)	C(1)–O(2)	1.252(4)
Y(1)–O(3)	2.330(2)	C(1)–O(1)	1.268(4)
Y(1)–O(7)	2.353(2)	O(2)–C(1)–O(1)	119.1(3)
Y(1)–O(1)	2.383(2)	C(4)–O(4)	1.246(4)
Y(1)–O(4)	2.394(2)	C(4)–O(3) ^I	1.274(4)
Y(1)–O(5)	2.399(2)	O(4)–C(4)–O(3) ^I	119.3(3)
Y(1)–O(6)	2.454(2)	C(5)–O(5)	1.267(4)
Y(1)–O(2)	2.489(2)	C(5)–O(6)	1.268(4)
Y(1)–O(3) ^{II}	2.606(2)	O(5)–C(5)–O(6)	118.0(3)
Y(1)–Y(1)	4.113(2)		
Compound 3			
Y(1)–O(12)	2.3053(14)	C(1)–O(2)	1.240(3)
Y(1)–O(14)	2.3460(15)	C(1)–O(1)	1.277(2)
Y(1)–O(8) ^{II}	2.3469(15)	O(2)–C(1)–O(1)	119.07(18)
Y(1)–O(6) ^{II}	2.3704(14)	C(4)–O(3)	1.236(3)
Y(1)–O(1)	2.3945(14)	C(4)–O(4) ^{IV}	1.285(3)
Y(1)–O(10) ^{II}	2.4172(14)	O(3)–C(4)–O(4) ^{IV}	119.63(19)
Y(1)–O(3) ^{III}	2.4599(16)	C(5)–O(5)	1.248(3)
Y(1)–O(4)	2.4816(15)	C(5)–O(6)	1.281(2)
Y(1)–O(9) ^{II}	2.5836(15)	O(5)–C(5)–O(6)	118.64(18)
Y(2)–O(7)	2.3075(14)	C(8)–O(7)	1.247(2)
Y(2)–O(9)	2.3189(15)	C(8)–O(8)	1.264(2)
Y(2)–O(1)	2.3917(14)	O(7)–C(8)–O(8)	124.89(18)
Y(2)–O(13)	2.3992(17)	C(9)–O(10)	1.256(3)
Y(2)–O(5)	2.4294(15)	C(9)–O(9)	1.267(2)
Y(2)–O(4)	2.4365(15)	O(10)–C(9)–O(9)	117.96(18)
Y(2)–O(11)	2.4623(15)	C(12)–O(12)	1.246(2)
Y(2)–O(2)	2.4802(16)	C(12)–O(11)	1.268(2)
Y(2)–O(6)	2.4810(14)	O(12)–C(12)–O(11)	124.96(18)
Y(1)–Y(2) ^{II}	4.0001(2)		

Symmetry code: (I) $-x, -y+1, -z$; (II) $x-1, y, z$; (III) $x, y-1, z$; (IV) $x, y+1, z$.

Table 1

Crystallographic data for **2** and **3**.

Compound	2	3
Identification code	ZY2	ZY3
Empirical formula	C6 H16 O11 Y1	C12 H16 O14 Y2
Formula weight/g mol $^{-1}$	353.10	562.07
Temperature/K	293(2)	293(2)
Wavelength	CuK α (1.54184 Å)	
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions		
<i>a</i> (Å)	6.5328(2)	7.59090(10)
<i>b</i> (Å)	9.7828(4)	8.4348(2)
<i>c</i> (Å)	10.4889(3)	13.8238(3)
α ($^\circ$)	80.2110(10)	97.104(2)
β ($^\circ$)	89.831(2)	98.377(2)
γ ($^\circ$)	71.378(2)	98.696(2)
Cell volume/Å 3	625.05(4)	855.94(3)
<i>Z</i>	2	2
Calc. Density/ mg m $^{-3}$	1.876	2.181
Absorption coefficient/ mm $^{-1}$	7.102	9.801
<i>F</i> (000)	358	556
Crystal size (mm 3)	0.204 \times 0.093 \times 0.016	0.197 \times 0.0489 \times 0.0108
Theta range for data collection/ $^\circ$	4.28–73.89	3.27–73.72
Index ranges	$-7 \leq h \leq 7, -12 \leq k \leq 12, -12 \leq l \leq 12$	$-9 \leq h \leq 9, -10 \leq k \leq 10, -17 \leq l \leq 17$
Reflections collected	8421	16920
Independent reflections	2385 [R(int)=0.0238]	3458 [R(int)=0.0245]
Completeness to theta= 67°	97%	99.8%
Absorption correction	Refined (XABS2)	Refined (XABS2)
Max. and min. transmission	0.6094 and 0.3171	1 and 0.51424
Refinement method	Full-matrix least-squares on <i>F</i> 2	Full-matrix least-squares on <i>F</i> 2
Data/restraints/parameters	2385/9/193	3458/0/265
Goodness-of-fit on <i>F</i> 2	1.265	1.069
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	R1=0.0251, wR2=0.0714	R1=0.0215, wR2=0.0581
<i>R</i> indices (all data)	R1=0.0266, wR2=0.0855	R1=0.0221, wR2=0.0586
Largest diff. peak and hole	0.505 and -0.54 e \AA^{-3}	0.584 and $-0.333 \text{ e \AA}^{-3}$

programs: CrysAlis CCD [44] for data collection; CrysAlis RED [45] for cell refinement, data reduction and empirical absorption correction; SHELX-97 [46] for structure solution; XABS2 [47] for refined absorption correction; SHELXL-97 for structure refinement and prepare materials for publication; PLATON [48] for the geometrical calculations; Diamond [49] for molecular graphics. Crystal data and structure refinement details for compounds **2** and **3** are outlined on Tables 1–3.

2.3. Thermal characterization

A Mettler-Toledo TGA/SDTA851^e and DSC822^e were used for the thermal analyses in oxygen dynamic atmosphere (50 mL/min) at a heating rate of 10 °C/min. In all cases, ca. 10 mg of powder sample was thermally treated, and blank runs were performed. In TG tests, a Pfeiffer Vacuum ThermoStarTM GSD301T mass spectrometer was used to determine the evacuated vapours. The masses 18 (H₂O) and 44 (CO₂) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

Table 3

Hydrogen-bond geometry in **1** [41], **2** and **3** (Å, °).

D–H...A	D–H [Å]	H...A [Å]	D...A [Å]	D–H...A [°]
Compound 1				
O7–H7A...O1 ^I	0.76(7)	1.96(7)	2.717(5)	170
O7–H7B...O3 ^{II}	0.88(3)	2.02(4)	2.867(5)	161
Compound 2				
O7–H7A...O1 ^{III}	0.72(5)	1.95(6)	2.675(3)	176
O7–H7B...O6 ^{IV}	0.74(6)	2.07(6)	2.799(4)	170
O8–H8A...O10 ^V	0.87(7)	1.88(7)	2.728(5)	167
O8–H8B...O11	0.71(7)	1.99(6)	2.690(4)	169
O9–H9A...O10	0.94(3)	1.99(3)	2.928(5)	176
O9–H9B...O2 ^V	0.94(3)	2.12(4)	2.973(4)	150
O10–H10A...O2	0.95(4)	2.25(4)	3.073(4)	145
O10–H10A...O6	0.95(4)	2.33(4)	3.072(3)	135
O10–H10B...O11 ^V	0.95(4)	1.97(3)	2.851(4)	154
O11–H11A...O9	0.94(2)	1.85(2)	2.740(5)	159
O11–H11B...O5 ^{VI}	0.94(3)	1.81(3)	2.751(4)	178
Compound 3				
O14–H14B...O10 ^{VII}	0.74(3)	2.00(3)	2.729(2)	174
O14–H14A...O11 ^{VIII}	0.78(3)	2.03(3)	2.791(2)	165
O13–H13A...O8	0.84(3)	2.05(3)	2.857(3)	162

Symmetry code: (I) 1/2 – x, 1/2 + y, 1/2 – z; (II) 1/2 – x, – 1/2 + y, 1/2 – z; (III) – x, 1 – y, – z; (IV) – 1 + x, y, z; (V) 1 – x, – y, 1 – z; (VI) – x, 1 – y, 1 – z; (VII) – x, 1 – y, – z; (VIII) 1 + x, – y, z.

3. Results and discussion

The structure of Y₂(C₄H₄O₄)₃(H₂O)₂ · H₂O (**1**) has already been found and described in the literature [41]. The asymmetric unit comprises one Y^{III} cation, one and half succinate anions, a coordinated water molecule and half uncoordinated water molecule. It is a three-dimensional framework, with empty channels running along the *c*-axis (Fig. 2a) with approximate dimensions of 7 × 3 Å, and with free water molecules located in the channels with approximate dimensions of 7 × 5 Å running along the *b*-axis (Fig. 2b). In the crystal structure, each Y^{III} cation coordinates to nine oxygen atoms (Fig. 3c) with tricapped trigonal prismatic coordination polyhedron joined in a chain edge-to-edge parallel to *b*-axis, the distance between adjacent Y in the chain is 4.0088(3) Å, these chains are in turn linked via succinate bridges in (001) and (101) directions, forming 3D framework. Eight of coordinated oxygen are carboxylic (O1–O2–O3–O4–O5–O6) and one from coordinated water molecule (O7). The three crystallographically independent carboxylate groups (coming from two different succinate anions one of them containing atoms O5 and O6 is situated on a crystallographic centre of inversion) may be divided into two groups according to their coordination mode: (i) the carboxylate group (O4–C4–O3) that acts as a bridge, coordinates each oxygen atom to a different Y^{III} cation; (ii) the two remaining carboxylate groups (O1–C1–O2) and (O6–C5–O5) coordinate one oxygen atom (O1, O6) to only one yttrium, and the other (O2, O5) acts as bridge between two different yttrium. In the structure, strong hydrogen bonds (see Table 3) between the aqua ligand (O7) and carboxylic oxygen atoms O1 and O3 contribute to strengthen the structure. We also suspect that the free water molecule (O8) participates in moderately strong hydrogen-bonding interactions with the aqua ligand (O7), in each case the aqua ligand acts as donor or acceptor, respectively.

Compound **2** is isostructural with several rare-earths succinates, M₂(C₄H₄O₄)₃(H₂O)₄ · 6H₂O (M=Ho, Er, Yb), previously reported [31,43,50]. The layered structure is built up from connections of Y^{III} cations and succinate ligands, with free water molecules located between the layers (Fig. 4). The asymmetric unit comprises one Y cation, one and half succinate anions, two coordinated water molecules and three uncoordinated water molecules. Each Y^{III} cation has nine-coordinated oxygen atoms (Fig. 3b), seven of them belonging to two succinate ligands and the two remaining belonging to two water molecules. The coordination polyhedra geometry can be described as a

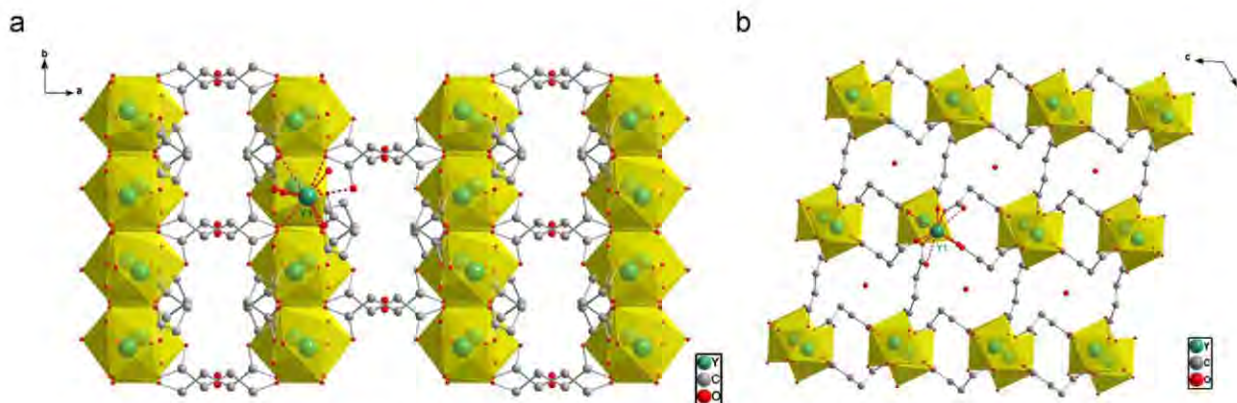


Fig. 2. Projection of the structure of **1** along the *c*-axis (a) and the *b*-axis (b).

monocapped square antiprism. Two edge sharing polyhedra, generate centrosymmetric dimmers Y_2O_{16} linked by succinate ions in (100) and (101) directions. The Y–O distances range from 2.318(2) to 2.606(2) Å and the average value is 2.414(2) Å. The distance between two adjacent Y cations within the

bi-polyhedron is 4.114(2) Å. In this structure, there are two crystallographically independent succinate anions which have different coordination modes, one of which is situated on a crystallographic centre of inversion. This generates two carboxylate groups according to two their coordination modes, the carboxylate groups (O2–C1–O1, O6–C5–O5) coordinate two oxygen atoms to only one yttrium (bond in chelating mode), and the remaining carboxylate group (O3–C4–O4) coordinates one oxygen atom (O4) to a single yttrium and the other (O3) bridges between two yttrium atoms. Moderate to strong interlayer hydrogen bonds are observed in **2** (see Table 3) providing 3D stability to the structure, involving uncoordinated water molecules (O8) which act as donor and uncoordinated water molecules (O10, O11) acting as acceptors, the latter (O10, O11) with (O9) act as donors with carboxylic oxygen atoms (O6, O5, and O2) of the succinate ligands, taking into account the contribution of hydrogen bonds between uncoordinated water molecules.

Compound **3**, $Y_2(C_4H_4O_4)_3(H_2O)_2$, is isostructural with the corresponding erbium-analogue [51]. The asymmetric unit comprises two Y cations, three succinate anions, and two coordinated water molecules. The structure of **3** consists of a 3D framework (Fig. 5a) built from the connections of Y^{III} cation and succinate ligands. There are two crystallographically independent Y^{III} , both are nine-coordinated (Fig. 3a) within a tricapped trigonal prismatic geometry joined in a edge-to-edge chain parallel to the a-axis (Fig. 5b), defined by eight O atoms, derived from six carboxylate groups belonging to three different succinate anions and one molecular water, the chains are linked via succinate bridges in b and c-axis, forming the 3D framework. The Y1–O distances range from 2.3053(14) to 2.5836(15) Å and the average value is 2.4117(14) Å; similarly, related values for Y2–O are from 2.3075(14) to 2.4810(14) Å, and 2.4119(15) Å. The distance between adjacent Y1–Y2 cations in the chain is 4.0001(2) Å. The six independent carboxylate groups may be divided into two groups according to their coordination mode: the carboxylate groups (O8–C8–O7) and (O12–C12–O11) that act as a bridge, coordinate each oxygen atom to the two independent Y^{III} , the four remaining carboxylates groups coordinate one oxygen atom (O2, O3, O5, O10) to only one Y^{III} , while the other (O1, O4, O6, O9) bridges between two independent Y^{III} and Y^{III} . In this structure, strong hydrogen bonds form (see Table 3) between the two coordinated water molecules (O13, O14) that act as donors, and carboxylic oxygen atoms of the bridging succinate ligands.

In the compounds **1** and **3**, the succinate ligands coordinated to yttrium adopt the same coordination modes, in contrast with compound **2** (see Scheme 1). Despite this, they present certain topological difference, which may be due to the different conformations of the succinate ligand. Although no free water molecules reside in the channels of **3**, in contrast with compound **1**, the structure is more compact and likely to be more stable than **1** and **2**. The presence of BTC in the reaction medium in the case of **3**, is manifested by more rich conformational modes (torsion angles) of succinate ligand, than **1** and **2**, and by maintained the same coordination modes of **1**. The presence of BDC in **2** is manifested by decreasing the carboxylate groups coordination number, and therefore high number of uncoordinated and coordinated water molecules in **2**.

The thermal stability of **1**, **2** and **3** was investigated. The TG/DTG, SDTA curves, and the mass spectrometric analysis, are depicted in the Fig. 6, while Fig. 7 shows DSC traces. TG /DTG curves of **1**, **2** and **3** reveal total mass losses of, respectively, 60.6% (cal. 61.05%), 69.3% (cal. 68.01%), and 58.6% (cal. 59.78%), from room temperature up to 1000 °C, in good agreement with X-ray crystallography study, assuming Y_2O_3 is the final product of the decomposition (this has been confirmed by powder XRD).

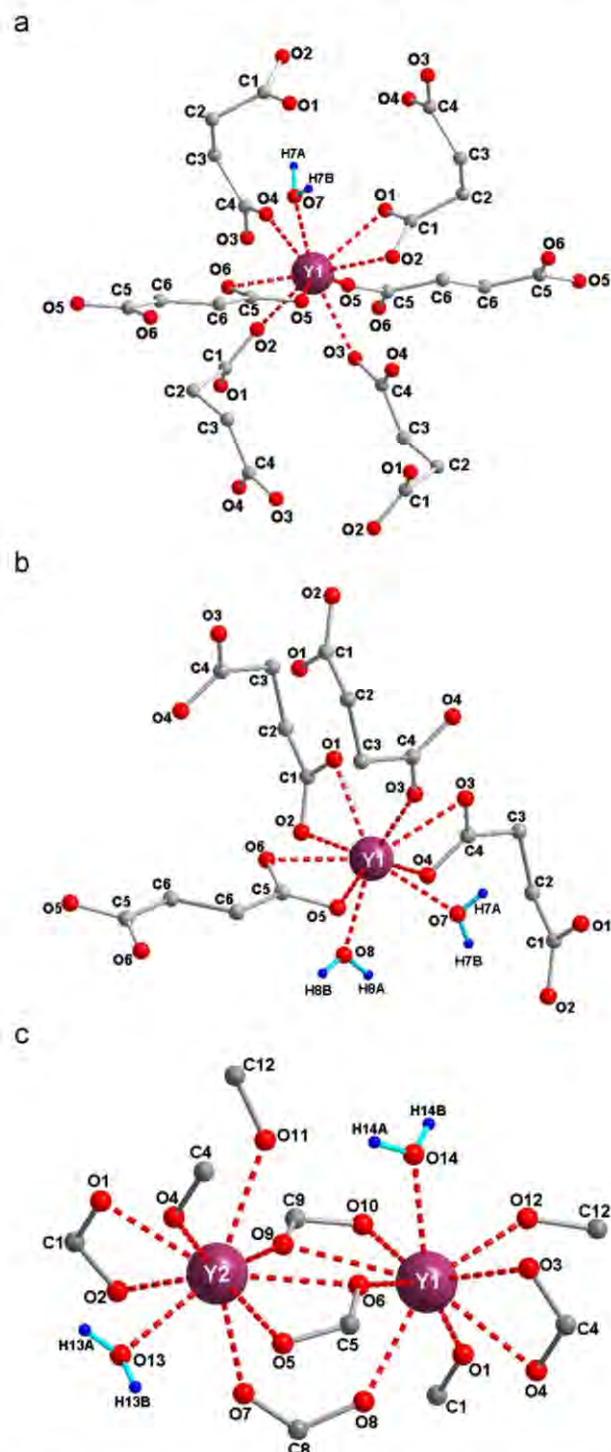
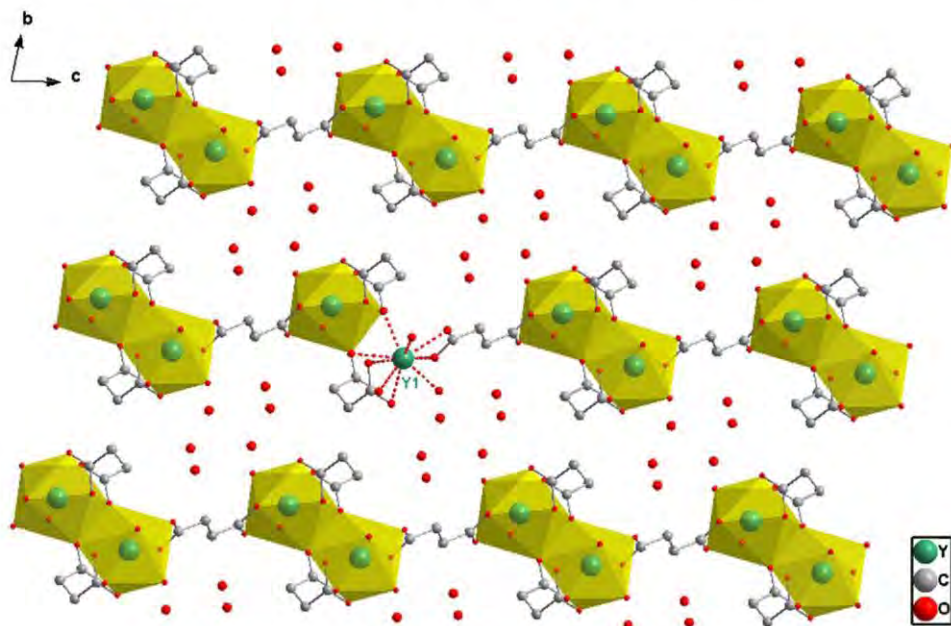
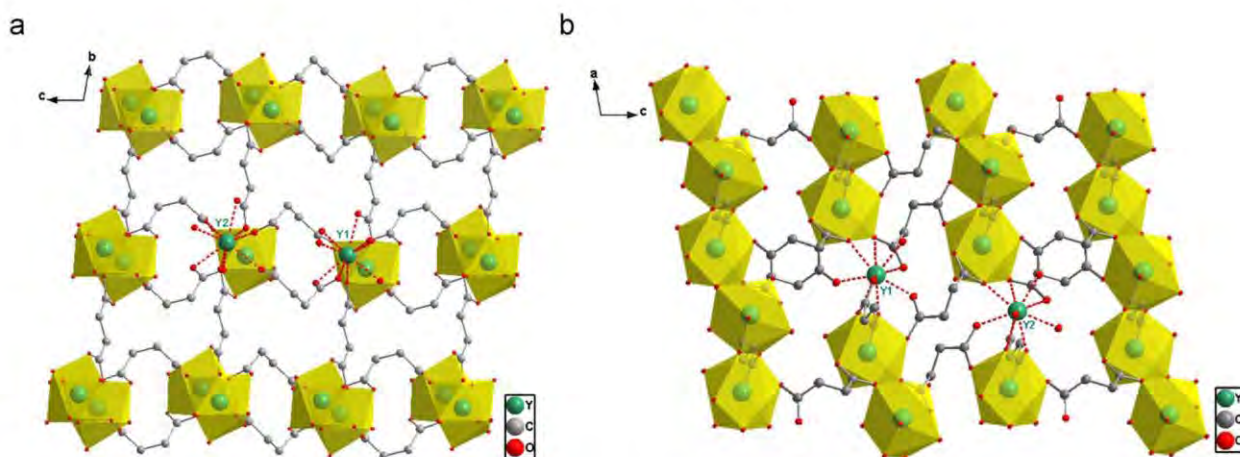


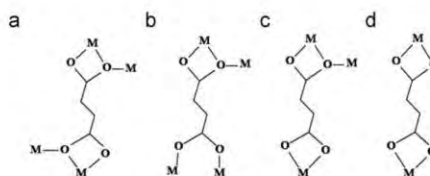
Fig. 3. Local coordination environment of the Y atom in **1** (a), **2** (b) and **3** (c).

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Fig. 4. Projection of the structure of **2** along the *a*-axis.Fig. 5. Projection of the structure of **3** along the *a*-axis (a) and the *b*-axis (b).

The mass loss of **1**, in air, proceeds by two separate and defined steps. The first step between 120 and 200 °C (which reaches its maximum velocity at 180 °C), with the mass loss of 8.4% (cal. 9.31%), associated with endothermic peak at 190 and 200 °C on the SDTA and DSC curves, respectively, corresponds to the loss of *ca.* 3 (2.7 moles) water molecules: the free water molecule located in the channels and the two coordinated water molecules. The second step, between 330–900 °C, is complex, and composed of two continuous and overlapping processes with total mass loss of 52.1% (which reach their maximum velocity at 390 and 435 °C), and associated with exothermic peak which consists of two shoulders (at 385 and 410 °C) and a main peak on the SDTA (at 445 °C) and DSC (at 455 °C) curves, is assigned to the decomposition (oxidation) of the succinate ligand in two processes, which may be due to the partial collapse of channels after the water removal (dehydration step), leading to Y_2O_3 . The



Scheme 1. (a) and (b): coordination modes of succinate ligands in compounds **1** and **3**; (c) and (d): coordination modes of succinate ligands in compound **2**.

associated mass spectrometry m/z 18 and 44 curves are in a good agreement with TG/DTG data. m/z 18 curve has two maxima, the first one at 190 °C corresponding to the loss of three water molecules, and the second at 445 °C (accompanied by a shoulder at 390 °C) coincides with the maximum of m/z 44 curve, which is

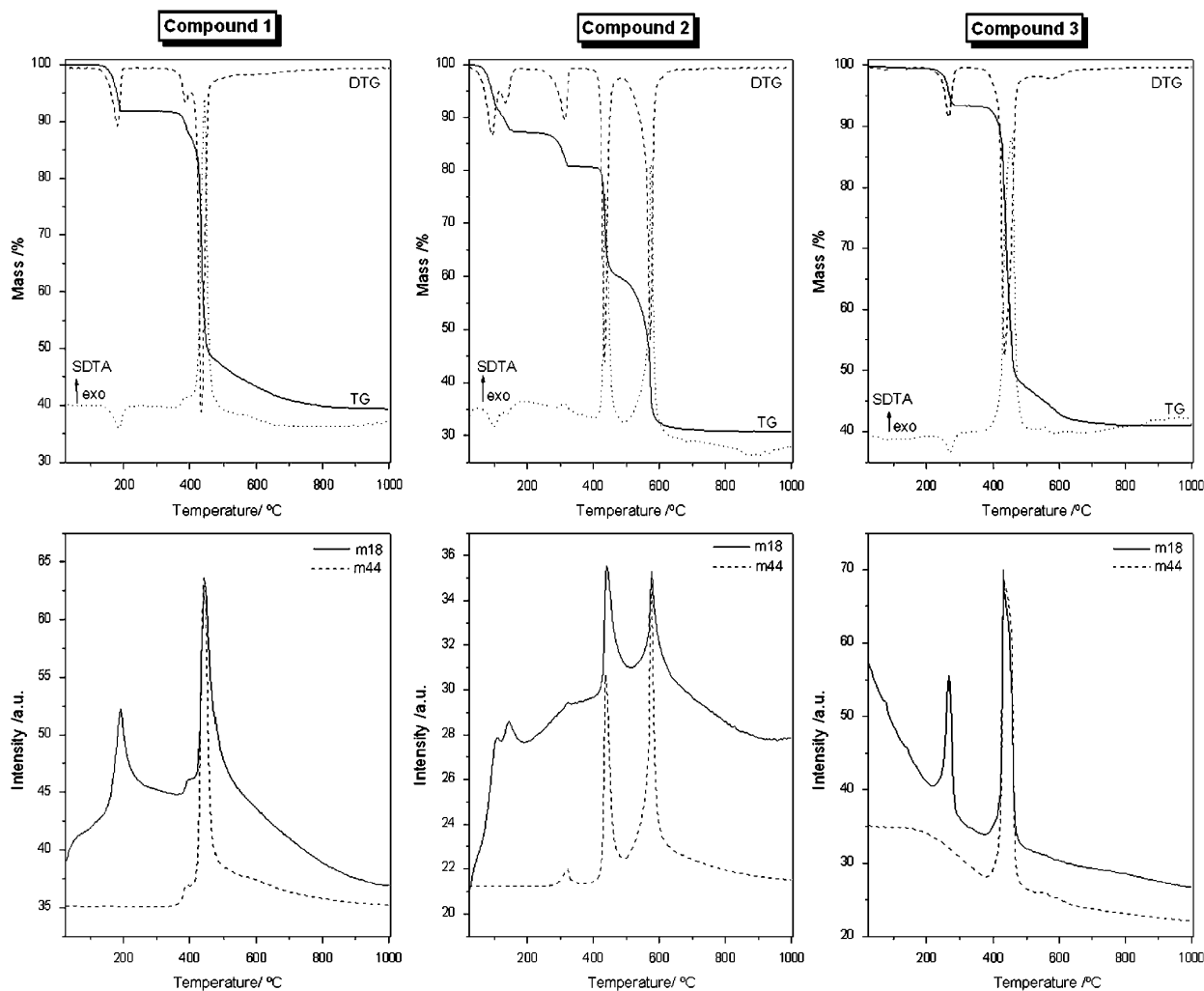


Fig. 6. TG-DTG-SDTA curves, and m/z 18 (H_2O) and m/z 44 (CO_2) MS signals of evacuated vapours, for 1, 2 and 3.

attributed to the decomposition step of the succinate ligand. Taking into account that the mass spectrometry analysis is a semiquantitative method, the integration of the first band (2868 nA) is almost half of the integration of the second one (5948 nA), proving the loss of six water molecules in the second step, corresponding exactly to the hydrogen atoms coming from the decomposition (or oxidation) of three succinic ligands in the formula of **1**. The rest of mass loss corresponding to the loss of CO_2 , is showed by the maximum of m/z 44 curve at 450 °C.

The mass loss of **2** in air takes place in five stages. The first and the second stages are continuous, with the total mass loss of 12.8% (cal. 12.75%) in the range 50–200 °C (which reach their maximum velocity at 90 and 135 °C, respectively), associated with two endothermic peaks on the SDTA (at 100 and 140 °C) and DSC curves (at 110 and 145 °C), attributed to the loss of five uncoordinated water molecules located between the layers. The third stage between 200–350 °C, with the mass loss of 6.5% (reaches its maximum velocity at 315 °C), is simultaneously associated with endothermic and exothermic effects on the SDTA curve, and may be attributed to the loss of the last uncoordinated water molecule, and the beginning of the succinic acid oxidation.

The DSC curve only exhibits an endothermic peak, which may be explained by a high endothermic effect making the exothermic peak unobservable. This multi-step dehydration behaviour of the uncoordinated water molecules can be explained as consequence of the hydrogen bonds existing between the uncoordinated water molecules, and their interactions with the coordinated water molecules. The fourth and the fifth stages are continuous, with mass losses of 20.9% and 28.9%, respectively, in the ranges 380–490 °C and 490–800 °C (reach their maximum velocity at 435 and 570 °C), associated with two exothermic peaks on the SDTA (at 435 and 570 °C) and DSC curve (at 440 and 580 °C), correspond to loss of the four coordinated water molecules and to the oxidation of the whole organic moiety leading to Y_2O_3 as residue. This three-step oxidation process may be due to the dimensionality of this compound (layered structures are known to undergo multistep decomposition processes). The associated mass spectrometry m/z 18 and 44 curves are in a good agreement with TG/DTG curves. The mass spectrometry m/z 18 curve has five maxima, the first and the second maxima at 110 and 145 °C, overlap and correspond to the loss of five interlayer water molecules; the third maximum at 450 °C coincides with the first

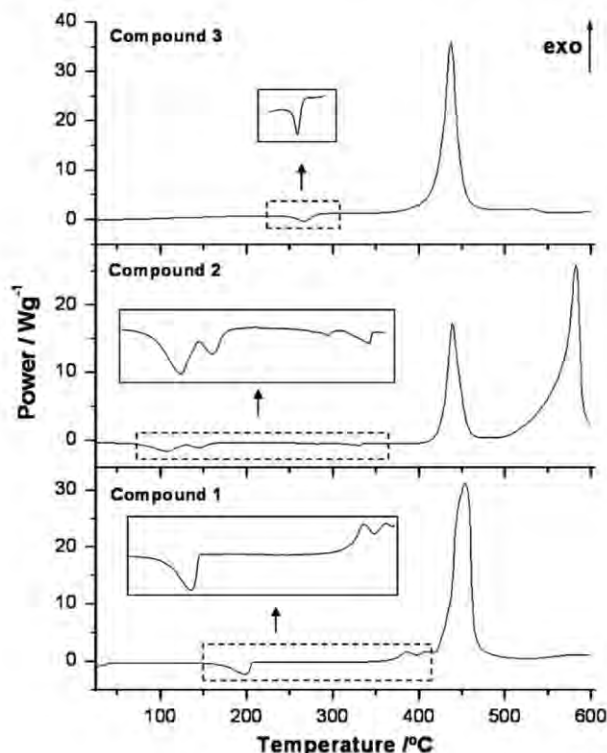


Fig. 7. DSC curves for 1, 2 and 3.

maximum of m/z 44 curve, which may be attributed to the loss of the last interlayer water molecule and to the first decomposition step of the succinic ligand. The fourth and the fifth maxima at 440 and 575 °C, coincide with the second and the third maxima of m/z 44 curve, and correspond to loss of the four coordinated water molecules and to the oxidation of the whole organic moiety leading to Y_2O_3 as residue. Taking in account that the mass spectrometry analysis is semiquantitative, the integration of the first three bands (4091 nA) is 0.78 of the integration of the fourth and fifth ones (5229 nA) in the m/z 18 curve, indicating the loss of approximately ten water molecules in the fourth and fifth step, corresponding to four coordinated water molecules, and six water molecules resulting from the oxidation of the three succinic ligands in **2**. In the mass spectrometric m/z 44 curve, the integration of the three bands shows the loss of 0.30, 2.85 and 8.85 moles of CO_2 in the third, fourth and the fifth stages, respectively.

Similarly to **1**, the mass loss of **3** in air proceeds by two separate and defined stages. The first stage, with the mass loss of 5.9% (cal. 5.69%) in range 200–300 °C (which reaches its maximum velocity at 275 °C), described by endothermic effect on the SDTA (at 270 °C) and DSC curves (at 265 °C), is attributed to the loss of the two coordinated water molecules. The second stage is observed in the range 350–800 °C, with the corresponding mass loss of 52.7% (which reaches its maximum velocity at 440 °C), and described by exothermic peak on the SDTA and DSC curve at 450 and 435 °C, respectively, is attributed to one-step decomposition process of the whole organic moiety leading to Y_2O_3 . The associated mass spectrometry m/z 18 and 44 curves are in a good agreement with TG/DTG data. m/z 18 curve has two maxima, the first one at 273 °C corresponding to the loss of the two coordinated water molecules, and the second one at 430 °C, which coincides

with the maximum of m/z 44 curve. The integration of the first band (2577 nA) is almost a third of the integration of the second one (7235 nA), proving the loss of six water molecules in the second stage, corresponding exactly to the hydrogen atoms coming from the decomposition of three succinic anions in the formula, and the rest of mass loss corresponding to the loss of CO_2 showing by the maxima of m/z 44 curve at 430 °C.

The TG/DTG curves show that the compounds **1** and **3** have similar thermal decomposition behaviours. From the point of view of dehydration and the decomposition temperatures, the compound **3** is the most stable, followed by **1** and **2**. These results show that the 3D compounds are more stable than the layered ones. After the dehydration, the anhydrous compounds of **1** and **3** are stable up to 370 and 400 °C, respectively, and they have comparable oxidative decomposition enthalpies, 2888 and 2710 kJ/mol, respectively. Unlike **2**, the decomposition and the rest of dehydration steps (corresponding to loss of coordinated water molecules) occur simultaneously, which is reflected by an exothermic higher oxidative decomposition enthalpy (3601 kJ/mol), and this can be explained by the fact that the intermediate compound, partially dehydrated, is different from the anhydrous one in the case of **1** and **2**.

The structural reasons for such stability trend are the high number of uncoordinated and coordinated water molecules in **2**; the uncoordinated water molecules residing in the channels of **1** which is manifested by large channels in **1** than in **3**; also the relatively shorter Y–O distances in **3** than in **1** and **2**, and finally the double infinite Y–O–Y connectivity along b -axis and a -axis in **1** and **3**, respectively, which is absent in the case of **2**, may explain the thermal stability order of the compounds.

4. Conclusions

The hydrothermal synthesis and crystal structure of new members in the yttrium-succinate family have been reported. The results suggest that the structural diversity obtained, in this system, is related to the coordination diversity and the conformational flexibility of the succinate ligand, which in turn depend on the synthesis conditions that play an important role in directing to one compound or another.

Supporting information available

CCDC nos. 735614 and 735615 contain the supplementary crystallographic data for compounds **2** and **3** described in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [10.1016/j.jssc.2009.09.027](http://dx.doi.org/10.1016/j.jssc.2009.09.027).

References

- [1] S.S. Kaye, A. Dailly, O.M. Yaghi, J.R. Long, *J. Am. Chem. Soc.* 129 (2007) 14176.
- [2] D.J. Collins, H.C. Zhou, *J. Mater. Chem.* 17 (2007) 3154.
- [3] D. Sun, S. Ma, Y. Ke, D.J. Collins, H.C. Zhou, *J. Am. Chem. Soc.* 128 (2006) 3896.
- [4] J.L.C. Rowsell, O.M. Yaghi, *J. Am. Chem. Soc.* 128 (2006) 1304.
- [5] S. Ma, H.C. Zhou, *J. Am. Chem. Soc.* 128 (2006) 11734.
- [6] A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, *J. Am. Chem. Soc.* 128 (2006) 3494.
- [7] B.L. Chen, N.W. Ockwig, A.R. Millward, D.S. Contreras, O.M. Yaghi, *Angew. Chem. Int. Ed.* 44 (2005) 4745.
- [8] J.L.C. Rowsell, O.M. Yaghi, *Micropor. Mesopor. Mater.* 73 (2004) 3.
- [9] G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guegan, *Chem. Commun.* (2003) 2976.
- [10] L. Pan, B. Parker, X. Huang, D.H. Olson, J.Y. Lee, J. Li, *J. Am. Chem. Soc.* 128 (2006) 4180.
- [11] M. Dinca, J.R. Long, *J. Am. Chem. Soc.* 127 (2005) 9376.
- [12] D.N. Dybtsev, H. Chun, S.H. Yoon, D. Kim, K. Kim, *Am. Chem. Soc.* 126 (2004) 32.
- [13] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem. Intl. Ed.* 42 (2003) 428.
- [14] R.Q. Zou, H. Sakurai, Q. Xu, *Angew. Chem. Int. Ed.* 45 (2006) 2542.
- [15] D.N. Dybtsev, A.L. Nuzhdin, H. Chun, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, K. Kim, *Angew. Chem. Int. Ed.* 45 (2006) 915.
- [16] W.B. Lin, *J. Solid State Chem.* 178 (2005) 2486.
- [17] C.D. Wu, A. Hu, L. Zhang, W.B. Lin, *J. Am. Chem. Soc.* 127 (2005) 8940.
- [18] L.G. Qiu, A.J. Xie, L.D. Zhang, *Adv. Mater.* 17 (2005) 689.
- [19] B. Kesanli, W.B. Lin, *Coord. Chem. Rev.* 246 (2003) 305.
- [20] O.M. Yaghi, H. Li, *J. Am. Chem. Soc.* 118 (1996) 295.
- [21] A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, *Angew. Chem. Int. Ed.* 39 (2000) 3130.
- [22] Q. Ye, D.W. Fu, H. Tian, R.G. Xiong, P.W.H. Chan, S.P.D. Huang, *Inorg. Chem.* 47 (2008) 772.
- [23] Q. Ye, Y.M. Song, G.X. Wang, K. Chen, D.W. Fu, P.W.H. Chan, J.S. Zhu, S.D. Huang, R.G. Xiong, *J. Am. Chem. Soc.* 128 (2006) 6554.
- [24] W.J. Rieter, K.M.L. Taylor, W.B. Lin, *J. Am. Chem. Soc.* 129 (2007) 9852.
- [25] B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E.B. Lobkovsky, *Adv. Mater.* 19 (2007) 1693.
- [26] X.P. Yang, R.A. Jones, W.K. Wong, V. Lynch, M.M. Oye, A.L. Holmes, *Chem. Commun.* (2006) 1836.
- [27] J.P. Zhang, Y.Y. Lin, X.C. Huang, X.M. Chen, *J. Am. Chem. Soc.* 127 (2005) 25495.
- [28] O.R. Evans, W.B. Lin, *Acc. Chem. Res.* 35 (2002) 511.
- [29] Y.F. Zhou, F.L. Jiang, D.Q. Yuan, B.L. Wu, M.Ch. Hong, *J. Mol. Struct.* 743 (2005) 21.
- [30] S.C. Manna, E. Zangrando, A. Bencini, C. Benelli, N.R. Chaudhuri, *Inorg. Chem.* 45 (2006) 9114.
- [31] N. Rahahla, K. Alioune, A.G. Laidoudi, S. Dahaoui, C. Lecomte, *Acta Crystallogr. Sect. E* 62 (2006) 2543.
- [32] H. Xu, J. Liang, J. Zhuang, H. Kou, R. Wang, Y. Li, *J. Mol. Struct.* 689 (2004) 177.
- [33] F. Li, *Acta Crystallogr. Sect. E* 63 (2007) 840.
- [34] Y.K. He, X.F. Wang, L.T. Zhang, Z.B. Hana, S.W. Ng, *Acta Crystallogr. Sect. E* 63 (2007) 3019.
- [35] Q. He, J.F. Zi, F.J. Zhang, *Acta Crystallogr. Sect. E* 62 (2006) 1266.
- [36] B. Yu, X.Q. Wang, R.J. Wang, G.Q. Shen, D.Z. Shen, *Acta Crystallogr. Sect. E* 62 (2006) 1620.
- [37] C.X. Wang, Y. Li, Q.H. Zhang, D.J. Cai, X.B. Xie, *Acta Crystallogr. Sect. E* 62 (2006) 545.
- [38] A. Seguatni, M. Fakhfakh, M.J. Vauley, N. Jouini, *J. Solid State Chem.* 177 (2004) 3402.
- [39] B. Yu, C.Z. Xie, X.Q. Wang, R.J. Wang, G.Q. Shen, D.Z. Shen, *J. Coord. Chem.* (2007) 1817.
- [40] G.H. Cui, J.R. Li, R.H. Zhang, X.H. Bu, *J. Mol. Struct.* 740 (2005) 187.
- [41] J. Perles, M. Iglesias, C.R. Valero, N. Snejko, *J. Mater. Chem.* 14 (2004) 2683.
- [42] J. Perles, M. Iglesias, C.R. Valero, N. Snejko, *Chem. Commun.* (2003) 346.
- [43] M.C. Bernini, E.V. Brusau, G.E. Narda, G.A. Echeverria, C.G. Pozzi, G. Punte, C.W. Lehmann, *Eur. J. Inorg. Chem.* (2007) 684.
- [44] CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.32.37 (release 24-10-2008 CrysAlis171 .NET) (compiled Oct 24 2008,09:44:38).
- [45] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.37 (release 24-10-2008 CrysAlis171 .NET) (compiled Oct 24 2008,09:44:38).
- [46] G.M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
- [47] S. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystallogr.* 28 (1995) 53.
- [48] [a] A.L. Spek, *Acta Crystallogr. Sect. A* 64 (1990) 34;
[b] A.L. Spek (Ed.), PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.
- [49] K. Brandenburg, DIAMOND. Version 3.1. 2007, Crystal Impact GbR, Bonn, Germany.
- [50] J. Sun, Y.Q. Zheng, J.L. Lin, *Z. Kristallogr., New Cryst. Struct.* 219 (2004) 99.
- [51] G.Y. Dong, G.H. Cuia, J. Linb, *Acta Crystallogr. Sect. E* 62 (2006) 738.

3.3. Polímeros de coordinación basados en itrio y ligandos dicarboxílicos.

Artículo II

Artículo publicado en el año 2010 (*Vol. 49, pp. 7917–7926*) en la revista *Inorganic Chemistry*, con el título “Metal Organic Frameworks Assembled from Y(III), Na(I), and Chiral Flexible-Achiral Rigid Dicarboxylates”

Resumen

El objetivo del trabajo presentado en este artículo fue la síntesis de nuevos polímeros de coordinación basados en itrio y ligandos mixtos de tipo dicarboxílico.

Este artículo describe la síntesis y caracterización de dos nuevos polímeros de coordinación bidimensionales, basados en itrio y ligandos mixtos dicarboxílicos rígido-flexible (ácido tartárico - ácido tereftálico / ácido bifenil-4,4'-dicarboxílico) de fórmulas $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$. Se ha descrito la síntesis hidrotermal y la estructura cristalina de ambos materiales, obtenida por difracción de rayos-X de monocristal, y su caracterización mediante diferentes técnicas: análisis elemental, microanálisis acoplado a microscopía electrónica de barrido (SEM/EDX), análisis térmico (TG-MS/SDTA y DSC), difracción de rayos-X de polvo cristalino, termodifracción de rayos-X, y resonancia magnética nuclear en estado sólido (SS-NMR).

El diseño de polímeros de coordinación quirales con diferentes arquitecturas y topologías sigue siendo un reto, y aún más cuando se utilizan lantánidos, en lugar de elementos metales de transición, como centros metálicos. Así, los intentos para construir polímeros de coordinación quirales basados en elementos lantánidos son todavía escasos, lo que debe atribuirse principalmente a la flexibilidad de la esfera de coordinación de los iones lantánidos. Sin embargo, esta flexibilidad, junto con la tendencia hacia un número de coordinación elevado, hace que sean atractivos para el diseño de nuevos materiales con arquitecturas y topologías reticulares inusuales, en adición a potenciales aplicaciones en muchos campos, entre los que caben citar los materiales magnéticos y luminiscentes, la adsorción selectiva de gases, y la catálisis heterogénea (tipo ácido de Lewis) en reacciones orgánicas de interés industrial.

Muchos de los informes recientemente publicados sobre polímeros de coordinación basados en lantánidos se han centrado en el uso de ligandos rígidos di- o poli-carboxílicos. Sin embargo, entre ellos, son escasos los que contienen simultáneamente ligandos dicarboxílicos rígidos y flexibles. En el presente trabajo, se presenta una nueva aproximación a la construcción de dos nuevos polímeros de coordinación heteronucleares quirales, basados en sistema mixtos metal-ligando que contienen un ligando dicarboxílico quiral flexible y otro aquiral lineal rígido. El ácido tartárico (**H₂Tart**) fue seleccionado como ligando flexible, ya que *i*) dispone de seis átomos dadores útiles para conseguir estructuras de alta dimensionalidad, *ii*) es un ligando fácilmente accesible que presenta dos centros quirales, y *iii*) existe en formas D(-), L(+), meso y racémica. El ácido tereftálico (**H₂BDC**), que ha sido utilizado ampliamente como un espaciador orgánico y, su análogo extendido, el ácido bifenil-4,4'-dicarboxílico (**H₂biBDC**), se han elegido como consecuencia de que estos ligandos rígidos *i*) son capaces de establecer puentes entre los centros metálicos ofreciendo armazones porosos, y *ii*) pueden potenciar las propiedades fluorescentes de los cationes lantánidos a través del proceso conocido como efecto antena. El número de polímeros de coordinación basados en itrio es relativamente limitado en comparación con los de cationes del bloque *f*, a pesar de que el itrio se utiliza ampliamente en cristales láser y materiales superconductores, por lo que los sistemas descritos aquí pueden generar polímeros de coordinación inusuales con propiedades interesantes.

Los dos nuevos polímeros de coordinación basados en itrio y ligandos mixtos dicarboxílicos rígido-flexible (ácido tartárico - ácido tereftálico / ácido bifenil-4,4'-

dicarboxílico), de fórmulas $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ (**1**) y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ (**2**), se han obtenido mediante la síntesis hidrotermal. Las condiciones de síntesis, en las que se obtuvieron monofases de cristales incoloros con forma de agujas, se resumen en la siguiente tabla:

Compuesto	$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$	Ácido tartárico	Ligando rígido	NaOH	$\text{H}_2\text{O}:\text{Etanol}$
1	1 mmol (0.31 g)	1.4 mmol (0.21 g)	Ácido tereftálico	3.5 mmol (0.14 g)	6 : 6 (mL)
	1 mmol (0.31 g)	1.4 mmol (0.21 g)	Ácido bifeníl-4,4'-dicarboxílico	3.5 mmol (0.14 g)	6 : 6 (mL)
2			0.5 mmol (0.12 g)		

La mezcla de reacción se agitó durante 2 horas en un recipiente de teflón (volumen interno de 40 mL) a temperatura ambiente hasta su homogenización y luego se introdujo en un autoclave de acero inoxidable que se mantuvo durante 72 horas en estufa a la temperatura de 180 °C.

Las estructuras cristalinas de **1** y **2** han sido resueltas utilizando la difracción de rayos X de monocristal. Ambos compuestos son quirales y presentan simetría ortorrómbica, cristalizando en el grupo espacial $C222_1$, con los siguientes parámetros de red: $a = 6.8854(2)$ Å, $b = 30.3859(7)$ Å, $c = 7.4741(2)$ Å para **1**, y $a = 6.8531(2)$ Å, $b = 39.0426(8)$ Å, $c = 7.4976(2)$ Å para **2**. Ambos compuestos son laminares, consecuencia del ensamblaje de los cationes Y(III) y Na (I) con los ligandos dicarboxílicos mixtos quiral flexible-aquiral rígido, **Tart-BDC** en el caso de **1**, y **Tart-biBDC** en el caso de **2**. En cada compuesto, el catión itrio está coordinado por ocho átomos de oxígeno, seis de ellos pertenecientes a los grupos carboxílicos, mientras que los otros dos provienen de grupos hidroxilos (Figura 3.3.1a,b), definiendo un poliedro de coordinación tipo prisma trigonal bicofiado distorsionado (Figura 3.3.1c,d), mientras que el catión sodio está coordinado a seis átomos de oxígeno, cuatro de ellos pertenecientes a los grupos carboxilo y los otros dos provenientes de dos moléculas de agua coordinadas (Figura 3.3.1e,f), definiendo un poliedro de coordinación tipo prisma trigonal distorsionado (Figura 3.3.1g,h). De los ocho átomos de oxígeno coordinados al catión itrio, seis provienen de cuatro aniones **Tarta**²⁻ cristalográficamente equivalentes: dos de ellos se

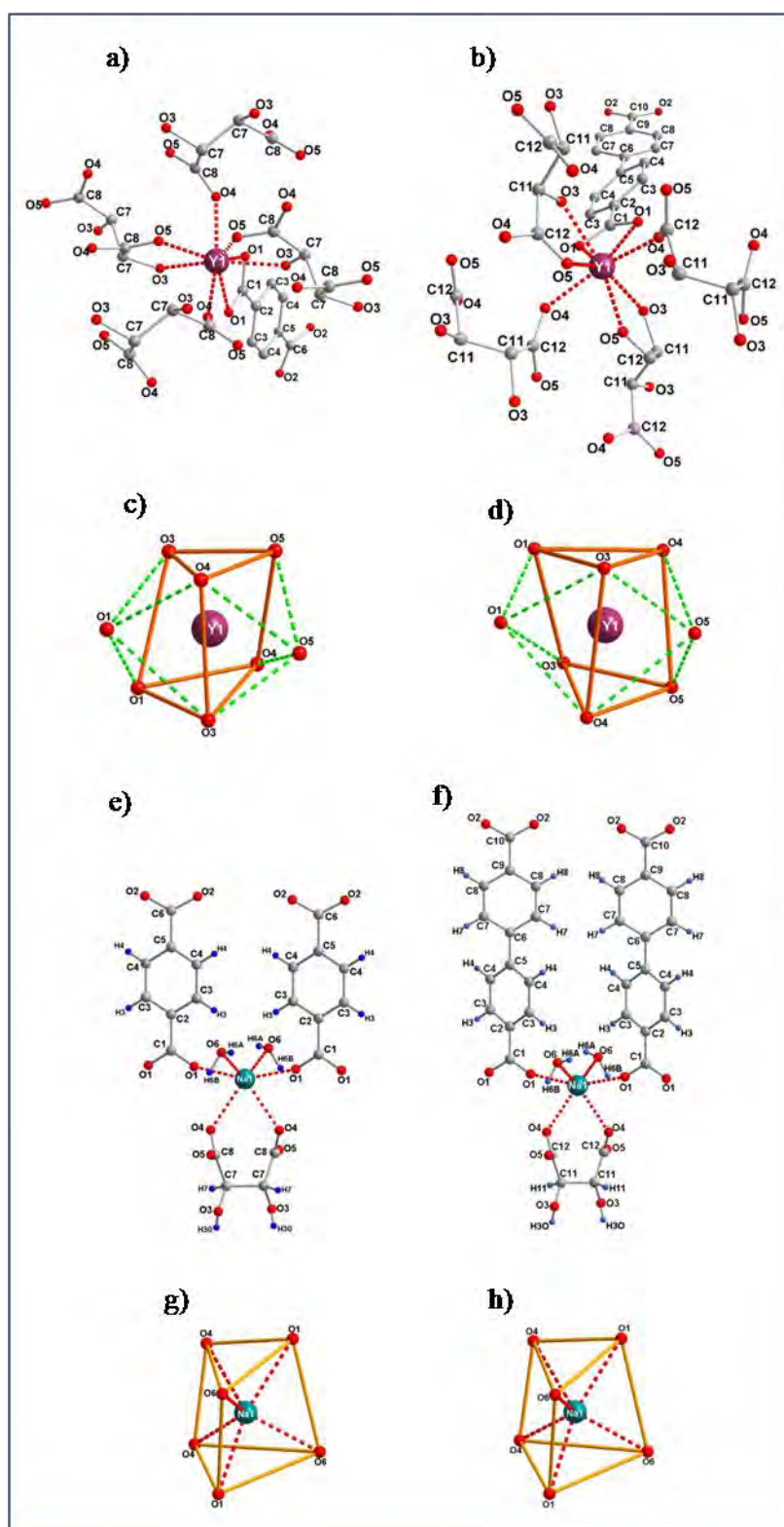


Figura 3.3.1. Entornos de coordinación local de itrio en **1** (a,c) y **2** (b,d), y sodio en **1** (e,g) y **2** (f,h).

coordinan al itrio en modo quelato a través del átomo de oxígeno carboxílico O5 y el hidroxilo O3, mientras que los dos otros actúan como puente entre cationes sodio e itrio mediante el átomo de oxígeno carboxílico O4. Los dos últimos átomos de oxígeno coordinados al catión itrio pertenecen a un anión BDC^{2-} (anión biBDC^{2-} en el caso de **2**), que actúa *i*) en modo de quelato a través del grupo carboxílico O1-C1-O1, y *ii*) como puente entre sodio e itrio mediante el átomo de oxígeno carboxílico O1. De los seis átomos de oxígeno coordinados al sodio, dos provienen del mismo anión Tart^{2-} , que actúa en modo quelato a través de los átomos de oxígeno carboxílicos O4, mientras que los cuatro restantes son proporcionados por una pareja (ambos componentes cristalográficamente equivalentes) de especies diferentes: *i*) moléculas de agua coordinadas, y *ii*) aniones BDC^{2-} (biBDC^{2-} en el caso de **2**), mediante la coordinación de los átomos O6 y O1, respectivamente. En **1**, las distancias Y—O y Na—O varían de 2.282(3) Å a 2.378(3) Å, y de 2.313(4) Å a 2.548(3) Å, con valores promedio de 2.342(4) Å y 2.421(3) Å, respectivamente. Del mismo modo, en **2** los valores correspondientes varían de 2.278(3) Å a 2.382(3) Å y de 2.316(4) Å a 2.554(3) Å, con los valores promedio de 2.345(5) Å y 2.417(3) Å, respectivamente. Los poliedros formados por itrio y sodio (Figura 3.3.2a) se alternan entre sí compartiendo aristas, originando cadenas infinitas paralelas al eje *a* (Figura 3.3.2b), con distancias entre cationes Y y Na adyacentes en la cadena de 3.819(2) Å y 3.808(4) Å en **1** y **2**, respectivamente. A su vez, estas cadenas están conectadas a través de aniones Tart^{2-} a lo largo de los ejes *a* y *c*, mostrando una disposición en zig-zag que conforma una doble lamina (Figura 3.3.2c). Estas láminas están conectadas por ligandos rígidos BDC^{2-} (biBDC^{2-} en el caso de **2**) paralelas al eje *b*, generando canales a lo largo de los ejes *a* (Figura 3.3.2d) y *c*, con dimensiones aproximadas de 6.3x3.5 Å² y 6.3x4.5 Å² en **1**, y de 10.6x3.5 Å² y 10.6x4.5 Å² en **2**. El espaciador rígido BDC^{2-} (biBDC^{2-} en el caso de **2**), que separa dos laminas dobles sucesivas, de un lado coordina a los cationes itrio y sodio, mientras que de otro está involucrado en fuertes enlaces de hidrógeno a través de los átomos de oxígeno O2 de los grupos carboxílicos (O2-C6-O2) no coordinados (O2-C10-O2 de biBDC^{2-} en el caso de **2**), que actúan como aceptores, y el átomo de oxígeno O3 de los grupos hidroxilo del ligando Tart^{2-} , junto con las moléculas de agua coordinadas (O6) al átomo de sodio, que actúan como donantes, lo que proporciona la estabilidad 3D de la estructura. El lado no coordinado del espaciador BDC^{2-} (o biBDC^{2-}) puede ser descrito como una nave anclada, donde el trinomio nave-ancla-anclaje es consecuencia de la estrecha relación

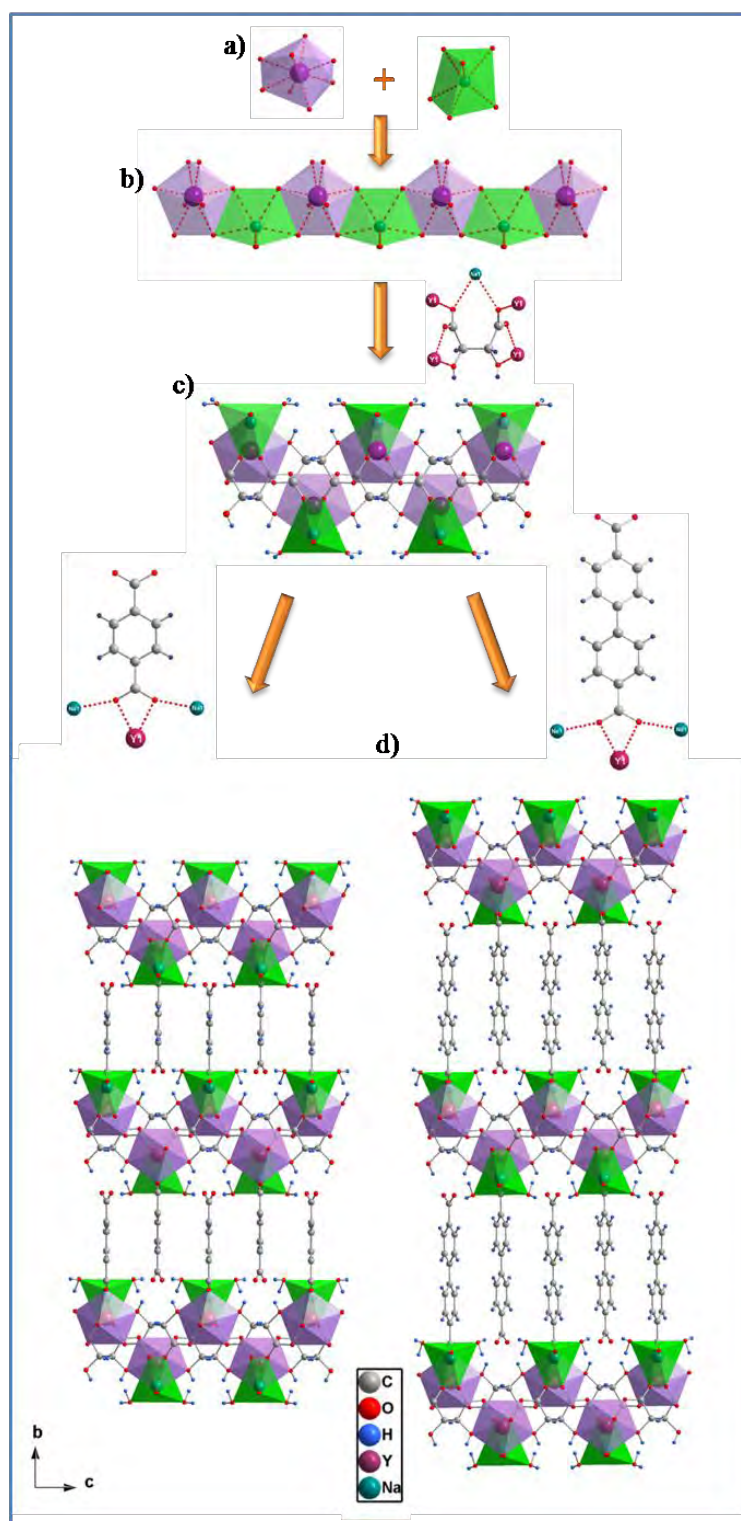


Figure 3.3.2. Estructuras cristalinas de 1 y 2: (a) geometría de coordinación de $Y(III)$ y $Na(I)$, (b) cadena inorgánica infinita $-Y-O-Na-O-Y-$, constituida por poliedros catiónicos que se alternan compartiendo aristas, visualizada a lo largo del eje c , (c) doble lámina, formada por cadenas infinitas conectadas entre sí a través de puentes de anión

tartrato, mostrando su disposición en zig-zag, (d) proyección de la estructura de 1 (izquierda) y 2 (derecha) a lo largo del eje *a*.

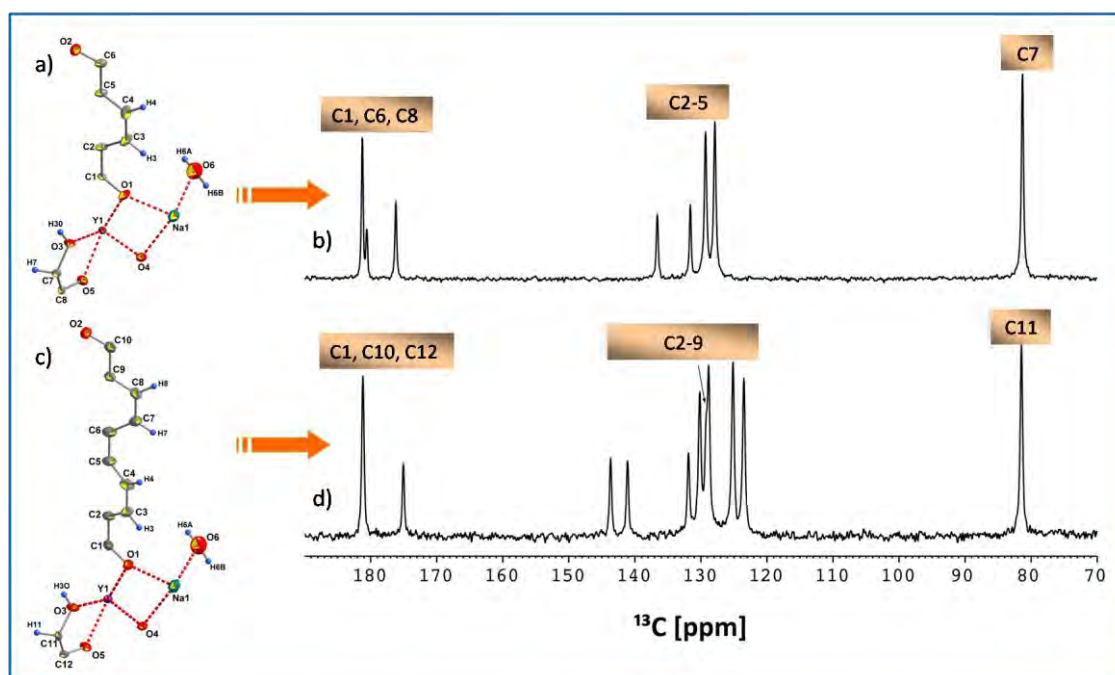


Figura 3.3.3. Espectros ^{13}C CPMAS NMR de 1 (b) y 2 (d) junto a sus unidades asimétricas (a,c). Los átomos asignados a cada señal se sitúan sobre los correspondientes picos de resonancia, mientras la flecha en (d) señala la existencia de un hombro (véase el texto).

entre los grupos carboxílicos no coordinados BDC^{2-} ó biBDC^{2-} (nave) y los grupos hidróxilo y/o las moléculas de agua coordinados (anclaje), mediante enlaces de hidrógeno (ancla). Finalmente, es destacable el inusual modo coordinación de BDC^{2-} (biBDC^{2-} en el caso de **2**), con inversión sucesiva, que da lugar a una superficie interlamina ondulante que se propaga en las direcciones cristalográficas *a* y *c*.

Los espectros de ^{13}C de resonancia magnética nuclear de estado sólido (CPMAS NMR) de **1** y **2** (Figura 3.3.3) confirman la elevada pureza y cristalinidad de sólidos obtenidos. En el espectro de **2**, sólo se observan 11 picos resonancia de los 12 esperados (incluyendo un hombro alrededor de 129 ppm), debido a la superposición de señales en el rango de desplazamiento químico del grupo carbonilo ($\delta > 170$ ppm). Las señales correspondientes a los carbonos aromáticos (BDC^{2-} y biBDC^{2-}) y a los grupos C-OH (Tart^{2-}) aparecen, tanto en **1** como de **2**, en el entorno $\delta = 120\text{-}150$ ppm y $\delta = 81$ ppm, respectivamente.

Mediante termogravimetría asociada al análisis por espectrometría de masas de los gases evacuados (TG-MS) y a análisis térmico diferencial (SDTA), junto con calorimetría diferencial de barrido (DSC), se ha investigado la estabilidad térmica de los nuevos materiales en atmósfera dinámica de oxígeno. Las curvas TG desde temperatura ambiente hasta 1000 °C de **1** y **2** muestran, respectivamente, una pérdida de masa total de 66.6% (cal. 68.69%) y 68.8% (cal. 73.14%). El producto final de la descomposición ha sido identificado como una mezcla de Y₂O₃ (detectado por difracción de rayos X del polvo cristalino residual), Na₂O amorfo (observado por microanálisis EDX acoplado a microscopía electrónica de barrido), y materia carbonosa (puesta de manifiesto por análisis elemental C-H-N).

Las curvas TG muestran que **1** y **2** tienen perfiles de descomposición térmica muy similares, lo que es esperable de compuestos que presentan composición química semejante, con estructuras relacionadas de idéntica dimensionalidad. La pérdida de masa de **1** (y **2**) procede en seis etapas. La primera transcurre entre 120 °C y 240 °C, con una pérdida de masa del 7.4% (cal. 7.82%) (6.2% (cal. 6.71%) para **2**) que se asocia a la evacuación de las dos moléculas de agua coordinadas al átomo de sodio. Las etapas segunda a quinta se superponen, en el rango 260-600 °C, con una pérdida de masa total del 53.0% (59.6% para **2**), correspondiendo a la descomposición de los ligandos orgánicos. La sexta etapa, 650-780 °C, se atribuye a la liberación de la fracción orgánica atrapada en la matriz inorgánica tras el colapso de la estructura original. La monitorización, mediante espectrometría de masas, de los gases evacuados en la descomposición térmica, unido a la semejanza en la variación de entalpía de deshidratación de ambos compuestos (-70 y -59 kJ/mol para **1** y **2**, respectivamente), la estabilidad de las fases anhidras hasta 250 °C, y su prácticamente idéntica variación de entalpía de descomposición oxidativa (-3545 y -3581 kJ/mol para **1** y **2**, respectivamente), corroboran esta interpretación.

La termodifracción de rayos X de polvocrystalino desveló que la deshidratación térmica de **1** y **2** es un fenómeno reversible en la atmósfera del laboratorio, con una cinética de rehidratación mucho más rápida en el caso de **1** que en el de **2**.

Finalmente, remarcar que se ha evaluado la actividad de **1** y **2** como catalizadores ácidos de Lewis en la acetalización del benzaldehído, comparando sus resultados con los obtenidos utilizando Y₂O₃ en las mismas condiciones. Ambos compuestos muestran un comportamiento muy similar, con actividades en exceso positivas, aunque muy modestas, probablemente consecuencia de la mayor

accesibilidad de los reactivos a sus centros metálicos en comparación con la estructura compacta del óxido.

Artículo II

Metal Organic Frameworks Assembled from Y(III), Na(I), and Chiral Flexible-Achiral Rigid Dicarboxylates

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New chiral metal organic frameworks, assembled from Y(III), Na(I), and chiral flexible-achiral rigid dicarboxylate ligands, formulated as $[\text{NaY}(\text{Tart})(\text{BDC})(\text{H}_2\text{O})_2]$ (**1**) and $[\text{NaY}(\text{Tart})(\text{biBDC})(\text{H}_2\text{O})_2]$ (**2**) (H_2Tart = Tartaric acid; H_2BDC = Terephthalic acid; H_2biBDC = Biphenyl-4,4'-dicarboxylic acid), were obtained as single phases under hydrothermal conditions. Their structures were solved by single-crystal X-ray diffraction (XRD), and characterized by ^{13}C CPMAS NMR, thermal analyses (thermogravimetry-mass spectrometry (TG-MS) and differential scanning calorimetry (DSC)), and X-ray thermogravimetry. Both compounds crystallize in the orthorhombic chiral space group $C22_21$ with $a = 6.8854(2)$ Å, $b = 30.3859(7)$ Å, $c = 7.4741(2)$ Å for **1**, and $a = 6.8531(2)$ Å, $b = 39.0426(8)$ Å, $c = 7.4976(2)$ Å for **2**. **1** and **2** are layered structures whose three-dimensional stability is ensured by strong hydrogen bond interactions. The dehydration of both compounds is accompanied by phase transformation, while the spontaneous rehydration process is characterized by different kinetics, fast in the case of **1** and slow for **2**.

Introduction

Metal–Organic Frameworks (MOFs), also known as coordination polymers, materials composed of metal ions or metal clusters as nodes and multifunctional organic linkers, are currently one of the most active and attractive research fields in materials science, owing to their wide variety of fascinating architectures and topologies and to their many

potential applications in gas storage^{1–9} and separation,^{10–13} catalysis,^{14,15} ion-exchange,^{16,17} magnetism,^{18,19} luminescence,^{20–23} and so on.

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- (1) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176.
- (2) Collins, D. J.; Zhou, H. C. *J. Mater. Chem.* **2007**, *17*, 3154.
- (3) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 3896.
- (4) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304.
- (5) Ma, S.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 11734.
- (6) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494.
- (7) Chen, B. L.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745.
- (8) Rowsell, J. L. C.; Yaghi, O. M. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.

- (9) Férey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guegan, A. *Chem. Commun.* **2003**, 2976–2977.
- (10) Pan, L.; Parker, B.; Huang, X.; Olson, D. H.; Lee, J. Y.; Li, J. *J. Am. Chem. Soc.* **2006**, *128*, 4180.
- (11) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376.
- (12) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32.
- (13) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428.
- (14) Zou, R. Q.; Sakurai, H.; Xu, Q. *Angew. Chem., Int. Ed.* **2006**, *45*, 2542.
- (15) Qiu, L. G.; Xie, A. J.; Zhang, L. D. *Adv. Mater.* **2005**, *17*, 689.
- (16) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, *118*, 295.
- (17) Kamiyama, A.; Noguchi, T.; Kajiwara, T.; Ito, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3130.
- (18) Ye, Q.; Fu, D. W.; Tian, H.; Xiong, R. G.; Chan, P. W. H.; Huang, S. P. D. *Inorg. Chem.* **2008**, *47*, 772.
- (19) Xu, N.; Shi, W.; Liao, D. Z.; Yan, S. P.; Cheng, P. *Inorg. Chem.* **2008**, *47*, 8748.
- (20) Rieter, W. J.; Taylor, K. M. L.; Lin, W. B. *J. Am. Chem. Soc.* **2007**, *129*, 9852.

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In MOFs, the functionality may be imparted by the inorganic or organic units. Nowadays, there is considerable interest in chiral metal–organic coordination polymers by virtue of their potential application in asymmetric catalysis and chiral separation,^{24–33} and nonlinear optical activity.^{34,35} The design of chiral coordination polymers with different architectures and topologies is still challenging, and more so when lanthanides, rather than transition metals, are used. The attempts at the construction of chiral lanthanides-based coordination polymers are still rare,^{36–40} which is due mainly to the flexibility of the lanthanide ions coordination sphere. However, their flexibility together with the tendency toward high coordination numbers makes them attractive for designing new materials with unusual architectures and network topologies as well as potential applications in many fields such as, magnetic^{18,19} and luminescent materials,^{20–23} liquid crystals,⁴¹ molecular-recognition and chirality-sensing agents in biology,⁴² selective gas absorption,⁴³ and as Lewis acid catalysts of various important organic reactions.^{44,45}

Many of the recent works based on lanthanide coordination polymers have been focused on the use of rigid polycarboxylate ligands. However, those containing both rigid and flexible dicarboxylates as mixed ligands are less deve-

loped.^{46–50} In this work, we report a new approach to the construction of two novel chiral heteronuclear metal–organic frameworks, based on a mixed-metals-ligands system containing both chiral flexible and achiral rigid linear ligands. Tartaric acid (**H₂Tart**) was selected as flexible ligand because it (i) has six donor atoms helpful in getting high dimensional structures, (ii) is a simple and inexpensive chiral ligand with two chiral centers, and (iii) exists in various forms such as D(–), L(+), meso and racemic. We have chosen terephthalic acid (**H₂BDC**) which has been used extensively as an organic spacer, and its extended analogue biphenyl-4,4′-dicarboxylic acid (**H₂biBDC**), because these rigid ligands (i) are able to establish a bridge between metal centers, affording frameworks with large pores,^{51–53} and (ii) may enhance the fluorescence of the Ln(III) ions, via the so-called antenna effect.^{54,55} The combination of this mixed-ligand system with rare-earth ions, such as the small Y(III),⁵⁶ allows the synthesis of unusual coordination polymers with interesting properties. The yttrium coordination polymers are relatively limited compared with the f-block metal ions, although yttrium is widely used in laser crystals,^{57–60} and superconductive materials.^{61–66}

Herein, we will confine ourselves to report the full structural characterization of the two novel chiral yttrium-based metal organic frameworks, NaY(C₄H₄O₆)(C₈H₄O₄)(H₂O)₂ (**1**) and NaY(C₄H₄O₆)(C₁₄H₈O₄)(H₂O)₂ (**2**), as the first examples of chiral structures containing Y(III), Na(I), and chiral flexible-achiral rigid dicarboxylic ligands, which have been synthesized hydrothermally. Their crystal structures were determined by single-crystal X-ray diffraction (XRD), and characterized by ¹³C CPMAS NMR, thermal analyses (thermogravimetry-mass spectrometry (TG-MS) and differential scanning calorimetry (DSC)), and X-ray thermodiffractionometry.

Experimental Section

Synthesis. NaY(C₄H₄O₆)(C₈H₄O₄)(H₂O)₂ (**1**) and NaY(C₄H₄O₆)(C₁₄H₈O₄)(H₂O)₂ (**2**) were synthesized under hydrothermal

- (21) Chen, B.; Yang, Y.; Zapata, F.; Lin, G.; Qian, G.; Lobkovsky, E. B. *Adv. Mater.* **2007**, *19*, 1693.
- (22) Song, X. Q.; Liu, W. S.; D, W.; Zheng, J. R.; Tang, X. L.; Zhang, H. R.; Wang, D. Q. *Dalton Trans.* **2008**, 3582.
- (23) Zhu, X.; Lu, J.; Li, X.; Gao, S.; Li, G.; Xiao, F.; Cao, R. *Cryst. Growth Des.* **2008**, *8*, 1897.
- (24) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.
- (25) Kesanli, B.; Lin, W. B. *Coord. Chem. Rev.* **2003**, *246*, 305.
- (26) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106.
- (27) Lin, W. J. *Solid State Chem.* **2005**, *178*, 2488.
- (28) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. J. *Am. Chem. Soc.* **2005**, *127*, 8940.
- (29) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273.
- (30) Cho, S. H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, *24*, 2563.
- (31) Nuzhdin, A. L.; Dybtshev, D. N.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P. *J. Am. Chem. Soc.* **2007**, *129*, 12958.
- (32) Li, G.; Yu, W. B.; Cui, Y. J. *Am. Chem. Soc.* **2008**, *130*, 4582.
- (33) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248.
- (34) Evans, O. R.; Lin, W. B. *Acc. Chem. Res.* **2002**, *35*, 511.
- (35) Liu, Y.; Xu, X.; Zheng, F. K.; Cui, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 4538.
- (36) Thushari, S.; Cha, J. A. K.; Sung, H. H. Y.; Chui, S. S. Y.; Leung, A. I. F.; Yen, Y. F.; Williams, I. D. *Chem. Commun.* **2005**, 5515.
- (37) Gu, X. J.; Xue, D. F. *Inorg. Chem.* **2006**, *45*, 9257.
- (38) Masu, H.; Tominaga, M.; Katagiri, K.; Kato, T.; Azumaya, I. *CrystEngComm* **2006**, *8*, 578.
- (39) Ma, Y. S.; Li, H.; Wang, J. J.; Bao, S. S.; Cao, R.; Li, Y. Z.; Ma, J.; Zheng, L. M. *Chem.—Eur. J.* **2007**, *13*, 4759.
- (40) Tang, Y.; Tang, K. Z.; Liu, W. S.; Tan, M. Y. *Sci. China, Ser. B: Chem.* **2008**, *51*, 614.
- (41) Binnemans, K.; Gorller-Walrand, C. *Chem. Rev.* **2002**, *102*, 2303.
- (42) Tsukube, H.; Shinoda, S. *Chem. Rev.* **2002**, *102*, 2389.
- (43) Pan, L.; Adams, K. M.; Hernandez, H. E.; Wang, X.; Zheng, C.; Hattori, Y.; Kaneko, K. *J. Am. Chem. Soc.* **2003**, *125*, 3062.
- (44) Imamoto, T. *Lanthanide in Organic Synthesis*; Academic: New York, 1994.
- (45) Perles, J.; Iglesias, M.; Valero, C. R.; Snejko, N. *J. Mater. Chem.* **2004**, *14*, 2683.
- (46) Wang, Z.; Xing, Y. H.; Wang, C. G.; Sun, L. X.; Zhang, J.; Ge, M. F.; Niu, S. Y. *CrystEngComm* **2010**, *12*, 762.
- (47) Wang, Z.; Bai, F. Y.; Xing, Y. H. *Inorg. Organomet. Polym.* **2010**, *20*, 242.
- (48) Wang, C. G.; Xing, Y. H.; Li, Z. P.; Li, J.; Zeng, X. Q.; Ge, M. F.; Niu, S. Y. *Cryst. Growth Des.* **2009**, *9*, 1525.
- (49) Wang, C. G.; Xing, Y. H.; Li, Z. P.; Li, J.; Zeng, X. Q.; Ge, M. F.; Niu, S. Y. *J. Mol. Struct.* **2009**, *921*, 126.
- (50) Hu, D. X.; Luo, F.; Che, Y. X.; Zheng, J. M. *Cryst. Growth Des.* **2007**, *7*, 1733.
- (51) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.
- (52) Guo, X. D.; Zhu, G. S.; Fang, Q. R.; Xue, M.; Tian, G.; Sun, J. Y.; Li, X. T.; Qiu, S. L. *Inorg. Chem.* **2005**, *44*, 3850.
- (53) Chen, J.; Chen, Z.; Yu, T.; Weng, L.; Tu, B.; Zhao, D. *Microporous Mesoporous Mater.* **2007**, *98*, 16.
- (54) Panigrahi, B. S.; Peter, S.; Viswanathan, K. S. *Spectrochim. Acta, Part A* **1997**, *53*, 2579.
- (55) Panigrahi, B. S. *J. Alloys Compd.* **2002**, *334*, 228.
- (56) Chen, S. P.; Ren, Y. X.; Gao, S. L. *Russ. J. Coord. Chem.* **2008**, *34*(4), 301.
- (57) Rasuleva, A. V.; Solomonov, V. I. *Laser Phys.* **2006**, *16*, 130.
- (58) Krennrich, D.; Knappe, R.; Henrich, B.; Wallenstein, R.; L’Huillier, J. A. *Appl. Phys. B: Lasers Opt.* **2008**, *92*, 175.
- (59) Coluccelli, N.; Galzerano, G.; Bonelli, L.; Toncelli, A.; Di Lieto, A.; Tonelli, M.; Laporta, P. *Appl. Phys. B: Lasers Opt.* **2008**, *92*, 519.
- (60) Yu, Y.; Wang, J.; Zhang, H.; Yu, H.; Wang, Z.; Jiang, M.; Xia, H.; Boughton, R. I. *J. Opt. Soc. Am. B.* **2008**, *25*, 995.
- (61) Chen, D. H.; Sheen, S. R.; Chang, C. T.; Shei, C. Y.; Hurng, W. M. *J. Chin. Chem. Soc.* **1992**, *39*, 137.
- (62) Ting, W.; Fosshem, K. *Int. J. Mod. Phys. B.* **1994**, *8*, 275.
- (63) Chen, D. H.; Liu, T. W.; Huang, J. C.; Cheng, C. H.; Chang, C. T.; Sheen, S. R.; Wang, T. C.; Wu, M. K. *Mater. Lett.* **1994**, *21*, 15.
- (64) Carr, C.; Eulenburg, A.; Romans, E. J.; Pegrum, C. M.; Donaldson, G. B. *Supercond. Sci. Technol.* **1998**, *11*, 1317.
- (65) Izumi, T.; Yuh, S. *J. Phys. Chem. Solids* **2005**, *66*, 535.
- (66) Prikhna, T. A. *J. Low Temp. Phys.* **2006**, *32*(4–5), 505.

Article

conditions and obtained as a single phase of colorless needle crystals by following similar procedures.

Compound 1: 0.31 g (1 mmol) of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 0.21 g (1.4 mmol) of L-tartaric acid (**H₂Tart**), 0.08 g (0.5 mmol) of terephthalic acid (**H₂BDC**), and 0.14 g (3.5 mmol) of NaOH were dissolved in a mixture of ethanol (6 mL) and distilled water (6 mL). (0.135 g, ca. 30% yield based on Y). Elemental analysis for **1**: $\text{C}_{12}\text{H}_{12}\text{O}_{12}\text{YNa}$ ($M_r = 460.12$). Calcd: C, 31.29; H, 2.61%. Found: C, 31.3; H, 2.3%.

Compound 2: 0.31 g (1 mmol) of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 0.21 g (1.4 mmol) of L-tartaric acid (**H₂Tart**), 0.12 g (0.5 mmol) of biphenyl-4,4'-dicarboxylic acid (**H₂biBDC**) and 0.14 g (3.5 mmol) of NaOH were dissolved in a mixture of ethanol (6 mL) and distilled water (6 mL). (0.176 g, ca. 32% yield based on Y). Elemental analysis for **2**: $\text{C}_{18}\text{H}_{16}\text{O}_{12}\text{YNa}$ ($M_r = 536.21$). Calcd: C, 40.28; H, 2.98%. Found: C, 39.0; H, 3.1%.

In both cases, the reaction mixture was stirred for 2 h at room temperature to homogeneity and then placed in a Teflon-lined stainless vessel (40 mL) and heated to 180 °C for 72 h under autogenous pressure and afterward cooled to room temperature. The resulting product was filtered off, washed thoroughly with ethanol and distilled water, and finally air-dried at room temperature.

Single-Crystal XRD Studies. Data collection was performed at 293 K on a Oxford Diffraction Gemini CCD diffractometer, using Cu K α radiation. Images were collected at a 55 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image. The crystal structure was solved by direct methods. The refinement was performed using full-matrix least-squares on F^2 . All non-H atoms were anisotropically refined. All H atoms were either geometrically placed riding on their parent atoms or obtained from the difference Fourier map, with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached. Crystallographic calculations were carried out using the following programs: CrysAlis CCD⁶⁷ for data collection; CrysAlis RED⁶⁸ for cell refinement, data reduction, and empirical absorption correction; SHELX-97⁶⁹ for structure solution; XABS2⁷⁰ for refined absorption correction; SHELXL-97 for structure refinement and preparation of materials for publication; PLATON⁷¹ for the geometrical calculations; Diamond⁷² for molecular graphics.

Thermal Characterization. A Mettler-Toledo TGA/SDTA851 and a DSC822 were used for the thermal analyses in oxygen dynamic atmosphere (50 mL/min) at a heating rate of 10 °C/min. In all cases, about 10 mg of powder sample was thermally treated, and blank runs were performed. In TG tests, a Pfeiffer Vacuum ThermoStar GSD301T mass spectrometer was used to determine the evacuated vapors. The masses 18 (H_2O), 44 (CO_2), and of the intense peaks corresponding to the cracking of the ligands used, were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

Elemental Analysis. The carbon and hydrogen contents were measured on a C–H–N Perkin-Elmer model 2400B elemental analyzer. X-ray microanalysis (SEM/EDX) confirmed the ratio Y:Na to be 1:1, by using a JEOL JSM-6100 scanning electron microscopy (SEM) coupled with an INCA Energy-200 energy

(67) CrysAlis CCD, Version 1.171.32.37 (release 24-10-2008 CrysAlis171.NET, compiled Oct 24, 2008,09:44:38); Oxford Diffraction Ltd.: Abingdon, U.K., 2008.

(68) CrysAlis RED, Version 1.171.32.37 (release 24-10-2008 CrysAlis171.NET, compiled Oct 24, 2008,09:44:38); Oxford Diffraction Ltd.: Abingdon, U.K., 2008.

(69) Sheldrick, G. M. *SHELXL-97, Program for refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(70) Parkin, S.; Moezzi, B.; Hope, H. J. *Appl. Crystallogr.* **1995**, *28*, 53.

(71) PLATON/PLUTON: (a) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.

(72) Brandenburg, K. *DIAMOND*, Version 3.1; Crystal Impact GbR: Bonn, Germany, 2007.

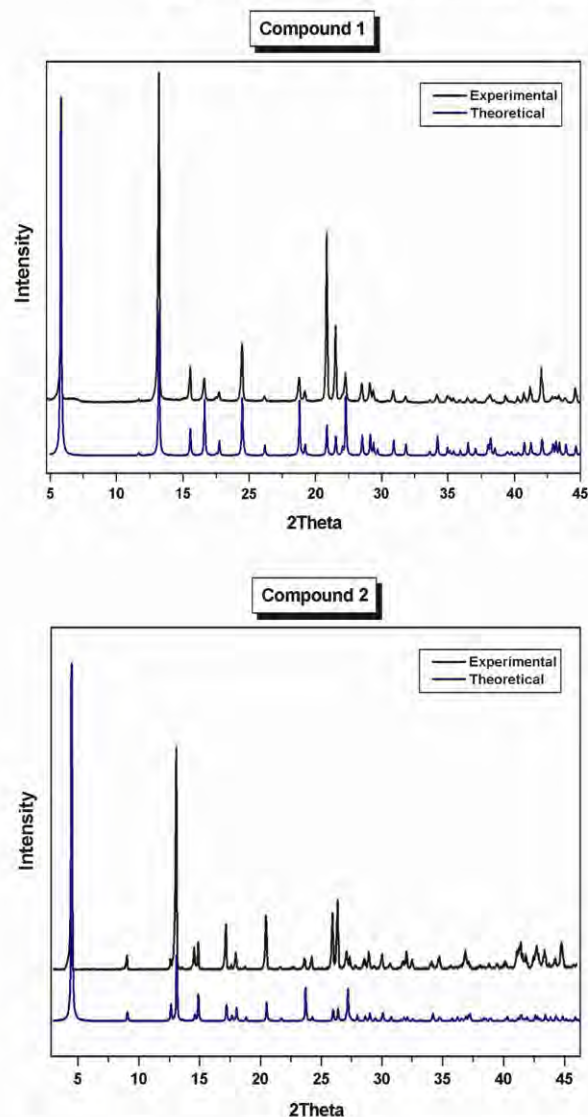


Figure 1. Powder XRD patterns of **1** and **2** compared with the theoretical ones.

dispersive X-ray microanalysis system (EDX) with a PentaFET ultrathin window detector.

Powder XRD Studies. Powder XRD (PXRD) patterns were recorded on X'Pert Philips diffractometer with Cu K α radiation. The samples were gently ground in an agate mortar to minimize the preferred orientation. All data were collected at room temperature over the angular 2θ range 3–46° with a step of 0.02° and a counting time of 0.4 s/step. The PXRD patterns of the compounds **1** and **2** were compared with the theoretical ones (see Figure 1), indicating that the products have been successfully obtained as pure crystalline phases.

Powder X-ray Thermodiffraction Studies. These studies were performed in air with the sample placed in an Anton Paar HTK 1200N oven-chamber, on a PANalytical XPERT-PRO diffractometer, using Cu K α radiation, equipped with a PIXcel linear detector with 255 channels. Each powder pattern was recorded in the 4–110° range (2θ) at intervals of 25 °C up to 200 °C and cooling down to 25 °C with a step of 0.013° and a counting time of 0.424 s/channel. The temperature ramp between two consecutive temperatures was 10 °C/min.

Table 1. Crystallographic Data for **1** and **2**

	Compound 1	Compound 2
identification code	ZA1	ZA2
empirical formula	C ₁₂ H ₁₂ NaO ₁₂ Y	C ₁₂ H ₁₂ NaO ₁₂ Y
formula weight/g mol ⁻¹	460.12	536.21
temperature/K	293(2) K	293(2) K
wavelength	1.54184 Å	1.54184 Å
crystal system	orthorhombic	orthorhombic
space group	C222 ₁	C222 ₁
unit cell dimensions		
<i>a</i> (Å)	6.8854(2)	6.8531(2)
<i>b</i> (Å)	30.3859(7)	39.0426(8)
<i>c</i> (Å)	7.4741(2)	7.4976(2)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
cell volume/ Å ³	1563.72(7)	2006.08(9)
<i>Z</i>	4	4
calc. density/mg m ⁻³	1.954	1.775
absorption coefficient/mm ⁻¹	6.184	4.928
<i>F</i> (000)	920	1080
crystal size (mm ³)	0.015 × 0.046 × 0.192	0.018 × 0.048 × 0.118
θ range for data collection/ deg	5.82 to 66.78	4.53 to 70.55
index ranges	-6 ≤ <i>h</i> ≤ 8 -23 ≤ <i>k</i> ≤ 35 -8 ≤ <i>l</i> ≤ 8	-4 ≤ <i>h</i> ≤ 8 -32 ≤ <i>k</i> ≤ 47 -9 ≤ <i>l</i> ≤ 7
reflections collected	2595	3491
independent reflections	1256 [<i>R</i> (int) = 0.0536]	1786 [<i>R</i> (int) = 0.0303]
completeness to θ_{\max}	98.3%	99.7%
absorption correction	refined (XABS2)	refined (XABS2)
max. and min. transmission	0.9255 and 0.6034	1 and 0.83103
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
data/restraints/parameters	1256/3/133	1786/3/158
goodness-of-fit on <i>F</i> ²	1.024	1.145
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0303 <i>wR</i> 2 = 0.0622	<i>R</i> 1 = 0.0278 <i>wR</i> 2 = 0.0715
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0334 <i>wR</i> 2 = 0.0627	<i>R</i> 1 = 0.0317 <i>wR</i> 2 = 0.0723
absolute structure parameter	0.01(3)	-0.01(2)
largest diff. peak and hole	0.491 and -0.415 e Å ⁻³	0.356 and -0.449 e Å ⁻³

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound **1** and **2**^a

Compound 1	Compound 2		
Y1—O1	2.377(2)	Y1—O1	2.381(2)
Y1—O3	2.378(3)	Y1—O3	2.382(3)
Y1—O4	2.282(3)	Y1—O4	2.278(3)
Y1—O5	2.332(3)	Y1—O5	2.341(3)
Na1—O1	2.399(3)	Na1—O1 ^{III}	2.382(2)
Na1—O4	2.548(3)	Na1—O4 ^{III}	2.554(3)
Na1—O6	2.313(4)	Na1—O6	2.316(4)
Y1—Na1	3.819(2)	Y1—Na1	3.808(4)
C1—O1	1.259(3)	C1—O1	1.264(3)
O1—C1—O1 ^I	119.7(4)	O1—C1—O1 ^{III}	120.0(4)
C6—O2	1.255(4)	C10—O2	1.254(4)
O2—C6—O2 ^I	123.5(5)	O2—C10—O2 ^{III}	123.7(5)
C7—O3	1.426(5)	C11—O3	1.429(5)
C8—O4 ^{II}	1.268(5)	C12—O4 ^{IV}	1.266(5)
C8—O5	1.253(5)	C12—O5	1.242(5)
O5—C8—O4 ^{II}	124.6(4)	O5—C12—O4 ^{IV}	125.2(4)

^aSymmetry code: (I) $-x, y, -z+3/2$; (II) $-x-1/2, -y+3/2, z-1/2$; (III) $-x+1, y, -z+3/2$; (IV) $-x+3/2, -y+1/2, z-1/2$.

Solid-State NMR Spectroscopy. ¹³C CPMAS NMR spectra were recorded on a Bruker AVANCE 400 (DSX) WB spectro-

Table 3. Hydrogen-Bond Geometry in **1** and **2** (Å, deg)^a

D—H···A	D—H [Å]	H···A [Å]	D···A [Å]	D—H···A [deg]
Compound 1				
O6—H6A···O2 ^I	0.99(4)	1.84(4)	2.817(7)	166(4)
O3—H3O···O2 ^I	0.81(5)	1.83(5)	2.628(4)	170(7)
Compound 2				
O6—H6A···O2 ^{II}	0.97(5)	1.86(5)	2.804(7)	163(5)
O3—H3O···O2 ^{III}	0.84(7)	1.77(6)	2.611(4)	171(7)

^aSymmetry code: (I) $1-x, -y, -1/2+z$; (II) $1-x, -y, -1/2+z$; (III) $x, -y, 1-z$.

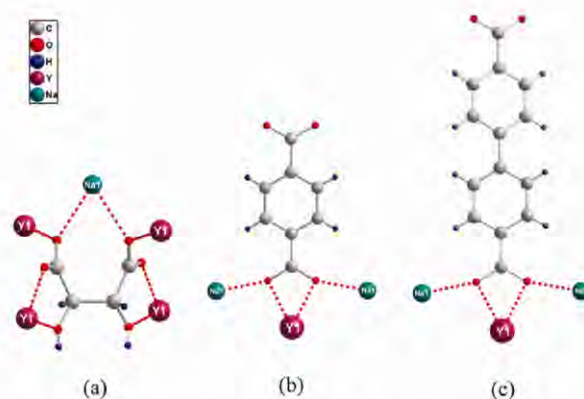


Figure 2. (a) Coordination modes of the **Tart**²⁻ ligand ($\mu 5-\eta^1: \eta^2: \eta^2: \eta^1: \eta^2$) in **1** and **2**, (b) and (c): coordination modes of **BDC**²⁻ ($\mu 3-\eta^1: \eta^2: \eta^1$) and **biBDC**²⁻ ($\mu 3-\eta^1: \eta^2: \eta^1$) ligands in **1** and **2**, respectively.

meter (9.4 T), using a double-resonance 4 mm VTN probe, at a Larmor frequency of 100.62 MHz. Samples were packed in a 4 mm diameter ZrO₂ rotor and spun at a MAS rate of 12 kHz. The spectra were recorded using a RAMP-CP shape (100–50% amplitude); radiofrequency (rf) field strengths between 50 and 70 kHz for Hartman-Hahn matching condition ($n = \pm 1$) in ¹³C and ¹H channels; recycle delay of 5 s; contact time of 1 ms; ¹H decoupling was employed using the Small phase Incremental Alternation (SPINAL-64) multiple pulse scheme, during ¹³C signal detection. A pulse length of 4.5 μ s (ca. 165° flip angle) and a ¹H rf decoupling strength ($\omega_1/2\pi$) of about 105 kHz were employed for the basic unit of the SPINAL64 scheme. Chemical shifts are quoted in parts per million (ppm) from solid glycine.

Catalysis Studies. The procedure followed for acetalization of benzaldehyde with trimethylorthoformate (TMOF) was as follows: to a suspension of the catalyst (0.01 mmol) in 3 mL of tetrachloromethane were added TMOF (5 mmol, 0.5 mL) and benzaldehyde (0.5 mmol, 0.05 mL). The reaction was carried out in a sealed tube under nitrogen atmosphere, mild conditions (70 °C), and under magnetic steering. Samples were taken at intervals and analyzed by gas chromatography.

Results and Discussion

The detailed crystallographic data and the structure refinement parameters are summarized in Table 1. Selected bond distances, angles, and hydrogen bonds for **1** and **2** are given in Tables 2 and 3. The coordination modes of **Tart**²⁻, **BDC**²⁻ and **biBDC**²⁻ ligands in compounds **1** and **2** are depicted in Figure 2. To the best of our knowledge, these coordination modes have not yet been reported.

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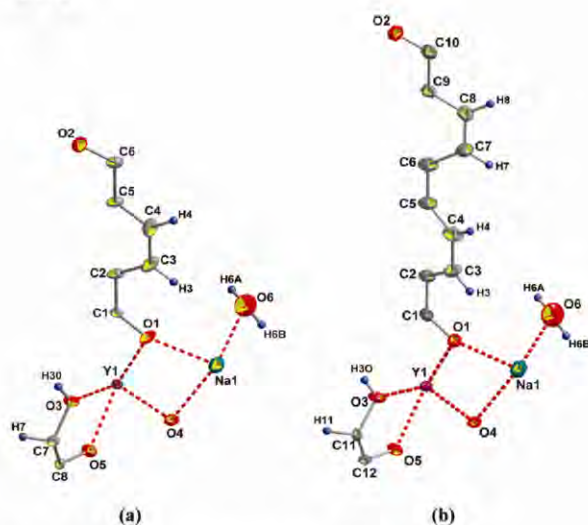


Figure 3. Asymmetric units of **1** (a) and **2** (b).

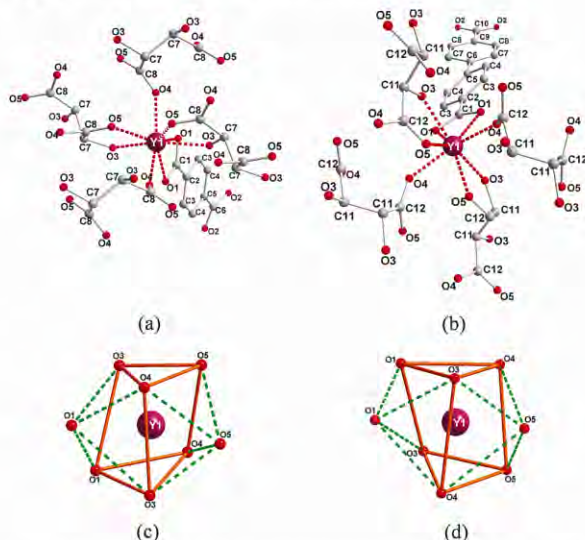


Figure 4. Perspective view of the coordination environment of Y(III) in **1** (a,c) and **2** (b,d).

1 and **2** are layered chiral coordination polymers, built up by mixing Y(III), Na(I), and chiral flexible-achiral rigid dicarboxylate ligands, **Tart-BDC** in the case of **1**, **Tart-biBDC** in the case of **2**. The single-crystal XRD measurements reveal that the compounds **1** and **2** crystallize in the orthorhombic chiral space group $C222_1$. The asymmetric unit of **1** and **2** comprises half Y^{3+} cation, half Na^+ cation, half **Tart**²⁻ anion, half **BDC**²⁻ anion in the case of **1** (half **biBDC**²⁻ anion in the case of **2**), and a coordinated water molecule (Figure 3), as a consequence of the fact that Y^{3+} and Na^+ cations, as well as **Tart**²⁻ and **BDC**²⁻ anions (**biBDC**²⁻ in the case of **2**), are situated on a crystallographic 2-fold axis along the *b*-direction. In each compound, the Y^{3+} cation is bonded to eight oxygen atoms, six of them carboxylic and two from hydroxyl groups (Figure 4a,b). Its coordination geometry may be described as a distorted bicapped trigonal-prism (Figure 4c,d), while the Na(I) cation is bonded to six oxygen

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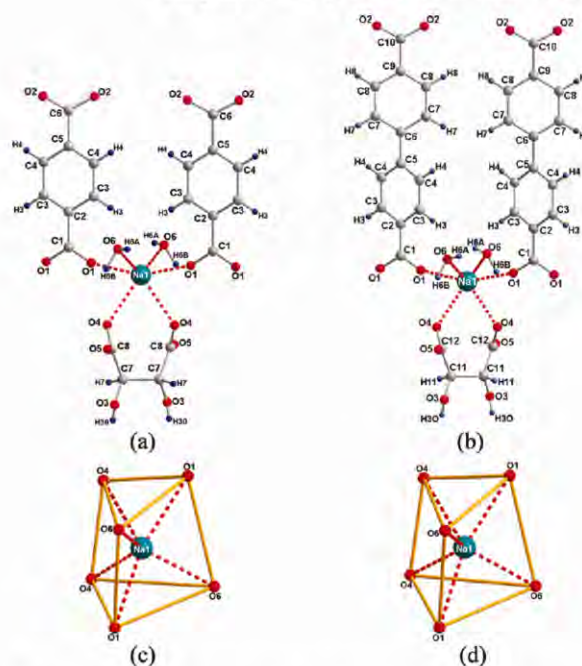


Figure 5. Perspective view of the coordination environment of Na(I) in **1** (a,c) and **2** (b,d).

atoms, four of them carboxylic and two from coordinated water molecules (Figure 5a,b), and its geometry may be described as distorted trigonal prism (Figure 5c,d). Out of the eight oxygen atoms coordinated to Y^{3+} , six come from four **Tart**²⁻ anions crystallographically equivalents: two of them are coordinated to Y^{3+} in chelating modes via the carboxylic oxygen atom O5 and the hydroxyl oxygen atom O3, and the last two act as a bridge between the Y^{3+} and Na^+ within the carboxylic oxygen atom O4. The two remaining oxygen atoms bonded to Y^{3+} belong to one **BDC**²⁻ anion (one **biBDC**²⁻ ligand in the case of **2**), which acts (i) in chelating mode via the carboxylate group O1–C1–O1 and (ii) in bridging mode between Y^{3+} and Na^+ within each carboxylate oxygen atom O1. From six oxygen atoms coordinated to Na^+ , two come from the **Tart**²⁻ anion which acts in chelating mode via the carboxylate oxygen atoms O4, and the four remaining, every two of them belonging to two crystallographically equivalents: (i) coordinated water molecules, (ii) **BDC**²⁻ anions (**biBDC**²⁻ anions in the case of **2**), by coordinating oxygen atoms O6 and O1, respectively. In **1**, the distances Y–O and Na–O range from 2.282(3) to 2.378(3) Å, and from 2.313(4) to 2.548(3) Å, with the average values of 2.342(4) Å and 2.421(3) Å, respectively. Similarly, the pertinent values in **2** range from 2.278(3) Å to 2.382(3) Å and from 2.316(4) Å to 2.554(3) Å, with the average values of 2.345(5) Å and 2.417(3) Å, respectively.

The Y^{3+} and Na^+ polyhedra alternate in a chain edge-to-edge parallel to the *a*-axis, and the distance between adjacent Y–Na cations in the chain is 3.819(2) Å and 3.808(4) Å in **1** and **2**, respectively. These chains are in turn connected via **Tart**²⁻ bridges along *a* and *c*-axis showing a zigzag arrangement, and forming a double layer. The resulting double layered network is then pillared by the rigid **BDC**²⁻ ligands (**biBDC**²⁻ in the case of **2**) which are parallel to the *b*-axis,

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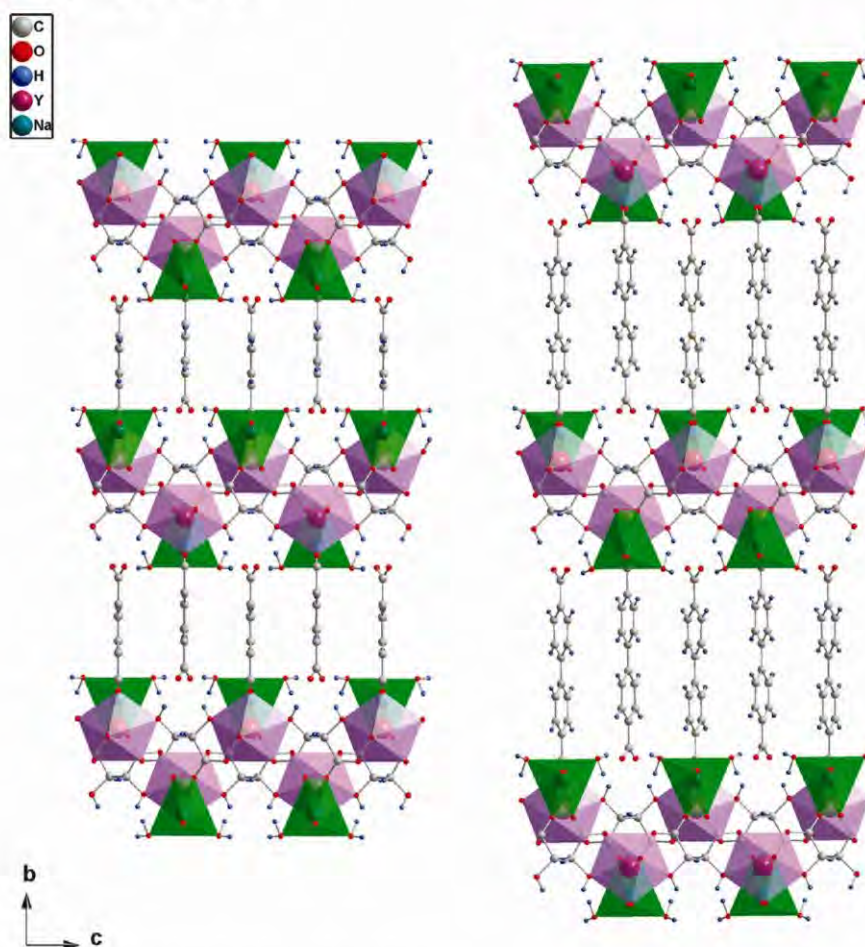


Figure 6. Projection of the structure of **1** (left) and **2** (right) along the *a*-axis.

forming channels running along *a* (Figure 6) and *c*-axis (Figure 7), with approximate dimensions of $6.3 \times 3.5 \text{ \AA}^2$ and $6.3 \times 4.5 \text{ \AA}^2$ in **1**, or $10.6 \times 3.5 \text{ \AA}^2$ and $10.6 \times 4.5 \text{ \AA}^2$ in **2**. The rigid BDC^{2-} (**biBDC** $^{2-}$ in the case of **2**) spacers, separating two successive double layers, are one-sided coordinated (to Y^{3+} and Na^+ cations), the other side being involved in strong hydrogen bond interactions between: the oxygen atoms O2 of the noncoordinated carboxylate group O2–C6–O2 of the BDC^{2-} ligand (O2–C10–O2 of the **biBDC** $^{2-}$ ligand, in the case of **2**) which acts as acceptor, and the oxygen atom O3 of the hydroxyl groups of the Tart^{2-} ligand, together with the coordinated water molecules O6 to the sodium atom which act as donors, therefore imparting 3D stability to the structure. The uncoordinated side of BDC^{2-} or **biBDC** $^{2-}$ ligands can be described as ship anchoring, forming ship-anchor-anchorage (with ship = uncoordinated carboxylate groups of BDC^{2-} or **biBDC** $^{2-}$, anchor = hydrogen bonds, anchorage = hydroxyl groups and coordinated water molecules found in the double layer). The unusual coordination mode of BDC^{2-} (**biBDC** $^{2-}$ in the case of **2**), in a successive switch manner, gives rise to an undulating interlayer surface propagating in *a* and *c*-directions.

The ^{13}C CP/MAS NMR spectra of **1** (a) and **2** (b) are shown in the Supporting Information, Figure S1 and confirm the

phase purity of the samples. In the spectrum of **2** (Supporting Information, Figure S1a) only 11 of the 12 resonances are observed (including a shoulder at about $\delta = 129$ ppm), because of peak overlap in the carbonyl chemical shift range ($\delta > 170$ ppm). The peaks from the aromatic ligands (BDC^{2-} and **biBDC** $^{2-}$) and from the Tart^{2-} C–OH groups appear at about $120 < \delta < 150$ ppm and about $\delta = 81$ ppm, respectively, in both structures of **1** and **2**.

The thermal stability in air of **1** and **2** was investigated. The TG/DTG, SDTA curves, and the mass spectrometry analysis, are depicted in the Supporting Information, Figure S2, while Supporting Information, Figure S3 shows DSC traces. TG/DTG curves of **1** and **2** reveal total mass losses of, respectively, 66.6% (calcd 68.69%) and 68.8% (calcd 73.14%), from room temperature up to 1000 °C. The final product of the decomposition is Y_2O_3 (detected by PXRD), amorphous Na_2O (by EDX microanalysis), and coal (by C–H–N elemental analysis).

In the case of **1**, the first stage between 120 and 245 °C (which reach its maximum velocity at 212 °C) with the total mass loss of 7.4% (calcd 7.82%), associated with endothermic peak at 215 and 210 °C on the SDTA and DSC curves respectively, corresponds to the loss of the two water molecules coordinated to the sodium atom. The second, third, and

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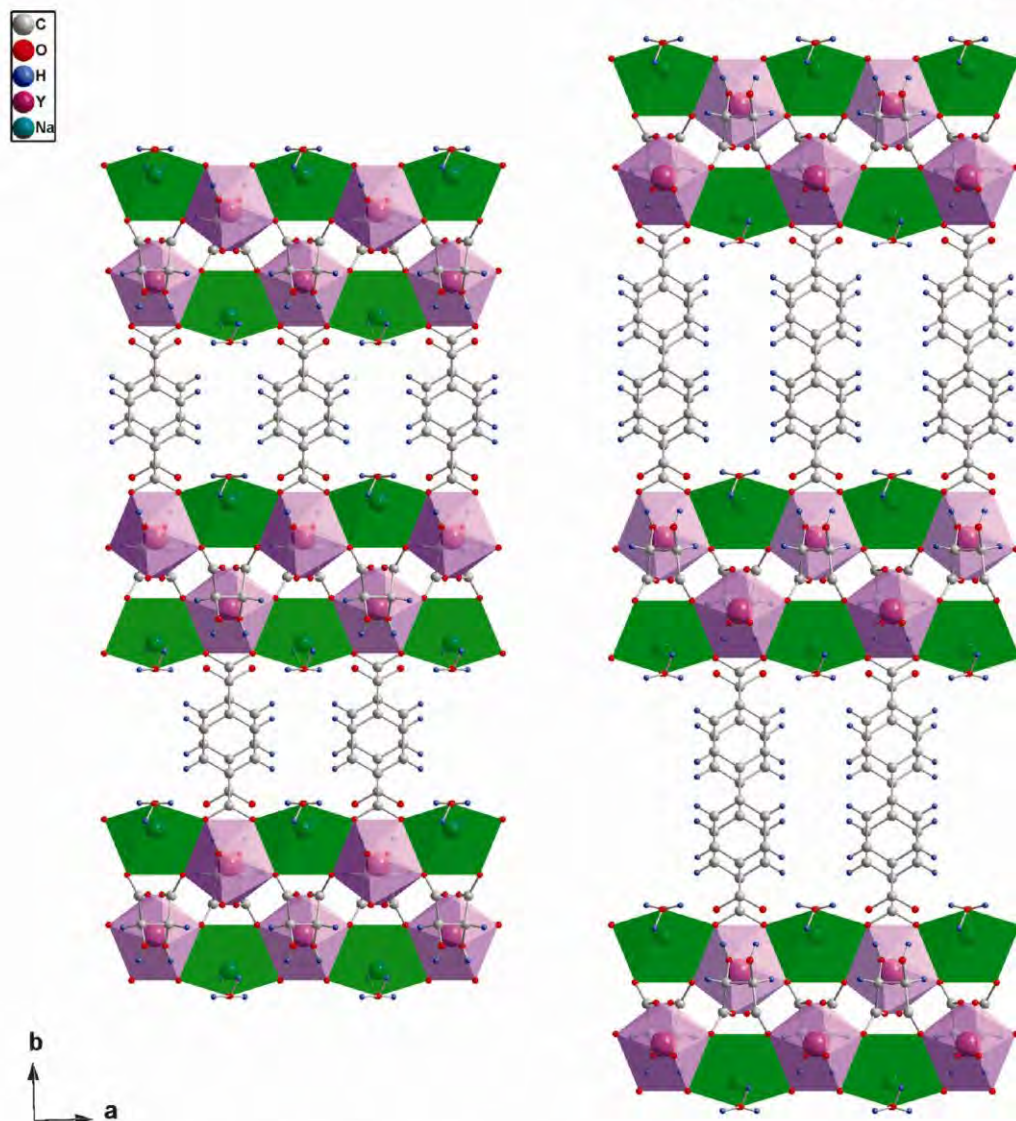


Figure 7. Projection of the structure of 1 (left) and 2 (right) along the c -axis.

fourth with shoulder (fifth stage) stages are continuous and overlapping, with the total mass loss of about 53%, in the range 270–580 °C, which reach their maximum velocity at 314, 402, and 485 °C respectively, associated with a large exothermic bound in the range 308–440 °C (maximum at 400 °C) and 306–435 °C (maximum at 403 °C) on the SDTA and DSC curves, respectively, corresponding to the second and third stages, and with a sharp exothermic peak at 484 °C accompanied by shoulder at 520 °C on the SDTA curve and with two peaks at 489 and 520 °C on the DSC curve corresponding to the fourth and fifth stages. This multistep decomposition behavior is assigned to a complex and overlapping oxidation process of the mixed-ligands. The sixth stage in the range 630–750 °C, which reaches its maximum velocity at 698 °C, with the mass loss of about 6%, described by exothermic effect at 700 °C on the SDTA curve, may be due to the liberation of some trapped organic part after the

structure collapse. The associated mass spectrometry m/z 18 and 44 curves are in a good agreement with the TG/DTG curves. The mass spectrometry m/z 18 curve has four maxima, the first one at 223 °C corresponding to the loss of the two water molecules coordinated to sodium atom, and the second, third, and fourth maxima at 324, 406, and 485 °C, respectively, coincide with the first, second, and third (accompanied by a shoulder at 520 °C) maxima of the m/z 44 curve, which may be attributed to multistep oxidation of the Tart^{2-} and BDC^{2-} ligands. The fifth maxima of m/z 44 curve at 700 °C confirm the liberation of some trapped organic part after the structure collapse. Other fragments of m/z 42 and 50, corresponding to Tart^{2-} and BDC^{2-} ligands respectively, have been also detected. The m/z 42 curve shows three maxima which coincide with the first, second, and third maxima of the m/z 44 curve, while the m/z 50 maxima at 485 °C coincide with the third maximum of m/z 44, showing

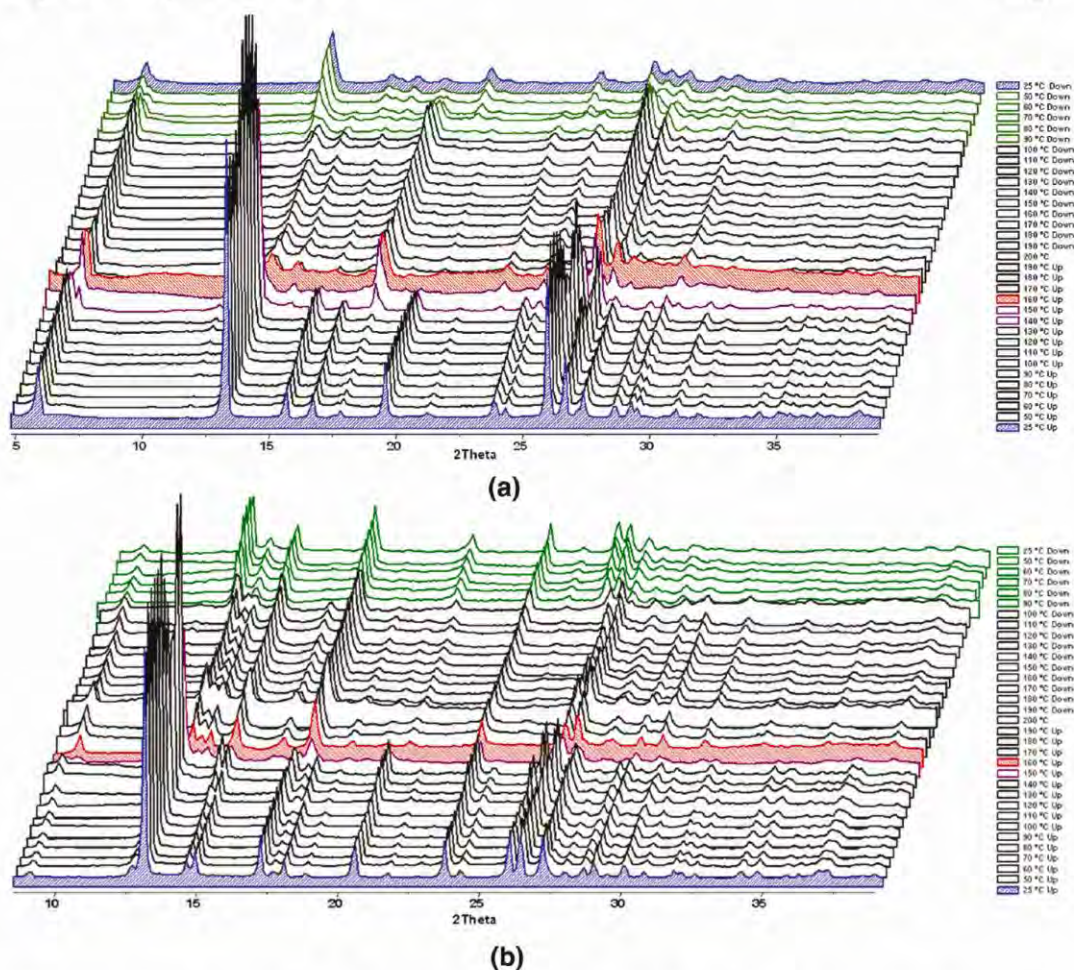


Figure 8. X-ray thermodiffractogram of **1** (a) and **2** (b) recorded in air heating up from 25 to 200 °C and cooling down to 25 °C. Color code corresponding to the structural changes, blue: compound **1** or **2**, purple: dehydration of compound **1** or **2**, red: dehydrated compound **1** or **2**, green: rehydration of compound **1** or **2** blue: rehydrated compound **1**.

the thermal resistance of the BDC^{2-} ligand up to 450 °C. And therefore, the second and third stages may be due to the oxidation of the Tart^{2-} ligand, while the fourth and fifth stages are shared between the oxidation of the Tart^{2-} and the BDC^{2-} ligands. Taking into account that the mass spectrometry analysis is a semiquantitative method, the integration of the first band (670 nA) is almost half of the integration of the second, third, and fourth ones (1553 nA) in the m/z 18 curve, indicating the loss of approximately four water molecules in the second, third, fourth, and fifth steps, corresponding to the amount of hydrogen atoms resulting from the decomposition of the both Tart^{2-} and BDC^{2-} ligands in the formula of **1**.

Similarly to **1**, the mass loss of compound **2** proceeds in six stages; the first stage between 125 and 240 °C with the total mass loss of 6.2% (calcd 6.71%) corresponds to the loss of the two coordinated water molecules to sodium atom. The second to the fifth stages are continuous and overlapping, in the range 260–600 °C, with the total mass loss of 59.6%, correspond to the decomposition of the mixed-ligands. The sixth stage, in the range 700–780 °C, is attributed to the liberation of some trapped organic part after the structure collapse.

The associated mass spectrometry m/z 18 and 44 curves are in a good agreement with those of TG/DTG, and they have four (at 230, 350, 510, and 548 °C) and five maxima (at 350, 416, 510, 548, and 753 °C), respectively. The integration of the first band (1943 nA) is almost a third of the integration of the second, third, and fourth ones (6125 nA) in the m/z 18 curve, proving the loss of approximately six water molecules in the second, third, fourth, and fifth stages, corresponding to the amount of hydrogen atoms resulting from the decomposition of the both Tart^{2-} and biBDC^{2-} ligands in the formula of **2**.

As it was suspected, the TG/DTG curves show that the compounds **1** and **2** have similar multistep decomposition profiles (both have the same dimensionality and related structures), with differences related with the thermal stability of the mixed-ligand system. In addition, the dehydration enthalpies (−70 kJ/mol and −59 kJ/mol for **1** and **2**, respectively) are comparable. After the dehydration, the anhydrous compounds of **1** and **2** are stable up to 250 °C, and their similarity is reflected by comparable oxidative decomposition enthalpies, 3545 and 3581 kJ/mol, respectively.

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The X-ray thermodiffraction analysis carried out under air heating up to 200 °C and cooling down to 25 °C (Figure 8) confirmed that compounds **1** and **2** show a phase transformation corresponding to the dehydration process by losing the two water molecules coordinated to sodium atom, which is a reversible process involving a spontaneous rehydration after cooling down to room temperature and which has been seen clearly in the thermodiffraction of compound **1** (blue curve at 25 °C down, Figure 8a); however, it is slowly reversible in the case of **2**.

In the case of **1**, no structural change occurs below 140 °C, and no significant change in the unit cell parameters has been observed. The beginning of the phase transformation to the anhydrous form without losing the crystallinity, is seen from 140 to 150 °C, the total transformation to the anhydrous form happens at 160 °C, and it is maintained until 200 °C (no significant changes in the unit cell parameters have been observed from 160 to 200 °C), which is consistent with the TG analysis even if the temperature profile of X-ray thermodiffraction analysis is different from that of TG. During the temperature decrease the anhydrous phase is preserved; the rehydration begins at 90 °C and continues until room temperature. The pattern of dehydrated compound **1** corresponds to the as-synthesized compound **1** with a noticeable diffraction intensity drop and peak broadening.

The behavior of **2** is similar to that of **1**, no phase transformation occurs below 150 °C, and no significant change in the unit cell parameters is observed; the phase transformation to the anhydrous form begins at 150 °C, and the total transformation takes place at 160 °C, and it is maintained until 200 °C, which is consistent with the TG analysis (no significant change in the unit cell parameters is observed from 160 to 200 °C). During the temperature decrease the anhydrous phase is preserved until 100 °C, the rehydration of **2** begins at 90 °C but, in contrast with **1**, it is not achieved at the end of the experiment, and takes a few days in air, indicating the slow reversibility of the process.

The bad quality of the patterns corresponding to dehydrated compounds, **1** and **2**, prevents any structural resolution of the dehydrated form of **1** or **2**. The powder XRD pattern of dehydrated compounds, **1** and **2**, treated at 160 °C in air, have been indexed in the orthorhombic system with the following unit cell parameters: $a = 6.7515(5) \text{ \AA}$, $b = 28.666(6) \text{ \AA}$, $c = 7.309(1) \text{ \AA}$, $V = 1414.5(4) \text{ \AA}^3$, in the case of **1**, and $a = 6.7195(3) \text{ \AA}$, $b = 37.886(4) \text{ \AA}$, $c = 7.5429(6) \text{ \AA}$, $V = 1920.2(3) \text{ \AA}^3$, in the case of **2**, by using the TREOR⁷³ ($M(20) = 13$, $F 20 = 18$) and DICVOL⁷⁴ ($M(20) = 21.7$, $F 20 = 38.4$) programs and refined using the FullProf software package.⁷⁵ The results reveal that the structure of **1** and **2** contract about 5.6% and 3%, respectively, along the b -axis, maintaining the orthorhombic symmetry, which is due to the loss of two water molecules coordinated to the sodium atoms. The a and c axis are almost unchanged in the case of **1** and **2**. The change in coordination environment of the sodium atom from octahedral to tetrahedral geometry is compensated by the contraction of the long axis (b -axis), owing to the fact that the

(73) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(74) Boulouf, A.; Louër, D. *J. Appl. Crystallogr.* **2004**, *37*, 724.

(75) Rodríguez-Carvajal, J. *Phys. B.* **1993**, *192*, 55.

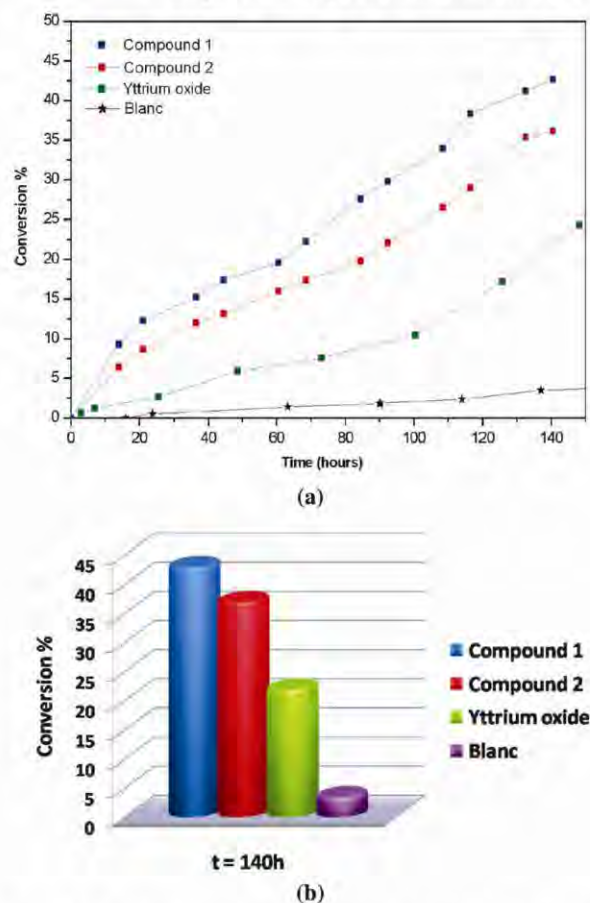


Figure 9. Catalytic activity of compounds **1** and **2** in acetalization of benzaldehyde, compared with that of yttrium oxide as a function of time (a), and at 140 h (b).

free carboxylate groups, O2–C6–O2 of BDC^{2-} or O2–C10–O2 of biBDC^{2-} ligands in **1** and **2**, respectively, are not coordinated, so that these carboxylate groups became closer to the sodium atom trying to keep an octahedral environment.

A test of catalytic activity has been performed to check the ability of compounds **1** and **2** to behave as acid Lewis catalysts, in acetalization of benzaldehyde (Figure 9), and their catalytic activity has been compared with that of yttrium oxide (Y_2O_3) which was tested under the same conditions. The results are quite modest, and both compounds show a similar catalytic behavior. However, these results may prove the positive effect of the framework to improve the catalytic activity of the yttrium center compared with the compact structure of the oxide.

Conclusions

The hydrothermal synthesis and the structural characterization of two novel chiral yttrium-based metal organic frameworks, the first examples of chiral MOFs containing mixed Y(III), Na(I), and chiral flexible-achiral rigid ligands, have been reported. Currently, our work is focused on obtaining members of $\text{Ln(III)-Na(I)-Tart}^{2-}\text{-BDC}^{2-}$ and $\text{Ln(III)-Na(I)-Tart}^{2-}\text{-biBDC}^{2-}$ (Ln = lanthanide element) families,

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as these may be promising materials in the fields of photoluminescence and heterogeneous catalysis.

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2006), FSE, and FEDER. The authors are also grateful to Prof. José Gimeno for helping us to carry out the catalysis studies.

Supporting Information Available: TG-DTG-SDTA-DSC-MS curves, and ^{13}C CPMAS NMR data of the compounds **1** and **2**. X-ray crystallographic information (CIF files) for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Metal Organic Frameworks Assembled from Y(III), Na(I) and Chiral Flexible-Achiral Rigid Dicarboxylates

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Electronic Supplementary Information

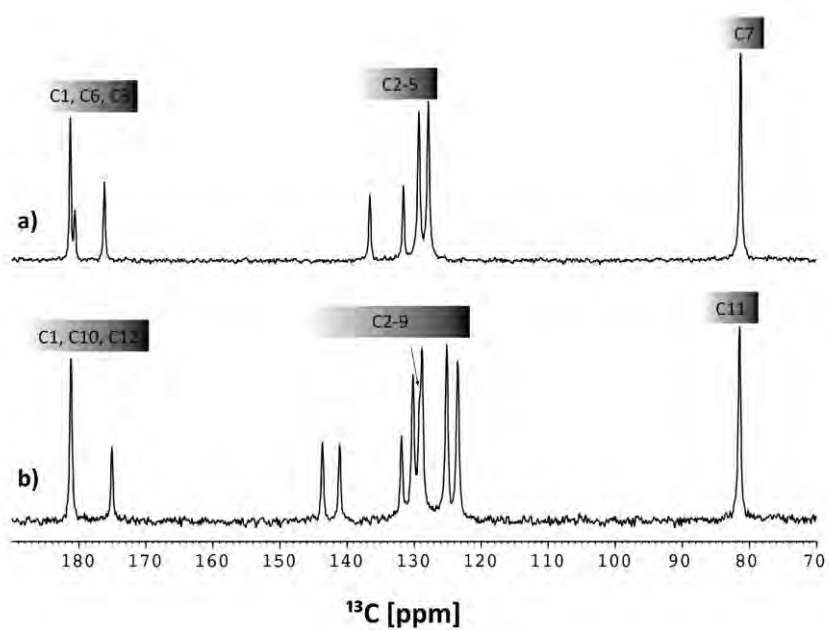


Figure S1. ^{13}C CPMAS NMR spectra of **1** (a) and **2** (b). Atom labels are located above the corresponding ^{13}C resonances. The arrow in (b) depicts a resonance which appears as a shoulder.

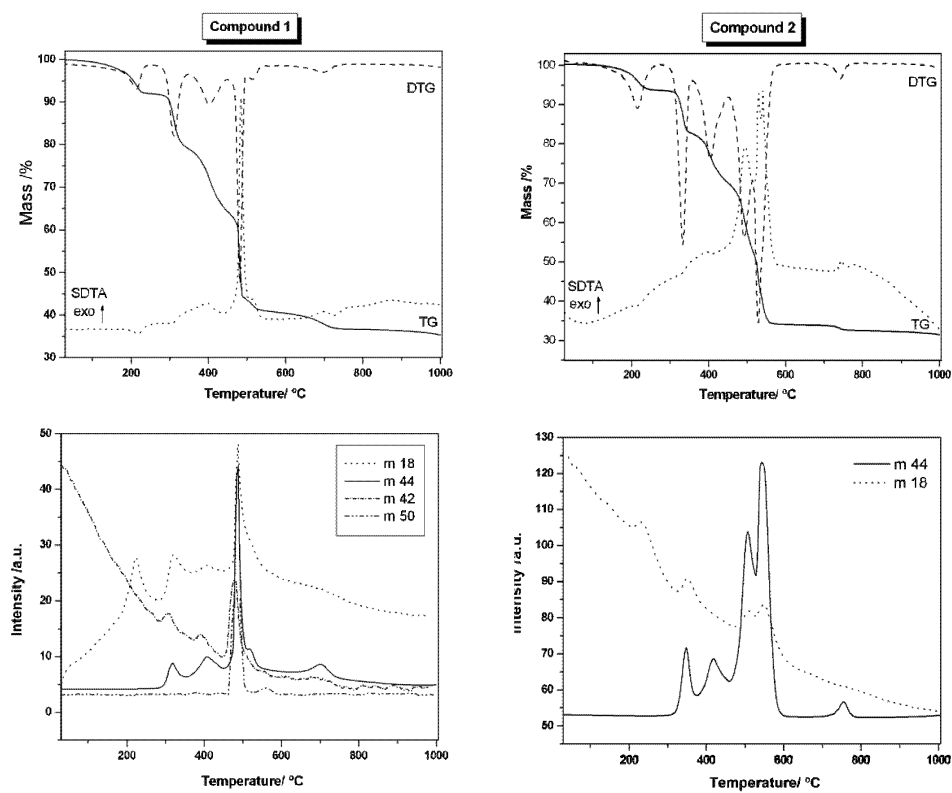


Figure S2. TG-DTG-SDTA curves, and m/z 18 (H_2O) and m/z 44 (CO_2) MS signals of evacuated vapours, of **1** and **2**.

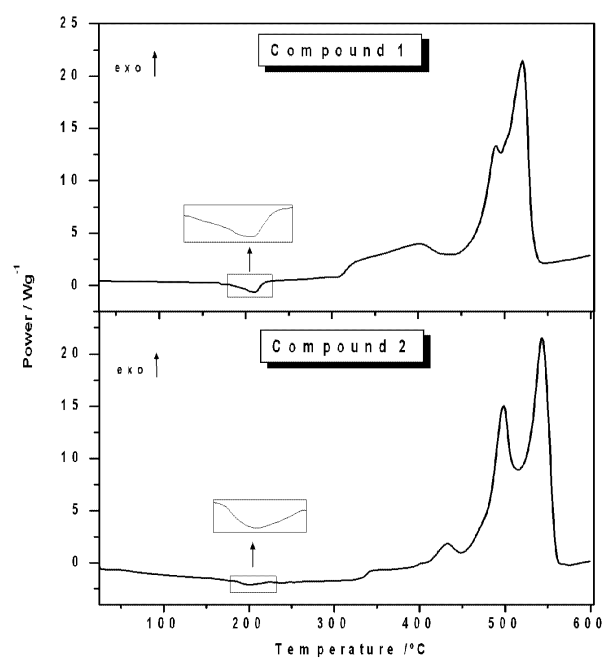


Figure S3. DSC curves of 1 and 2.

3.4. Modelización estructural de fases anhidras.

Artículo III

Artículo publicado en el año 2011 (*Vol. 1, pp. 361–366*) la revista *Zeitschrift für Kristallographie Proceedings*, con el título “Phase transformation on mixed yttrium/sodium-MOFs, X-ray thermogravimetry and structural modeling”

Resumen

El trabajo presentado en este artículo abordará la modelización estructural de las fases anhidras, $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)$ (**D1**) y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)$ (**D2**), de los compuestos **1** y **2** comentados en el capítulo anterior.

Los estudios de termodifracción de rayos X de polvo cristalino, realizados en atmósfera de aire calentando desde temperatura ambiente hasta 200 °C y enfriando posteriormente a 25 °C (Figura 3.4.1), desvelaron que **1** y **2** sufren una transformación de fase que acompaña al proceso de descomposición causado por la pérdida de las dos moléculas de agua coordinadas, siendo éste un proceso reversible que involucra una rápida rehidratación tras el enfriamiento a temperatura ambiente en el caso de **1**, que mucho más lenta en el caso de **2**, precisando varios días de exposición al aire para alcanzar su total reconversión.

Los termodifractogramas recogidos a 200 °C, que corresponden a los compuestos **D1** y **D2**, se han indexado en el sistema ortorrómbico con los siguientes parámetros de celda unidad: $a = 6.7515(5) \text{ \AA}$, $b = 28.666(6) \text{ \AA}$, $c = 7.309(1) \text{ \AA}$ ($V = 1414.5(4) \text{ \AA}^3$) para **1**, y $a = 6.7195(3) \text{ \AA}$, $b = 37.886(4) \text{ \AA}$, $c = 7.5429(6) \text{ \AA}$ ($V = 1920.2(3) \text{ \AA}^3$) para **2**, con figuras de mérito aceptables utilizando, respectivamente, los programas TREOR ($M(20) = 18$) y DICVOL ($M(20) = 21,7$). Los resultados desvelan que tanto la estructura de **1** como la de **2** se comprimen tras la deshidratación, respectivamente, un 5.6% y un 3.0% a lo largo del eje b , manteniendo la simetría ortorrómbica, con un descenso en el volumen de sus celdas unidad estimado en el 10% y el 5%, respectivamente.

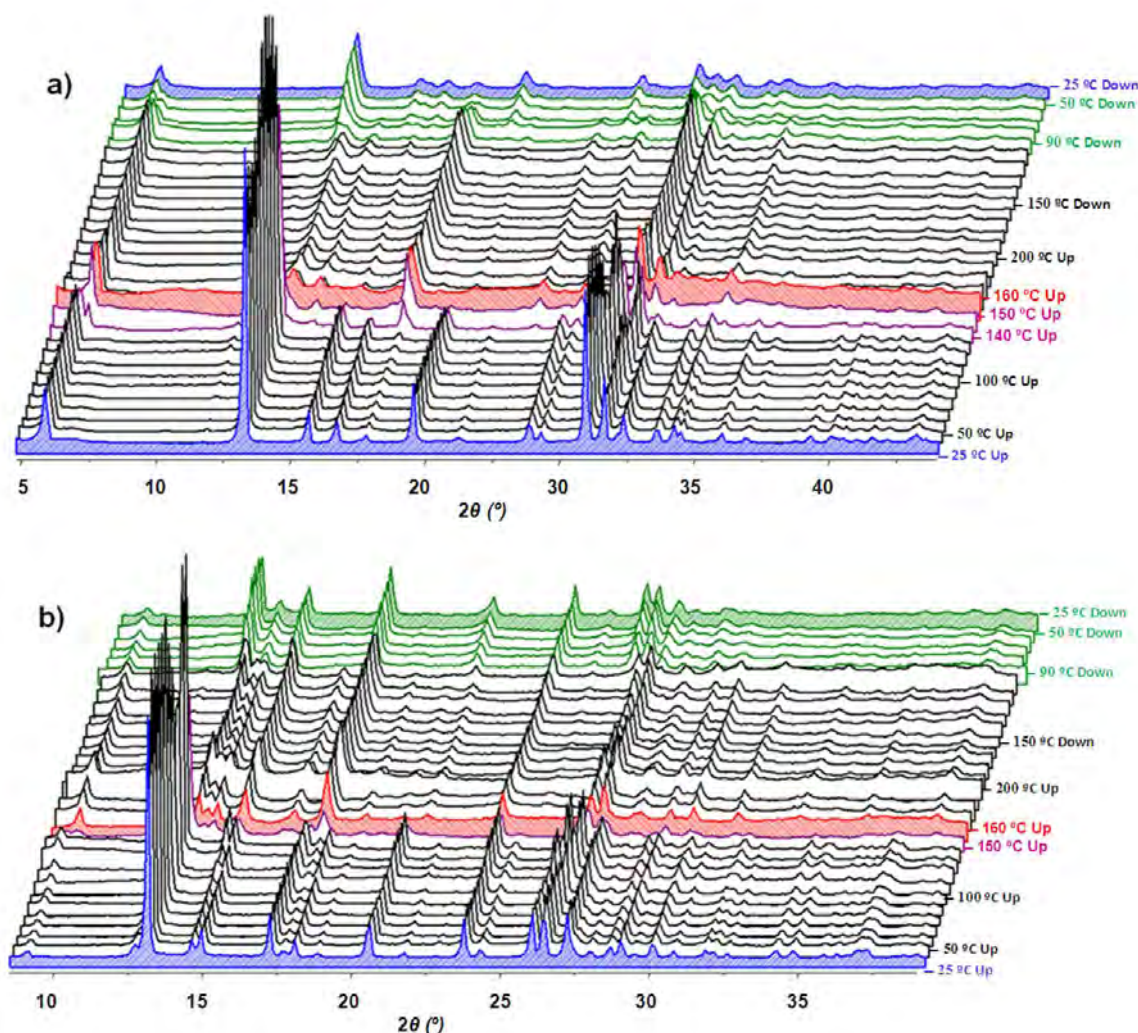


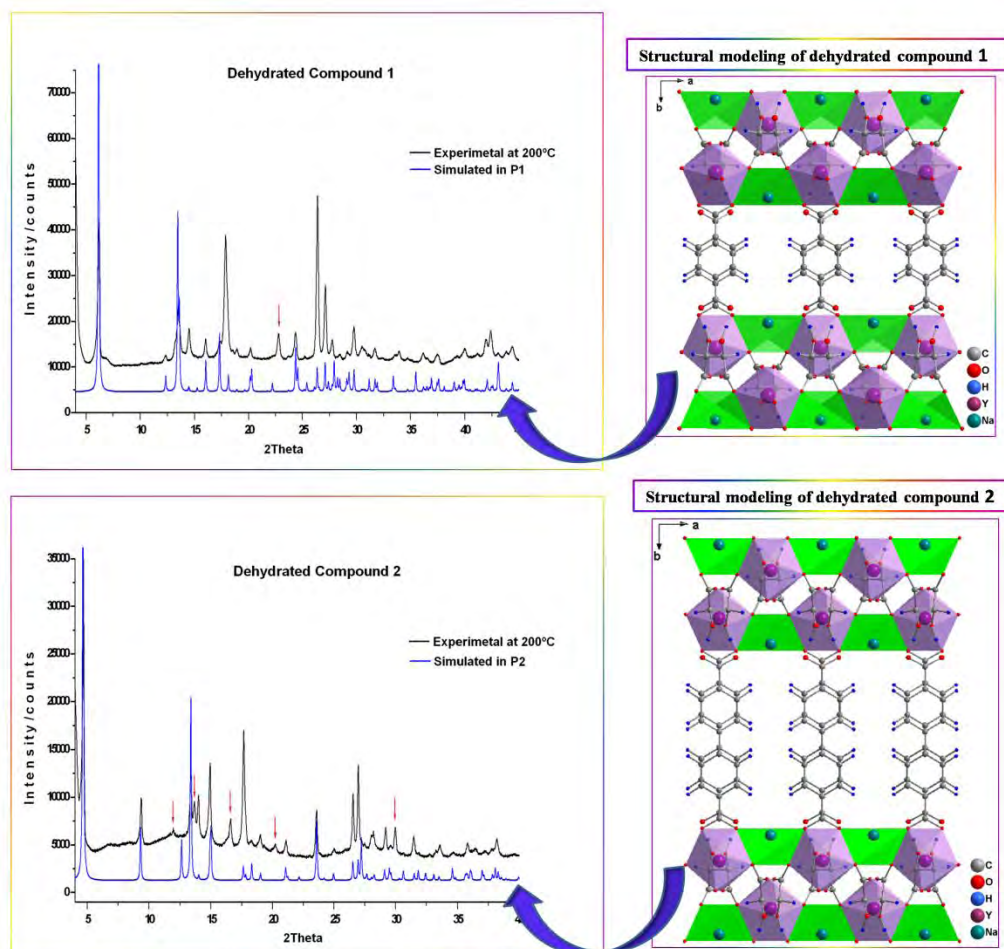
Figura 3.4.1. Termodifractogramas de rayos-X de **1** (a) y **2** (b) registrados al aire (calentamiento: 25→200 °C; enfriamiento: 200→25 °C). Código de colores: azul

(compuesto **1** ó **2**), púrpura (deshidratación de **1** ó **2**), rojo (compuesto **D1** ó **D2**), verde (rehidratación de **D1** ó **D2**).

Los intentos de elucidación estructural de las fases anhidras se han topado con un gran número de obstáculos, que se resumen a continuación. Debido a la baja calidad de los diagramas de polvo de **D1** y **D2**, no se ha logrado su determinación estructural por métodos *ab-initio*. Tampoco los intentos de refinamiento estructural por método de *Rietveld* han tenido éxito, incluso usando los parámetros de celdilla obtenidos del índice de los termodifractogramas a 200 °C y el uso de un modelo derivado de las estructuras de **1** y **2**, probablemente como consecuencia del cambio del grupo espacial centrosimétrico ($C222_1$) a uno primitivo. Por otra parte, estudios *in-situ* mediante la difracción de rayos X de monocristal a temperatura variable, tampoco proporcionaron un camino para determinar las estructuras de **D1** y **D2**, debido a que el monocristal se deteriora como consecuencia de la deshidratación. Así, finalmente, se recurrió a la modelización estructural, presentándose los modelos estructurales de las fases anhidras, **D1** y **D2**, obtenidos mediante cálculos teóricos utilizando el método DFT en su aproximación de densidad local (LDA), mediante el programa *DMOL3*, implementado en *Materials Studio* (como se describe en la sección 2.3 de este artículo). Los modelos obtenidos fueron refinados por el método de *Rietveld*. Los parámetros de celda y los índices de acuerdo del ajuste se recogen en la Tabla 3.4.1, mientras que el perfil observado (en negro), y calculado (en azul) del ajuste *Rietveld* final se muestran en la Figura 3.4.2.

Tabla 3.4.1. Datos cristalográficos y refinamiento estructural de las fases anhidras **D1** y **D2**.

	D1	D2
Fórmula	$NaY(C_4H_4O_6)(C_8H_4O_4)$	$NaY(C_4H_4O_6)(C_{14}H_8O_4)$
Sistema cristalino	Triclínico	Monoclínico
Grupo espacial	<i>P1</i>	<i>P2</i>
<i>a</i> (Å)	6.75(1)	7.58(1)
<i>b</i> (Å)	28.68(4)	6.718(9)
<i>c</i> (Å)	7.308(9)	37.91(5)
α (°)	89.7(1)	90
β (°)	89.7(1)	85.89(6)
γ (°)	89.8(2)	90
R_p	0.136	0.0947
R_{wp}	0.219	0.1479

Figura 3.4.2. Termogravimogramas (a la izquierda) de **D1** y **D2** obtenidos a 200 °C (en negro) comparados con los calculados (en azul) a partir de los modelos estructurales (a la derecha).

Las diferencias en las intensidades de los picos de difracción entre los diagramas experimentales recogidos a 200 °C y los calculados a partir de los modelos estructurales obtenidos para **D1** y **D2**, y la casi anulación de la intensidad (no la posición) de algunos picos de difracción en los diagramas calculados (indicados por flechas de color rojo en Figura 3.4.2) se puede explicar asumiendo que no se ha incluido en el cálculo un factor importante como es el desorden de los anillos fenilo y los grupos carboxílicos no coordinados (este efecto es especialmente intenso en el caso de **D2**). Asumiendo que el desorden estructural es muy difícil de modelar, los modelos estructurales obtenidos pueden calificarse como satisfactorios.

Artículo III

Phase transformation on mixed yttrium/sodium-MOFs, X-ray thermodiffractometry and structural modeling

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Keywords: MOFs, X-ray thermodiffractometry, phase transformation, structural modeling

Abstract. New chiral MOFs, assembled from Y(III), Na(I) and chiral flexible-achiral rigid dicarboxylate ligands, have been obtained as single phase under hydrothermal conditions and their structures were solved by single-crystal XRD. The powder X-ray thermodiffractometry study was performed, and reveals that the dehydration of both compounds is accompanied by phase transformation, while the spontaneous rehydration process is characterized by different kinetics. The crystal structures of anhydrous compounds have been modeled.

1. Introduction

Metal-organic frameworks (MOFs), also known as coordination polymers, continue receiving a great attention, since they are a very attractive class of materials due to, the great deal of extended structures and to their potential applications in several fields such as gas storage [1,2], catalysis [3], magnetism [4,5], luminescence [6,7], and so on. In the last decade, large variety of bi- or multi-functional organic linkers and transition or rare earth metals units have been applied as building blocks, leading to numerous 2D and 3D structures. Nevertheless, to the best of our knowledge, only some of them exhibit interesting features, such as reversible phase transition [8-10].

Previously [11] we have reported the hydrothermal synthesis and the full structural characterization of two novel chiral yttrium-based metal organic frameworks, both exhibited phase transformation corresponding to the dehydration process. In continuation of this work, and in the aim to determine the structures of the dehydrated forms, powder X-ray thermodiffraction data and the structural modelling have been performed.

2. Experimental

2.1 Synthesis

Compounds **1** and **2**, formulated as $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ and $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$, respectively, were synthesized under hydrothermal conditions, and obtained as a single phase of colorless needle crystals, as described in the ref. 11.

2.2 Powder X-ray thermodiffraction studies

Powder X-ray thermodiffraction studies were performed in air. The sample was placed in an Anton Paar HTK 1200N oven-chamber, on a PANalytical XPERT-PRO diffractometer, using Cu K α radiation, equipped with PIXcel linear detector with 255 channels. Each powder pattern was recorded in the 4–110° range (2θ) at intervals of 25 °C up to 200 °C and cooling down to 25 °C with a step of 0.013° and a counting time of 0.424 s/channel. The temperature ramp between two consecutive temperatures was 10 °C/min.

2.3 Structural modeling

The structures of **1** and **2** were used as initial models. After (i) removing the two water molecules (coordinated to sodium atoms), and (ii) using the following initial unit cell parameters, $a = 6.7515(5)$ Å, $b = 28.666(6)$ Å, $c = 7.309(1)$ Å, and $a = 6.7195(3)$ Å, $b = 37.886(4)$ Å, $c = 7.5429(6)$ Å, obtained from the indexation of powder XRD patterns at 200 °C corresponding, respectively, to dehydrated forms of **1** (**D1**) and **2** (**D2**), and (iii) keeping the fractional coordinates fixed during the lattice changes. The full geometry optimizations of the resulting structures, in the space group $P1$, were performed in *DMOL3* module implemented in *Materials Studio* [12], by using the local density functional (LDA) of Vosko-Wilk-Nusair (VWN) [13] with a double numerical basis set with polarization functions (DNP) and a “medium” K-point set. During the optimization, the unit cell parameters were kept fixed. The structures were considered to be converged when the change in energy between two iterations was smaller than 1.10^{-5} hartree and gradient and displacement were, respectively, less than 2.10^{-3} hartree a_0^{-1} and 5.10^{-3} a_0 . Between 23 and 66 iterations were required to reach convergence. The symmetry test was performed of the models obtained in $P1$ for **D1** and **D2**, and it was found to be higher, $P2$, in case of **D2**. Rietveld refinement of the obtained models was carried out with *Reflex*, a powder diffraction module implemented in *Materials Studio*. The PXRD profiles have been modeled as a pseudo-Voigt function in the range $2\theta = 4\text{--}45^\circ$. The parameters refined were: the zero offset, the scale factor, 20 background terms, the U, V and W profile parameters, the unit cell parameters, Finger-Cox-Jephcoat asymmetry correction for peaks below $2\theta = 20^\circ$, global isotropic temperature factor, and the preferred orientation using March-Dollase function in the directions [010] (for **D1**) and [001] (for **D2**). The unit cell parameters and the final values of figures of merit are listed in Table 1.

3. Results and discussion

Compounds **1** and **2** crystallize in the orthorhombic chiral space group $C222_1$ with unit cell parameters $a = 6.8854(2)$ Å, $b = 30.3859(7)$ Å, $c = 7.4741(2)$ Å for **1**, and $a = 6.8531(2)$ Å, $b = 39.0426(8)$ Å, $c = 7.4976(2)$ Å for **2**. The X-ray thermodiffraction analysis indicates that **1** and **2** show a phase transformation corresponding to the dehydration process (Figure 1), by losing the two water molecules coordinated to sodium atom, which is a re-

versible process involving a spontaneous rehydration after cooling down to room temperature, which has been seen clearly in the thermodiffractogram of **1** (blue curve at 25 °C down, Figure 1a), however, it is slowly reversible in the case of **2**, and takes few days in air after the end of the experiment.

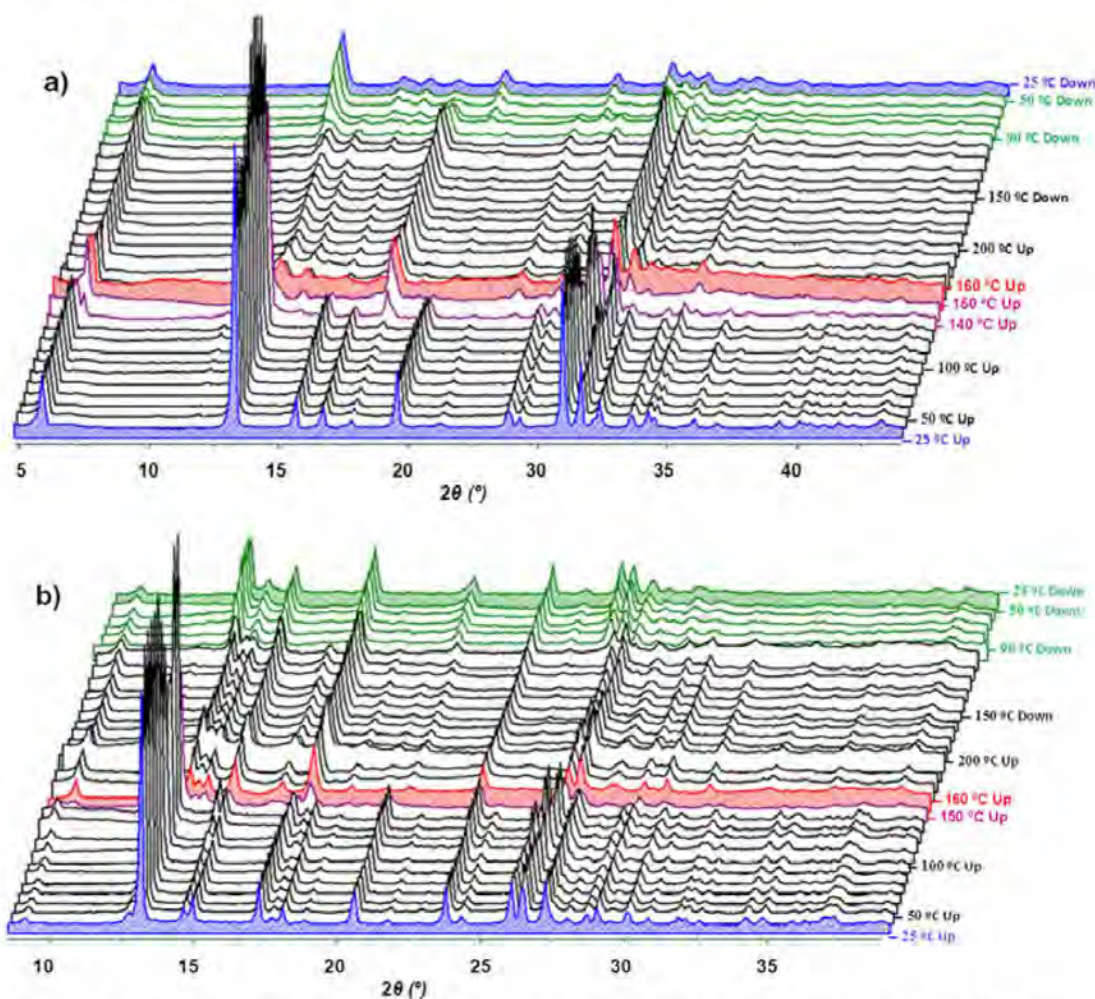


Figure 1. X-ray thermodiffractograms of **1** (a) and **2** (b) recorded in air heating up from 25 °C to 200 °C and cooling down to 25 °C. Colour code corresponding to the structural changes, blue: compound **1** or **2**, purple: dehydration of compound **1** or **2**, red: dehydrated compound **1** or **2**, green: rehydration of compound **1** or **2**, blue: rehydrated compound **1**.

Since the dehydration of **1** and **2** begins respectively at 140 °C and 150 °C, the variation of the unit cell parameters of **1** and **2** from 50 °C to 130 °C (for **1**), and from 50 °C to 140 °C (for **2**), obtained by Rietveld refinement using the structural models of **1** and **2** (hydrated), are illustrated in Figure 2 (a) and (b), respectively. A slight contraction of the cell volume of *ca.* 1% has been observed from room temperature to 130 °C. The powder XRD pattern of dehydrated compounds, **1** and **2**, treated at 200 °C in air, have been indexed in the orthorhombic system with these unit cell parameters: $a = 6.7515(5) \text{ \AA}$, $b = 28.666(6) \text{ \AA}$, $c = 7.309(1) \text{ \AA}$, $V = 1414.5(4) \text{ \AA}^3$, in the case of **1**, and $a = 6.7195(3) \text{ \AA}$, $b = 37.886(4) \text{ \AA}$, $c =$

7.5429(6) Å, $V = 1920.2(3)$ Å³, in the case of **2**, by using respectively, TREOR ($M(20) = 18$) and DICVOL ($M(20) = 21.7$). The results reveal that the structure of **1** and **2** contract of *ca.* 5.6 % and 3 % along the *b*-axis, and the cell volume of *ca.* 10% and 5%, respectively, maintaining the orthorhombic crystal system.

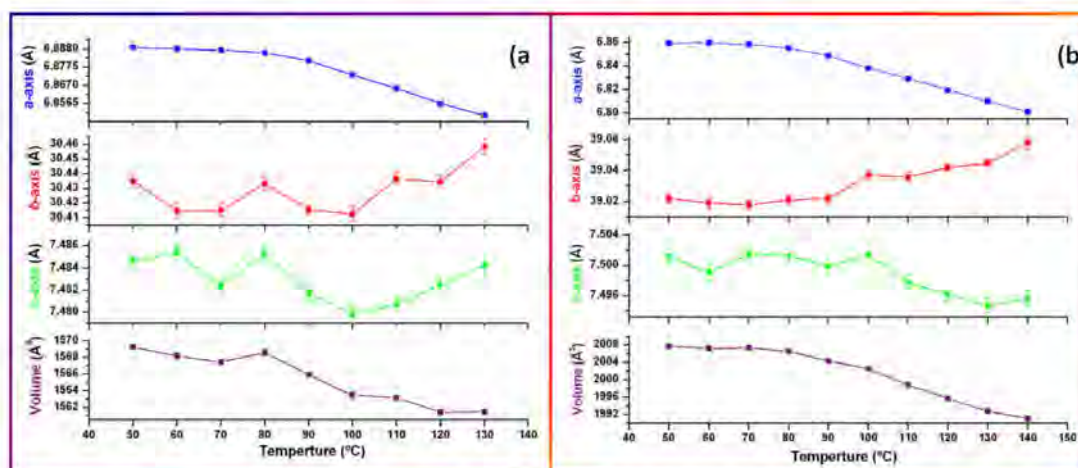


Figure 2. The variation of the unit cell parameters of compound **1** (a) and **2** (b), from 50 °C to 140 °C.

The attempts for Rietveld refinement of **D1** and **D2** (after removing water molecules from the initial structural models of **1** and **2** and using the corresponding unit cell parameters found previously for **D1** and **D2**) have been failed, we suspect that the space group have been changed from the centrosymmetric $C222_1$ to a primitive. Also, *ab-initio* structural resolution was not reached due to the low quality of powder patterns. Moreover, *in-situ* variable temperature single-crystal XRD studies were not able to determine the structures of the dehydrated forms, due to the single-crystal deterioration. Thus finally, we resorted to structural modeling. Herein, we have presented the **D1** and **D2** models obtained by LDA as described in the Section 2.3. The Rietveld refinements of the obtained models have been performed. Cell parameters and refinement indexes of agreement are represented in Table 1. The observed (black) and calculated (blue) profiles for the final Rietveld refinement are showed in the Figure 3. The relative differences of peak intensities between the experimental patterns at 200 °C and the simulated from the models, and disappearance of some peaks in the models, but not the Bragg-peak positions (Figure 3, red arrows), reflected by the high values of refinement indexes of agreement, may be explained by the fact that an important factor not taken into consideration (not included during the calculation of the models), the temperature factor, supposing that may lead to disorder of the phenyl rings and uncoordinated carboxylate groups (specially in case of dehydrated compound **2**, which exhibits the large difference between the experimental and simulated patterns). Given the fact that the disorder is difficult to model, to summarize, the models obtained at this stage are considered quite satisfactory.

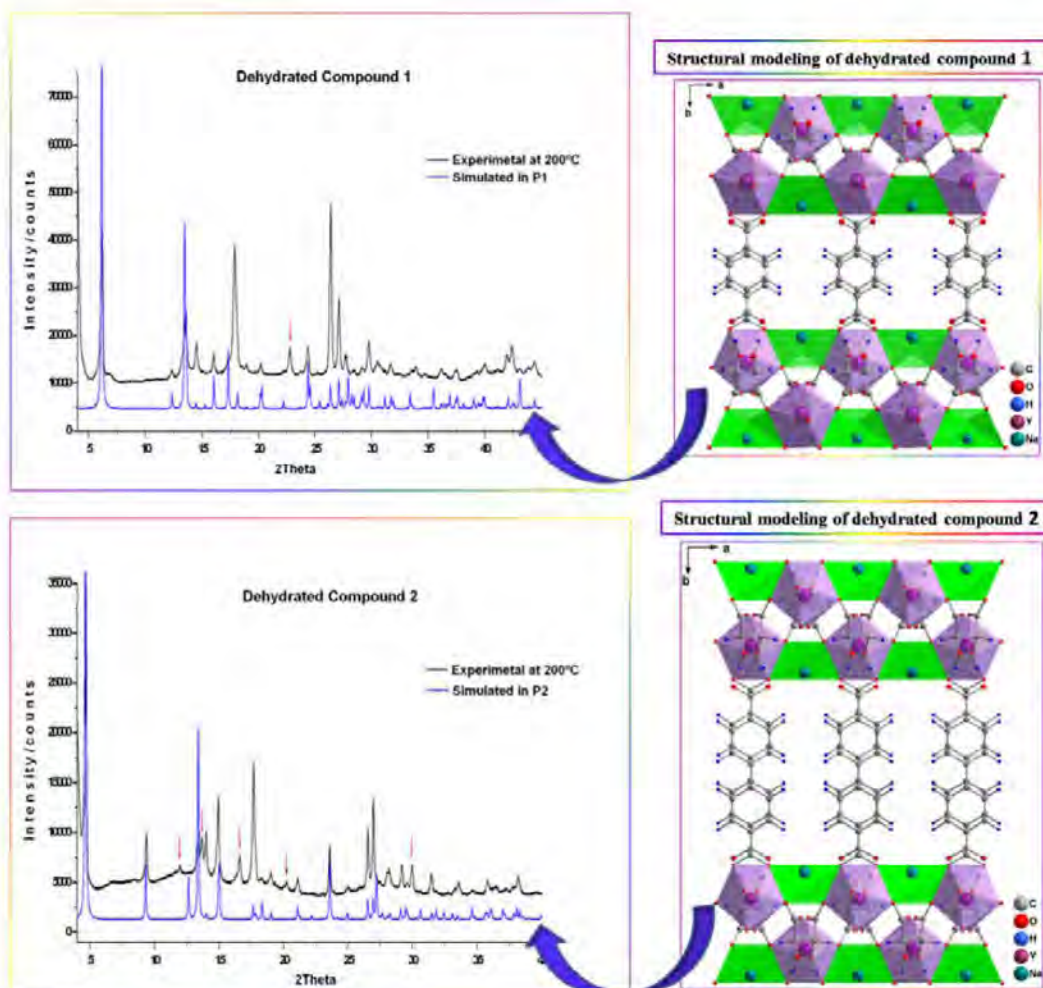


Figure 3. PXRD patterns of dehydrated compounds 1 and 2 at 200 °C compared with the simulated from the structural modelling.

Table 1. Crystal data and structure refinements for 1 and 2 dehydrated compounds.

	Dehydrated 1	Dehydrated 2
Formula	$\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)$	$\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)$
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1	<i>P</i> 2
<i>a</i> (Å)	6.75(1)	7.58(1)
<i>b</i> (Å)	28.68(4)	6.718(9)
<i>c</i> (Å)	7.308(9)	37.91(5)
α (°)	89.7(1)	90
β (°)	89.7(1)	85.89(6)
γ (°)	89.8(2)	90
<i>R</i>_p	0.136	0.0947
<i>R</i>_{wp}	0.219	0.1479

4. Conclusions

The phase transformation, corresponding to the dehydration process of compounds **1** and **2**, has been confirmed by X-ray thermodiffraction analysis. The low quality of the patterns corresponding to dehydrated compounds prevents *ab-initio* structural resolution of the dehydrated forms of **1** and **2**. *In-situ* variable temperature single-crystal XRD studies, were not able to determine the structures of the dehydrated forms, due to the single-crystal deterioration. The structural modeling of the dehydrated form of **1** or **2** has been performed using LDA approach, and the best models obtained so far have been presented.

References

1. Kaye, S.S., Dailly, A., Yaghi, O.M. & Long, J.R., 2007, *J. Am. Chem. Soc.*, **129**, 14176.
2. Collins, D.J. & Zhou., H.C., 2007, *J. Mater. Chem.*, **17**, 3154.
3. Corma, A., Gracia, H. & Llabrés i Xamena, F.X., 2010, *Chem. Rev.*, **110**, 4606.
4. Wang, Z., Hu, K., Gao, S. & Kobayashi, H., 2010, *Adv. Mater.*, **22**, 1526.
5. Rogez, G., Viart, N. & Drillon, M., 2010, *Angew. Chem. Int. Ed.*, **49**, 1921.
6. Liu, K., You, H., Zheng, Y., Jia, G., Song, Y., Huang, Y., Yang, M., Jia, J., Guo, N. & Zhang, H., 2010, *J. Mater. Chem.*, **20**, 3272.
7. Wang, M.S., Guo, S.P., Li, Y., Cai, L.Z., Zou, J.P., Xu, G., Zhou, W.W., Zheng, F.K. & Guo, G.C., 2009, *J. Am. Chem. Soc.*, **131**, 13572.
8. Gustafsson, M., Bartoszewicz, A., Martín-Matute, B., Sun, J., Grins, J., Zhao, T., Li, Z., Zhu, G. & Zou, X., *Chem. Mater.*, **22**, 3316.
9. Shi, F.N., Cunha-Silva, L., Sa Ferreira, R.A., Mafra, L., Trindade, T., Carlos, L.D., Almeida Paz, F.A. & Rocha, J., 2008, *J. Am. Chem. Soc.*, **130**, 150.
10. Wu, C.D. & Lin, W., 2005, *Angew. Chem. Int. Ed.*, **44**, 1958.
11. Amghouz, Z., Roces, L., García-Granda, S., García, J.R., Souhail, B., Mafra, L., Fanian, S. & Rocha, J., 2010, *Inorg. Chem.*, **49**, 7917.
12. <http://accelrys.com/products/materials-studio/>.
13. Vosko, S.H., Wilk, L. & Nusair, M., 1980, *Can. J. Phys.*, **58**, 1200.

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3.5. Polímeros de coordinación basados en lantánidos y ligandos dicarboxílicos.

Artículo IV

Artículo en trámite de aceptación en la revista *Inorganic Chemistry*, con el título “Series of Metal Organic Frameworks Assembled from Ln(III), Na(I), and Chiral Flexible-Achiral Rigid Dicarboxylates Exhibiting Tunable UV-VIS-IR Light Emission”

Resumen

En este trabajo se describe la síntesis y caracterización de polímeros de coordinación basados en lantánidos, sodio, y ligandos mixtos de tipo dicarboxílico, así como el estudio de sus propiedades luminiscentes.

La síntesis de dos nuevas series de compuestos conteniendo un metal lantánido, sodio, y ligandos dicarboxílicos mixtos quirales-flexibles y aquirales-rígidos, $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ y $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) propició la determinación de la estructura cristalina de cada miembro individual, utilizando para ello datos de difracción de rayos-X de monocristal, soportados por otras técnicas instrumentales: análisis elemental, microanálisis acoplado a microscopía electrónica de barrido (SEM/EDX), análisis térmico (TG-MS/SDTA y DSC), espectroscopia vibracional (FTIR), difracción de rayos X de polvo cristalino y

termodifracción de rayos X, culminando con la descripción de su actividad catalítica y sus propiedades fotoluminiscentes.

Los iones lantánidos atraen un gran interés científico, debido a las propiedades luminiscentes que derivan de las transiciones internas $4f$, útiles en una gran variedad de aplicaciones fotónicas, destacando su uso como amplificadores ópticos en sistemas para telecomunicación, diodos emisores de luz (LED), láseres o láseres sintonizables, y como marcadores fluorescentes en inmuno-ensayos. Los iones lantánidos trivalentes que emiten luz visible, como el europio y terbio, son útiles en dispositivos de iluminación fluorescente y pantallas a color, mientras que los emisores en la región del infrarrojo cercano son ideales para la obtención de imágenes biológicas, diagnóstico médico y aplicaciones en el campo de la telecomunicación. El erbio(III) se utiliza actualmente como componente activo en amplificadores de fibra óptica (EDFA) de uso habitual en dispositivos de telecomunicación, mientras los sistemas emisores de luz ultravioleta (UVLEDs) son fuertes candidatos para ser usados en equipos de iluminación y almacenamiento óptico. Por lo tanto, aquellos materiales luminiscentes que puedan generar emisiones luminosas sintonizables en el rango UV-VIS-IR son un objetivo enormemente atractivo en el ámbito tanto de la investigación fundamental como de sus aplicaciones prácticas.

En particular, los MOFs (o polímeros de coordinación) basados en lantánidos trivalentes (LnMOFs) pueden constituir la base de una plataforma sólida para hacer frente a los retos de la ingeniería de materiales luminiscentes multipropósito. Dado que los MOFs se desarrollaron inicialmente alrededor de sus posibles aplicaciones en el almacenamiento y separación de gases, los estudios sobre sus propiedades fotoluminiscentes se encuentran aún en un periodo de desarrollo incipiente, siendo inexistente un enfoque integrado para el diseño de LnMOFs eficientes, estables, baratos, respetuosos con el medio ambiente, y multi-luminiscentes. Así, los estudios sobre las propiedades luminiscentes de LnMOFs se han centrado en sus características como emisores en el visible, limitándose en su mayoría a estructuras que contienen europio(III) y/o terbio(III), en un estrecho rango espectral (rojo-verde). Además, la disposición relativa de los niveles de energía electrónica permite su uso como sonda sensible al entorno local, lo que unido a su posible sensibilización a través de los ligandos (efecto antena), convierte a sus compuestos en un objeto atractivo de investigación. Sin embargo, aquellos que emiten en la región del infrarrojo cercano (NIR) han sido muy escasamente estudiados como consecuencia de que las propiedades

de absorción vibracional de las matrices orgánicas congelan los estados excitados de los elementos lantánidos. No obstante, aparentemente, es posible superar estas limitaciones mediante un enfoque racional de su diseño estructural, habiéndose descrito unos pocos casos LnMOFs que emiten en NIR, basados en cationes lantánidos trivalentes poco comunes (erbio, neodimio, iterbio).

Recientemente, la cantidad de esfuerzos dedicados al campo de la fotoluminiscencia de MOFs están aumentando, habiéndose descubierto algunos nuevos e interesantes fenómenos, entre los que cabe citar la emisión sintonizable de luz UV-VIS mediante el control de las moléculas huésped, la emisión sintonizable de color amarillo-blanco o blanco-azul púrpureo variando la longitud de onda de la excitación, la emisión sintonizable VIS-IR cambiando la concentración del elemento dopante, o la detección de iones y moléculas pequeñas. Sin embargo, parece que aún no se ha descrito ningún ejemplo de emisión sintonizable de luz UV-VIS-NIR de LnMOFs quirales por sustitución del elemento dopante.

Se han obtenido hidrotermalmente dos series de polímeros de coordinación que, basados en un elemento lantánido, sodio, y ligandos mixtos dicarboxílicos rígido-flexible (ácido tartárico - ácido tereftálico / ácido bifenil-4,4'-dicarboxílico), se han preparado por vías sintéticas análogas, obteniéndose productos relacionados, de fórmulas $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ (**S1**) y $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ (**S2**) (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb).

El análisis estructural mediante de difracción de rayos X de monocristal desvela que todos los compuestos de cada serie (**S1** y **S2**) son isoestructurales, cristalizando en el grupo espacial ortorrómbico $C222_1$. Los parámetros de celda, así como las distancias Ln-Na, varían en una función de los radios iónicos efectivos de los cationes lantánidos, disminuyendo linealmente a medida que desciende el tamaño de los cationes lantánidos al avanzar en el período.

Las curvas TG muestran que, como es esperable de sistemas con composición química semejante y estructuras relacionadas de idéntica dimensionalidad, todos los compuestos de las series **S1** y **S2** presentan perfiles de descomposición térmica muy similar. La monitorización, mediante espectrometría de masas, de los gases evacuados en la descomposición térmica, unido a la semejanza en la variación de entalpía de deshidratación y descomposición oxidativa en ambas serie de compuestos, **S1** y **S2**, corroboran esta interpretación.

La termodifracción de rayos X de polvocrystalino desveló que la deshidratación térmica de **S1** y **S2** es un fenómeno reversible en la atmósfera del laboratorio, con una cinética de rehidratación mucho más rápida en el caso de **S1** que en el de **S2**.

Se ha evaluado la actividad de los compuestos basados en erbio e iterbio de la serie **S1** como catalizadores ácidos de Lewis en la acetalización del benzaldehído, comparando los resultados obtenidos con los descritos en el capítulo III para el compuesto **1**, basado en itrio, en las mismas condiciones. La actividad catalítica está favorecida cuando la estructura contiene Yb ó Er como centros catalíticos, probablemente como consecuencia del aumento del carácter ácido al disminuir el radio iónico del catión lantánido.

Finalmente, se han estudiado las propiedades fotoluminiscentes de algunos compuestos seleccionados, empleado varias técnicas espectroscópicas (excitación, emisión y tiempo de vida), siendo destacable que estos materiales presentan emisión sintonizable de luz UV-VIS-IR mediante una efectiva sensibilización de los cationes lantánidos trivalentes a través de los ligandos aromáticos BDC²⁻ y biBDC²⁻.

Artículo IV

Submitted to *Inorganic Chemistry*

**Series of Metal Organic Frameworks Assembled from
Ln(III), Na(I), and Chiral Flexible-Achiral Rigid
Dicarboxylates Exhibiting Tunable UV-VIS-IR Light Emission**

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Series of Metal Organic Frameworks Assembled from Ln(III), Na(I), and Chiral Flexible-Achiral Rigid Dicarboxylates Exhibiting Tunable UV-VIS-IR Light Emission

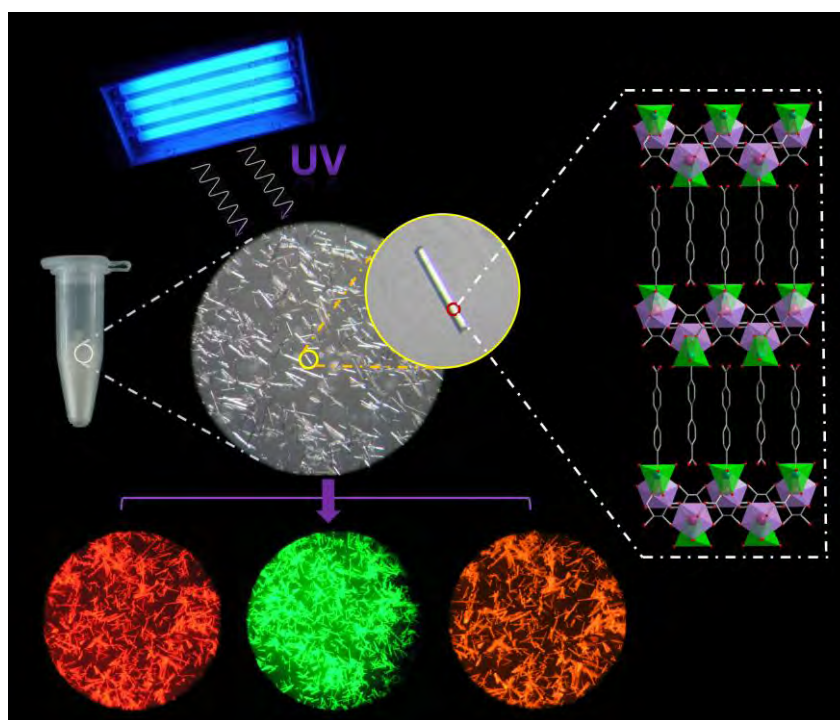
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Abstract

Two series of isorecticular chiral metal-organic frameworks assembled from Ln(III) (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), Na(I), and chiral flexible-achiral rigid dicarboxylate ligands, formulated as [NaLn(Tart)(BDC)(H₂O)₂] (**S1**) and [NaLn(Tart)(biBDC)(H₂O)₂] (**S2**) (H₂Tart = Tartaric acid; H₂BDC = Terephthalic acid; H₂biBDC = Biphenyl-4,4'-dicarboxylic acid), were obtained as single phases under hydrothermal conditions. The compounds have been studied by single-crystal and powder X-ray diffraction, thermal analyses (TG-MS and DSC), vibrational spectroscopy (FTIR), scanning electron microscopy (SEM-EDX), elemental analysis, and X-ray thermodiffraction. The activity catalytic has been also investigated. The photoluminescence properties of selected compounds have been investigated, exhibiting room temperature tunable UV-VIS-IR light emission.

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16 isorecticular chiral lanthanide-organic frameworks materials based on Ln(III), Na(I) and chiral flexible-achiral rigid dicarboxylates ligands, have been synthesized and characterized, undergo spontaneous rehydration upon dehydration process, and exhibiting multi-wavelength emission at room temperature through an effective Ln(III) sensitization via aromatic ligands.

Introduction

Lanthanide ions attract a great deal of interest, because their luminescence properties are useful in a variety of photonic applications, the most prominent are optical amplification for telecommunication,¹ light emitting diodes,² lasers or tunable lasers,³ low-energy scintillators,⁴ and fluoro-immuno assays.⁵ The luminescence of the lanthanide ions stems from intra 4f-transitions, which are in principal forbidden transitions resulting in relatively long-lived excited states, and hence makes them suited for laser applications. The luminescence of lanthanide(III) ions emitting in visible, such as europium and terbium are useful for fluorescent lighting and color displays.⁶ Those emitting in the near-infrared region are ideally suited for biological imaging and telecommunication applications.⁷ Er(III) is actually used as the active component in optical amplification in Erbium Doped Fiber Amplifiers (EDFAs)¹ in telecommunication devices. Ultraviolet light-emitting devices (UVLEDs) are strong candidates in lighting equipment and optical storage devices.⁸ Therefore, luminescent materials which can give tunable emissions between UV-Visible-Infrared wavelengths are attractive targets for both fundamental research and practical applications.

Particular class of materials known as Metal–Organic Frameworks (or coordination polymers) based on trivalent lanthanides (LnMOFs), composed of metal ions or metal clusters as nodes and multifunctional organic linkers as molecular building blocks through strong bonds, are a very promising class of materials and may constitute a robust platform for addressing the challenges in engineering of luminescent centers for multi-purposes. MOFs have emerged as a new class of materials, basically due to their potential applications in gas storage⁹⁻¹⁷ and separation.¹⁸⁻²¹

Studies on the photoluminescence of MOFs are still in their infancy,^{22,23} and missing for an integrated approach towards the design of efficient, stable, cheap, environmentally-friendly and multi-luminescent LnMOFs.²³ The research on luminescent LnMOFs has been focused on their visible emission features, As remarked in the majority of reported LnMOFs, the studies of luminescence properties are limited to structures containing Eu(III) and/or Tb(III),²⁴⁻⁴⁰ owing to their efficient and spectrally

narrow red and green emissions and their energy level scheme that allows their use as a sensitive local probe of the metal neighbourhood, in addition to their sensitization via ligand levels (the well-known antenna effect), which makes their compounds an attractive target. However, emissive Near-Infrared (NIR) LnMOFs have been barely investigated mainly because in organic matrices molecular vibrations like C-H and O-H stretching modes quench the lanthanide excited states. Nevertheless, it is possible to overcome such limitations through rational structural design. A few instances so far of NIR emitting LnMOFs from less common lanthanides, such as Er(III), Nd(III), and Yb(III) have been reported.⁴¹⁻⁴⁸

Recently, the amount of efforts devoted to the field of photoluminescence of MOFs are increasing, and some novel interesting phenomena have been discovered, such as tunable UV-to-visible emission by controlling the guest molecules,⁴⁹ tunable yellow-to-white emission or white-to-purplish blue by variation of excitation wavelength,⁵⁰ color tunable by changing the doping concentration,²⁵ tunable visible-IR changing the doping element,⁵¹ tunable emissions by controlling the type of guest species,⁵² and ion and small molecules sensing.^{53,54} However, to the best of our knowledge, no tunable UV-VIS-NIR luminescent chiral LnMOFs have been reported so far.

Herein, we report the synthesis and structural characterization of two new families (**S1** and **S2**) which consists of 16 isorecticular trivalent lanthanide-organic frameworks containing Ln(III), Na(I), and both flexible and rigid dicarboxylate ligands, motivated by our previous report,⁵⁵ as a tunable platform for the design of stable, cheap, and efficient multi-wavelength emission materials with intriguing architectures.

Experimental Section

Synthesis. $\text{LnNa}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ (**Series 1**) and $\text{LnNa}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ (**Series 2**) were synthesized under hydrothermal conditions and obtained as a single phase of colorless needle crystals by following similar procedures.

Series 1 (S1): In a typical synthesis, 0.21 g (1.4 mmol) of L-tartaric acid (**H₂Tart**), 0.08 g (0.5 mmol) of terephthalic acid (**H₂BDC**), 0.14 g (3.5 mmol) of NaOH, and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (Sm: 0.30 g, 0.82 mmol; Eu: 0.28 g, 0.76 mmol; Gd: 0.29 g, 0.77 mmol; Tb: 0.30 g, 0.80 mmol; Dy: 0.30 g, 0.80 mmol; Ho: 0.33 g, 0.88 mmol; Er: 0.36 g, 0.94 mmol; Yb: 0.40 g, 1 mmol) were dissolved in a mixture of ethanol (6 mL) and distilled water (6 mL).

Series 2 (S2): In a typical synthesis, 0.21 g (1.4 mmol) of L-tartaric acid (**H₂Tart**), 0.12 g (0.5 mmol) of biphenyl-4,4'-dicarboxylic acid (**H₂biBDC**), 0.14 g (3.5 mmol) of NaOH, and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (Sm: 0.30 g, 0.82 mmol; Eu: 0.27 g, 0.74 mmol; Gd: 0.28 g, 0.75 mmol; Tb: 0.33 g, 0.88 mmol; Dy: 0.31 g, 0.82 mmol; Ho: 0.34 g, 0.90 mmol; Er: 0.37 g, 0.97 mmol; Yb: 0.39 g, 1 mmol) were dissolved in a mixture of ethanol (6 mL) and distilled water (6 mL).

In both cases, the reaction mixture was stirred for two hours at room temperature to homogeneity and then placed in a Teflon-lined stainless vessel (40 mL) and heated to 170 °C for 60 h under autogenous pressure and afterwards cooled slowly to room temperature at a rate of 5 °C/h. The resulting product was filtered off, washed thoroughly with ethanol and distilled water, and finally air-dried in an oven at 60 °C. Elemental analyses were performed in a C-H-N Perkin-Elmer model 2400B elemental analyzer. The yields based on lanthanides elements, the calculated and found percentages of C-H, and the total mass losses of the two series of compounds are represented in the Table 1.

Doped yttrium compounds. Compounds based on Ce, Pr, and Nd, unfortunately have not been obtained, thus, we have restored to the doping approach of yttrium-based compounds by following procedure: 0.21 g (1.4 mmol) of L-tartaric acid (**H₂Tart**), 0.08 g (0.5 mmol) of terephthalic acid (**H₂BDC**) and 0.14 g (3.5 mmol) of

NaOH were added to, 6 mL of a solution of Y:Ln with ratio 20:1 previously prepared by dissolving 0.29 g (0.95 mmol) of $YCl_3 \cdot 6H_2O$ and $LnCl_3 \cdot 6H_2O$ (for Ce: 0.019 g, 0.05 mmol; Pr: 0.013g, 0.08 mmol; Nd: 0.018 g, 0.05 mmol) in 6 mL and stirred for 24h. Finally, 6 mL of ethanol were added to the mixture. The reaction mixture was stirred for one hour at and then placed in a Teflon-lined stainless vessel (40 mL) and heated to 180 °C for 72 h. (for Ce: 0.08g, *ca.* 20% yield based on Y; Pr: 0.10g, *ca.* 28%; Nd: 0.12g, *ca.* 30%).

Single-Crystal X-Ray Diffraction Studies. Data collection was performed at 293 K on an Agilent Gemini CCD diffractometer, using $CuK\alpha$ radiation. Images were collected at a 55 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image. The crystal structure was solved by direct methods. The refinement was performed using full-matrix least squares on F^2 . All non-H atoms were anisotropically refined. All H atoms were either geometrically placed riding on their parent atoms or located from the difference Fourier map, with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached. Crystallographic calculations were carried out using the following programs: CrysAlis CCD⁵⁶ for data collection; CrysAlis RED⁵⁷ for cell refinement, data reduction and empirical absorption correction; SHELXS-97⁵⁸ or SIR-2004⁵⁹ for structure solution; XABS2⁶⁰ for refined absorption correction; SHELXL-97⁵⁸ for structure refinement and prepare materials for publication; PLATON⁶¹ for the geometrical calculations; Diamond⁶² for molecular graphics. The detailed crystallographic data and the structure refinement parameters are summarized in Table 2. Selected bond distances, angles, and hydrogen bonds for **S1** and **S2** are given in Tables 3 and 4.

Thermal Characterization. A Mettler-Toledo TGA/SDTA851[°] and a DSC822[°] were used for the thermal analyses in oxygen dynamic atmosphere (50 mL/min) at a heating rate of 10 °C/min. In all cases, *ca.* 20 mg of powder sample was thermally treated, and blank runs were performed. In TG tests, a Pfeiffer Vacuum ThermoStarTM GSD301T mass spectrometer was used to determine the evacuated vapours. The masses 18 (H_2O), 44 (CO_2), and of the intense peaks corresponding to the cracking of the ligands **BDC**²⁻ and **biBDC**²⁻, were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

Morphological Characterization. Micrographs and X-ray microanalysis (SEM/EDX) were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV coupled with an INCA Energy-200 energy dispersive X-ray microanalysis system (EDX) with a PentaFET ultrathin window detector. SEM images show needle shaped crystals with length of *ca.* 50-400 μm (See Figure 1), and EDX confirmed that the ratio Ln:Na is *ca.* 1:1.

Infrared spectra. The infrared data were collected at RT using a FT-IR Bruker Tensor-27 spectrometer from KBr pellets. The spectra were collected over the range 4000–400 cm^{-1} by averaging 15 scans at a maximum resolution of 4 cm^{-1} .

Powder X-Ray Diffraction Studies. Powder X-ray diffraction patterns were recorded on X'pert Philips diffractometer with $\text{CuK}\alpha$ radiation. The samples were gently ground in an agate mortar in order to minimize the preferred orientation. All data were collected at room temperature over the angular 2θ range 3-46° with a step of 0.01° and a counting time of 1.5 s/step. The PXRD patterns of the compounds **1** and **2** were compared with the theoretical ones (see Figure 2), indicating that the products have been successfully obtained as pure crystalline phases.

Powder X-Ray Thermodiffraction Studies. In two different diffractometer, the powder X-ray thermodiffraction studies were performed in : (a) air, the sample was placed in an Anton Paar HTK 1200N oven-chamber, on a PANalytical XPERT-PRO diffractometer, using $\text{CuK}\alpha$ radiation, equipped with PIXcel linear detector with 255 channels. Each powder pattern was recorded in the 4-110° range (2θ) at intervals of 25 °C up to 200 °C and cooling down to 25 °C with a step of 0.013° and a counting time of 0.424 s/channel. The temperature ramp between two consecutive temperatures was 10 °C/min. (b) air, the sample was placed in an Anton Paar XRK 900 Reactor Chamber on a Bruker D8 Advance diffractometer with *DAVINCI* design, using $\text{CuK}\alpha$ radiation, equipped with LynxEye detector. Each powder pattern was recorded in the 4-60° range (2θ) from RT to 200 °C and cooling to RT with a step of 0.02° and a counting time of 0.4 s. The temperature ramp between two consecutive temperatures was 10 °C/min. (c) vacuum; the sample was placed in an Anton Paar XRK 900 Reactor Chamber on a

Bruker D8 Advance diffractometer with *DAVINCI* design, using $\text{CuK}\alpha$ radiation, equipped with LynxEye detector. Each powder pattern was recorded in the $4\text{--}60^\circ$ range (2θ) from RT to 900°C with a step of 0.02° and a counting time of 0.3 s, the temperature ramp was $10^\circ\text{C}/\text{min}$ and XRPD patterns were recorded every 50°C .

Catalysis Studies. The procedure established for acetalization of benzaldehyde with trimethylorthoformate (TMOF) is described as follows: TMOF (5 mmol, 0.5 mL) and benzaldehyde (0.5 mmol, 0.05 mL) were added to a suspension of the catalyst (0.01 mmol) in 3 mL of tetrachloromethane. The reaction was carried out in a sealed tube under nitrogen atmosphere, mild conditions (70°C), and magnetic steering. Samples were taken at intervals and analyzed by gas chromatography.

Photoluminescence Studies. The photoluminescence spectra in the visible and NIR spectral ranges were recorded at room temperature with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 and H9170 Hamamatsu photomultipliers, respectively, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. The time-resolved measurements were acquired with the set-up above described for the photoluminescence spectra using a pulsed Xe-Hg lamp (6 μs pulse at half width and 20–30 μs tail). The NIR emission and excitation spectra were acquired with 20–50 scans.

Results and Discussion

Single-crystal X-ray diffraction analyses reveal that all the compounds crystallize in the orthorhombic chiral space group $C222_1$, and the compounds of each series (**S1** or **S2**) are isostructural, tuned by the influence of the Ln^{3+} cations (see Table 2). The variation of unit cell parameters show dependency to the Shannon's effective ionic radii,⁶³ and the expected tendencies are observed: the ionic radii decrease linearly as the unit cell parameters (a , b , c , and volume) and distances Ln—Na do. These tendencies are illustrated in Figure 3. The coordination modes of carboxylate groups of

Tart²⁻, **BDC**²⁻ and **biBDC**²⁻ ligands in **S1** and **S2** are shown in Figure 5g. To the best of our knowledge, these coordination modes are uncommon and have not yet been reported.

The structures of the compounds of both series **S1** and **S2** consist of infinite chains, along the *a*-axis, of alternating {LnO₈} and {NaO₆} polyhedra edge-shared through two carboxylate oxygen atoms, O(1) (from **BDC**²⁻ or **biBDC**²⁻) and O(4) (from **Tart**²⁻). The distance between adjacent Ln-Na cations in the chain, from the beginning to the end of **S1** and **S2**, is ranging from 3.861(1) Å (for **Za3**, Sm) to 3.798(1) Å (for **Za17**, Yb), and from 3.849(1) Å (**Za4**, Sm) to 3.786(1) Å (**Za18**, Yb), with the average values of 3.831 Å and 3.820 Å, respectively. The flexible **Tart**²⁻ ligand serves as bridge to link the ∙∙Ln-Na-Ln-Na∙∙ chains along *a* and *c*-axis to create a double layer in a zig-zag fashion, while the rigid **BDC**²⁻ in **S1** or **biBDC**²⁻ ligands in **S2**, are parallel to the *b*-axis and act as pillars separating two successive double layered network. The distance centroid-to-centroid between neighboring **BDC**²⁻ ligands in **S1** or **biBDC**²⁻ in **S2** along *c*-axis ranges, respectively, from 3.83 Å (for **Za3**) to 3.78 Å (for **Za17**), and from 3.84 Å (**Za4**) to 3.80 Å (**Za18**), thus indicating the possibility of the weak noncovalent π-π interactions, which is an offset stacking, where the ring normal forms an angle of about 10° with the vector between the rings centroids. In the case of **S2**, **biBDC**²⁻ is not planar and has a torsion angle ranging from a maximum value of 36.61° (for **Za4**) to minimum of 34.13° (for **Za18**). The slight decrease in distance centroid-to-centroid, as well as the torsion angle in the case of **S2**, show dependency to ionic radii of Ln³⁺ cations. The spacers **BDC**²⁻ in **S1** or **biBDC**²⁻ in **S2**, are one-sided coordinated and binding three cations (one Ln³⁺ and two Na⁺) in a tetradentate chelating-bridging mode (μ₃ - η¹: η²: η¹). However, the opposite side being involved in strong hydrogen bond interactions between the oxygen atoms O2 of the non-coordinated carboxylate groups O2-C6-O2 of the **BDC**²⁻ ligand in **S1**, or O2-C10-O2 of the **biBDC**²⁻ ligand in the case of **S2**, which acts as acceptor, and the oxygen atom O3 of the hydroxyl groups of the **Tart**²⁻ ligand, together with the coordinated water molecules O6 to the sodium atom which act as donors, therefore imparting 3D stability to the structure. The unusual coordination mode of **BDC**²⁻ (**biBDC**²⁻ in the case of **S2**), in a successive switch manner, gives rise to an undulating interlayer surface propagating in *a* and *c*-directions. The resulting isorecticular layered chiral Ln/Na-organic frameworks have channels running along *a* (Figure 4a,b) and *c*-axis (Figure 4c,d), with approximate dimensions of 6.3 × 3.5 Å² and 6.3 × 4.5 Å² in **S1**, and 10.6 × 3.5 Å² and 10.6 × 4.5 Å² in **S2**. Both series of

compounds, contain single crystallographically independent Ln^{3+} and Na^+ cations, each with half occupancy sit on a twofold crystallographic axis along b -direction. Around each Ln^{3+} cation are eight oxygen atoms (Figure 5a,c), six of them carboxylic (O1 from BDC^{2-} or biBDC^{2-} , and O4 and O5 from Tart^{2-}) and two from hydroxyl groups (O3 from Tart^{2-}). Its coordination geometry may be described as a distorted bicapped trigonal-prism (Figure 5b), while the Na^+ cation is bonded to six oxygen atoms (Figure 5d,f), four of them carboxylic (O1 and O4) and two from coordinated water molecules (O6), and its geometry may be described as distorted trigonal prism (Figure 5e). Out of the eight oxygen atoms coordinated to Ln^{3+} , six come from four symmetry-related Tart^{2-} anions: two of them are coordinated to Ln^{3+} in chelating modes *via* the carboxylic oxygen atom O5 and the hydroxyl oxygen atom O3, and the last two act as a bridge between the Ln^{3+} and Na^+ through the carboxylic oxygen atom O4. The two remaining oxygen atoms bonded to Ln^{3+} belong to one BDC^{2-} anion in **S1** or biBDC^{2-} in the case of **S2**, which acts (i) in chelating mode *via* the carboxylate group O1–C1–O1 and (ii) in bridging mode between Ln^{3+} and Na^+ within each carboxylate oxygen atom O1. Out of the six oxygen atoms coordinated to Na^+ , two come from the Tart^{2-} anion which acts in chelating mode *via* the carboxylate oxygen atoms O4, and the four remaining, every two of them are belonging to two symmetry-related: (i) coordinated water molecules, (ii) BDC^{2-} anions (or biBDC^{2-} anions in the case of **S2**), by coordinating oxygen atoms O6 and O1, respectively. In **S1**, the distances Ln–O and Na–O range from maximum average value of 2.408 Å and 2.434 Å (for **Za3**, Sm) to minimum average values of 2.315 (3) Å and 2.407 Å (for **Za17**, Yb). Similarly, the pertinent values in **S2** range from 2.405 Å and 2.431 Å (for **Za4**, Sm) to 2.319 Å and 2.406 Å (for **Za18**, Yb), respectively, which are usual values for oxygen-coordinated lanthanides or sodium atoms compounds with carboxylic acids.

Series of compounds **S1** and **S2** display very similar IR spectra as depicted on Figures 6a and 6b. The strong and broad adsorption bands in the region 3600–3400 cm^{-1} are attributed to the characteristic O—H stretching vibrations from hydroxyl groups of Tart^{2-} ligands and coordinated water molecules to sodium atom, the existence of these two different types of chemical species is evident in the spectra which show two markedly distinct bands at *ca.* 3590 cm^{-1} and 3470 cm^{-1} assigned, respectively, to water molecules and hydroxyl groups. The weak two bands at *ca.* 3065 cm^{-1} are assigned to =C—H stretching vibrations of phenylene rings of BDC^{2-} or biBDC^{2-} ligands, and those

at *ca.* 2960 cm⁻¹ and 2920 cm⁻¹ are attributed to C—H stretching vibrations of the alkane chain of **Tart**²⁻ ligand. The two coordination modes adopted by the carboxylate groups of **Tart**²⁻, and **BDC**²⁻ or **biBDC**²⁻ ligands in all the compounds are clearly distinguished from the spectra. The characteristic bands for the asymmetric and symmetric stretching vibrations of the carboxylate groups appear at *ca.* 1640-1545 cm⁻¹ and 1470-1360 cm⁻¹, respectively. The values of $\Delta\nu = \nu_{\text{asym}}(\text{CO}_2^-) - \nu_{\text{sym}}(\text{CO}_2^-)$ of *ca.* 140-180 cm⁻¹ may confirm the bridging mode of the carboxylate groups found in these compounds. The band at 1670 cm⁻¹ may be assigned to the uncoordinated and deprotonated carboxylate group of **BDC**²⁻ or **biBDC**²⁻ involved in strong hydrogen bonds. The strong band at *ca.* 1510 cm⁻¹ corresponding to C=C stretching vibrations (skeletal vibrations). Bands at *ca.* 1350 cm⁻¹ and 1304 cm⁻¹ may be assigned to O—H stretching vibrations of hydroxyl **Tart**²⁻. Band at *ca.* 1242 cm⁻¹ is attributed to C—O stretching vibrations of carboxylate groups. The bands corresponding to C—OH stretching vibrations of **Tart**²⁻ appear at *ca.* 1074 cm⁻¹. The band at *ca.* 865 cm⁻¹ is may be attributed to scissoring vibrations of carboxylate groups. The aromatic =C—H out-of-plane deformation vibrations are confirmed by the strong bands at *ca.* 798 cm⁻¹ (strong) and 710 cm⁻¹ (weak). Band corresponding to C—C—O stretching vibrations of **Tart**²⁻ appear at *ca.* 740 cm⁻¹. Bands at *ca.* 534 cm⁻¹ and 424 cm⁻¹ may be assigned, respectively, to in-plane rocking vibration and out-of-plane of deformation vibrations of carboxylate groups bonded to aromatic rings. The main difference between **S1** and **S2** is the fact that in **S2** appeared additional sharp strong band centered around 690 cm⁻¹ which due to C—H out-of-plane deformation vibrations arising from the second aromatic ring of **biBDC**²⁻.⁶⁴⁻⁶⁶

The thermal stability in air of **S1** and **S2** was investigated. Comparison TG curves for each series of compounds **S1** or **S2** are depicted in Figure 7a and 7b, respectively. For each compound, the TG/DTG/SDTA curves with the corresponding mass spectrometry analysis, are provided in the Figure S1, while Figure S2 (see Supporting Information) shows DSC traces. TG curves of **S1** and **S2** reveal the observed total mass losses, presented in the Table S1 (see Supporting Information), from room temperature up to 1000 °C. The final product was identified as a 1:1 mixture of Ln₂O₃ (detected by PXRD) and amorphous Na₂O (by EDX microanalysis), and coal (by C-H-N elemental analysis). The TG curves of **S1** or **S2**, as well as comparing between **S1** and **S2**, very closely resemble each other, isostructural frameworks lead to the similar thermal decomposition processes, which may be divided into two main

stages. The first mass loss corresponds to the release of the coordinated water molecules, while the second mass loss, composed of several continuous and overlapping processes, is attributed to the decomposition of the ligands.

In the case of **S1**, **Za9** has been taken as representative example. As shown in Figure S1d (see Supporting Information), the thermal decomposition process of **Za9** proceeds in five stages. The first mass loss between 140-260 °C (reaching maximum velocity at 222 °C) with the total mass loss of 6.5 % (cal. 6.79%), associated with endothermic peak at 212 °C and 228 °C on the SDTA and DSC curves, respectively, corresponds to the gradual loss of the two water molecules coordinated to the sodium atom. The rest of stages, from second to fifth, in the range 270-560 °C, are continuous and overlapping (reaching their maximum velocity at 310 °C, 410 °C, 493 °C, and 518 °C, respectively) with the total mass loss of *ca.* 48.2 %. The second stage (range 270-360 °C) is associated with endothermic peak at 312 °C and 311 °C on the SDTA and DSC curves, respectively, while the third (range 360-442 °C), and fourth-fifth stages (range 442-560 °C) are associated, respectively, with exothermic band (maximum at 402 °C) and sharp exothermic peak at 485 °C with shoulder at 515 °C on SDTA curve, and with exothermic band (maximum at 403 °C) and exothermic peak at 478 °C on the DSC curve which correspond to the third and fourth stages, respectively. This multi-step decomposition behavior is assigned to a complex and overlapping oxidation process of the mixed-ligands as well as desorption of some fragments. Additional mass loss of *ca.* 2% have been observed in the range 950–1000 °C, which is assigned to the liberation of some trapped organic part after the structure collapse. The associated mass spectrometry *m/z* 18 (H₂O) and 44 (CO₂) curves are in a good agreement with TG/DTG curves. The mass spectrometry *m/z* 18 curve has four maxima, the first one at 208 °C corresponding to the loss of the two water molecules coordinated to sodium atom, while the second, third and the fourth maxima, at 307 °C, 398 °C and 490 °C respectively, which coincide with the first, second and the third maxima of *m/z* 44 curve, are attributed to multi-step oxidation of the **Tart**²⁻ and **BDC**²⁻ ligands. Other fragments of *m/z* 58 and 39, corresponding to **Tart**²⁻ and **BDC**²⁻ ligands, respectively, have been also detected. *m/z* 58 curve shows two maxima at 304 °C and 380 °C which coincide with the first maximum and the shoulder of second one of *m/z* 44 curve, while *m/z* 39 maxima at 392 °C and 485 °C coincide with second and the third maxima of *m/z* 44. The first maximum of *m/z* 58 curve at 304 °C explain the endothermic peaks at 311 °C and 312

°C on the SDTA and DSC curves associated to the second stage. Desorption of the fragment m/z 58 is followed by oxidation in air, thus the reason why m/z 18 and 44 are also detected at the second stage. Taking into account that the mass spectrometry analysis is a semiquantitative method, the integration of the first band (608 nA) is almost half of the integration of the second, third and the fourth ones (1367 nA) in the m/z 18 curve, indicating the loss of approximately four water molecules in the second, third, fourth and fifth steps, corresponding to the amount of hydrogen atoms resulting from the decomposition of the both **Tart**²⁻ and **BDC**²⁻ ligands in the formula of **Za9**.

In the same way, **Za10** is taken as representative example of **S2** (Figure S1d, Supporting Information). **Za10** undergo five steps of mass loss, the first step (exp. 5.6%) at 150-240 °C, corresponds to the gradual loss of coordinated water molecules (calcd. 5.94%). The rest of steps (exp. 54.5%; calcd. 58.77%) in the range 290–540 °C are continuous and overlapping, correspond to the progressive decomposition of the ligands. Additional mass loss (ca. 2%) between 900–1000 °C is attributed to the liberation of some trapped organic moieties after the structure collapse. The associated mass spectrometry m/z 18, m/z 44, and m/z 78 (C₆H₆) curves are fairly agreeing with those of TG/DTG. and they have, respectively, four maxima (at 197 °C, 324 °C, 396 °C, 458 °C, and shoulder at 508 °C), three maxima (324 °C, 397 °C, 450 °C, and shoulder at 504 °C), and one maximum (450 °C). m/z 78 (C₆H₆) curve shows that the desorption of phenyl group starts basically in the fourth stage manifested by the contraction of interlayer spacing from ca. 18.3 Å (of dehydrated phase) to ca. 14.7 Å due the desorption and oxidation of one phenyl group of **biBDC**²⁻ ligand (confirmed by powder X-ray thermodiffraction studies, see violet powder pattern at 450 °C Figure 8d), however, no endothermic has been observed on the SDTA or DSC curve, due to the fact that the oxidation process of phenyl group is dominant than the desorption. The integration of the first band (440 nA) is almost a third of the integration of the second, third and fourth ones (1296 nA) in the m/z 18 curve, which proves the loss of approximately six water molecules in the second, third, fourth and fifth stages, corresponding to the hydrogen atoms resulting from the decomposition of the both **Tart**²⁻ and **biBDC**²⁻ ligands in the formula of **Za10**.

For the remaining compounds of **S1** and **S2**, numerical values of TG-DTG-MS and SDTA/DSC curves and are represented in the Table S1 (see Supporting Information). To summarize, the first stage is attributed to the release of two

coordinated water molecules, the second stage correspond to desorption of **Tart**²⁻ fragments followed by oxidation in air. The third stage shared between the continuation of **Tart**²⁻ oxidation and the beginning of **BDC**²⁻ or **biBDC**²⁻ oxidation, and finally, the fourth and fifth stages are attributed to **BDC**²⁻ or **biBDC**²⁻ oxidation and desorption.

In addition, the dehydration enthalpies for **S1** and **S2**, are in the range -36 kJ/mol to -105 kJ/mol and -34 kJ/mol to -107 kJ/mol, respectively, which are fairly close and comparable. However, oxidative decomposition enthalpies are found to be higher in **S2** than **S1**, varying in the range 3571–6690 kJ/mol and 2051–3889 kJ/mol, respectively, which is related to difference between oxidative decomposition enthalpies of **BDC**²⁻ and **biBDC**²⁻ and estimated *ca.* 2200 kJ/mol.

The X-ray thermodiffraction analysis carried under air heating up from 25 °C to 200 °C and cooling down to 25 °C were performed for **Za7**, **Za13**, and **Za16** (see Figures 8a, 8b, and 8c, respectively), and under vacuum heating up from room temperature to 900 °C for **Za16** (Figure 8d). The results confirm that **S1** and **S2** exhibit a phase transformation corresponding to the dehydration process by losing the two water molecules coordinated to sodium atom, which is a reversible process for **S1**, involving a spontaneous rehydration after cooling down to room temperature, clearly illustrated by thermodiffractogram of **Za7** and **Za13** (blue powder patterns at 25 °C down, Figure 8a and 8b). However, rehydration is slowly reversible in the case of **S2** illustrated by thermodiffractogram of **Za16** (green powder patterns on the Figure 8c), and estimated to be approximately half rehydrated at the end of experiment (confirmed by TG analysis).

For **Za7**, **Za13**, or **Z16**, no structural change occurs below 160 °C, and no significant change in the unit cell parameters has been observed. The phase transformation to the anhydrous form beginning at 170 °C, the total transformation to the anhydrous form is reached at 180 °C and maintained until 200 °C, which is consistent with the TG analyses. During the temperature decrease the anhydrous phase is preserved, the rehydration begins at 120 °C, 140 °C, and 100 °C for **Za7**, **Za13**, and **Z16**, respectively, and continues until room temperature. The patterns of dehydrated compounds of **Za7** and **Za13** correspond to the as-synthesized compounds with some diffraction intensity drop and peak broadening. In contrast with **S1** compounds, the rehydration of **S2** compounds (**Za16**) is not achieved at the end of the experiment, and takes a few days in air, indicating the slow reversibility of the process.

X-ray thermodiffractogram of **Za16** under vacuum heating up to 900 °C (see Figure 8d) indicates that no structural change below 100 °C, at 150 °C the dehydrate phase appear and progressively increase until reaching the total transformation at 250 °C, the anhydrous phase is preserved until 300 °C. At 350 °C and 400 °C, powder patterns show broad peak at $2\theta \sim 5.4^\circ$ corresponding to the interlayer distance and practically no other diffraction peaks have been observed at higher angles, which due to phase amorphization due to desorption of the organic ligands. At 450 °C and 500 °C the broad peak became sharp, its intensity markedly increase, and is shifted toward higher angles due to contraction of interlayer spacing from *ca.* 18.3 Å (of dehydrated phase) to *ca.* 14.7 Å caused by desorption of phenyl rings, moreover, second peak corresponding to the interlayer distance at $2\theta \sim 11.8^\circ$ also appears. This behavior is explained by the fact that desorption of **Tart**²⁻ (incorporated in the layer) fragments is stopped and desorption of phenyl rings of **biBDC**²⁻ (pillaring the layers) is continued. Above 550 °C, practically no diffraction peak has been observed due to the structure collapse. These results are consistent with TG analyses. However, new phase has been formed characterized by series of broad diffraction peaks corresponding to the formation of Er₂O₃.

X-ray powder diffraction patterns of dehydrated forms for **Za7**, **Za13** and **Za16** at 200 °C, have been indexed in the orthorhombic system with the following unit cell parameters: $a = 6.818(2)$ Å, $b = 28.634(8)$ Å, $c = 7.297(5)$ Å, $V = 1424.5(6)$ Å³, for **Za7**, $a = 6.7713(4)$ Å, $b = 28.728(2)$ Å, $c = 7.3292(8)$ Å, for **Za13**, and $a = 6.7357(6)$ Å, $b = 37.875(4)$ Å, $c = 7.5869(7)$ Å, $V = 1935.5(4)$ Å³, for **Za16**. The results reveal that the structure contract of *ca.* 7% (for **Za7**), *ca.* 6% (**Za13**) and *ca.* 3% (**Za16**) along the *b*-axis, maintaining the orthorhombic symmetry, after the loss of two water molecules coordinated to the sodium atoms. The *a* and *c*-axis are almost unchanged in all cases.

Two compounds **Za15** (Er compound) and **Za17** (Yb compound) of **S1** have been selected to test their catalytic activity to behave as Lewis acid catalysts in acetalization of benzaldehyde (Figure 9), and their catalytic activity has been compared with that of yttrium-based compound (compound **1**) previously reported.⁵⁵ The results show that the activity catalytic is quite improved when the catalytic centre is Yb or Er. The greater catalytic effect of Yb-based compound (**Za15**) may be explained in terms of more acidic character when the ionic radii decrease.

Series of compounds **S1** and **S2** have been examined under UV-light and exhibit color tunable emission over the whole visible light range by changing the doping Ln^{3+} cation or concentration, as exemplified in Figure 10. For instance, the crystals of **Za5** display a red-light emission visible at the naked eyes, as exemplified in Figure 10e,f. In order to monitor the excitation paths that induce such emission features, the excitation spectra were monitored within the $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$ transition (Figure 11). The spectra of crystals **Za6** and **Za5** are very similar being formed of a large band with three peaks around 250 nm, 270 nm, and 310 nm ascribed to the excited states of the **biBDC**²⁻ or **BDC**²⁻ ligands (Figure S3, Supporting Information) and of a series of straight lines ascribed to the intra-4f⁶ $\ ^7\text{F}_{0,1} \rightarrow \ ^5\text{D}_{4-1}, \ ^5\text{G}_{2-6}, \ ^5\text{L}_6$ transitions. The low-relative intensity of the intra-4f⁶ lines, point out that the Eu^{3+} ions sensitization process is more efficient when compared with direct intra-4f⁶ excitation. The excitation paths in the presence of Gd^{3+} ions were also monitored for the **DZa7** crystal (synthesis, crystallographic data and structural characterization for **DZa7** are given in Supporting Information), Figure 11. This spectrum resemble the ones acquired for the pure Eu^{3+} samples being, however, observed changes in the relative intensity of the broad band components and a decrease in the relative intensity of the intra-4f⁶ lines, which indicates a better Eu^{3+} sensitization process in the presence of Gd^{3+} ions. Nevertheless, the absence on Gd^{3+} lines in the excitation spectrum monitored within the Eu^{3+} emission lines indicates the absence of efficient room-temperature Gd^{3+} -to- Eu^{3+} energy transfer mechanism. Figure 12 compares the emission features of **Za6**, **Za5** and **DZa7** under excitation via the broad band (270 nm) and directly into the intra-4f⁶ levels (395 nm, $\ ^5\text{L}_6$). The spectra are formed of the $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_{0-4}$ transitions, and for the **Za6** crystal a low-intensity broad band originated from the ligands excited states in which a series of intra-4f⁶ self-absorptions are superimposed is also detected. For the **Za6** and **Za5** the presence of a single line for the non-degenerated $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ transition, the Stark splitting into 2 and 3 clearly express components for the $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_{1,2}$ transitions and the high relative intensity of the $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$ transition are in accord with the Eu^{3+} local site symmetry (C_2) determined based on the crystal structures. Moreover, the energy and full width at half maximum (fwhm) of the intra-4f⁶ lines are almost independent of the excitation wavelength, in good agreement with the presence of a single average local environment for the Eu^{3+} in both crystals. Nevertheless, the **Za6** crystal emission lines display a higher fwhm value, when compared with that of **Za5**, as well exemplified by the fwhm

value of the ${}^5D_0 \rightarrow {}^7F_0$ transition illustrated in the inset in Figure 12 (15.4 ± 0.4 and $26.6 \pm 0.9 \text{ cm}^{-1}$ for **Za5** and **Za6**, respectively). The presence of Gd^{3+} induces both an enlargement of the Eu^{3+} emission lines (e.g. $40.6 \pm 1.0 \text{ cm}^{-1}$ for the ${}^5D_0 \rightarrow {}^7F_0$ transition) and variations in the energy of the components, suggesting a larger distribution of Eu^{3+} similar local environments compared with that found in **Za6** and **Za5**. Moreover, the relative intensity of the ${}^5D_0 \rightarrow {}^7F_{0-4}$ transition depends on the excitation wavelength, reinforcing this assumption. The emission features of the three crystals were further quantified by the measurement of the 5D_0 decay curves monitored within the ${}^5D_0 \rightarrow {}^7F_2$ transition, under direct intra- $4f^6$ excitation (395 nm, 5L_6), Figure 13. Whereas the emission of **DZa7** is well reproduced by a single exponential function yielding a lifetime value of $0.574 \pm 0.002 \text{ ms}$, the emission decay curves of the **Za6** and **Za5** display a rise-time behaviour for time values below 1 ms (inset in Figure 13) probably ascribed to the contribution of the 5D_1 or ligands levels. For time values higher than 1 ms, the decay curves reveal a single exponential decay with lifetime values of $0.588 \pm 0.002 \text{ ms}$ and $0.608 \pm 0.002 \text{ ms}$ for **Za6** and **Za5**, respectively.

Figures 14a,b shows the emission spectra of Dy^{3+} -based materials under distinct excitation wavelengths. The spectra of **Za12** are formed of a high-relative intensity broad band (380-500 nm) and a series of Dy^{3+} lines attributed to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2-11/2}$ transitions. For the **Za11** the emission is characterized by a low-relative intensity broad band (380-650 nm) and by the typical Dy^{3+} ${}^4F_{9/2} \rightarrow {}^6H_{15/2-11/2}$ transitions. The large broad band in each sample can be ascribed to the excited states of the **BDC**²⁻ or **biBDC**²⁻ ligands (Figure S3, Supporting Information). The excitation spectra were selectively monitored within the large broad band (410-450 nm) and within the Dy^{3+} emission lines (575 nm), as exemplified in the inset of Figures 14a and 14b for **Za12** and **Za11**, respectively. The latter spectrum reveals a broad band (240-380 nm) superimposed on a series of Dy^{3+} -related lines assigned to the ${}^6H_{15/2} \rightarrow {}^4P_{7/2,3/2}$, ${}^4F_{7/2}$, ${}^4G_{21/2}$, ${}^4P_{7/2,3/2}$, and ${}^4H_{15/2}$ transitions. The UV-band is also present in the excitation spectrum monitored within the **BDC**²⁻ and **biBDC**²⁻ ligands emission spectra (inset of Figures 14a,b), pointing out an efficient Dy^{3+} sensitization. Moreover, the higher relative intensity of the ligands broad band with respect to the Dy^{3+} lines indicates that the main excitation path for the metal ions is via the **BDC**²⁻ or **biBDC**²⁻ excited states. For the **Za12** sample the excitation spectrum monitored within the Dy^{3+} lines also reveals a broad band (390-480 nm). Figure 15 show the emission features of the Ho^{3+} and Er^{3+} -based materials

containing **biBDC**²⁻ ligands. The spectra reveals a broad band assigned to the ligands excited states (Figure S3, Supporting Information) and a series of Ho³⁺ and Er³⁺-related self-absorptions ascribed to the Er³⁺ and Ho³⁺-related transitions, respectively. The Ho³⁺ and Er³⁺-doped materials containing the **BDC**²⁻ ligands do not show efficient room temperature emission. This observation suggest that the ligands absorbed energy is probably being efficiently transfer to the lanthanide ions, since the ligands are optically active at 300 K (Figure S3, Supporting Information). Under UV excitation the Er³⁺-containing samples display the typical NIR emission ascribed to the intra-4f¹¹ ⁴I_{13/2}→⁴I_{15/2}, Figure 16. The excitation spectra were monitored around this transition revealing a broad band ascribed to the **BDC**²⁻ and **biBDC**²⁻ excited states for **Za15** and **Za16**, respectively, and a series of Er³⁺ lines attributed to the ⁴I_{15/2}→³G_{11/2}, ⁴F_{7/2} transitions. As above mentioned for the Dy³⁺-based materials (Figure 14), the higher-relative intensity of the ligands excited states when compared with the Er³⁺ lines points out that the lanthanide ions are mainly populated via an efficient sensitization process rather than by direct intra-4f excitation.

Conclusions

In summary, the field of metal-organic frameworks chemistry has advanced quickly over recent years. Recent reports tend to focus on the functionality of these materials, but much of them are centered on transition metal rather than lanthanides containing materials, due the fact that the lanthanides provide a challenge in the assembly of topologies of interest. However, it is important to harness the unique feature of the luminescent lanthanide ions and direct attention to exploring and exploiting this property for potential applications. In this context, two series NaLn(C₄H₄O₆)(C₈H₄O₄)(H₂O)₂ (**S1**) and NaY(C₄H₄O₆)(C₁₄H₈O₄)(H₂O)₂ (**S2**) made up of 16 isorecticular chiral lanthanide-organic frameworks materials based on Ln(III), Na(I) and chiral flexible-achiral rigid dicarboxylates ligands, have been synthesized and characterized. **S1** and **S2** undergo phase transformation upon dehydration process, while the spontaneous rehydration is characterized by different kinetics, fast in the case of **S1** and slow for **S2**. Catalytic activity has been is quite improved through judicious choice of the Ln³⁺ cation. Photoluminescence studies of the investigated materials show room

temperature tunable UV-VIS-IR light emission through an effective Ln³⁺ sensitization via **BDC**²⁻ and **biBDC**²⁻ ligands.

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Supporting Information Available

TG/DTG/SDTA-MS and DSC curves for series of compounds **S1** and **S2**, emission and excitation spectra of yttrium-based compounds **Za1** and **Za2**, section of synthesis and structural characterization for **DZa7**, and X-ray crystallographic information (CIF files) for series of compounds **S1-S2-DZa7** can be obtained free of charge *via* the internet at <http://pubs.acs.org>.

References

- (1) (a) Kuriki, K.; Koike, Y.; Okamoto, Y. *Chem. Rev.* **2002**, 102, 2347. (b) Polman, A.; van Veggel, F. C. J. M. *J. Opt. Soc. Am. B.* **2004**, 21, 871
- (2) (a) Justel, T.; Nikol, H.; Ronda, C. *Angew. Chem., Int. Ed.* **1998**, 37, 3084. (b) Feldmann, C.; Justel, T.; Ronda, C. R.; Schmidt, P. J. *Adv. Funct. Mater.* **2003**, 13, 511.
- (3) (a) Yokoyama, H. *Science*, **1992**, 256, 66. (b) Adam, J. L. *Chem. Rev.* **2002**, 102, 2461. (c) S. Kuck, *Appl. Phys. B*, **2001**, 72, 515.
- (4) Dorenbos, P. *IEEE. Trans. Nucl. Sci.*, **2010**, 57, 1162.
- (5) (a) Hemmila, I.; Laitala, V. *J. Fluoresc.* **2005**, 15, 529. (b) Hemmila, I.; Dakubu, S.; Mukkala, V. M.; Siitari, H.; Lovgren. T. *Anal. Biochem.* **1984**, 137, 335. (c) Westerlund-Karlsson, A.; Suonpaa, K.; Ankelo, M.; Ilonen, J.; Knip, M.; Hinkkanen, A. E. *Clin. Chem.* **2003**, 49, 916. (d) Ankelo, M.; Westerlund-Karlsson, A.; Ilonen, J.; Knip, M.; Savola, K.; Kankaanpaa, P.; Merio, L.; Siitari, H.; Hinkkanen, A. *Clin. Chem.* **2003**, 49, 908. (e) Haese, A.; Vaisanen, V.; Finlay, J. A.; Pettersson, K.; Rittenhouse, H. G.; Partin, A.W.; Bruzek, D. J.; Sokoll, L. J.; Lilja, H.; Chan. D. W. *Clin. Chem.* **2003**, 49, 601. (f) Korpimaki, T.; Hagren, V.; Brockmann, E. C.; Tuomola. M. *Anal. Chem.* **2004**, 76, 3091.
- (6) Justel, T.; Nikol, H.; Ronda, C. *Angew. Chem. Int. Ed.* **1998**, 37, 3084.
- (7) Bunzli, J. C. G.; Piguet, C. *Chem. Soc. Rev.*, **2005**, 34, 1048.
- (8) (a) Chao, T. C.; Lin, Y. T.; Yang, C. Y.; Hung, T. S.; Chou, H. C.; Wu, C. C.; Wong, K. T. *Adv. Mater.*, **2005**, 17, 992. (b) Hu, X.; Deng, J.; Zhang, J. P.; Lunev, A.; Bilenko, Y.; Katona, T.; Shur, M. S.; Gaska, R.; Shatalov. M.; Khan, A. *Phys. Status Solidi A*, **2006**, 203, 1815. (c) Mochizuki, S.; Minami, S.; Fujishiro, F. *J. Lumin.*, **2005**, 112, 267.
- (9) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, 129, 14176.
- (10) Collins, D. J.; Zhou. H. C. *J. Mater. Chem.* **2007**, 17, 3154.
- (11) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou. H. C. *J. Am. Chem. Soc.* **2006**, 128, 3896.
- (12) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, 128, 1304.
- (13) Ma, S.; Zhou. H. C. *J. Am. Chem. Soc.* **2006**, 128, 11734.
- (14) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, 128, 3494.
- (15) Chen, B. L.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2005**, 44, 4745.
- (16) Rowsell, J. L. C.; Yaghi, O. M. *Micropor. Mesopor. Mater.* **2004**, 73, 3–14.

- (17) Férey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guegan, A. *Chem. Commun.* **2003**, 2976–2977.
- (18) Pan, L.; Parker, B.; Huang, X.; Olson, D. H.; Lee, J. Y.; Li, J. *J. Am. Chem. Soc.* **2006**, 128, 4180.
- (19) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, 127, 9376.
- (20) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *Am. Chem. Soc.* **2004**, 126, 32.
- (21) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem. Intl. Ed.* **2003**, 42, 428.
- (22) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, 38, 1330.
- (23) Rocha, J.; Carlos, D. C.; Almeida Paz, F. A.; Ananias, D. *Chem. Soc. Rev.* **2011**, 40, 926.
- (24) Guo, H.; Zhu, Y.; Qiu, S.; Lercher, J. A.; Zhang, H. *Adv. Mater.* **2010**, 22, 4190.
- (25) Liu, K.; You, H.; Zheng, Y.; Jia, G.; Song, Y.; Huang, Y.; Yang, M.; Jia, J.; Guo, N.; Zhang, H. *J. Mater. Chem.* **2010**, 20, 3272.
- (26) Black, C. A.; Costa, J. S.; Fu, W. T.; Massera, C.; Roubeau, O.; Teat, S. J.; Aromi, G.; Gamez, P.; Reedijk, J. *Inorg. Chem.* **2009**, 48, 1062.
- (27) Zhu, Q.; Sheng, T.; Fu, R.; Hu, S.; Chen, J.; Xiang, S.; Shen, C.; Wu, X. *Cryst. Growth Des.* **2009**, 9, 5128.
- (28) Ma, D. Y.; Liu, H. L.; Li, Y. W. *Inorg. Chem. Commun.* **2009**, 12, 883.
- (29) Li, X.; Zhang, Y. B.; Shi, M.; Li, P. Z. *Inorg. Chem. Commun.* **2008**, 11, 869.
- (30) Van der Horst, M. G.; Van Albada, G. A.; Ion, R. M.; Mutikainen, I.; Turpeinen, U.; Tanase, S.; Reedijk, J. *Eur. J. Inorg. Chem.*, **2008**, 2170.
- (31) Song, X. Q.; Liu, W. S.; Dou, W.; Wang, Y. W.; Zheng, J. R.; Zang, Z. P. *Eur. J. Inorg. Chem.* **2008**, 1901.
- (32) Lill, D. T.; Bettencourt-Dias, A.; Cahill, C. L. *Inorg. Chem.* **2007**, 46, 3960.
- (33) Chandler, B. D.; Yu, J. O.; Cramb, D. T.; Shimizu, G. K. H. *Chem. Mater.* **2007**, 19, 4467.
- (34) Li, Z.; Zhu, G.; Guo, X.; Zhao, X.; Jin, Z.; Qiu, S. *Inorg. Chem.* **2007**, 46, 5174.
- (35) Shi, Q.; Zhang, S.; Wang, Q.; Ma, H.; Yang, G.; Sun, W. H. *J. Mol. Struct.* **2007**, 837, 185.
- (36) Mahata, P.; Natarajan, S. *Inorg. Chem.* **2007**, 46, 1250.
- (37) Sonnauer, A.; Nather, C.; Hoppe, H. A.; Senker, J.; Stock, N. *Inorg. Chem.* **2007**, 46, 9968.

- (38) Zhang, X. J.; Xing, Y. H.; Sun, Z.; Han, J.; Zhang, Y. H.; Ge, M. F.; Niu, S. Y. *Cryst. Growth Des.* **2007**, *7*, 2041.
- (39) Sun, Y. Q.; Yang, G. Y. *Dalton Trans.* **2007**, 3771.
- (40) Yue, Q.; Yang, J.; Li, G. H.; Li, G. D.; Chen, J. S. *Inorg. Chem.* **2006**, *45*, 4431.
- (41) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S. *J. Am. Chem. Soc.* **2009**, *131*, 18069.
- (42) Marchal, C.; Filinchuk, Y.; Chen, X.-Y.; Imbert, D.; Mazzanti, M. *Chem.–Eur. J.*, **2009**, *15*, 5273.
- (43) White, K. A.; Chengelis, D. A.; Zeller, M.; Geib, S. J.; Szakos, J.; Petoud, S.; Rosi, N. L. *Chem. Commun.* **2009**, 4506.
- (44) Wang, H.-Y.; Cheng, J.-Y.; Ma, J.-P.; Dong, Y.-B.; Huang, R.-Q. *Inorg. Chem.*, **2010**, *49*, 2416.
- (45) Gandara, F.; Garcia-Cortes, A.; Cascales, C.; Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, A.; Snejko, N. *Inorg. Chem.* **2007**, *46*, 3475.
- (46) Chen, B.; Yang, Y.; Zapata, F.; Qian, G.; Luo, Y.; Zhang, J.; Lobkovsky, E. B. *Inorg. Chem.* **2006**, *45*, 8882.
- (47) Herrera, J.-M.; Pope, S. J. A.; Adams, H.; Faulkner, S.; Ward, M. D. *Inorg. Chem.*, **2006**, *45*, 3895.
- (48) Guo, X.; Zhu, G.; Fang, Q.; Xue, M.; Tian, G.; Sun, J.; Li, X.; Qiu, S. *Inorg. Chem.* **2005**, *44*, 3850.
- (49) Huang, Y. Q.; Ding, B.; Song, H. B.; Zhao, B.; Ren, P.; Cheng, P.; Wang, H. G.; Liao, D. Z.; Yan S. P. *Chem. Commun.* **2006**, 4906.
- (50) (a) Wang, M. S.; Guo, S. P.; Li, Y.; Cai, L. Z.; Zou, J. P.; Xu, G.; Zhou, W. W.; Zheng, F. K.; Guo, G. C. *J. Am. Chem. Soc.* **2009**, *131*, 13572. (b) Joao, R.; Almeida, P. F. A.; Shi, F. N.; Ferreira R. A. S.; Tito, T.; Carlos, L. D. *Eur. J. Inorg. Chem.* **2009**, 4931.
- (51) (a) Bo, Q.-B.; Sun, G.-X.; Geng, D.-L. *Inorg. Chem.* **2010**, *49*, 561. (b) Wang, H.-S.; Zhao, B.; Zhai, B.; Shi, W.; Cheng, P.; Liao, D.-Z.; Yan, S.-P. *Cryst. Growth Des.*, **2007**, *7*, 1851.
- (52) (a) Wang, P.; Ma, J. P.; Dong, Y. B.; Huang, R. Q. *J. Am. Chem. Soc.* **2007**, *129*, 10620. (b) Wang, P.; Ma, J. P.; Dong, Y. B. *Chem.–Eur. J.* **2009**, *15*, 10432.
- (53) Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2008**, *130*, 6718.
- (54) (a) Harbuzaru, B. V.; Corma, A.; Rey, F.; Atienzar, P.; Jordá, J. L.; García, H.; Ananias, D.; Carlos, L. D.; Rocha, J. *Angew. Chem. Int. Ed.* **2008**, *47*, 1080. (b) Chen, B.; Yang, Y.; Zapata, F.; Lin, G.; Qian, G.; Lobkovsky, E. B. *Adv. Mater.* **2007**, *19*, 1693. (c) Guo, Z.; Xu, H.; Su, S.; Cai, J.; Dang, S.; Xiang, S.; Qian, G.; Zhang, H.; O’Keeffe, M.; Chen, B. *Chem. Commun.* **2011**, *47*, 5551.

- (55) Amghouz, Z.; Roces, L.; García-Granda, S.; García, J. R.; Souhail, B.; Mafra, L.; Fa-nian, S.; Rocha, J. *Inorg. Chem.* **2010**, 49, 7917.
- (56) CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.32.37 (release 24-10-2008 CrysAlis171 .NET) (compiled Oct 24 2008,09:44:38)
- (57) CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.37 (release 24-10-2008 CrysAlis171 .NET) (compiled Oct 24 2008,09:44:38)
- (58) Sheldrick, G. M. SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, **1997**.
- (59) Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2005**, 38, 381.
- (60) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, 28, 53.
- (61) PLATON/PLUTON - (a) Spek, A. L. *Acta Crystallogr. Sect A*, **1990**, 46, C34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.
- (62) Brandenburg, K. DIAMOND. **2007**, Version 3.1. Crystal Impact GbR, Bonn, Germany.
- (63) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.
- (64) Socrates, G. *Infrared and Raman Characteristic Group Frequencies*. 3rd ed, Wiley, Chichester, England, **2001**.
- (65) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*. 3rd ed, Chapman and Hall, London, **1975**.
- (66) Wang, Y. Y.; Shi, Q.; Shi, Q. Z.; Gao, Y. C.; Zhou, Z. Y. *Polyhedron* **1999**, 18, 2009.

Table 1. The yields based on lanthanides elements and the calculated and found percentages of C-H of the two series of compounds.

	Compound	<i>Mr</i> (g/mol)	<i>Yield</i> (%)	<i>Calc. C</i> (%)	<i>Calc. H</i> (%)	<i>Exp. C</i> (%)	<i>Exp. H</i> (%)
Series 1	C ₁₂ H ₁₂ NaSmO ₁₂	521.57	62	27.61	2.3	27.21	2.08
	C ₁₂ H ₁₂ NaEuO ₁₂	523.17	53	27.52	2.29	26.8	2.10
	C ₁₂ H ₁₂ NaGdO ₁₂	528.46	73	27.25	2.27	27.78	2.08
	C ₁₂ H ₁₂ NaTbO ₁₂	530.14	61	27.16	2.26	27.72	2.26
	C ₁₂ H ₁₂ NaDyO ₁₂	533.71	65	26.98	2.25	26.88	2.38
	C ₁₂ H ₁₂ NaHoO ₁₂	536.14	68	26.86	2.24	26.64	2.11
	C ₁₂ H ₁₂ NaErO ₁₂	538.47	50	26.74	2.23	26.91	2.33
	C ₁₂ H ₁₂ NaYbO ₁₂	544.25	18	26.46	2.21	26.2	2.13
Series 2	C ₁₈ H ₁₆ NaSmO ₁₂	597.66	51	36.14	2.68	36.32	1.99
	C ₁₈ H ₁₆ NaEuO ₁₂	599.27	71	36.04	2.67	35.8	2.60
	C ₁₈ H ₁₆ NaGdO ₁₂	604.55	65	35.73	2.65	35.07	2.57
	C ₁₈ H ₁₆ NaTbO ₁₂	606.23	64	35.63	2.64	35.15	2.41
	C ₁₈ H ₁₆ NaDyO ₁₂	609.8	71	35.42	2.62	34.83	2.84
	C ₁₈ H ₁₆ NaHoO ₁₂	612.23	72	35.28	2.61	34.98	2.48
	C ₁₈ H ₁₆ NaErO ₁₂	614.56	58	35.15	2.6	34.78	2.36
	C ₁₈ H ₁₆ NaYbO ₁₂	620.34	35	34.82	2.58	34.82	2.47

Table 2. Crystallographic data for series of compounds **S1** and **S2**.

Compound	3	4	5	6
<i>Identification code</i>	Za3	Za5	Za7	Za9
<i>Empirical formula</i>	C12 H12 Sm Na O12	C12 H12 Eu Na O12	C12 H12 Gd Na O12	C12 H12 Tb Na O12
<i>Formula weight/g mol⁻¹</i>	521.57	523.17	528.46	530.14
<i>Temperature/ K</i>	293(2)	293(2)	293(2)	293(2)
<i>Wavelength/ Å</i>	1.54184	1.54184	1.54184	1.54184
<i>Crystal system</i>	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
<i>Space group</i>	C222 ₁	C222 ₁	C222 ₁	C222 ₁
<i>Unit cell dimensions</i>				
<i>a (Å)</i>	6.94220(10)	6.9287(3)	6.920(2)	6.9031(3)
<i>b (Å)</i>	30.5658(5)	30.460(2)	30.559(7)	30.4533(11)
<i>c (Å)</i>	7.58420(10)	7.5611(4)	7.5478(14)	7.5215(2)
<i>Cell volume/ Å³</i>	1609.32(4)	1595.7(1)	1596.1(7)	1581.2(1)
<i>Z</i>	4	4	4	4
<i>Calc. Density/ mg m⁻³</i>	2.153	2.178	2.199	2.227
<i>Absorption coefficient/ mm⁻¹</i>	28.3	28.98	27.79	22.91
<i>F(000)</i>	1012	1016	1020	1024
<i>Crystal size (mm³)</i>	0.01 x 0.02 x 0.11	0.01 x 0.01 x 0.17	0.01 x 0.04 x 0.13	0.01 x 0.03 x 0.32
<i>Theta range for data collection/°</i>	5.79 to 70.52	2.89 to 71.94	5.79 to 71.49	5.81 to 70.56
<i>Index ranges</i>	-7<=h<=8, -33<=k<=36, -9<=l<=8	-8<=h<=8, -37<=k<=21, -6<=l<=9	-8<=h<=8, -37<=k<=36, -9<=l<=8	-7<=h<=8, -36<=k<=35, -9<=l<=5
<i>Reflections collected</i>	3417	2939	14896	3163
<i>Independent reflections</i>	1537 [R(int) = 0.04]	1556 [R(int) = 0.05]	1554 [R(int) = 0.06]	1498 [R(int) = 0.04]
<i>Completeness to theta_{max}</i>	99.70%	99.50%	99.80%	99.50%
<i>Absorption correction</i>	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)
<i>Max. and min. transmission</i>	0.751 and 0.275	0.772 and 0.223	0.406 and 0.146	0.853 and 0.191
<i>Refinement method</i>	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
<i>Data / restraints / parameters</i>	1537 / 5 / 133	1556 / 3 / 133	1554 / 4 / 133	1554 / 4 / 133
<i>Goodness-of-fit on F²</i>	1.101	1.131	1.023	1.101
<i>Final R indices [I>2sigma(I)]</i>	R1 = 0.0278, wR2 = 0.0700	R1 = 0.0500, wR2 = 0.1366	R1 = 0.0472, wR2 = 0.1043	R1 = 0.0409, wR2 = 0.1100
<i>R indices (all data)</i>	R1 = 0.0307, wR2 = 0.0713	R1 = 0.0549, wR2 = 0.1393	R1 = 0.0653, wR2 = 0.1140	R1 = 0.0437, wR2 = 0.1123
<i>Absolute structure parameter</i>	-0.03(3)	-0.02(1)	-0.001(13)	-0.04(8)
<i>Largest diff. peak and hole/ e.Å⁻³</i>	0.82 and -0.60	2.02 and -1.11	0.83 and -1.03	1.22 and -1.10

Compound	7	8	9	10
<i>Identification code</i>	Za11	Za13	Za15	Za17
<i>Empirical formula</i>	C12 H12 Dy Na O12	C12 H12 Ho Na O12	C12 H12 Er Na O12	C12 H12 Yb Na O12
<i>Formula weight/g mol⁻¹</i>	533.71	536.14	538.47	544.25
<i>Temperature/ K</i>	293(2)	293(2)	293(2)	293(2)
<i>Wavelength/ Å</i>	1.54184	1.54184	1.54184	1.54184
<i>Crystal system</i>	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
<i>Space group</i>	C222 ₁	C222 ₁	C222 ₁	C222 ₁
<i>Unit cell dimensions</i>				
<i>a (Å)</i>	6.89600(10)	6.8860(3)	6.8781(7)	6.8598(2)
<i>b (Å)</i>	30.4341(8)	30.3878(12)	30.389(3)	30.3257(8)
<i>c (Å)</i>	7.4984(2)	7.4722(4)	7.4593(6)	7.4274(2)
<i>Cell volume/ Å³</i>	1573.7(1)	1563.6(1)	1559.1(3)	1545.1(1)
<i>Z</i>	4	4	4	4
<i>Calc. Density/ mg m⁻³</i>	2.253	2.278	2.294	2.34
<i>Absorption coefficient/ mm⁻¹</i>	26.33	10.38	10.92	12.13
<i>F(000)</i>	1028	1032	1036	1044
<i>Crystal size (mm³)</i>	0.01 x 0.02 x 0.11	0.01 x 0.01 x 0.11	0.01 x 0.03 x 0.11	0.02 x 0.03 x 0.14
<i>Theta range for data collection/°</i>	5.82 to 68.25	5.82 to 70.61	2.91 to 70.69	5.84 to 68.17
<i>Index ranges</i>	-8<=h<=8, -34<=k<=36, -7<=l<=8	-8<=h<=6, -36<=k<=36, -8<=l<=8	-8<=h<=6, -36<=k<=36, -8<=l<=9	-7<=h<=8, -35<=k<=36, -8<=l<=4
<i>Reflections collected</i>	4447	3015	7667	2809
<i>Independent reflections</i>	1429 [R(int) = 0.06]	1460 [R(int) = 0.05]	1508 [R(int) = 0.06]	1405 [R(int) = 0.03]
<i>Completeness to theta_{max}</i>	99.20%	99.60%	99.80%	99.70%
<i>Absorption correction</i>	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)
<i>Max. and min. transmission</i>	0.771 and 0.264	1 and 0.464	0.838 and 0.445	0.756 and 0.541
<i>Refinement method</i>	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
<i>Data / restraints / parameters</i>	1429 / 4 / 133	1460 / 5 / 133	1508 / 5 / 133	1405 / 5 / 133
<i>Goodness-of-fit on F²</i>	1.032	0.985	0.987	1.078
<i>Final R indices [I>2sigma(I)]</i>	R1 = 0.0297, wR2 = 0.0637	R1 = 0.0353, wR2 = 0.0736	R1 = 0.0297, wR2 = 0.0560	R1 = 0.0204, wR2 = 0.0439
<i>R indices (all data)</i>	R1 = 0.0345, wR2 = 0.0660	R1 = 0.0428, wR2 = 0.0776	R1 = 0.0378, wR2 = 0.0575	R1 = 0.0222, wR2 = 0.0446
<i>Absolute structure parameter</i>	-0.004(10)	-0.03(2)	-0.02(2)	-0.02(2)
<i>Largest diff. peak and hole/ e.Å⁻³</i>	0.55 and -0.64	0.65 and -0.52	0.57 and -0.64	0.47 and -0.64

Compound	11	12	13	14
<i>Identification code</i>	Za4	Za6	Za8	Za10
<i>Empirical formula</i>	C18 H16 Sm Na O12	C18 H16 Eu Na O12	C18 H16 Gd Na O12	C18 H16 Tb Na O12
<i>Formula weight/g mol⁻¹</i>	597.66	599.27	604.55	606.23
<i>Temperature/K</i>	293(2)	293(2)	293(2)	293(2)
<i>Wavelength/Å</i>	1.54184	1.54184	1.54184	1.54184
<i>Crystal system</i>	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
<i>Space group</i>	C222 ₁	C222 ₁	C222 ₁	C222 ₁
<i>Unit cell dimensions</i>				
<i>a (Å)</i>	6.9094(2)	6.8969(4)	6.89120(10)	6.8767(2)
<i>b (Å)</i>	39.2050(8)	39.176(2)	39.1425(5)	39.1054(14)
<i>c (Å)</i>	7.5963(2)	7.5752(4)	7.55970(10)	7.5359(3)
<i>Cell volume/Å³</i>	2057.7(1)	2046.8(2)	2039.15(5)	2026.5(1)
<i>Z</i>	4	4	4	4
<i>Calc. Density/mg m⁻³</i>	1.929	1.945	1.969	1.987
<i>Absorption coefficient/mm⁻¹</i>	22.24	22.75	21.86	17.98
<i>F(000)</i>	1172	1176	1180	1184
<i>Crystal size (mm³)</i>	0.01 x 0.04 x 0.25	0.01 x 0.02 x 0.19	0.03 x 0.09 x 0.12	0.01 x 0.02 x 0.22
<i>Theta range for data collection/°</i>	3.38 to 70.37	4.51 to 70.62	4.52 to 70.57	3.38 to 70.30
<i>Index ranges</i>	-8<=h<=7, -47<=k<=47, -7<=l<=9	-8<=h<=8, -43<=k<=47, -9<=l<=9	-7<=h<=8, -38<=k<=47, -9<=l<=9	-8<=h<=8, -47<=k<=34, -8<=l<=6
<i>Reflections collected</i>	5933	5895	9182	3722
<i>Independent reflections</i>	1958 [R(int) = 0.03]	1951 [R(int) = 0.05]	1960 [R(int) = 0.03]	1874 [R(int) = 0.04]
<i>Completeness to theta_{max}</i>	99.40%	99.80%	99.90%	99.10%
<i>Absorption correction</i>	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)
<i>Max. and min. transmission</i>	1 and 0.288	0.721 and 0.450	0.538 and 0.186	1 and 0.944
<i>Refinement method</i>	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
<i>Data / restraints / parameters</i>	1958 / 5 / 161	1951 / 3 / 161	1960 / 4 / 161	1960 / 4 / 161
<i>Goodness-of-fit on F²</i>	1.041	1.058	1.083	0.934
<i>Final R indices [I>2sigma(I)]</i>	R1 = 0.0181, wR2 = 0.0412	R1 = 0.0314, wR2 = 0.0701	R1 = 0.0152, wR2 = 0.0369	R1 = 0.0282, wR2 = 0.0563
<i>R indices (all data)</i>	R1 = 0.0196, wR2 = 0.0417	R1 = 0.0357, wR2 = 0.0732	R1 = 0.0153, wR2 = 0.0370	R1 = 0.0355, wR2 = 0.0575
<i>Absolute structure parameter</i>	-0.02(1)	-0.03(1)	-0.006(3)	-0.013(7)
<i>Largest diff. peak and hole/ e.Å⁻³</i>	0.46 and -0.28	0.54 and -0.55	0.44 and -0.36	0.91 and -0.65

Compound	15	16	17	18
<i>Identification code</i>	Za12	Za14	Za16	Za18
<i>Empirical formula</i>	C18 H16 Dy Na O12	C18 H16 Ho Na O12	C18 H16 Er Na O12	C18 H16 Yb Na O12
<i>Formula weight/g mol⁻¹</i>	609.8	612.23	614.56	620.34
<i>Temperature/K</i>	293(2)	293(2)	293(2)	293(2)
<i>Wavelength/Å</i>	1.54184	1.54184	1.54184	1.54184
<i>Crystal system</i>	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
<i>Space group</i>	C222 ₁	C222 ₁	C222 ₁	C222 ₁
<i>Unit cell dimensions</i>				
<i>a (Å)</i>	6.8673(2)	6.8571(2)	6.8454(2)	6.8290(1)
<i>b (Å)</i>	39.0815(9)	39.0412(13)	39.0033(10)	38.9781(6)
<i>c (Å)</i>	7.5196(2)	7.4984(2)	7.4816(2)	7.4568(1)
<i>Cell volume/Å³</i>	2018.1(1)	2007.4(1)	1997.5(1)	1984.86(5)
<i>Z</i>	4	4	4	4
<i>Calc. Density/mg m⁻³</i>	2.007	2.026	2.043	2.076
<i>Absorption coefficient/mm⁻¹</i>	20.64	8.19	8.65	9.56
<i>F(000)</i>	1188	1192	1196	1204
<i>Crystal size (mm³)</i>	0.01 x 0.03 x 0.17	0.01 x 0.01 x 0.12	0.01 x 0.02 x 0.21	0.02 x 0.03 x 0.20
<i>Theta range for data collection/°</i>	4.53 to 73.35	4.53 to 71.83	4.53 to 70.51	4.54 to 70.47
<i>Index ranges</i>	-7<=h<=8, -48<=k<=47, -6<=l<=9	-7<=h<=8, -47<=k<=42, -9<=l<=7	-8<=h<=8, -47<=k<=46, -9<=l<=8	-7<=h<=8, -47<=k<=35, -9<=l<=3
<i>Reflections collected</i>	3871	3900	5476	4026
<i>Independent reflections</i>	1991 [R(int) = 0.03]	1943 [R(int) = 0.03]	1901 [R(int) = 0.05]	1886 [R(int) = 0.03]
<i>Completeness to theta_{max}</i>	99.60%	99.60%	99.70%	99.80%
<i>Absorption correction</i>	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)	Refined (XABS2)
<i>Max. and min. transmission</i>	0.851 and 0.264	0.953 and 0.627	1 and 0.928	0.742 to 0.493
<i>Refinement method</i>	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
<i>Data / restraints / parameters</i>	1991 / 5 / 161	1943 / 4 / 161	1901 / 5 / 161	1886 / 5 / 161
<i>Goodness-of-fit on F²</i>	1.085	1.083	1.023	1.061
<i>Final R indices [I>2sigma(I)]</i>	R1 = 0.0302, wR2 = 0.0802	R1 = 0.0304, wR2 = 0.0766	R1 = 0.0299, wR2 = 0.0667	R1 = 0.0273, wR2 = 0.0681
<i>R indices (all data)</i>	R1 = 0.0325, wR2 = 0.0816	R1 = 0.0347, wR2 = 0.0780	R1 = 0.0342, wR2 = 0.0688	R1 = 0.0297, wR2 = 0.0694
<i>Absolute structure parameter</i>	-0.001(8)	-0.03(1)	-0.04(2)	-0.03(2)
<i>Largest diff. peak and hole/e.Å⁻³</i>	0.73 and -1.23	0.98 and -0.39	0.90 and -0.70	2.19 and -0.53

Table 3. Selected bond lengths (Å) and bond angles (°) for series of compounds **S1** and **S2**.

	Za3 (Ln = Sm)	Za5 (Ln = Eu)	Za7 (Ln = Gd)	Za9 (Ln = Tb)	Za11 (Ln = Dy)	Za13 (Ln = Ho)	Za15 (Ln = Er)	Za17 (Ln = Yb)
Ln1—O1	2.433 (3)	2.422(6)	2.410 (6)	2.402 (4)	2.391 (3)	2.381 (3)	2.371 (3)	2.343 (3)
Ln1—O3	2.449 (4)	2.444(7)	2.423 (6)	2.418 (6)	2.400 (4)	2.383 (5)	2.363 (4)	2.350 (3)
Ln1—O4	2.341 (4)	2.313(7)	2.412 (6)	2.301 (5)	2.296 (4)	2.282 (4)	2.277 (4)	2.252 (3)
Ln1—O5	2.407 (4)	2.396(6)	2.385 (6)	2.373 (5)	2.359 (4)	2.340 (4)	2.332 (4)	2.313 (3)
Na1—O1	2.427 (3)	2.419(6)	2.412 (6)	2.409 (5)	2.411 (3)	2.392 (3)	2.396 (3)	2.388 (3)
Na1—O4	2.565 (5)	2.557(8)	2.562 (8)	2.545 (7)	2.543 (5)	2.551 (4)	2.542 (4)	2.530 (4)
Na1—O6	2.310 (6)	2.306(9)	2.302 (9)	2.310 (7)	2.307 (5)	2.299 (5)	2.294 (5)	2.305 (4)
Ln1—Na1	3.861(1)	3.850(2)	3.848(2)	3.834(2)	3.824(1)	3.821(1)	3.813(1)	3.798(1)
C1—O1	1.267 (5)	1.260(8)	1.267 (8)	1.259 (7)	1.256 (5)	1.267 (5)	1.264 (4)	1.262 (4)
O1—C1—O1	119.4 (6)	120.7(11)	119.4 (10)	119.9 (8)	119.9 (6)	119.8 (6)	119.0 (5)	118.7 (4)
C6—O2	1.256 (6)	1.254(9)	1.260 (9)	1.249 (8)	1.260 (5)	1.264 (5)	1.249 (5)	1.258 (4)
O2—C6—O2	123.1 (7)	122.4(12)	122.6 (11)	122.6 (9)	122.2 (7)	122.2 (6)	123.2 (6)	122.9 (5)
C7—O3	1.433 (7)	1.440(11)	1.417 (11)	1.419 (10)	1.423 (7)	1.416 (7)	1.435 (6)	1.430 (5)
C8—O4	1.262 (7)	1.274(12)	1.275 (11)	1.281 (9)	1.261 (7)	1.257 (7)	1.266 (7)	1.270 (6)
C8—O5	1.251 (8)	1.235(11)	1.248 (12)	1.242 (9)	1.245 (7)	1.253 (8)	1.244 (7)	1.241 (6)
O5—C8—O4	124.3 (5)	125.7(4)	124.9 (9)	124.0 (7)	125.0 (6)	125.5 (6)	125.1 (5)	125.4 (4)
	Za4 (Ln = Sm)	Za6 (Ln = Eu)	Za8 (Ln = Gd)	Za10 (Ln = Tb)	Za12 (Ln = Dy)	Za14 (Ln = Ho)	Za16 (Ln = Er)	Za18 (Ln = Yb)
Ln1—O1	2.439 (2)	2.426(3)	2.4152 (14)	2.399 (3)	2.393 (3)	2.380 (3)	2.369 (3)	2.353 (3)
Ln1—O3	2.446 (2)	2.442(4)	2.4240 (16)	2.399 (4)	2.392 (4)	2.388 (3)	2.371 (4)	2.353 (4)
Ln1—O4	2.337 (2)	2.317(4)	2.3196 (16)	2.296 (3)	2.285 (3)	2.288 (3)	2.261 (4)	2.249 (4)
Ln1—O5	2.399 (2)	2.393(4)	2.3813 (15)	2.360 (3)	2.354 (3)	2.344 (3)	2.338 (3)	2.322 (4)
Na1—O1	2.415 (2)	2.403(3)	2.4027 (15)	2.399 (3)	2.395 (3)	2.387 (3)	2.385 (3)	2.377 (3)
Na1—O4	2.571 (2)	2.569(4)	2.5636 (19)	2.560 (4)	2.553 (4)	2.545 (4)	2.544 (4)	2.529 (4)
Na1—O6	2.308 (3)	2.307(5)	2.310 (2)	2.307 (4)	2.302 (5)	2.314 (4)	2.314 (4)	2.314 (5)
Ln1—Na1	3.849(1)	3.841(1)	3.835(1)	3.824(1)	3.818(1)	3.808(1)	3.799(1)	3.786(1)
C1—O1	1.262 (3)	1.273(4)	1.268 (2)	1.266 (4)	1.263 (4)	1.268 (4)	1.267 (4)	1.265 (4)
O1—C1—O1	120.4 (3)	119.4(5)	119.4 (2)	119.2 (5)	119.2 (5)	119.2 (4)	118.5 (5)	118.6 (5)
C10—O2	1.259 (3)	1.267(5)	1.259 (2)	1.253 (5)	1.256 (5)	1.260 (4)	1.262 (5)	1.250 (5)
O2—C10—O2	122.5 (4)	122.5(6)	122.8 (3)	122.9 (6)	123.1 (6)	123.3 (5)	122.2 (5)	122.8 (6)
C11—O3	1.429 (4)	1.424(7)	1.429 (3)	1.435 (6)	1.422 (6)	1.427 (5)	1.422 (6)	1.429 (6)
C12—O4	1.269 (4)	1.273(7)	1.264 (3)	1.274 (6)	1.280 (6)	1.261 (5)	1.274 (6)	1.279 (6)
C12—O5	1.252 (4)	1.245(6)	1.244 (3)	1.247 (6)	1.245 (6)	1.244 (5)	1.240 (6)	1.238 (6)
O5—C12—O4	124.4 (3)	124.8(5)	124.5 (2)	125.4 (5)	124.8 (5)	125.1 (4)	125.2 (5)	124.7 (5)

Table 4. Hydrogen-bond geometry in series of compounds **S1** and **S2**.

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
Za3				
O3-H3O...O2 ⁽¹⁾	0.83	1.8	2.62	168
O6-H6A...O2 ⁽¹⁾	0.95	1.98	2.866	153
O6-H6B...O2 ⁽²⁾	0.97	2.21	3.145	163
Za4				
O3-H3O...O2 ⁽¹⁾	0.83	1.78	2.61	176
O6-H6A...O2 ⁽³⁾	0.96	1.91	2.822	158
O6-H6B...O2 ⁽⁴⁾	0.98	2.32	3.193	148
Za5				
O3-H3O...O2 ⁽⁵⁾	0.84	1.79	2.611	165
O6-H6A...O2 ⁽⁵⁾	0.97	1.97	2.849	151
O6-H6B...O2 ⁽⁶⁾	0.97	2.2	3.148	167
Za6				
O3-H3O...O2 ⁽⁵⁾	0.85	1.78	2.612	169
O6-H6A...O2 ⁽⁷⁾	0.97	1.93	2.81	150
O6-H6B...O2 ⁽⁸⁾	0.99	2.33	3.177	144
Za7				
O3-H3O...O2 ⁽⁵⁾	0.84	1.81	2.63	164
O6-H6A...O2 ⁽⁷⁾	0.97	1.88	2.853	177
O6-H6B...O2 ⁽⁸⁾	0.97	2.3	3.137	145
Za8				
O3-H3O...O2 ⁽⁵⁾	0.84	1.77	2.605	174
O6-H6A...O2 ⁽⁹⁾	0.94	1.94	2.816	155
O6-H6B...O2 ⁽⁸⁾	0.95	2.32	3.18	149
Za9				
O3-H3O...O2 ⁽⁵⁾	0.86	1.76	2.612	171
O6-H6A...O2 ⁽⁷⁾	0.97	1.92	2.845	157
O6-H6B...O2 ⁽⁸⁾	0.97	2.21	3.132	159
Za10				
O3-H3O...O2 ⁽⁵⁾	0.84	1.78	2.616	174
O6-H6A...O2 ⁽⁷⁾	0.97	2.05	2.81	134
O6-H6B...O2 ⁽⁸⁾	0.94	2.36	3.174	144

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
Za11				
O3-H3O...O2 ⁽¹⁰⁾	0.86	1.77	2.624	178
O6-H6A...O2 ⁽¹¹⁾	0.99	2.18	3.13	162
O6-H6B...O2 ⁽¹⁰⁾	0.98	2.06	2.84	135
Za12				
O3-H3O...O2 ⁽⁵⁾	0.84	1.79	2.62	173
O6-H6A...O2 ⁽⁸⁾	0.98	2.33	3.178	144
O6-H6B...O2 ⁽⁹⁾	0.99	1.9	2.793	149
Za13				
O3-H3O...O2 ⁽⁵⁾	0.86	1.77	2.622	172
O6-H6A...O2 ⁽⁹⁾	0.97	1.97	2.827	147
O6-H6B...O2 ⁽⁸⁾	0.97	2.19	3.126	162
Za14				
O3-H3O...O2 ⁽⁵⁾	0.86	1.76	2.613	168
O6-H6A...O2 ⁽⁸⁾	0.96	2.24	3.149	158
O6-H6B...O2 ⁽⁷⁾	0.98	1.93	2.801	148
Za15				
O3-H3O...O2 ⁽¹⁾	0.84	1.81	2.633	169
O6-H6A...O2 ⁽³⁾	0.97	2.24	3.13	153
O6-H6B...O2 ⁽¹⁾	0.97	1.9	2.84	162
Za16				
O3-H3O...O2 ⁽⁵⁾	0.85	1.77	2.613	172
O6-H6A...O2 ⁽⁵⁾	0.97	1.93	2.772	144
O6-H6B...O2 ⁽⁶⁾	0.97	2.28	3.174	154
Za17				
O3-H3O...O2 ⁽¹⁾	0.83	1.81	2.623	165
O6-H6A...O2 ⁽¹⁾	0.96	1.87	2.816	170
O6-H6B...O2 ⁽²⁾	0.96	2.27	3.116	146
Za18				
O3-H3O...O2 ⁽¹⁾	0.85	1.77	2.615	172
O6-H6A...O2 ⁽²⁾	0.98	2.31	3.171	146
O6-H6B...O2 ⁽³⁾	0.98	1.88	2.774	150

FIGURE CAPTIONS

Figure 1. SEM images of the two series of compounds.

Figure 2. Powder XRD patterns of compounds **S1** (a) and **S2** (b), compared with the theoretical ones for **Za11** and **Za12**, respectively.

Figure 3. Variation of cell parameters (*a*, *b*, and *c*), volume, and distance Ln-Na vs. Shannon's ionic radii (Å) of Ln³⁺ cations in the two series of compounds.

Figure 4. Projection of the structure of compounds **S1** (a, c) and **S2** (b, d) along *a* and *c*-axis.

Figure 5. Perspective view of the coordination environment of : Ln³⁺ in **S1** (a, b) and **S2** (b, c), and Na⁺ in **S1** (d, e) and **S2** (e, f). Coordination modes of **Tart**²⁻, **BDC**²⁻ and **biBDC**²⁻ ligands (g).

Figure 6. IR spectra of compounds **S1** (a) and **S2** (b).

Figure 7. Comparison TG curves for each series of compounds **S1**(a) or **S2** (b).

Figure 8. X-ray thermodiffractogram of **Za7** (a), **Za13** (b) and **Za16** (c) recorded in air heating up from 25 °C to 200 °C and cooling down to 25 °C. Colour code corresponding to the structural changes, blue: **Za7**, **Za13** or **Za16**, pink: dehydration of **Za7**, **Za13** or **Za16**, red: dehydrated **Za7**, **Za13** or **Za16**, green: rehydration **Za7**, **Za13** or **Za16**, blue: rehydrated **Za7** or **Za13**. X-ray thermodiffractogram of **Za16** (d) recorded in vacuum heating up from 50 °C to 900 °C, the colour code corresponding to the structural changes.

Figure 9. Catalytic activity of **Za15** and **Za17** in the acetalization of benzaldehyde compared with that of yttrium-based compound (**Za1**) as a time function (a), and catalytic activity after 100 hours (b).

Figure 10. Digital photographs under UV radiation (254 nm) of **Za3**-red (a), **Za4**-pink (b), **Za9**-green (c, d), **Za5**-red (e, f), **Za11**-yellowish-orange (g), **Za12**-blue (h), **Za13**-deep-purple (i), and **Tb-doped-Y-compound**-yellow (j). Photographs (d) and (f) were taken by optical microscopy.

Figure 11. Excitation spectra of **Za6** (a), **Za5** (b) and **DZa7** (c) monitored within 616-618 nm. The spectrum of **Za6** monitored at 420 nm is also shown (solid line and open circles); the asterisk denotes the intra-4f⁶ self absorption ascribed to the ⁷F₀→⁵L₆ transition. The inset shows a magnification of the ⁷F₀→⁵D_{0,1} transitions for **DZa7**.

Figure 12. Emission spectra of **Za6** (a), **Za5** (b) and **DZa7** (c) under different excitation wavelengths. The insets show a magnification of the (left) ⁵D₀→⁷F₀

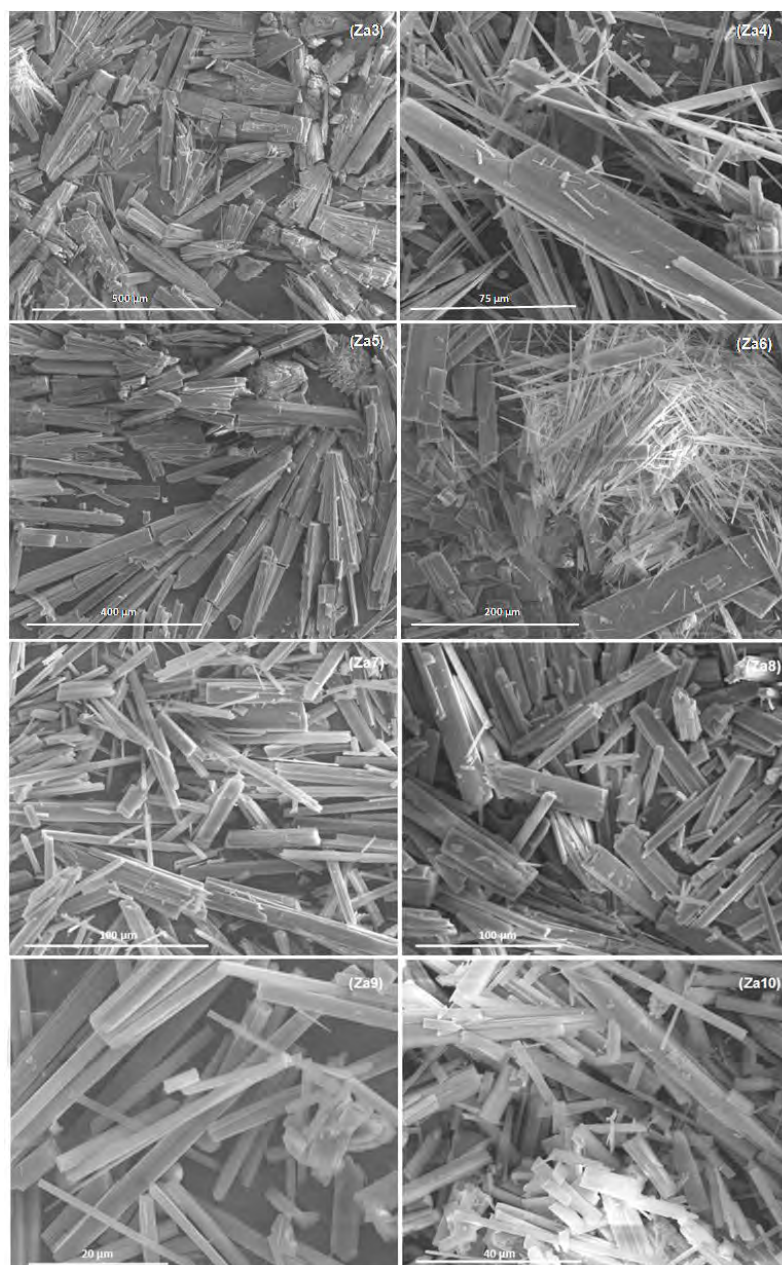
transitions excited at 393 nm and (right) the broad emission observed for **Za6**: (*) and (**) denote the intra-4f⁶ self absorptions ascribed to the ${}^7F_0 \rightarrow {}^5L_6$, 5D_2 transitions. The excitation wavelengths were 270 nm (black line), 315 nm (red line) and 393 nm (blue line).

Figure 13. Emission decay curves of **Za6** (1, pen circles) and **Za5** (2, solid squares) (a) and of **DZa7** monitored at 616 nm and excited at 395 nm (b). The solid lines represent the data best fit using a single exponential function. The respective residual plots and the reduced- χ^2 (χ^2_{red}) values are also shown for a better judgment of the fits quality.

Figure 14. Emission spectra of **Za12** (a) and **Za11** (b) excited at (1) 270 nm, (2) 340-350 nm. The insets show the excitation spectra monitored at (3) 410 nm and (4) 575 nm.

Figure 15. Emission spectra of (1) **Za16** and (2) **Za14** excited at 325 nm.

Figure 16. Excitation (dashed line) and NIR emission (solid line) spectra of (1) **Za16** and (2) **Za15** monitored around 1530 nm and excited at 325 nm, respectively.



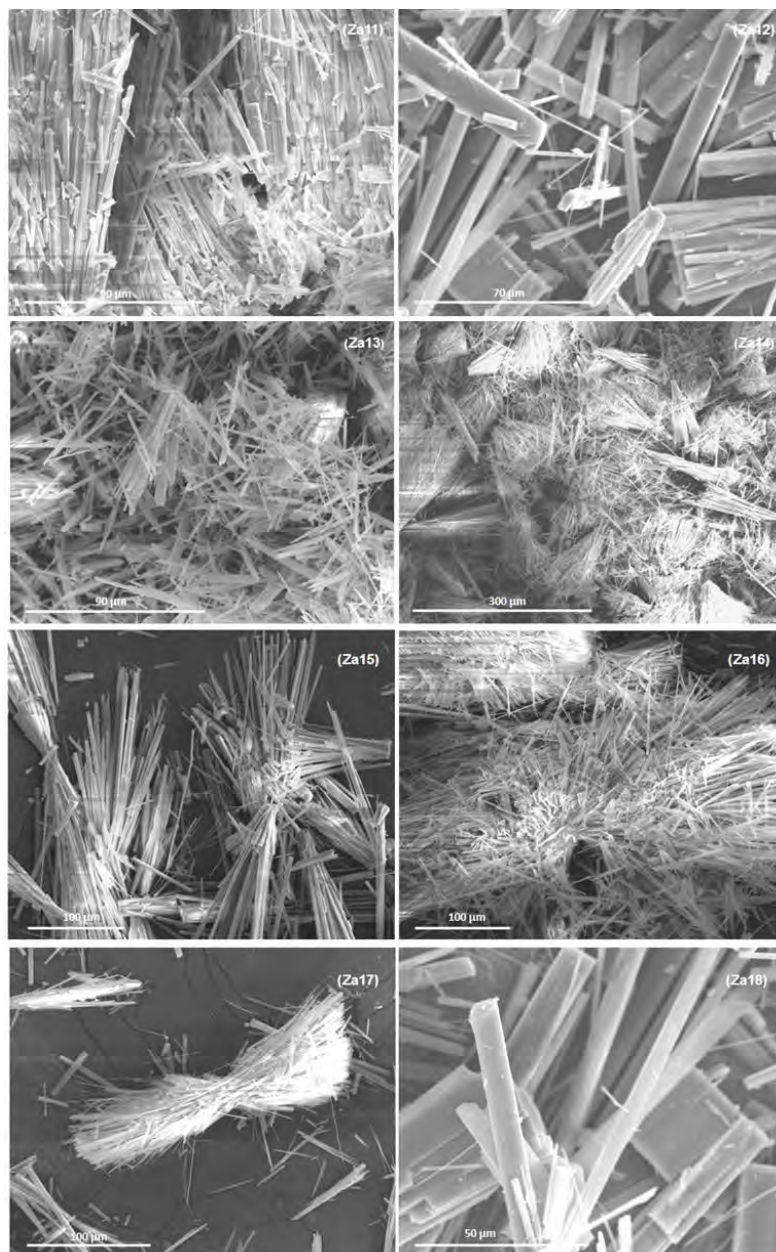


Figure 1

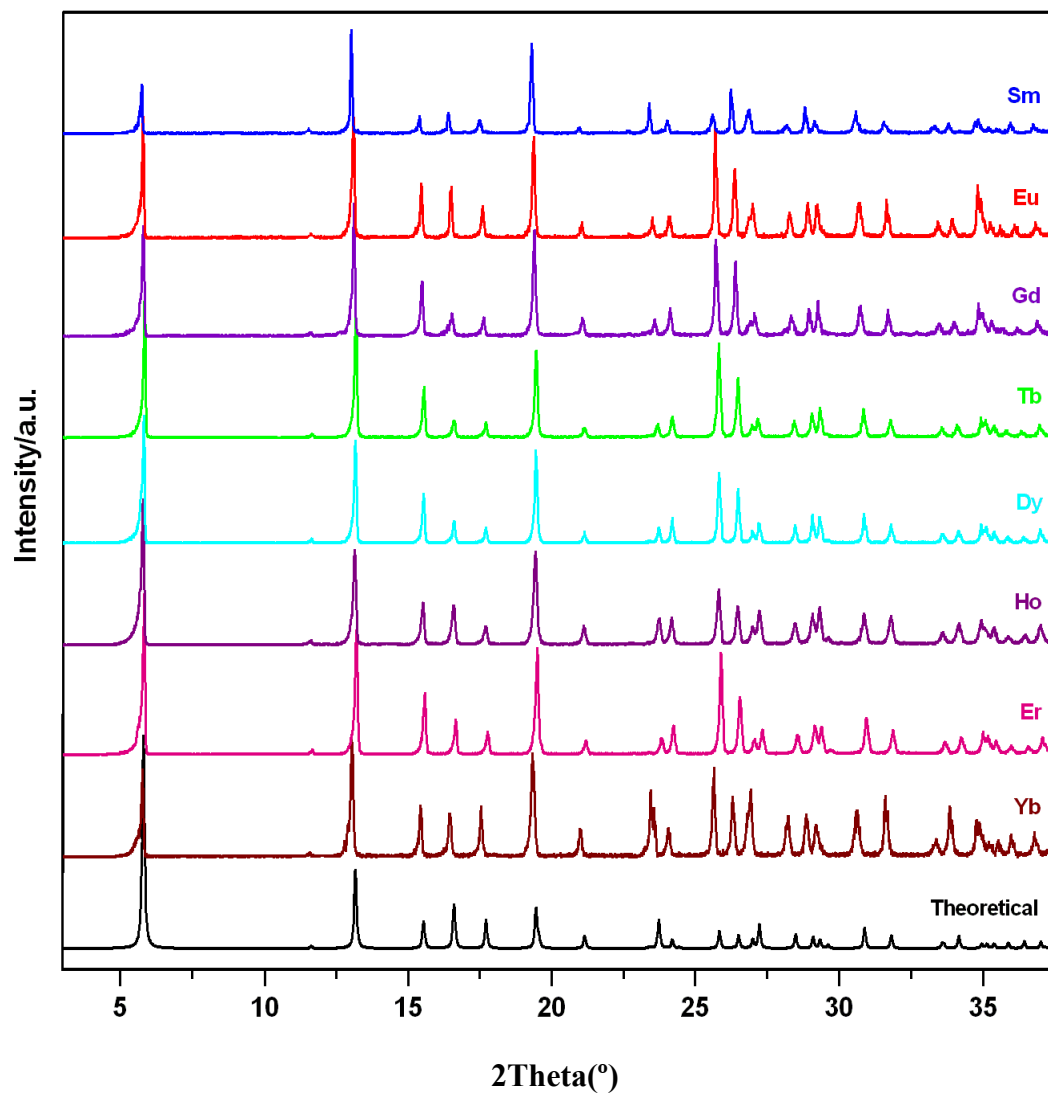


Figure 2a

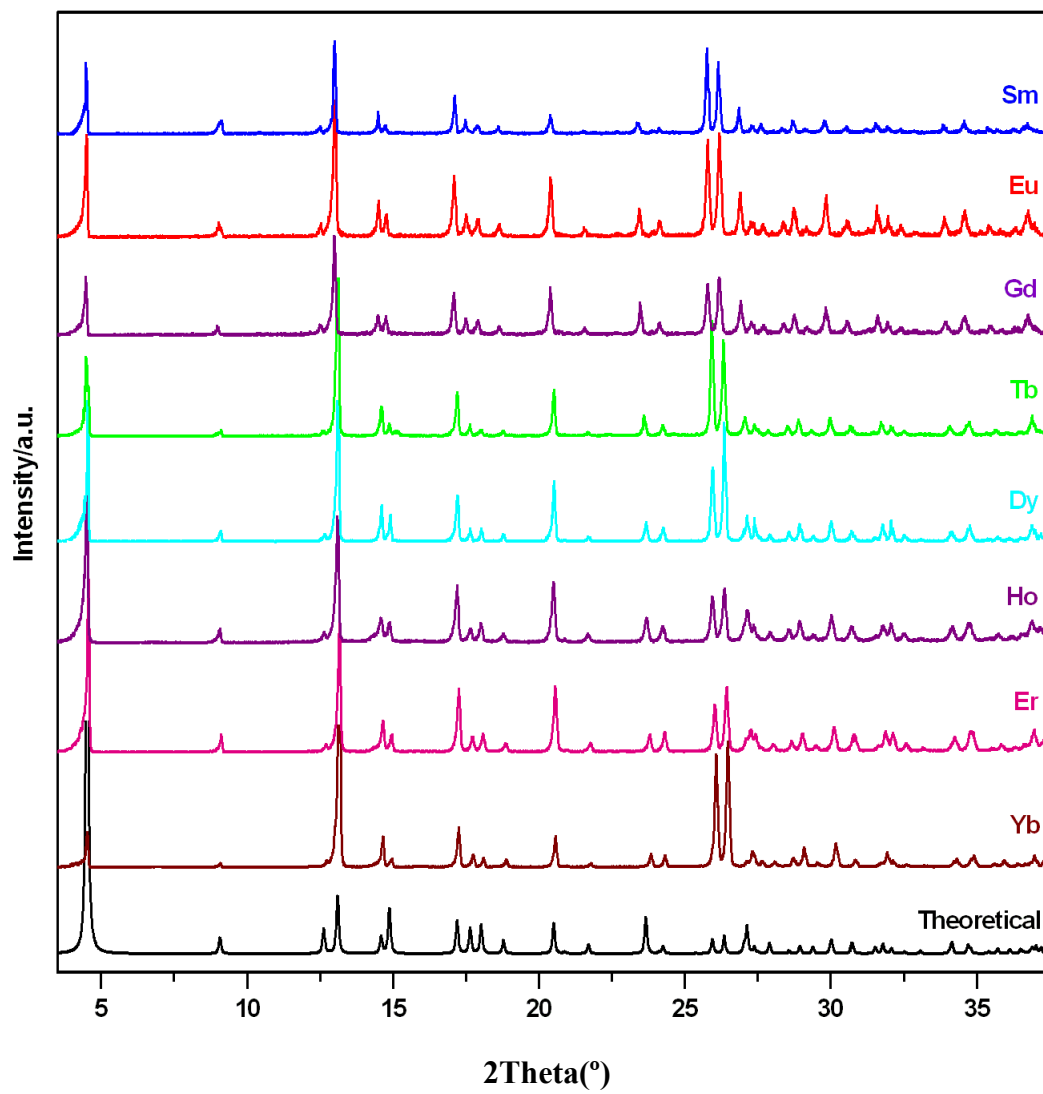


Figure 2b

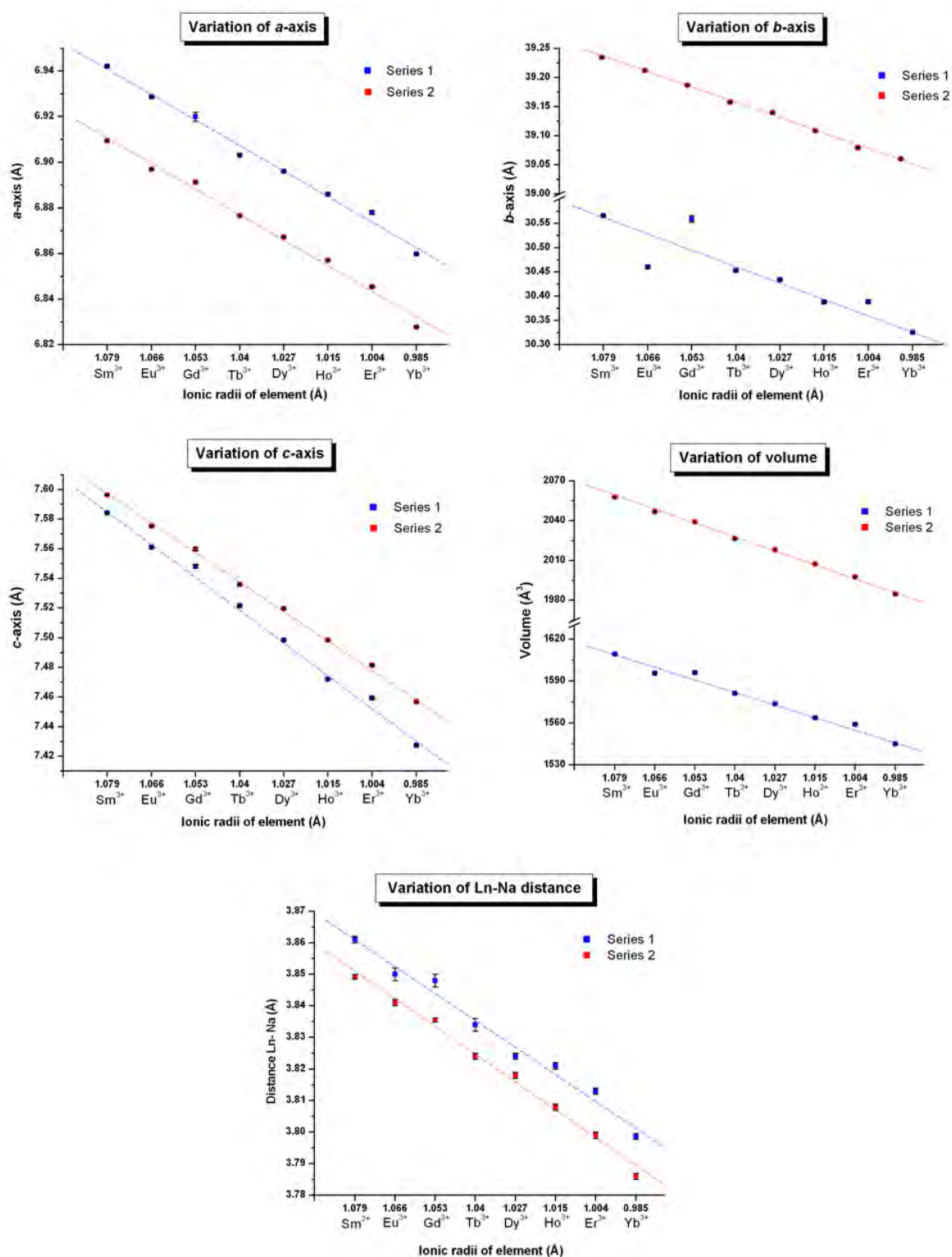


Figure 3

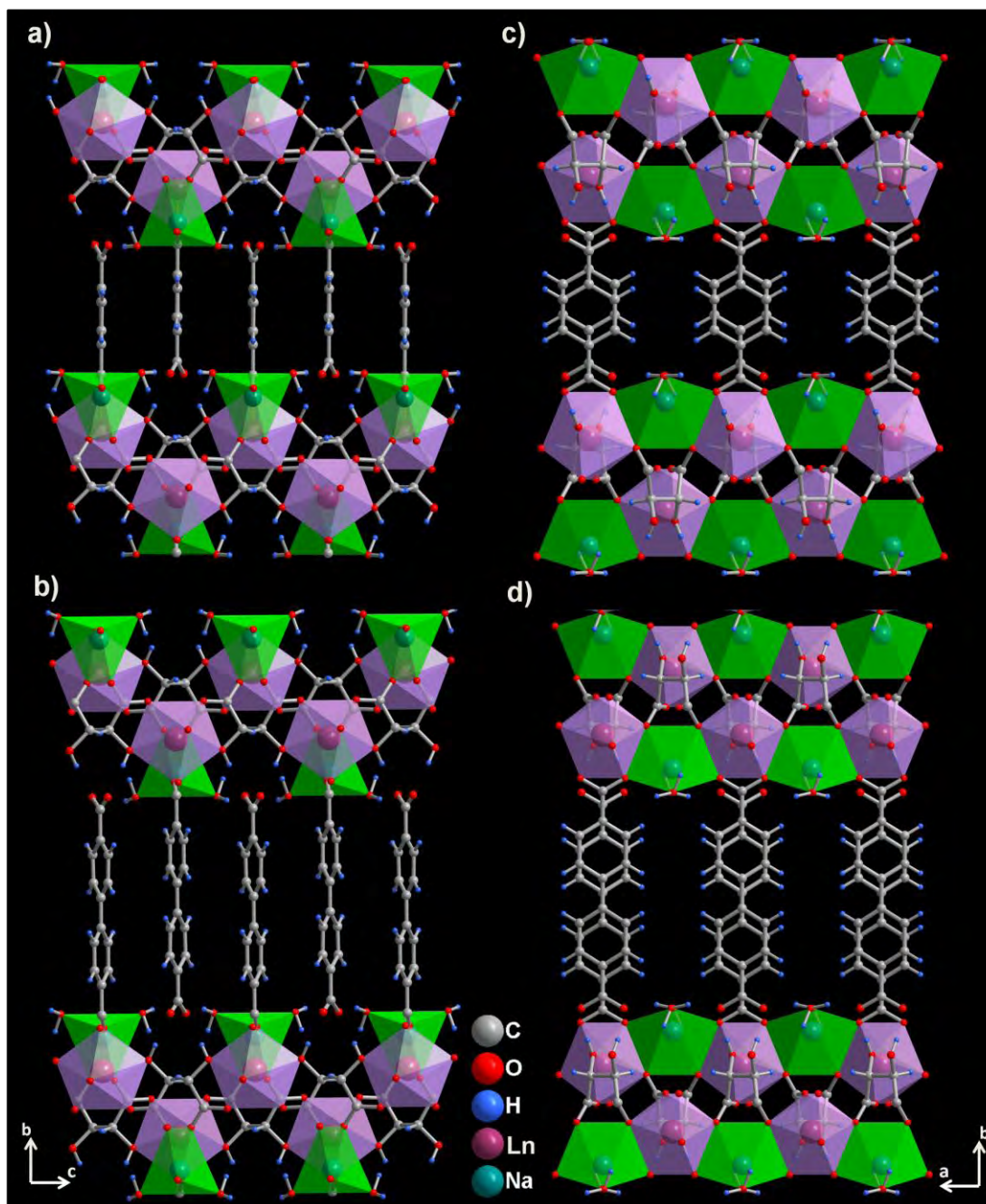


Figure 4

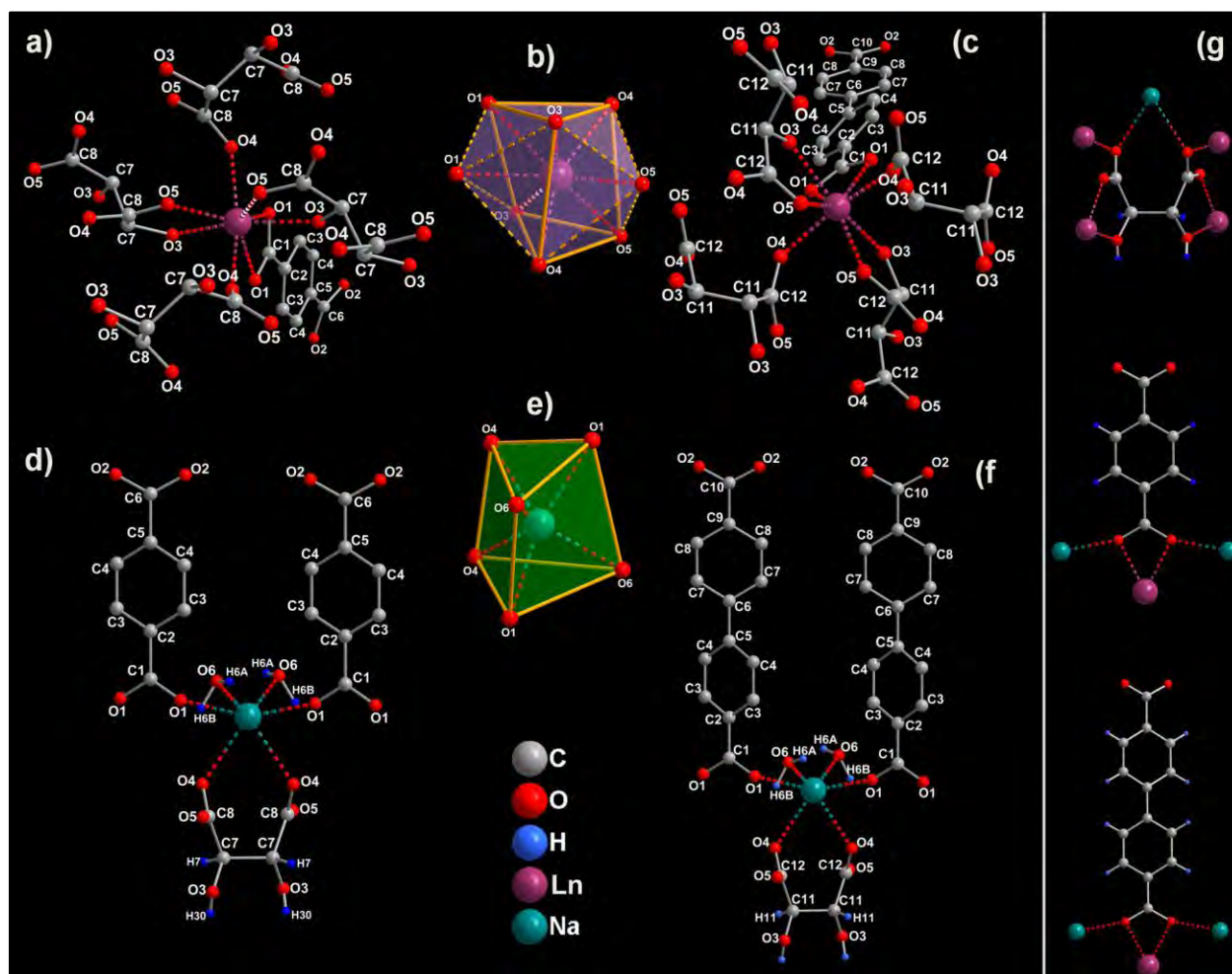


Figure 5

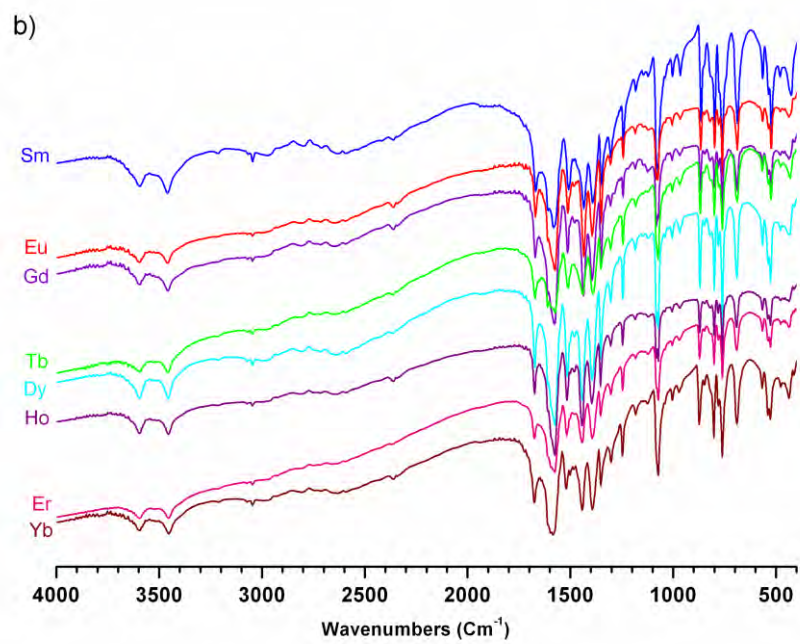
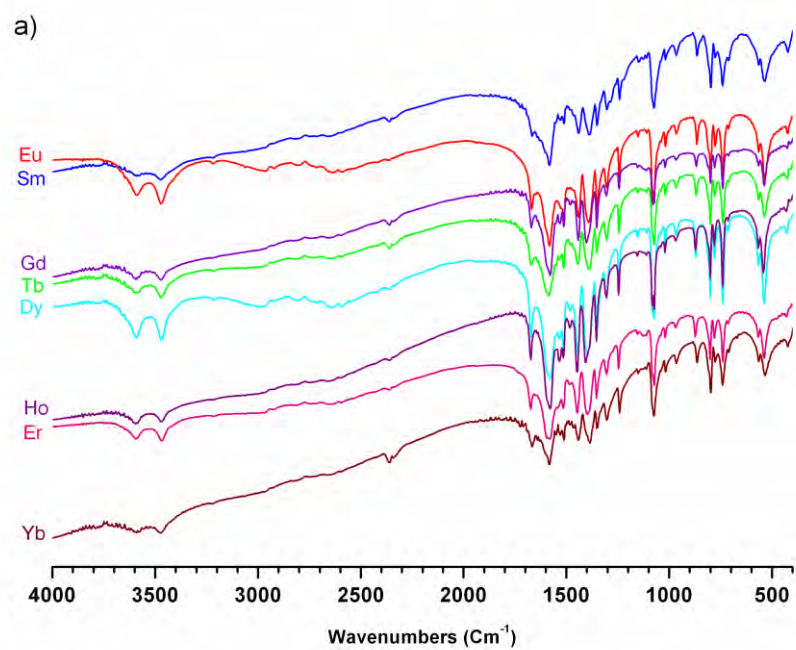


Figure 6

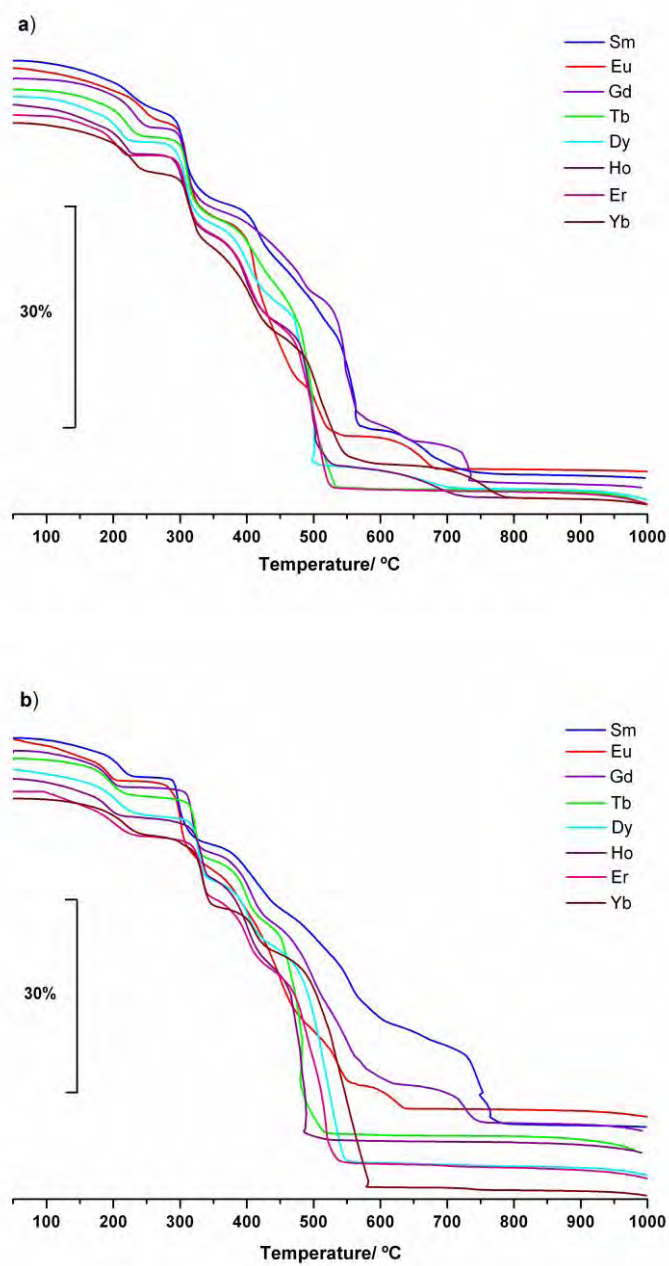


Figure 7

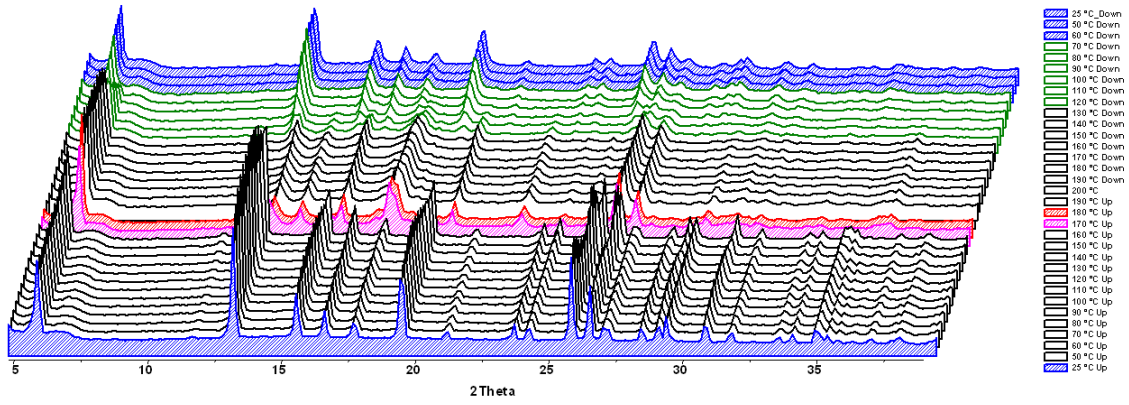


Figure 8a

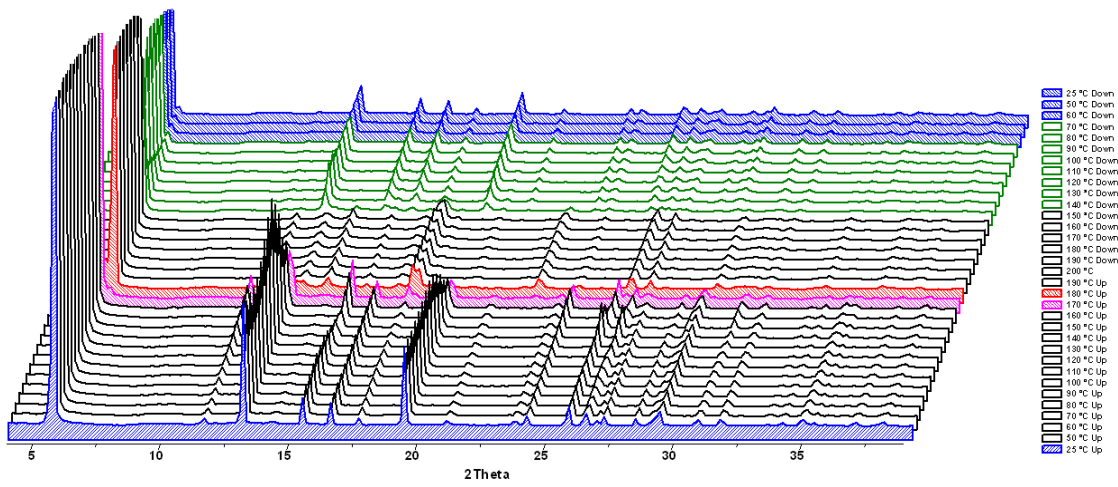


Figure 8b

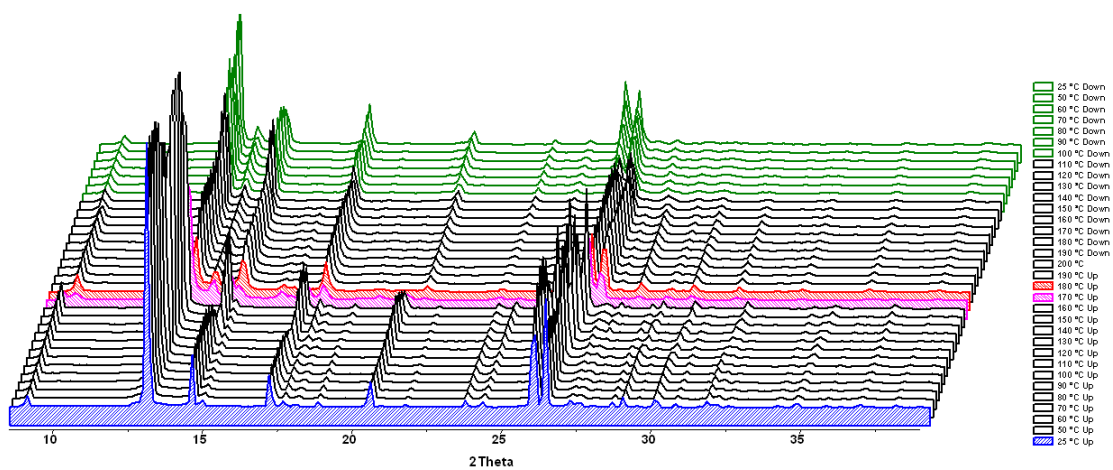


Figure 8c

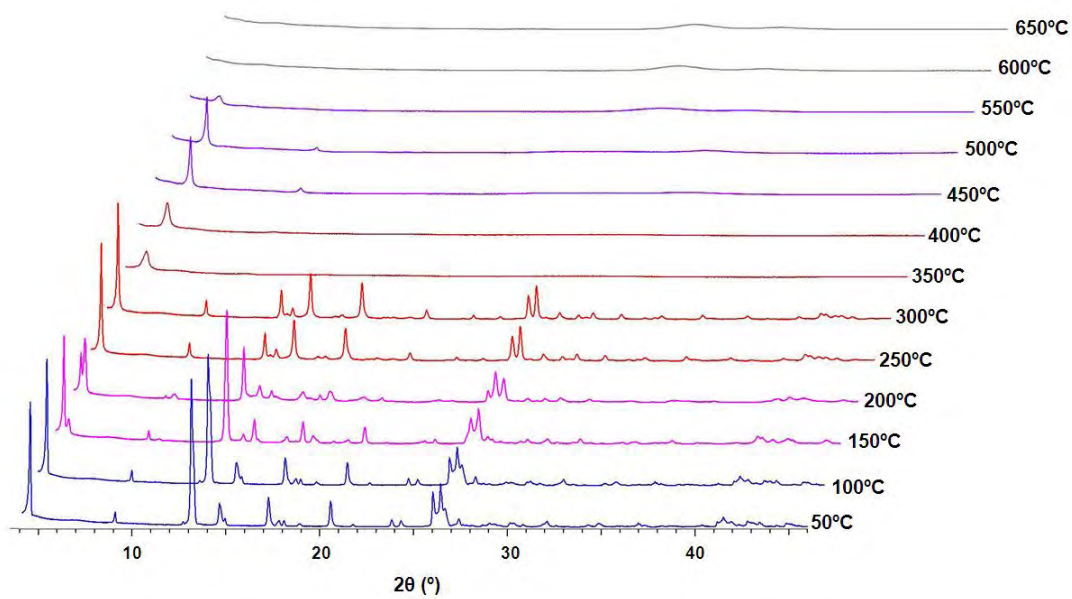


Figure 8d

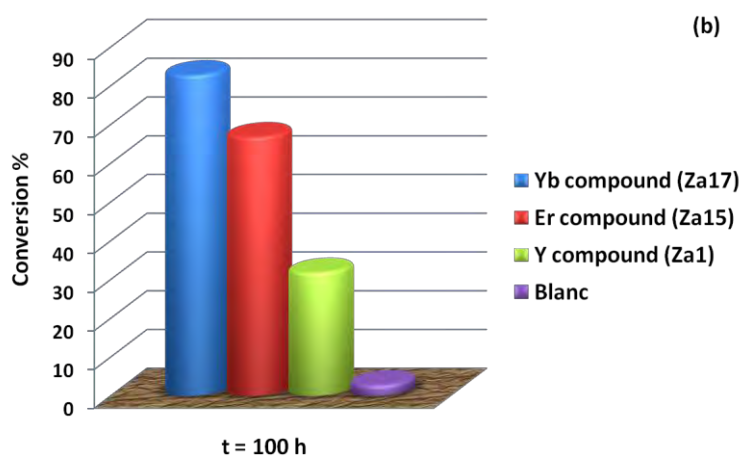
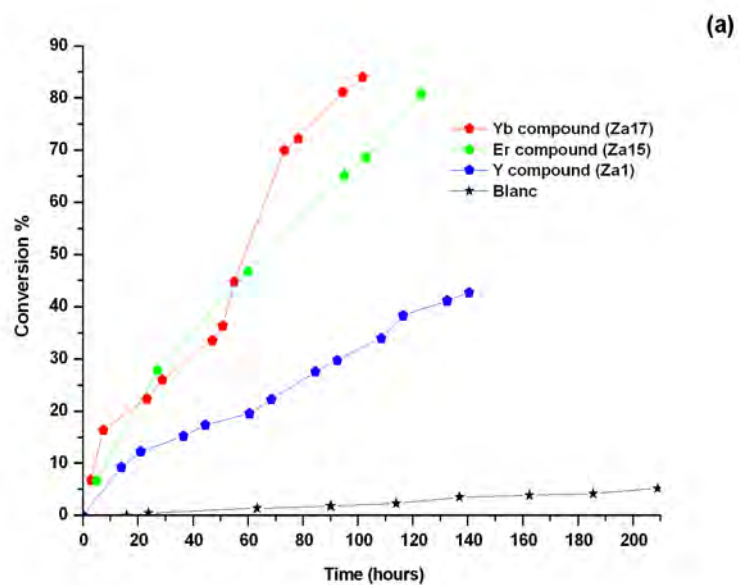


Figure 9

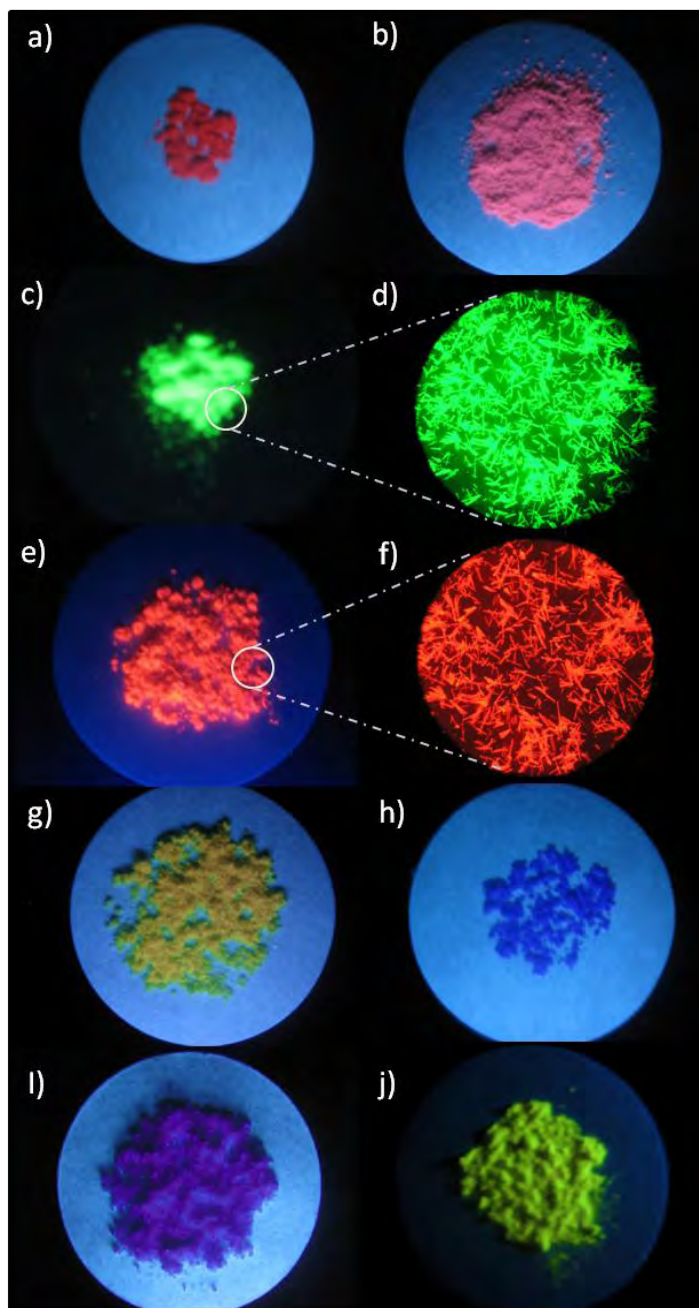


Figure 10

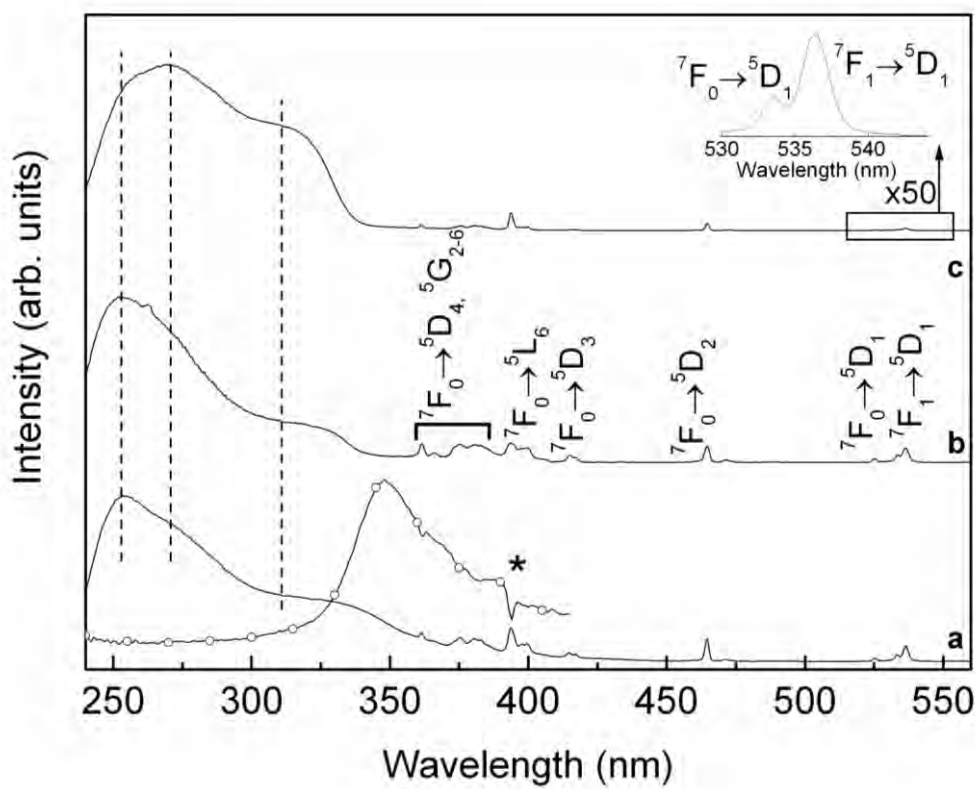


Figure 11

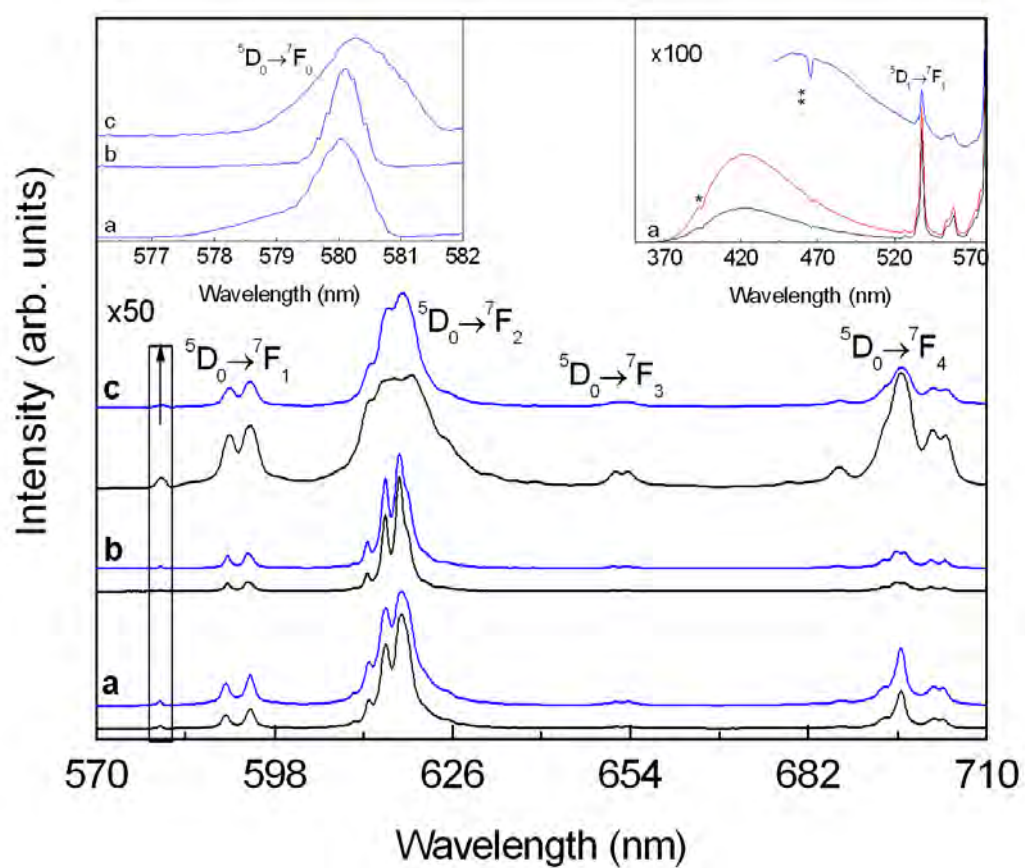


Figure 12

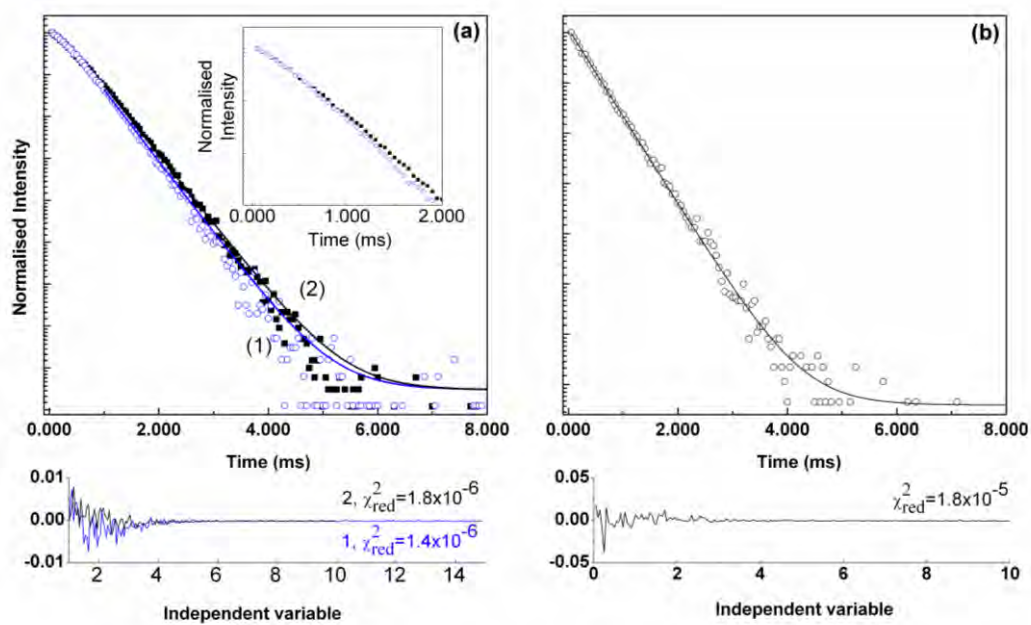


Figure 13

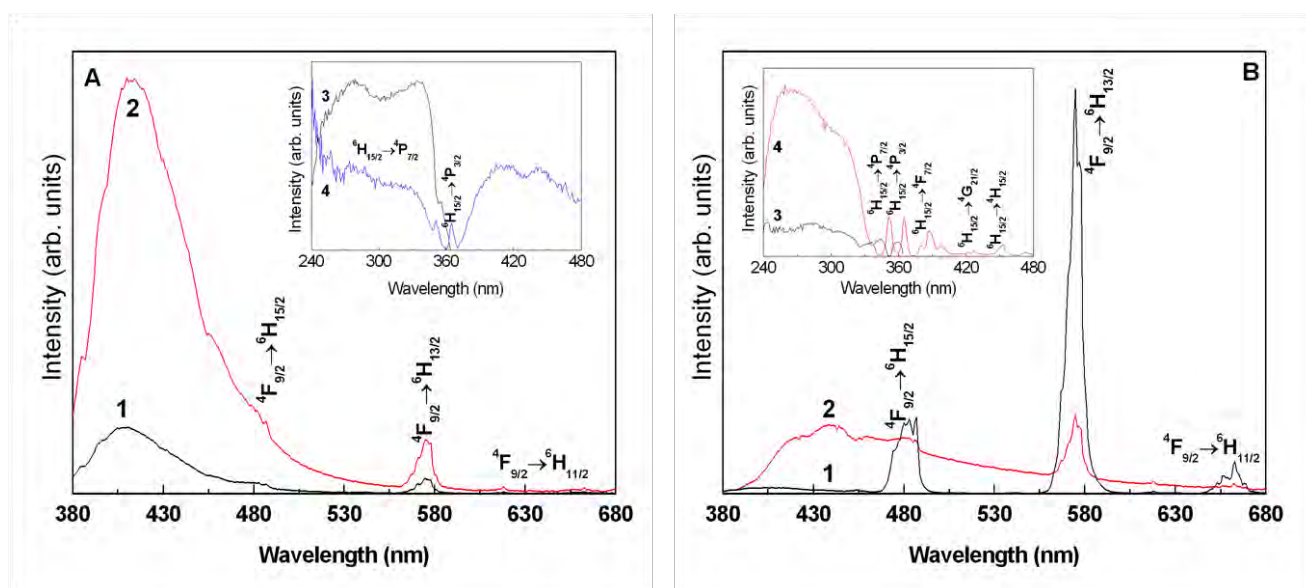


Figure 14

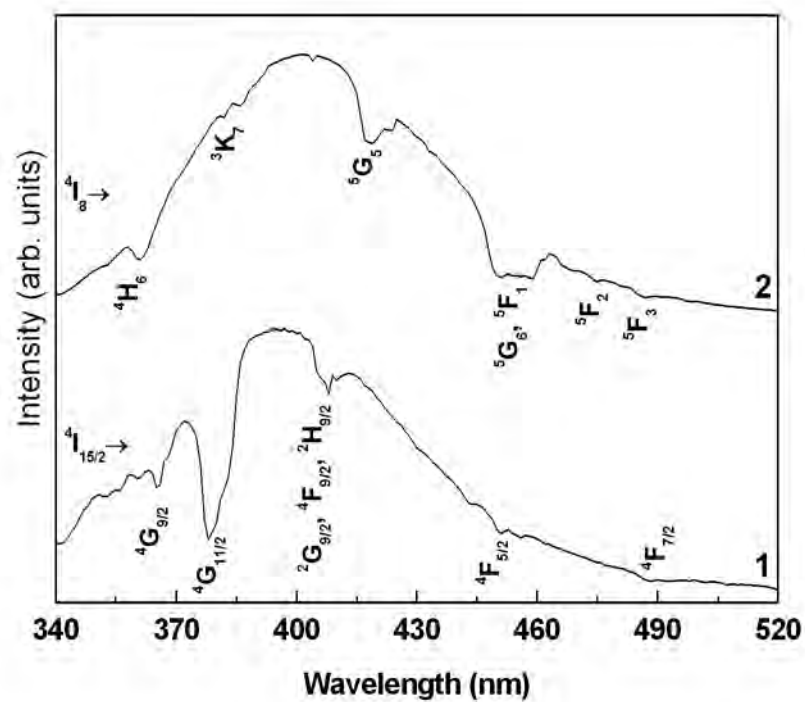


Figure 15

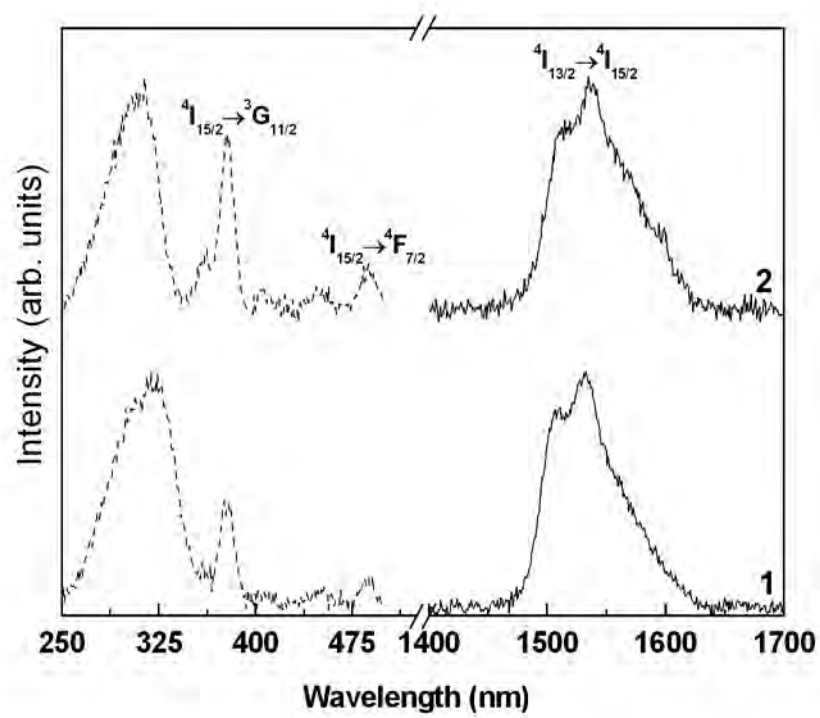


Figure 16

Series of Metal Organic Frameworks Assembled
from Ln(III), Na(I), and Chiral Flexible-Achiral
Rigid Dicarboxylates Exhibiting Tunable UV-VS-IR
Light Emission

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Electronic Supporting Information

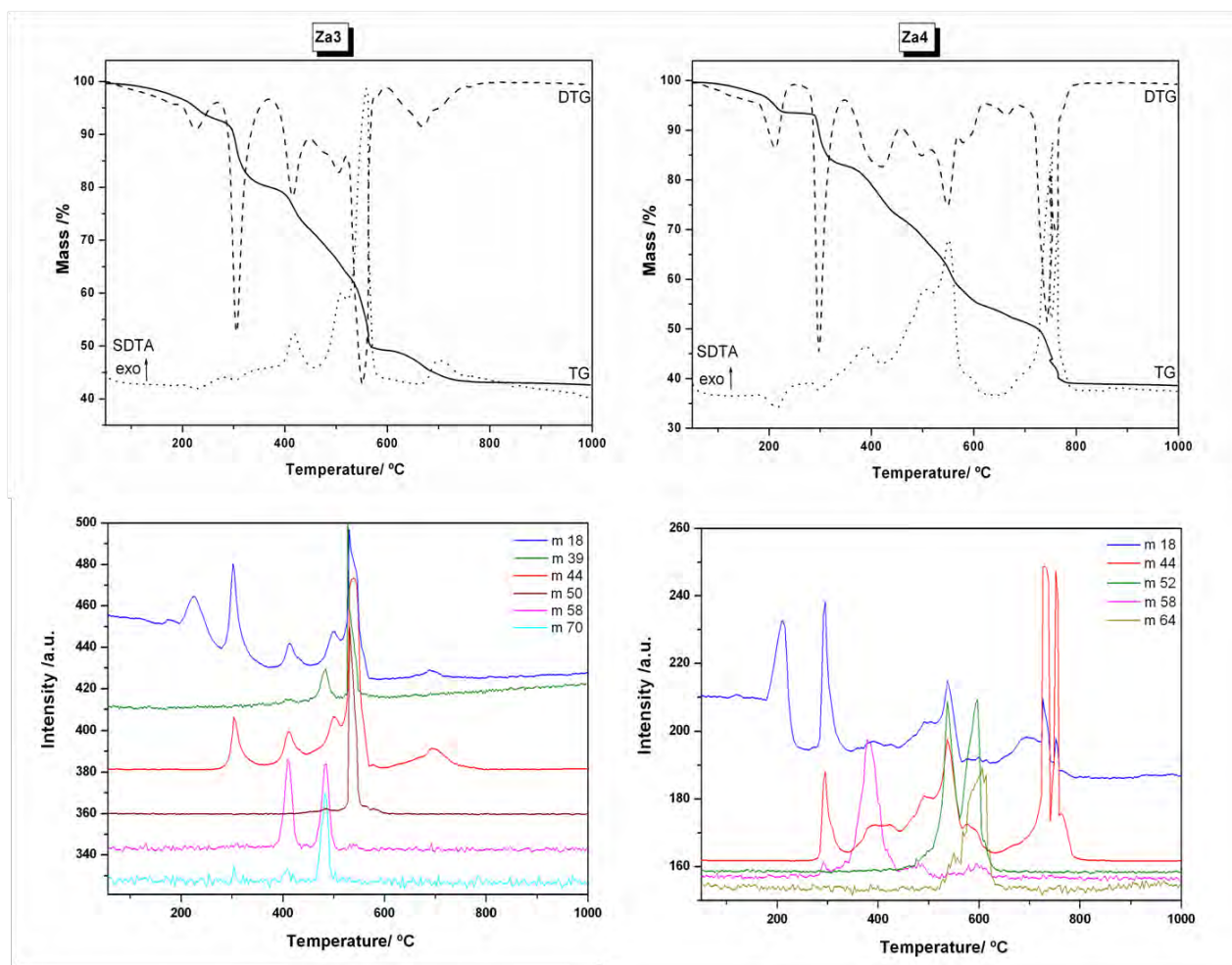


FIGURE S1a

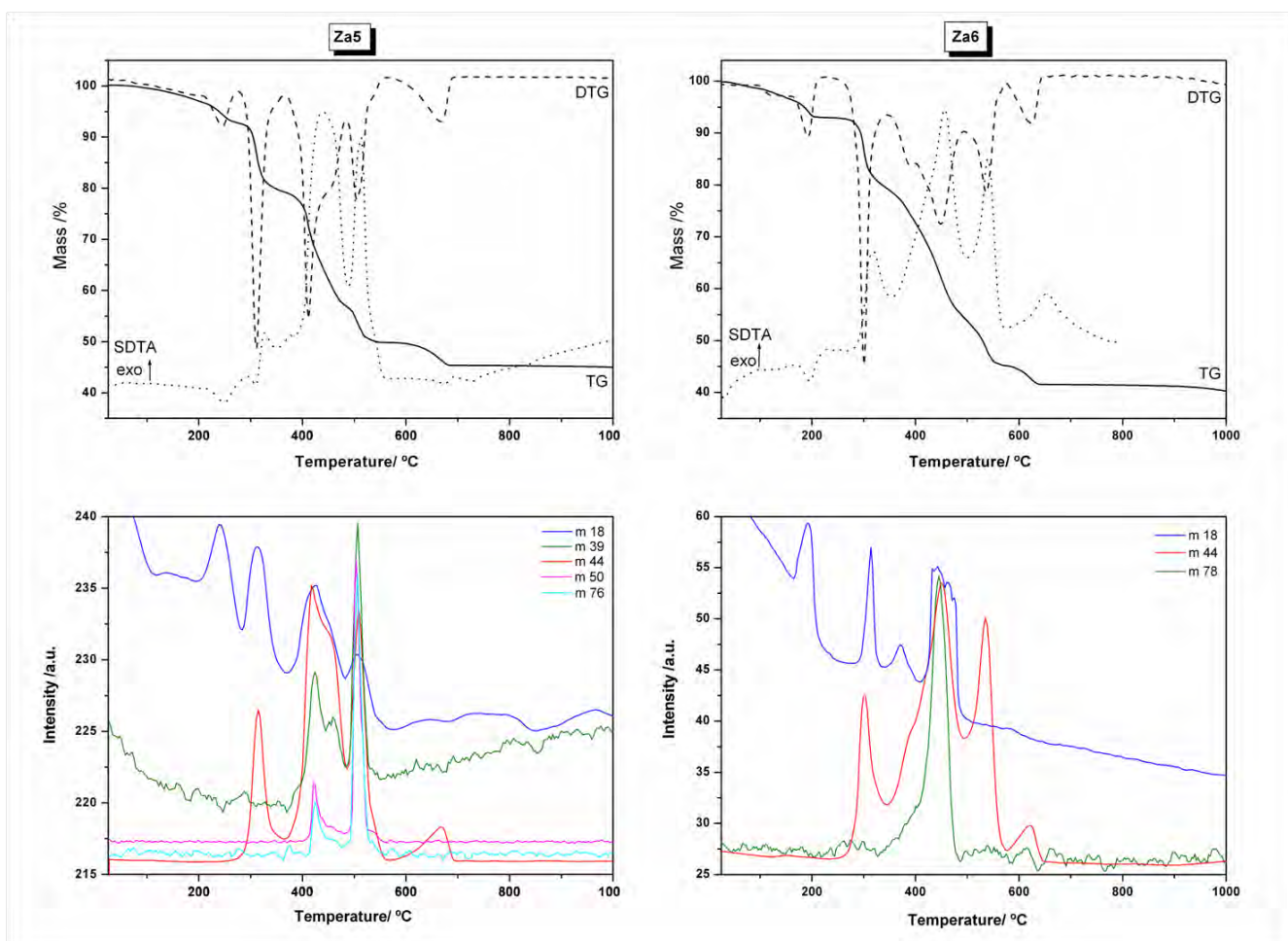


FIGURE S1b

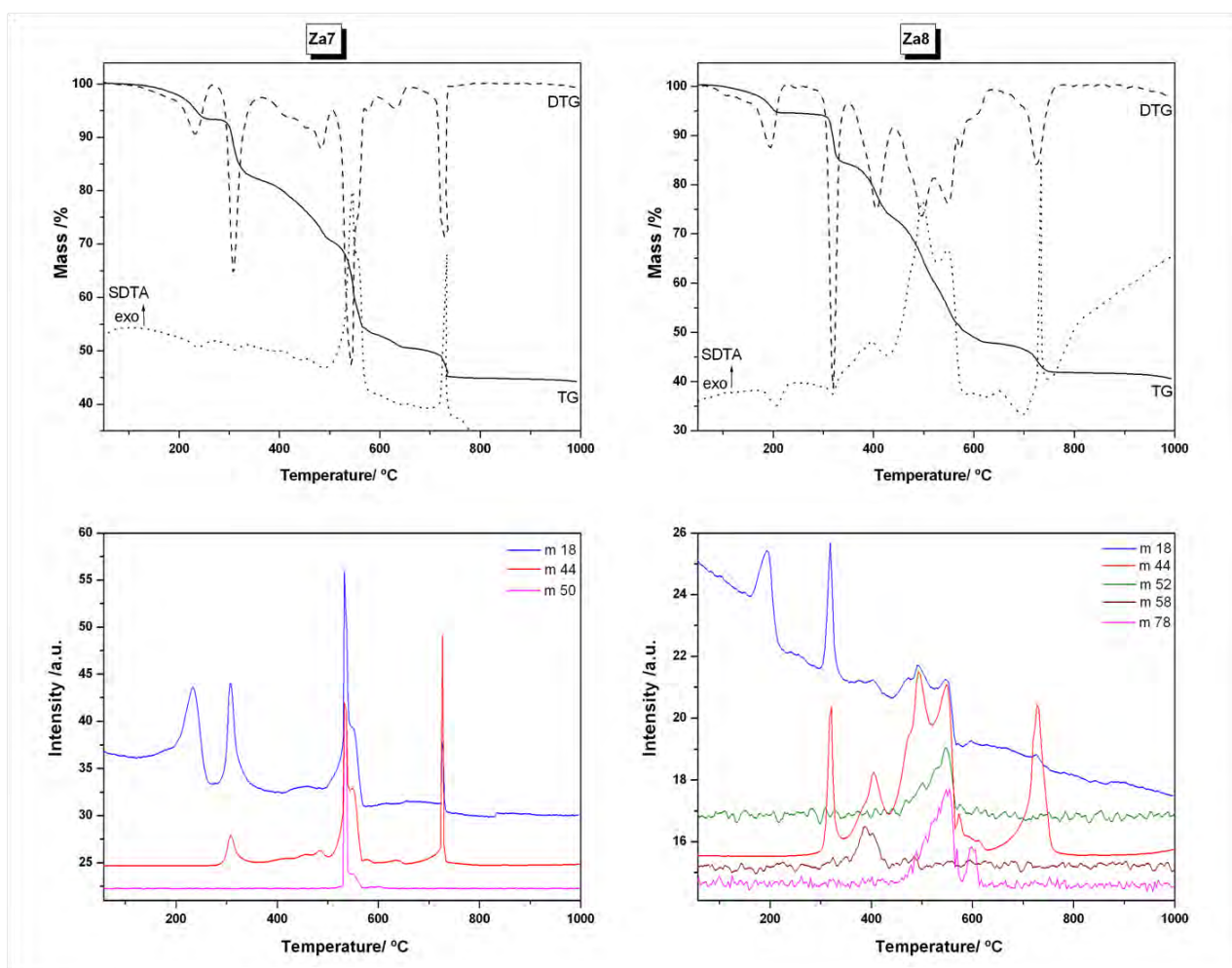


FIGURE S1c

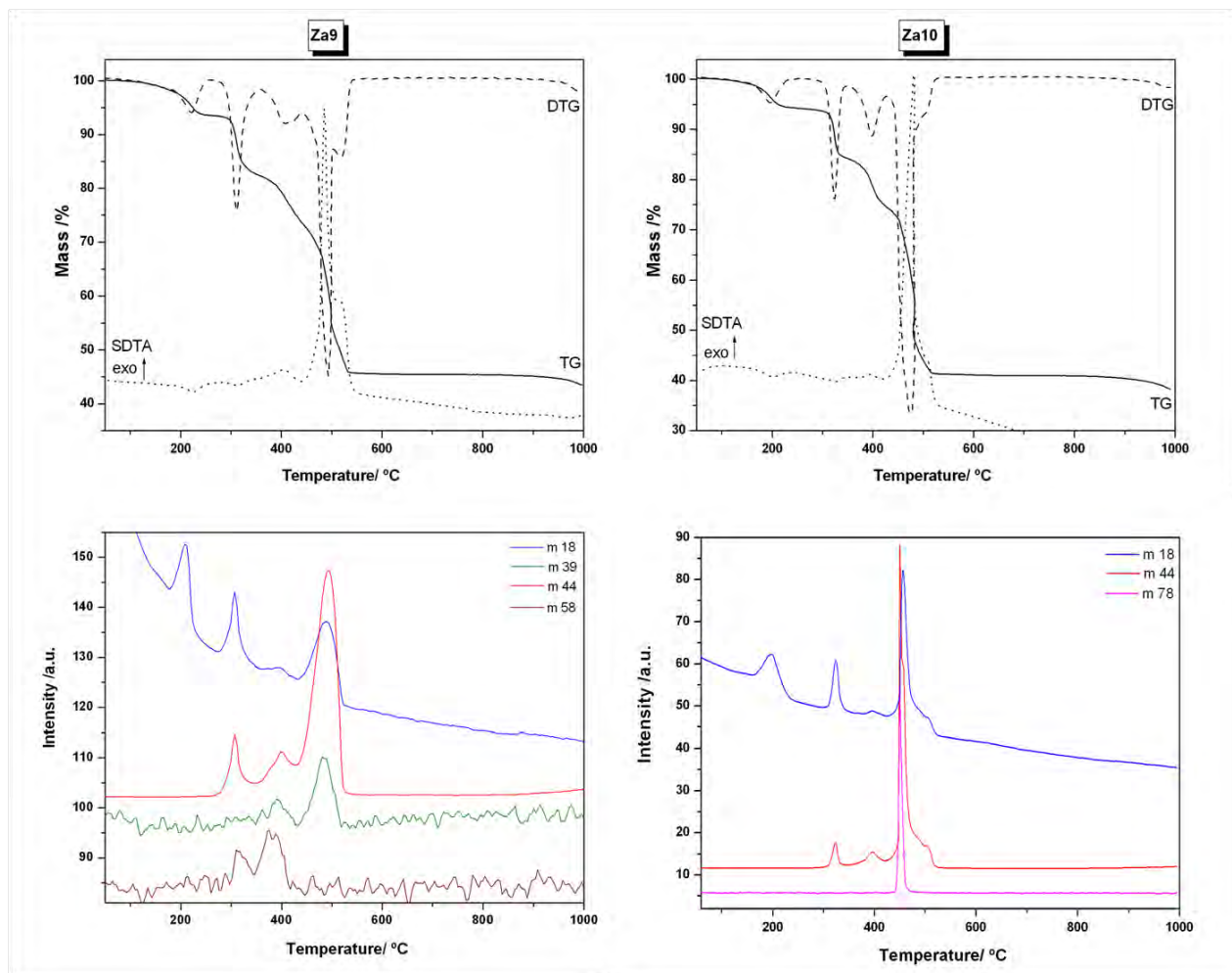


FIGURE S1d

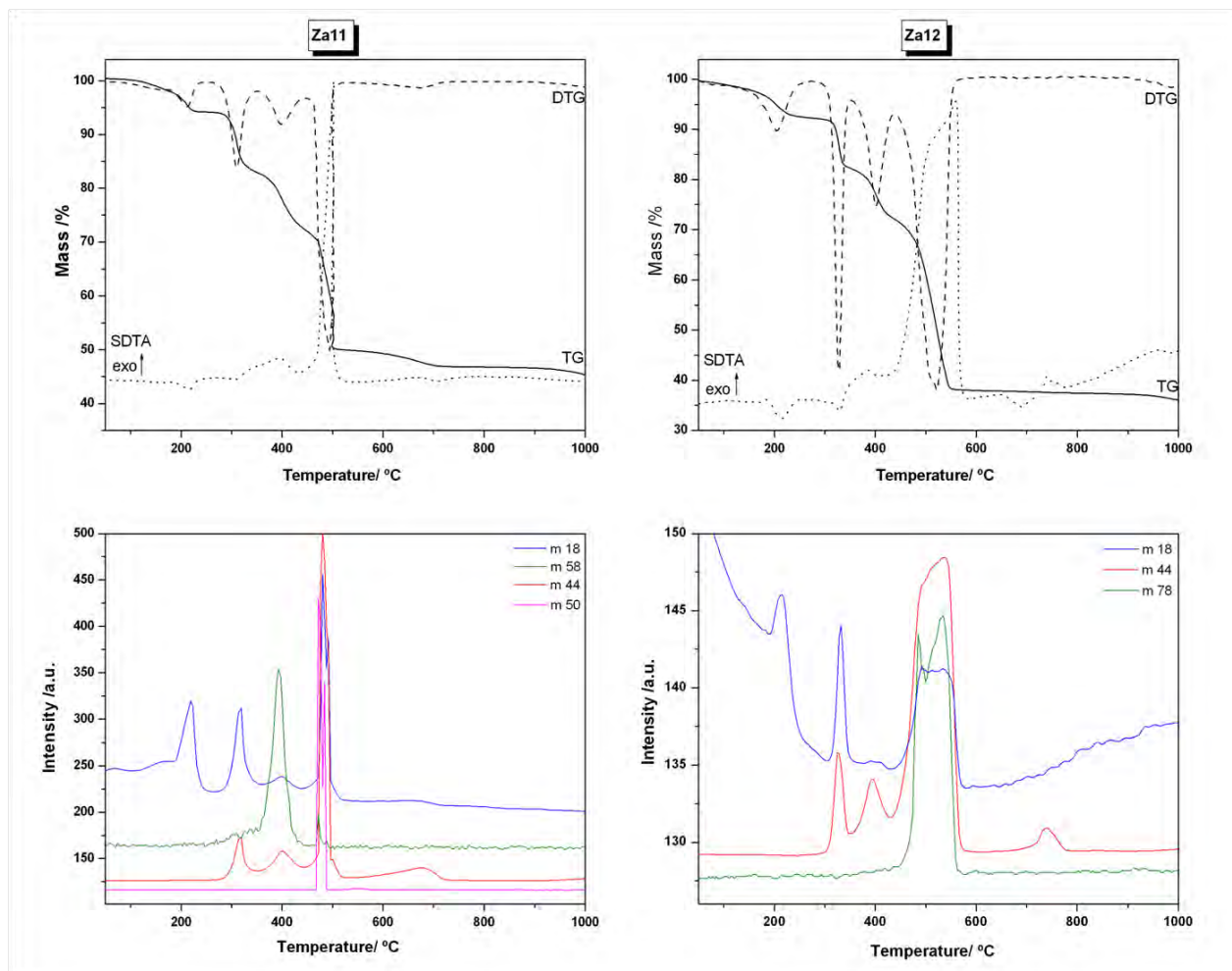


FIGURE S1e

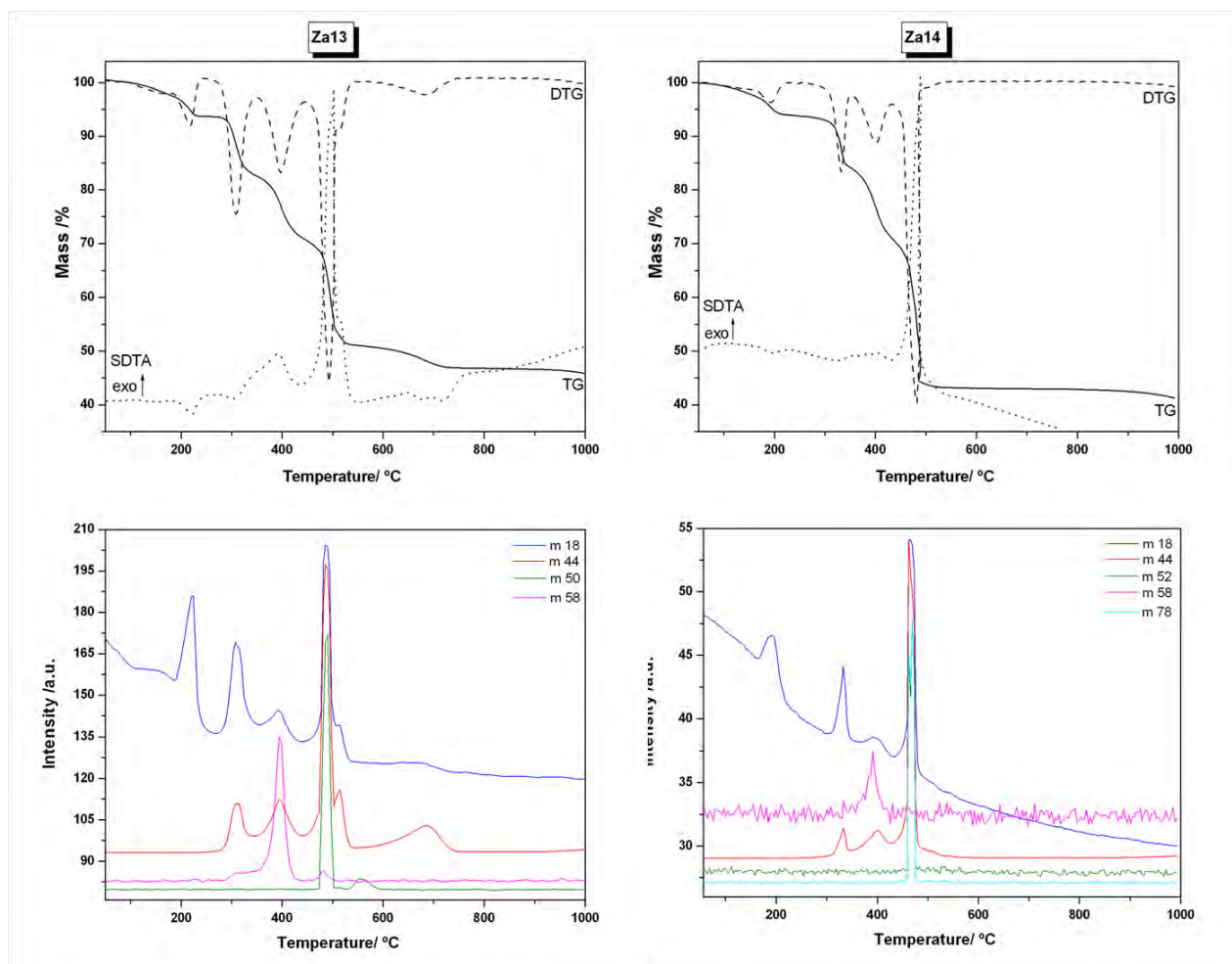


FIGURE S1f

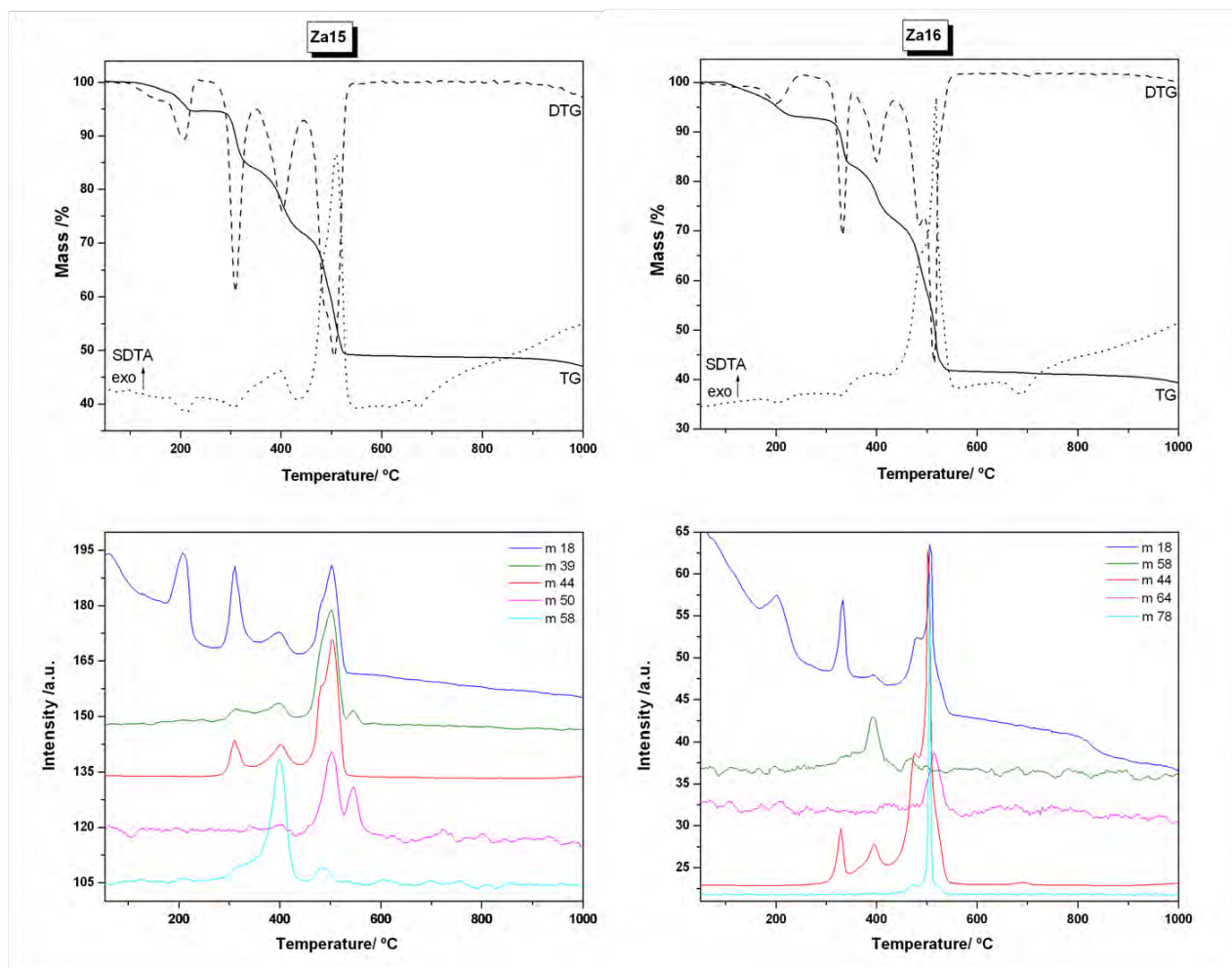


FIGURE S1g

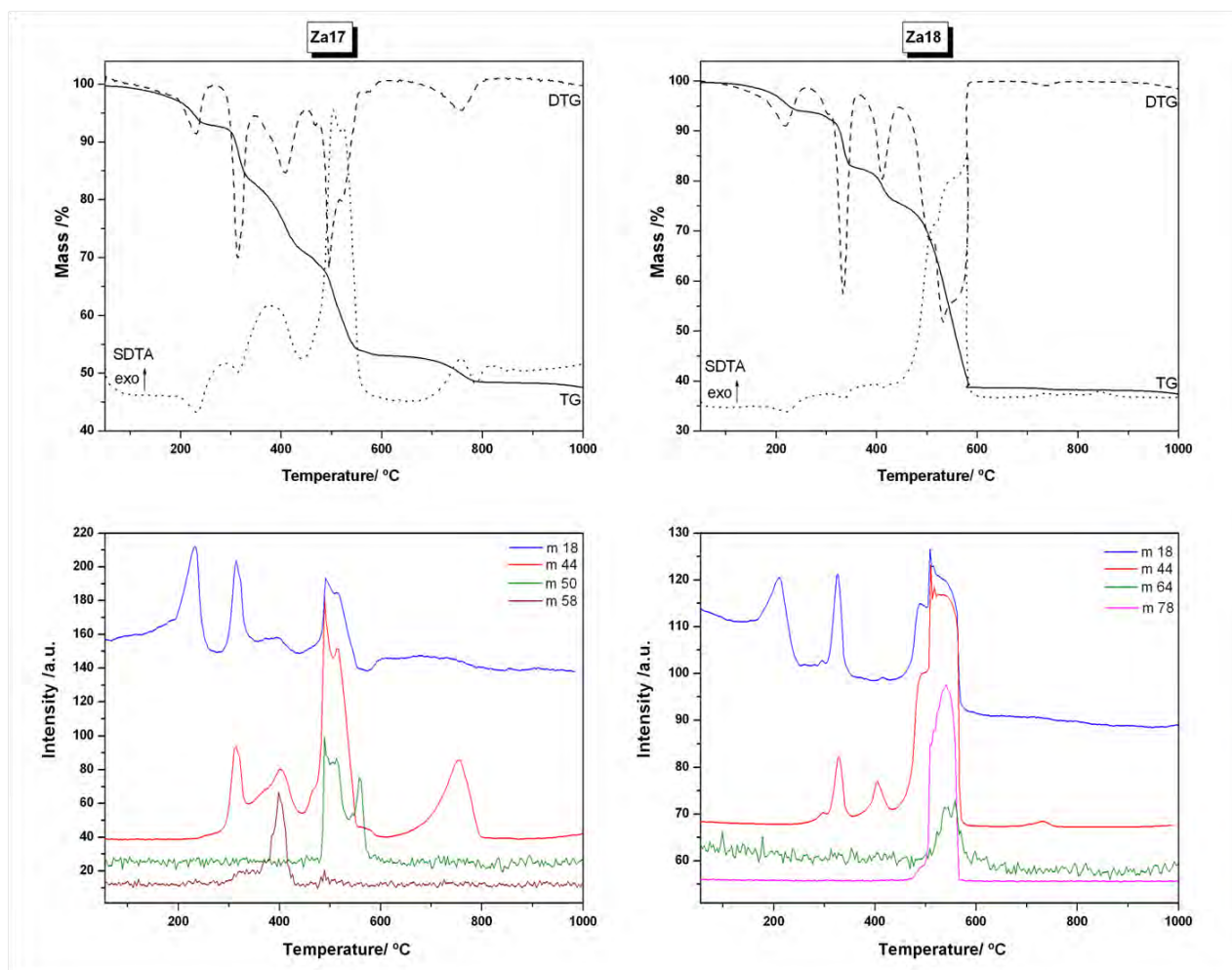


FIGURE S1h

Figure S1. TG-DTG-SDTA curves, and m/z 18 (H_2O), m/z 44 (CO_2) and of the intense m/z corresponding to the cracking of the ligands BDC^{2-} and biBDC^{2-} MS signals of evacuated vapours of the two series of compounds.

Table S1. Numerical values of TG-DTG -MS curves and SDTA/DSC traces for series of compounds **S1** and **S2**.

	Za3	Za4	Za5	Za6	Za7	Za8	Za9	Za10
Total Mass loss (%)								
Calc.	60.63	65.64	60.44	65.46	59.84	64.89	59.65	64.71
Exp.	56.88	61	58.1	61.8	55.85	59.7	56.7	61.9
First stage								
Range (°C)	120-267	120-250	130-270	120-230	120-267	140-228	140-260	150-240
Maximum velocity (°C)	227	211	244	193	232	195	222	195
First Stage Mass loss (%)								
Calc.	6.91	6.03	6.89	6.01	6.82	5.96	6.79	5.94
Exp.	6.2	5.8	7.2	5.8	6.7	5.7	6.5	5.6
Endothermic peaks associated (°C)								
SDTA peak	229	216	250	196	237	207	228	201
DSC peak	207	173	213	192	221	190	212	195
Rest of stages (°C)								
Range of 2 ^d stage	273-368	275-348	280-365	260-343	280-364	290-350	270-360	290-350
Range of 3 ^d stage	368-448	348-457	370-485	343-493	364-506	350-442	360-442	350-430
Range of 4 th stage	448-520	457-620	485-565	493-574	506-594	442-522	442-560	430-540
Range of 5 th stage	520-598	620-688	565-700	574-650	594-656	522-630	--	--
Range of 6 th stage	602-780	694-820	--	--	656-740	650-780	--	--
Total range	273-780	275-820	280-700	260-650	280-750	290-780	270-560	290-540
Maximum velocity (°C)								
max 2 ^d range	305	297	312	300	310	320	310	324
max 3 ^d range	415	421	412(450(s))	388(s)/448	420(450/483)	407	410	397
max 4 th range	506	500	507	538	542/577	495	493(518(s))	475(508(s))
max 5 th range	550	548(580(s))	670	626	634	550(572/612)	--	--
max 6 th range	670	664(s)/743/759	--	--	730	724	--	--
Rest of stages mass loss (%)								
Cal.	53.72	59.61	53.55	59.45	53.02	58.93	52.86	58.77
Exp.	50.7	55.2	50.9	56.0	49.1	54.0	48.2	54.5
SDTA exothermic peaks								
peak2	302(endo)	297(endo)	310(endo)/326	320	310(endo)	318(endo)	312(endo)	324(endo)
peak3	417	390	377(s)/440	420(s)/457	408/457	380(s)/397	402	396
peak4	512	505	514	541	547	496	485/515	481/510
peak5	560	550/585(s)	674(s)/690	652	654	549	--	--
peak6	701	690(s)/753/764	--	--	734	--	--	--
DSC exothermic peaks								
peak2	302(endo)	291(endo)	309(endo)/ 320	311/318	307(endo)	314(endo)	311(endo)	324(endo)
peak3	411	366	shd430/475	428	413.5	380/414	403	400
peak4	496(s)/549	429	520	506	504(s)/537	475(s)/494	478	474(s)/502
peak5	--	496(s)/552/574(s)	--	--	--	552	--	--
m/z 18 maxima (°C)								
max1	175/ 227	216	240	194	233	193	208	197
max2	302	300	311	314	307	319	307	324
max3	414	396(b)	235	371	460(b)	374(b)/403(b)	398(b)	396
max4	502	500(b)	506	443/464/475	533(550(s))	shd473/492	490	458/508
max5	530	540/ 600(b)	--	583(b)	655(b)	546/593	--	--
max6	690	697(b)/728/753	--	--	726	726	--	--
m/z 44 maxima (°C)								
max1	304	300	315	303	308	321	307	324
max2	413	410(b)	417	450	453/484	405	398	397
max3	500	500	510	385(s)/435	532/550/578	493	494	450/504
max4	538	540/ 580(s)	668	534	640	573/590/614	--	--
max5	692	730/757/765(s)	--	--	727	728	--	--
Other fragments maxima (°C)								
m/z 39	--	--	424/460/507	--	--	--	392/485	--
m/z 50	531	--	424/503	--	533(550(s))	--	--	--
m/z 52	--	540/600	--	--	--	548	--	--
m/z 58	413/486	381	--	--	--	388	304/380	--
m/z 64	--	550/606	--	--	--	--	--	--
m/z 70	483	--	--	--	--	--	--	--
m/z 76	--	--	424/503	--	--	--	--	--
m/z 78	--	--	--	532	--	550/570/603	--	450
Integration of m/z 18 curve bands (nA)								
First band	2022	1882	618	405	798	98	608	440
Rest of bands	4684	6253	1341	1251	1594	315	1367	1296
Ratio	2.3	3.3	2.1	3.1	1.99	3.2	2.2	2.9
DSC curve								
Dehydration enthalpies (kJ/mol)	-36	-107	-42	-55	-51	-69	-105	-87
Oxidative decomposition enthalpies (kJ/mol)	3021	3571	3253	4739	2666	4737	3889	6565

	Za11	Za12	Za13	Za14	Za15	Za16	Za17	Za18
Total Mass loss (%)								
Calc.	59.25	64.33	58.98	64.08	58.72	63.84	58.1	63.24
Exp.	57.62	63.2	57.81	59.8	55.8	62.2	52.8	62.3
First stage								
Range (°C)	150-250	140-270	120-245	120-230	120-230	120-250	150-260	125-260
Maximum velocity (°C)	212	203	218	193	207	202	231	217
First Stage Mass loss (%)								
Calc.	6.75	5.91	6.72	5.88	6.69	5.86	6.62	5.81
Exp.	6.2	5.9	6.4	5.4	5.8	5.7	6.3	5.6
Endothermic peaks associated (°C)								
SDTA peak	215	216	220	198.6	212	204	234	220
DSC peak	211	204	191	176	192	191	225	209
Rest of stages (°C)								
Range of 2 nd stage	270-353	290-353	270-350	290-352	280-350	300-354	280-346	280-364
Range of 3 rd stage	353-448	353-438	350-446	352-432	350-444	354-436	346-450	364-446
Range of 4 th stage	448-524	438-600	446-545	432-550	444-550	436-570	450-600	446-600
Range of 5 th stage	600-750	--	570-760	--	--	--	670-810	690-770
Range of 6 th stage	--	--	--	--	--	--	--	--
Total range	270-750	290-600	270-760	290-550	280-550	300-570	280-810	280-770
Maximum velocity (°C)								
max 2 nd range	312	329	308	332	309	333	315	305(s)/333
max 3 rd range	398	401	396	403	402	400	408	411
max 4 th range	494	521	492/514(s)	482	485(s)/505	484/515	468(s)/495/521(s)	507(s)/532/570
max 5 th range	675	--	683	--	--	--	760	738
max 6 th range	--	--	--	--	--	--	--	--
Rest of stages mass loss (%)								
Calc.	52.50	58.42	52.26	58.20	52.03	57.98	51.48	57.43
Exp.	51.4	57.3	51.4	54.4	50.0	56.5	46.5	56.7
SDTA exothermic peaks								
peak2	312(endo)	330(endo)	302(endo)	332(endo)/350	306(endo)	333(endo)	312(endo)	335(endo)
peak3	394	388	393	407	396	397	374/402	398(b)
peak4	502	510(s)/560	503/514(s)	488/ 515(s)	485(s)/510	487(s)/518	504/524	515/548/582
peak5	675	--	650/692	--	--	--	760	--
peak6	--	--	--	--	--	--	--	--
DSC exothermic peaks								
peak2	310(endo)	328(endo)	304(endo)	328(endo)/340	305(endo)	334(endo)	307(endo)	330(endo)
peak3	401	400	397	402	398	404	374(b)/400	397(b)
peak4	490	494/517	487/501	480/498(s)	480/508	485/514	488/514/524(s)	488/517
peak5	--	--	--	--	--	--	--	--
m/z 18 maxima (°C)								
max1	220	214	224	192	208	203	232	220
max2	320	332	307	333	310	333	314	302(s)/334
max3	400	400(b)	394	395	398	394	396	420(b)
max4	480/492	492/535	487/514(s)	466	482/502	480/506	490/510	496/513/545
max5	654(b)	--	672	--	--	--	--	--
max6	--	--	--	--	--	--	--	--
m/z 44 maxima (°C)								
max1	319	325	311	333	310	330	314	302(s)/331
max2	401	396	395	402	402	395	402	410
max3	480	535	488/515(s)	464	482/503	477(s)/502	464(s)/489/516	500(s)/514/520/540
max4	680	740	684	--	--	--	757	733
max5	--	--	--	--	--	--	--	--
Other fragments maxima (°C)								
m/z 39	--	--	--	--	315/398/502/548	--	--	--
m/z 50	472/484	--	490/556	--	502/548	--	489/513/558	--
m/z 52	--	--	--	462/469	--	--	--	--
m/z 58	394	--	395/482	392	398/486	394	398	--
m/z 64	--	--	--	--	--	514	--	546/563
m/z 70	--	--	--	--	--	--	--	--
m/z 76	--	--	--	--	--	--	--	--
m/z 78	--	485/535	--	462/469	--	473/506	--	596(s)/545
Integration of m/z 18 curve bands (nA)								
First band	4046	343	1817	202	1119	300	1959	896
Rest of bands	8012	1048	3930	571	2470	985	4265	3018
Ratio	1.98	3	2.2	2.83	2.2	3.3	2.2	3.3
DSC curve								
Dehydration enthalpies (kJ/mol)	-75	-34	-61	-44	-67	-46	-82	-55
Oxidative decomposition enthalpies (kJ/mol)	3554	6690	2836	4971	2782	5284	2501	5532

(b): band; (s): shoulder; (--): Stage not observed or peak not detected; (endo): endothermic peak, if not indicated, the peak is exothermic.

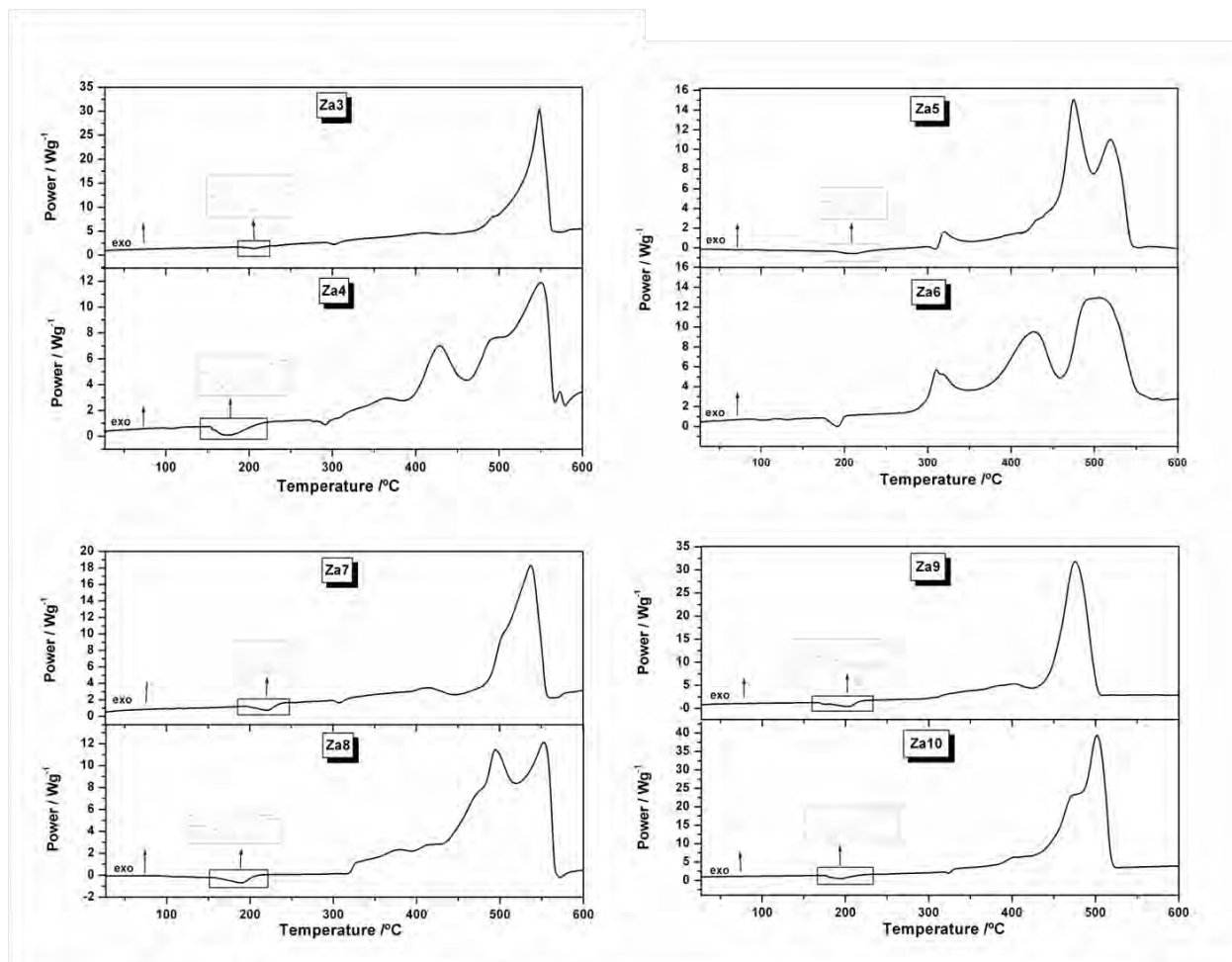


FIGURE S2a

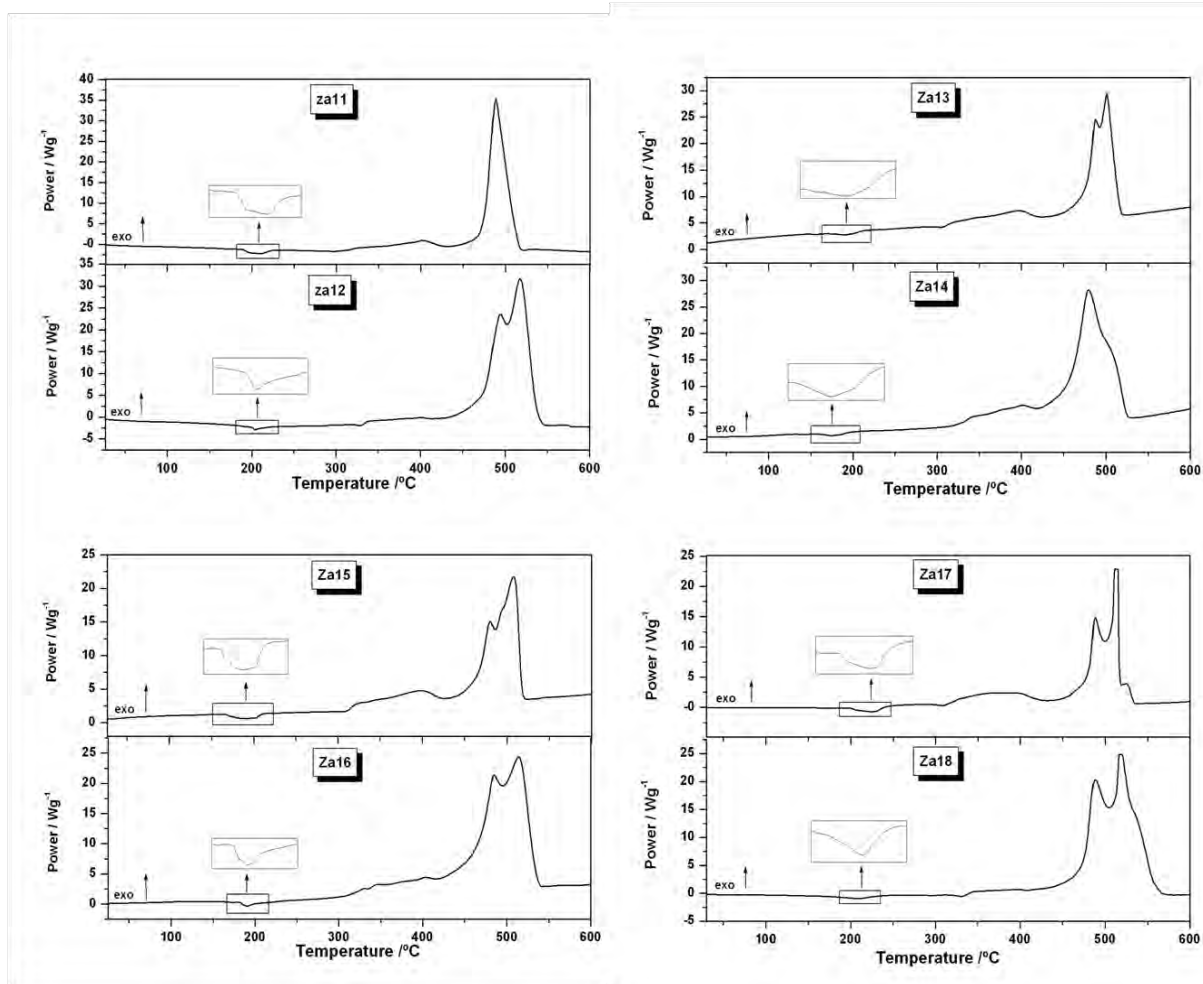


FIGURE S2b

Figure S2. DSC curves of the two series of compounds.

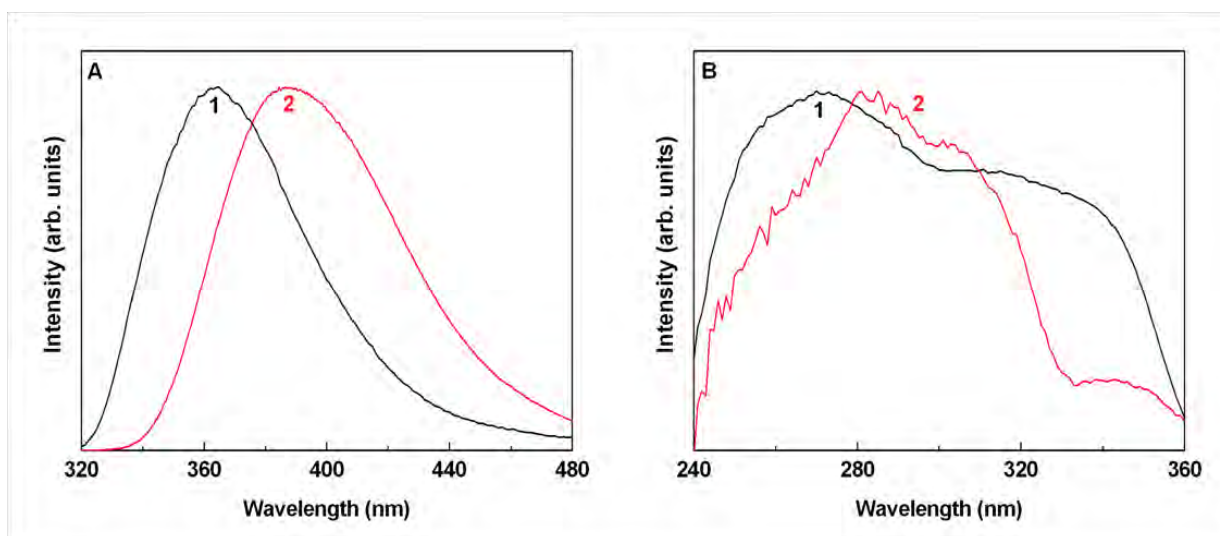


Figure S3. A: Emission and B: excitation spectra of (1) **Za1** (**Za141**) and (2) **Za2** (**Za167**) excited at 270 nm and monitored at 410 nm, respectively.

Synthesis. $\text{NaGd}_{0.86}\text{Eu}_{0.14}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ (**DZa7**) was synthesized under hydrothermal conditions and obtained as a single phase of colorless needle crystals by following procedure: 0.21 g (1.4 mmol) of L-tartaric acid (H_2Tart), 0.08 g (0.5 mmol) of terephthalic acid (H_2BDC) and 0.14 g (3.5 mmol) of NaOH were added to 6 mL of a solution of Gd:Eu with ratio 9:1 previously prepared by dissolving 0.27 g (0.73 mmol) of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.027 g (0.07 mmol) $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ in 6 mL and stirred for 24h, and finally 6 mL of ethanol was added. The mixture was stirred for two hours at room temperature to homogeneity and then placed in a Teflon-lined stainless vessel (40 mL) and heated to 170 °C for 60 h under autogenous pressure and afterwards cooled slowly to room temperature at a rate of 5 °C/h. The resulting product was filtered off, washed thoroughly with ethanol and distilled water, and finally air-dried at room temperature. (0.23 g, *ca.*56% yield based on Gd). Elemental analysis for **DZa7**: $\text{C}_{12}\text{H}_{12}\text{Gd}_{0.86}\text{Eu}_{0.14}\text{Na O}_{12}$ ($M_r = 527.72$). Calcd: C, 27.36; H, 2.28%. Found: C, 27.5; H, 2.4%.

Table S2. Crystallographic data for **DZa7**.

Compound	7
<i>Identification code</i>	DZa7
<i>Empirical formula</i>	C ₁₂ H ₁₂ Gd _{0.86} Eu _{0.14} NaO ₁₂
<i>Formula weight/g mol⁻¹</i>	527.72
<i>Temperature/K</i>	293(2)
<i>Wavelength/Å</i>	1.54184
<i>Crystal system</i>	Orthorhombic
<i>Space group</i>	C222 ₁
<i>Unit cell dimensions</i>	
<i>a (Å)</i>	6.9220(1)
<i>b (Å)</i>	30.5039(6)
<i>c (Å)</i>	7.5457(2)
<i>Cell volume/ Å³</i>	1593.26(6)
<i>Z</i>	4
<i>Calc. Density/ mg m⁻³</i>	2.198
<i>Absorption coefficient/ mm⁻¹</i>	28.15
<i>F(000)</i>	1019.4
<i>Crystal size (mm³)</i>	0.01 x 0.02 x 0.26
<i>Theta range for data collection/°</i>	5.79 to 70.45
<i>Index ranges</i>	-8<=h<=7, -33<=k<=36
<i>Reflections collected</i>	3599
<i>Independent reflections</i>	1488[R(int) = 0.04]
<i>Completeness to theta_{max}</i>	99.70%
<i>Absorption correction</i>	Refined (XABS2)
<i>Max. and min. transmission</i>	1 and 0.469
<i>Refinement method</i>	Full-matrix least-squares on F ²
<i>Data / restraints/ parameters</i>	1488 / 4 / 131
<i>Goodness-of-fit on F²</i>	1.05
<i>Final R indices [I>2sigma(I)]</i>	R1 = 0.0290, wR2 = 0.0736
<i>R indices (all data)</i>	R1 = 0.0316, wR2 = 0.0747
<i>Absolute structure parameter</i>	-0.009(9)
<i>Largest diff. peak and hole/ e.Å⁻³</i>	0.66 and -0.70

Table S3. Selected bond lengths (Å) and bond angles (°) for DZa7.

DZa7	
Gd1—O1 ^I	2.416 (3)
Gd1—O3	2.420 (4)
Gd1—O4 ^I	2.316 (4)
Gd1—O5	2.386 (4)
Na1—O1 ^{II}	2.417 (4)
Na1—O4	2.549 (5)
Na1—O6	2.305 (6)
Gd1—Na1 ^I	3.8450 (14)
C1—O1	1.259 (5)
O1—C1—O1 ^{VI}	120.3 (6)
C6—O2	1.260 (5)
O2—C6—O2 ^{VI}	123.4 (7)
C7—O3	1.423 (7)
C8—O4	1.283 (7)
C8—O5	1.235 (7)
O5—C8—O4	124.3 (5)

Symmetry code: (I) $-x+5/2, -y+3/2, z+1/2$; (II) $-x+2, y, -z+1/2$; (III) $-x+3, y, -z+1/2$.

Table S4. Hydrogen-bond geometry in DZa7 (Å, °)

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
DZa7				
O3-H3O...O2 ^I	0.86	1.77	2.627	176
O6-H6A...O2 ^{II}	0.95	2.27	3.151	153
O6-H6B...O2 ^{III}	0.96	1.88	2.839	175

Symmetry code: (I) 1/2+ x, 1/2+y, z; (II) 1+x, -y, 1-z; (III) -x, -y, 1/2+z

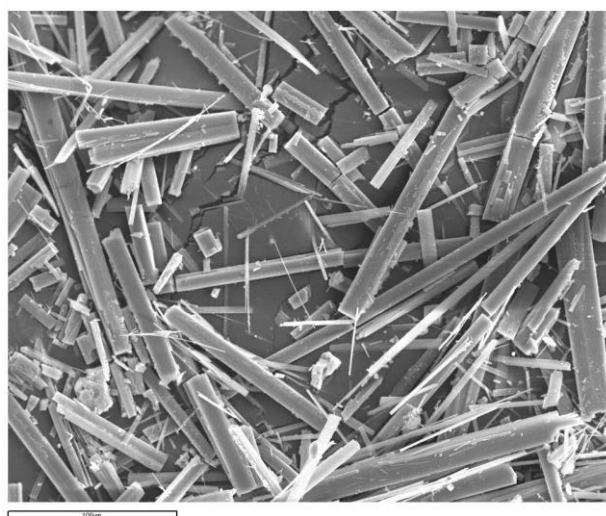


Figure S4. SEM image of **DZa7**.

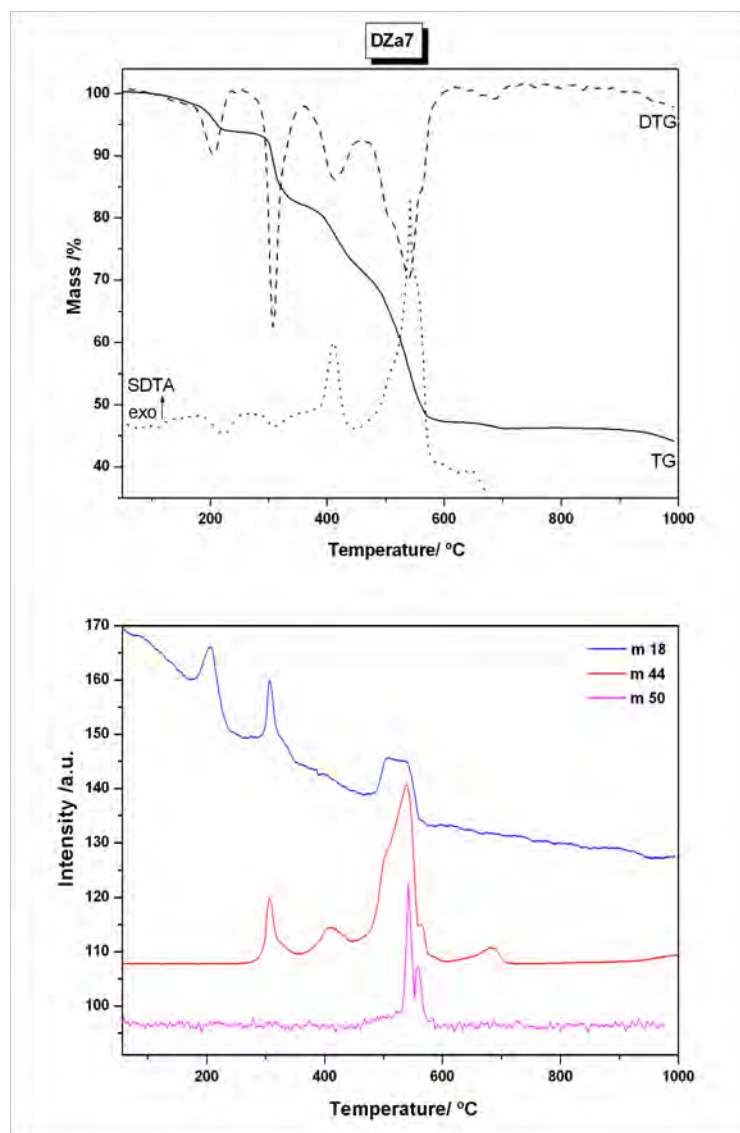


Figure S5. TG-DTG-SDTA curves, and m/z 18 (H_2O) and m/z 44 (CO_2) MS signals of evacuated vapours of **DZa7**.

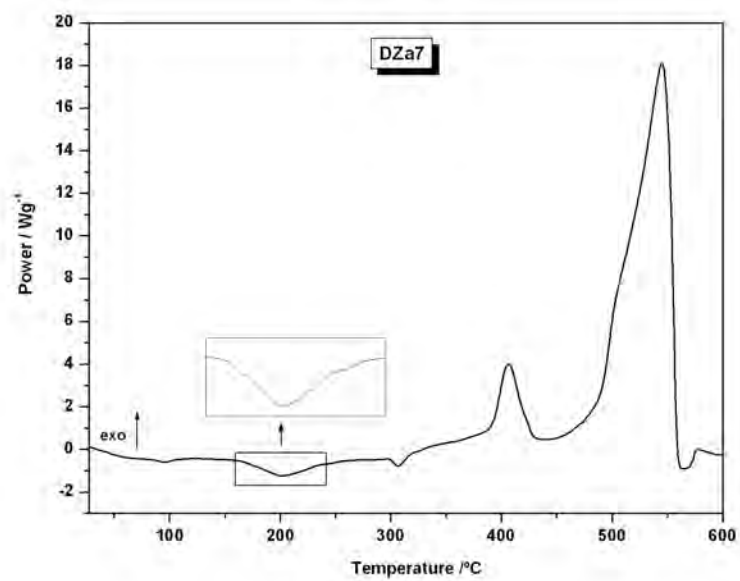


Figure S6. DSC curves of **DZa7**.

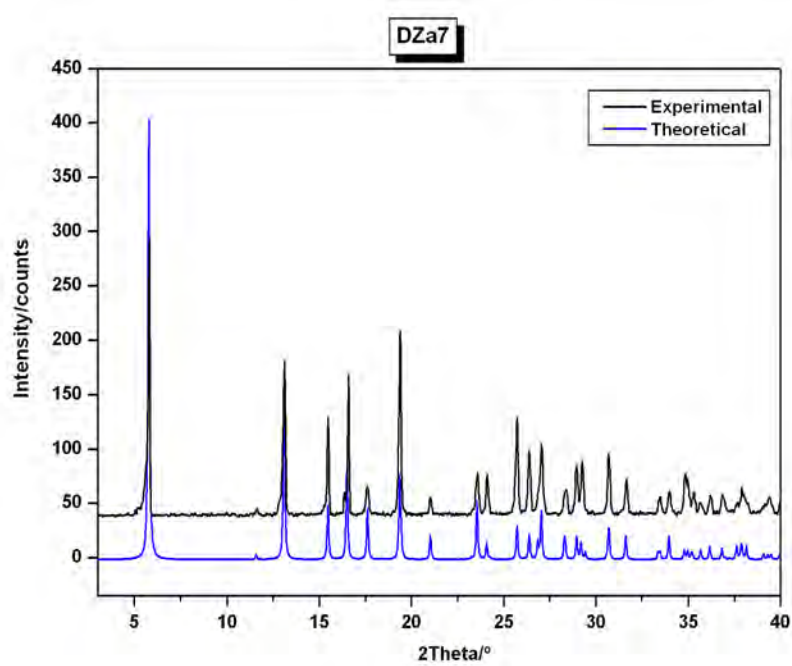


Figure S7. Powder XRD patterns of **DZa7** compared with the theoretical one.

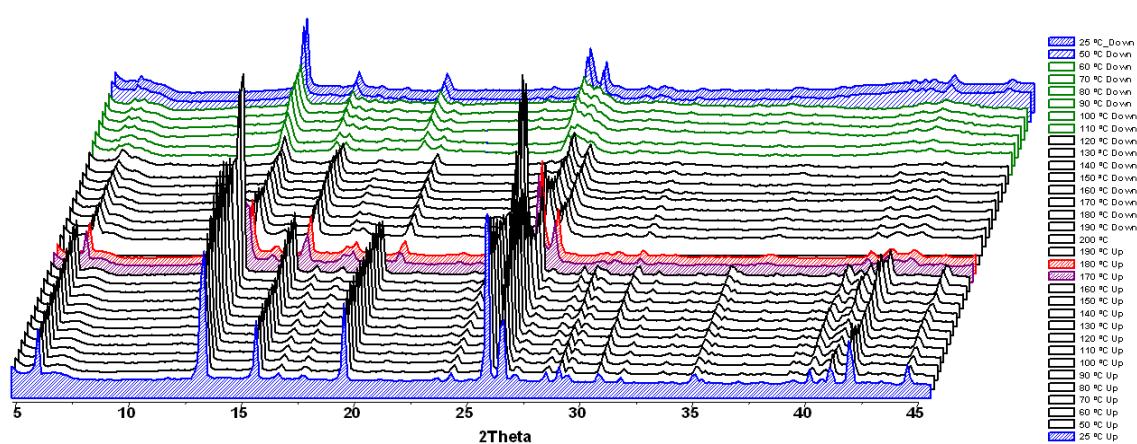


Figure S8. X-ray thermodiffractogram of **DZa7** recorded in air heating up from 25 °C to 200 °C and cooling down to 25 °C. Colour code corresponding to the structural changes, blue: compound **DZa7**, purple: dehydration, red: dehydrated compound, green: rehydration, blue: rehydrated compound.

3.6. Híbridos organo-inorgánicos basados en fosfonatos de lantánidos.

Artículo V

Artículo que será publicado en el año 2011 (DOI: 10.1021/cg2008254) en la revista *Crystal Growth & Design*, con el título “Organic-inorganic hybrids assembled from lanthanide and 1,4-phenylenebis(phosphonate)”.

Resumen

En este trabajo se recoge la síntesis de nueva familia de polímeros de coordinación basados en cationes lantánidos y un ligando rígido tipo difosfonato, así como el estudio de sus propiedades fotoluminiscentes.

La síntesis hidrotermal precedió a la caracterización estructural de nueva familia de híbridos organo-inorgánicos tridimensionales, isoestructurales, basados en elementos lantánidos y el ligando de vinculación bidentado rígido 1,4-fenilbis(fosfonato), de fórmula $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho). Sus estructuras cristalinas se determinaron a partir de datos difracción de rayos X de monocristal del compuesto de praseodimio y refinamiento Rietveld de los datos de difracción de rayos X de polvo cristalino del resto de los miembros de la serie. La caracterización mediante análisis elemental, microanálisis asociado a microscopia electrónica de barrido (SEM/EDX), espectroscopia de infrarrojo (IR), análisis térmico

(TG-MS/SDTA) y termodifracción de rayos X, precederá al estudio de sus propiedades fotoluminiscentes.

Los híbridos organo-inorgánicos en general, y los MOFs en particular, constituyen una clase importante de materiales que constituyen una novedosa área de investigación en el campo del diseño de materiales avanzados, que aún se encuentra en fase exploratoria, siendo los fosfonatos metálicos un campo particularmente versátil para la investigación. Así, en el pasado más reciente, se ha dedicado considerable atención a la investigación de la química de los fosfonatos metálicos como consecuencia de sus potenciales aplicaciones como intercambiadores iónicos, catalizadores, y sensores. La amplia gama de metales (mono-, di-, tri-, tetra-, penta-, y hexavalentes) y gran la variedad de ligandos orgánicos de vinculación que pueden ser utilizados para preparar fosfonatos metálicos, ofrece un amplio margen de opciones de síntesis posibles. Es necesario recordar aquí que la mayor parte de los compuestos orgánicos se pueden incorporar al ácido fosfórico mediante reacciones bien conocidas, siendo posible la incorporación de ligandos de vinculación tipo fosfonato con grupos funcionales muy variados en la estructura híbrida, lo que abre la posibilidad de diseñar estructuras adaptadas a funciones muy específicas.

Los fosfonatos metálicos pueden presentar estructuras poliméricas mono-, bi- o tri-dimensionales, siendo posible vincularlas mediante el uso de ligandos fosfonatos bidentados, así como prescindir de parte de esas uniones vinculantes con la introducción de especies espaciadoras, como el ácido fosfórico o ácido fosforoso, que contribuyen a crear estructuras porosas. En este ámbito, se han sintetizado recientemente fosfonatos de metales di-, tri-, y tetra-valentes con una enorme diversidad estructural, incluyendo materiales de marco abierto y sistemas laminares pilareados porosos.

A pesar de que los materiales basados en fosfonatos de metales lantánidos deben poseer interesantes propiedades ópticas y magnéticas, el número de informes publicados en estos campos es relativamente escaso, probablemente debido al hecho de que los fosfonatos de lantánidos suelen poseer muy baja solubilidad tanto en agua como en disolventes orgánicos, siendo difícil obtener monocristales adecuados para su determinación estructural mediante técnicas de difracción convencionales, lo que es un gran problema para una correcta interpretación de las útiles propiedades luminiscentes que suelen presentar tanto en la región del visible como del infrarrojo cercano.

En el trabajo descrito en esta memoria, el ácido 1,4-fenilenbis(fosfónico) (H_4BDP), ligando de vinculación bidentado rígido, se ha sintetizado siguiendo un

procedimiento previamente establecido, para ser usado como precursor en la síntesis hidrotermal de nueva familia de materiales híbridos de fórmula $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$. Las condiciones de síntesis, en las que se obtuvieron sólidos monofásicos, se describen a continuación: a 0.2 mmol (0.05 g) de H_4BDP , y 0.2 mmol de $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($x = 5, 6$; $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$) se han añadido 6 mL de agua destilada, agitando posteriormente la mezcla de reacción hasta su homogenización en un recipiente de teflón (volumen interno de 15 mL), para luego introducirla en un autoclave de acero inoxidable que se mantuvo a 180 °C durante 5 días.

En el compuesto de praseodimio (**Za1**) ha sido posible aislar cristales individuales de tamaño suficiente para determinar su estructura mediante difracción de rayos X de monocristal. **Za1** tiene simetría monoclinica, cristalizando en el grupo espacial $C2/c$, con los siguientes parámetros de red: $a = 5.6060(4) \text{ \AA}$, $b = 20.251(7) \text{ \AA}$, $c = 8.2740(6) \text{ \AA}$, $\beta = 108.52(1)^\circ$. La unidad asimétrica de **Za1** es relativamente simple, y contiene la mitad de cation Pr^{3+} y la mitad del ligando HBDP^{3-} , tal como se muestra en la Figura 3.6.1a, donde el catión Pr^{3+} está atravesado por un eje cristalográfico binario a lo largo del eje b , mientras el anión HBDP^{3-} ocupa un centro de inversión. El modo de coordinación de ligando HBDP^{3-} se muestra en la Figura 3.6.1b. Cada catión Pr^{3+} está coordinado por ocho átomos de oxígeno, que provienen de seis grupos fosfonato cristalográficamente equivalentes (Figura 3.6.1c), definiendo un poliedro de coordinación tipo prisma trigonal bicofiado distorsionado (Figura 3.6.1d). De los seis grupos fosfonato coordinados al cation Pr^{3+} , dos de ellos se coordinan en modo quelato a través de los átomos de oxígeno O1 y O2, los otros dos actúan como puente entre dos cationes Pr^{3+} adyacentes, mientras que los dos restantes se coordinan a través del oxígeno O3. Las distancias $\text{Pr}-\text{O}$ varían de 2.371(9) Å a 2.516 (9) Å, con un valor promedio de 2.44(1) Å. Los poliedros de coordinación del praseodimio se alternan entre sí compartiendo aristas, originando cadenas infinitas paralelas a la dirección [101], con distancia entre cationes Pr^{3+} adyacentes de 4.2503(6) Å. A su vez, estas cadenas se conectan a través de grupos fosfonato a lo largo de la dirección [101], conformando una región inorgánica laminar (Figura 3.6.1e). Estas laminas se conectan entre sí mediante pilares orgánicos, constituidos por los grupos fenilo del ligando HBDP^{3-} , provocando una alternancia a lo largo del eje c de fragmentos orgánicos e inorgánicos, como se muestra en la Figura 3.6.1(f,g), generando canales inaccesibles a lo largo de los ejes a y c , con unas dimensiones aproximadas de $6.5 \times 4.2 \text{ \AA}^2$ y $6.5 \times 5,6 \text{ \AA}^2$, respectivamente.

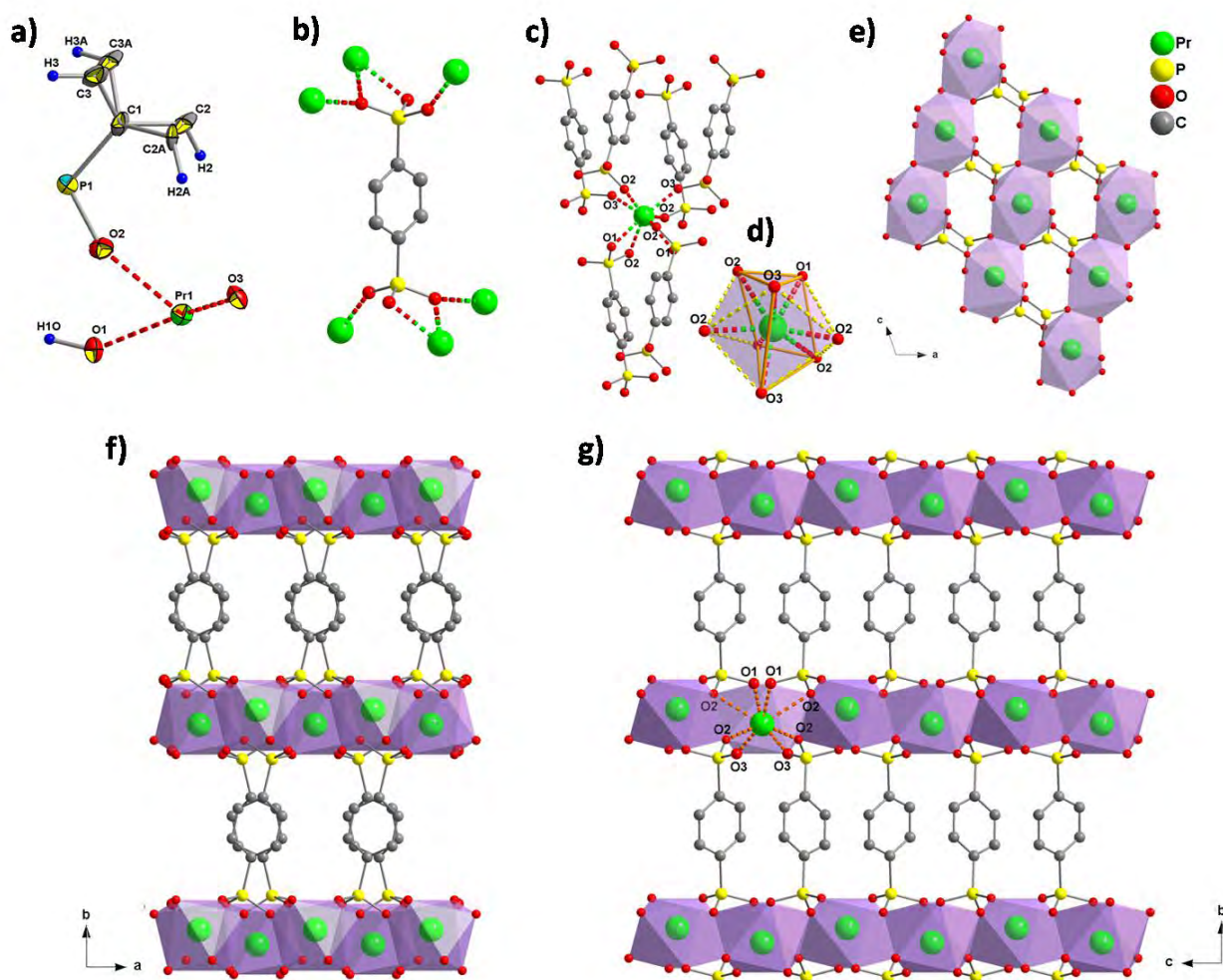


Figure 3.6.1. (a) Unidad asimétrica del compuesto $\text{Pr}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$. (b) Modos de coordinación del ligando HBDP^{3-} [$\mu_6 - 2(\eta^1 : \eta^2 : \eta^1)$]. (c, d) Entorno de coordinación local del catión Pr^{3+} . (e) Proyección de la lamina inorgánica a lo largo del eje b . (f, g) Proyección de la estructura a lo largo de los ejes a (g) y c (f).

Los demás compuestos de la serie, obtenidos en forma de polvo microcristalino, son isoestructurales con **Za1**, y sus estructuras se refinaron a partir de datos de difracción de rayos X de polvo cristalino (como ejemplo, véase la Figura 3.6.2) alcanzando, en todos los casos, valores muy aceptables para los índices de calidad del ajuste, observándose, como era de esperar, que los parámetros de las celdas unidad de los compuestos de esta familia son función del tamaño del catión lantánido que forma parte de cada estructura.

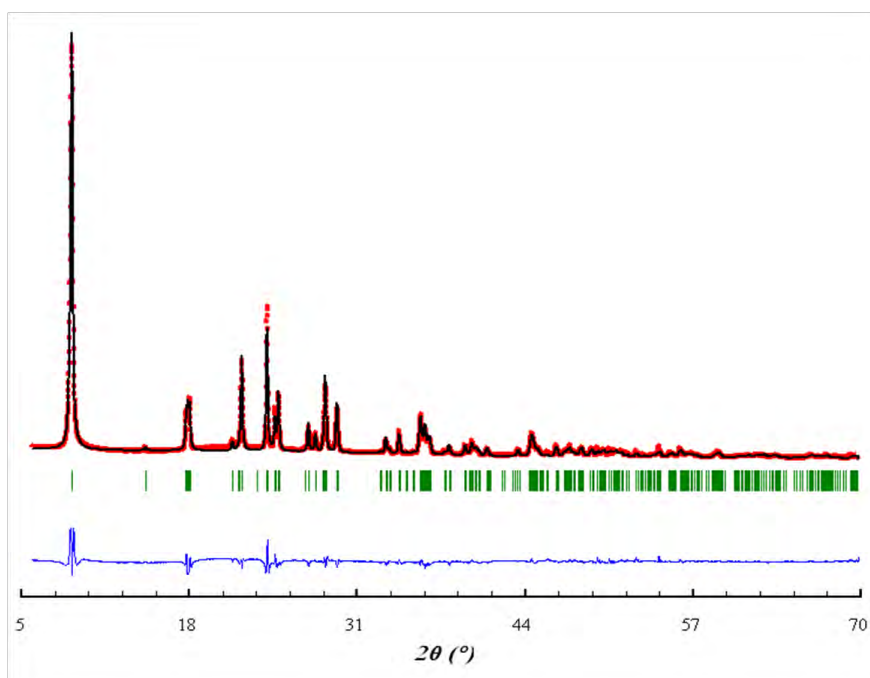


Figura 3.6.2. Difractograma observado (rojo), y calculado (negro) al final del refinamiento Rietveld del compuesto $\text{Ho}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$. La curva de diferencia (azul) está en la misma escala.

Las curvas de TG muestran que todos los compuestos de esta serie poseen perfiles de descomposición térmica muy similares, caracterizados por una alta estabilidad térmica, más que notable en el caso de los compuestos basados en Dy y Ho. La descomposición transcurre en etapas continuas y solapadas, con pérdidas de masa del 18-19%, asignables a la pérdida del grupo fenilo. Los estudios por termodifracción de rayos X de polvocrystalino son consistentes con los resultados del análisis térmico (TG-MS/SDTA), y confirman la alta estabilidad térmica de estos compuestos.

Finalmente, se han estudiado las propiedades fotoluminiscentes de los compuestos basados en europio y terbio, empleado varias técnicas espectroscópicas (excitación, emisión y tiempo de vida), siendo destacable que estos materiales presentan una fuerte emisión de luz en el visible, respectivamente, de color rojo y verde.

Artículo V

Organic–Inorganic Hybrids Assembled from Lanthanide and 1,4-Phenylenebis(phosphonate)

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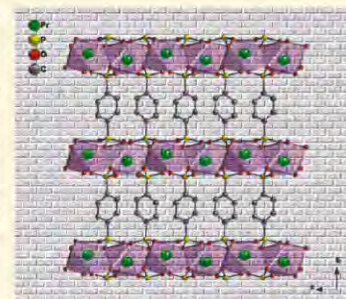
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S Supporting Information

ABSTRACT: A series of novel organic–inorganic hybrids based on trivalent lanthanide (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) and 1,4-phenylenebis(phosphonate) formulated as $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ has been obtained as single phases under hydrothermal conditions. In the praseodymium compound (**Za1**), single crystals have been obtained and the crystal structure has been determined. **Za1** crystallizes in the monoclinic space group, $C2/c$, with $a = 5.6060(4)$ Å, $b = 20.251(7)$ Å, $c = 8.2740(6)$ Å, $\beta = 108.52(1)^\circ$. All other compounds are isostructural to **Za1** as confirmed by Rietveld refinement using X-ray powder diffraction data. Compounds are characterized by thermal analyses (TG-MS and SDTA), elemental analysis, IR spectra, and X-ray thermogravimetric analysis. Their visible photoluminescence properties are also discussed.



INTRODUCTION

Organic–inorganic hybrids in general and metal–organic frameworks (MOFs) in particular constitute an important class of compounds in the exploratory research area of advanced materials design. In particular, metal phosphonates represent a particularly versatile field for investigation because of the great latitude open to the investigator. During the past two decades, a considerable amount of research attention has been devoted to the chemistry of metal phosphonates for their potential applications in ion exchange, catalysis, and sensor devices.^{1–5} The wide choice of metals (mono-, di-, tri-, tetra-, penta-, and hexavalent) and the variety of organic ligands that can be utilized to prepare the metal phosphonate mean that a wide latitude of choices is possible. Because almost any desired organic compound may be converted into a phosphonic acid by known reactions, it is thus possible to introduce phosphonate ligands with different functional groups into the hybrid structure, which suggests the possibility of tailored structures for highly specific functions,⁶ and even with unusual properties.⁴ Often, metal phosphonates exhibit polymeric structures consisting of chains, layers, or three-dimensional networks. By utilizing diphosphonates, it is possible to cross-link the layers and to space the cross-links by using spacer molecules, such as phosphorus or phosphoric acid, to create a porous structure. Recently, investigations of di-, tri-, and tetravalent metal phosphonates have yielded exciting structural diversity with interesting chemistries and applications,^{7–31} including open framework structures^{20–26} and porous pillared layered structures.^{7,8} The synthesis of lanthanide phosphonates has drawn the scientist's attention for their possible optical and

magnetic properties. However, reports on lanthanide phosphonates are rather limited because lanthanide phosphonates normally have low solubility in water and organic solvents, and hence it is difficult to obtain single crystals suitable for X-ray structural determination.²⁸ Nevertheless, the elucidation of the structures of lanthanide phosphonates is very important since these compounds may exhibit useful luminescent properties in both the visible and near IR regions. In particular, reports on the structure and photoluminescence properties of lanthanide (Ln) arylphosphonates or arylphosphonates are still scarce,^{28,32,33} although this kind of ligand may enhance the fluorescence of the lanthanide ions, via the so-called antenna effect.

Hydrothermal reaction of lanthanide(III) salts with 1,4-phenylenebis(phosphonic acid), afforded a series of new isostructural compounds, with three-dimensional networks formulated as $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ (where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho). Herein we report their synthesis, crystal structure, thermal behavior, and luminescent properties through luminescence and excitation spectroscopy and the excited-state lifetimes.

EXPERIMENTAL SECTION

Synthesis of 1,4-Phenylenebis(phosphonic acid) (H_4BDP).

To a three-necked round-bottom flask, 5 g of 4,4'-dibromobenzene

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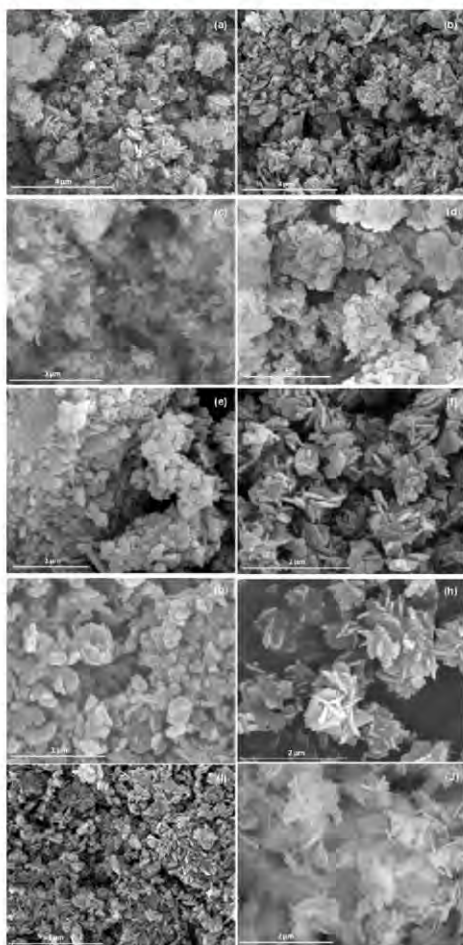


Figure 1. SEM images of $[\text{Ln}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$, (where Ln = La (a), Ce (b), Pr (c), Nd (d), Sm (e), Eu (f), Gd (g), Tb (h), Dy (i), and Ho (j)).

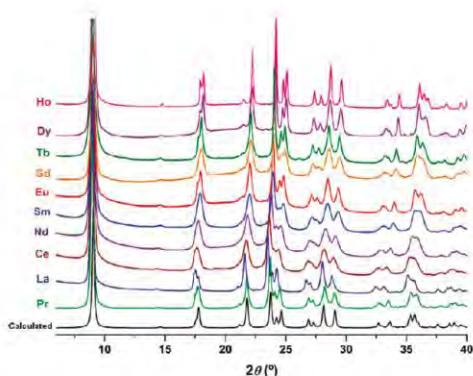


Figure 2. Powder XRD patterns of $[\text{Ln}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$ compared with that calculated for $\text{Pr}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$.

Table 1. Crystallographic Data for **Za1**

empirical formula	$\text{C}_6\text{H}_5\text{P}_2\text{O}_6\text{Pr}$
formula weight/ g mol^{-1}	375.95
temperature/K	296(2)
wavelength/Å	0.71073
crystal system	monoclinic
space group	$\text{C2}/c$
unit cell dimensions	
a (Å)	5.6060(4)
b (Å)	20.251(7)
c (Å)	8.2740(6)
α (°)	90
β (°)	108.522(11)
γ (°)	90
cell volume/Å ³	890.7(3)
Z	4
calc density/ mg m^{-3}	2.804
absorption coefficient/ mm^{-1}	5.833
$F(000)$	692
crystal size (mm^3)	$0.22 \times 0.09 \times 0.06$
theta range for data collection/°	2.01–27.1
index ranges	$-7 \leq h \leq 7, -25 \leq k \leq 25,$ $-10 \leq l \leq 10$
reflections collected	4543
independent reflections	971 [$R_{\text{int}} = 0.115$]
completeness to θ_{max}	98.30%
absorption correction	refined (XABS2)
max and min transmission	1 and 0.3984
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	971/5/85
goodness-of-fit on F^2	1.053
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.054, wR_2 = 0.122$
R indices (all data)	$R_1 = 0.112, wR_2 = 0.151$
largest diff peak and hole/ $e \cdot \text{Å}^{-3}$	1.449 and -1.914

(Aldrich, 98%) and 50 mL of 1,3-diisopropylbenzene (TCI America) were added. The system was flushed with N_2 and 0.5 g of NiBr_2 (Aldrich) was added. The reaction was slowly heated to 160 °C, while 10 mL of triethyl phosphate (Aldrich, 98%) was added over a 6-h period. The system was heated to 180 °C and stirred for 24 h. NiBr_2 and triethylphosphite were sequentially added twice, with half the amount each time. After such additions, the temperature was reduced to 120 °C and the system was left open to the atmosphere for 48 h. The reaction was distilled to remove solvents and byproducts; extractions were completed using hexanes. After recrystallization from hexanes, a hydrolysis using a 1:1 ratio of H_2O and HCl was carried out at 110 °C. The product was then washed and dried.¹⁰ Yield: ca. 2 g (40%).

Synthesis of Lanthanide 1,4-Phenylenebis(phosphonate) ($\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$). In a typical synthesis, 0.2 mmol (0.05 g) of 1,4-phenylenebis(phosphonic acid), 0.2 mmol of $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($x = 5, 6$) (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho), and 6 mL of water were mixed. The reaction mixture was stirred until a homogeneous gel was formed ($\text{pH} = 1-2$), sealed in a PTFE-lined stainless steel autoclave with an internal volume of 15 mL and heated at 180 °C for 5 days under autogenous pressure. After cooling, the resulting products were filtered off, washed with water, and dried in an oven at 80 °C. In the case of $\text{Pr}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ (**Za1**), the product contains a mixture of pale green powder and tiny plate-shaped crystals. A suitable single crystal was selected to perform the single-crystal X-ray diffraction studies.

96 Elemental analyses were performed in a C–H–N Perkin-Elmer model
97 2400B elemental analyzer, the calculated and found percentages of
98 C–H are represented in Table S.

99 **Single-Crystal X-ray Diffraction Studies.** Data collection was
100 performed at 115 K on a Bruker Smart APEX-II CCD diffractometer

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for Za1^a

Pr1–O3	2.371 (9)
Pr1–O2	2.435 (8)
Pr1–O1	2.516 (9)
P1–O3 ⁱ	1.519 (10)
P1–O ⁱⁱ	1.542 (9)
P1–O1 ⁱⁱⁱ	1.574 (9)
Pr1–Pr1	4.2503(6)
O3 ⁱ –P1–C1	107.5 (5)
O1 ⁱⁱⁱ –P1–C1	107.9 (5)
O2 ⁱⁱ –P1–C1	110.6(5)
O2 ⁱⁱ –P1–O1 ⁱⁱⁱ	103.0(5)
O3 ⁱ –P1–O1 ⁱⁱⁱ	110.7 (5)
O3 ⁱ –P1–O2 ⁱⁱ	116.9 (5)

^a Symmetry codes: (i) $-x - 1/2, -y + 1/2, -z + 1$; (ii) $-x + 1/2, -y + 1/2, -z + 1$; (iii) $-x, y, -z + 1/2$.

Table 3. Hydrogen-Bond Geometry in Za1 (Å, °)^a

D–H...A	D–H [Å]	H...A [Å]	D...A [Å]	D–H...A [deg]
O1–H10...O1 ⁱ	1.0(1)	1.54(8)	2.47(1)	151(14)

^a Symmetry codes: (i) $-x + 1, +y, -z + 1/2$.

101 with a Mo K α source operated at 40 kV and 40 mA. The crystal structure
102 was solved by direct methods. The refinement was performed using full-
103 matrix least-squares on F^2 . All non-H atoms were anisotropically refined.
104 All H atoms were either geometrically placed riding on their parent
105 atoms or located from the difference Fourier map, with isotropic
106 displacement parameters set to 1.2 times the U_{eq} of the atoms to which
107 they are attached. Crystallographic calculations were carried out using
108 the following programs: APEX2³⁴ for data collection, SAINT³⁴ for cell
109 refinement and data reduction, SADABS³⁵ for empirical absorption
110 correction, SHELXS-97³⁶ for structure solution, XABS2³⁷ for refined
111 absorption correction, SHELXL-97³⁶ for structure refinement and to
112 prepare materials for publication, PLATON³⁸ for the geometrical calculations,
113 and Diamond³⁹ for molecular graphics.

114 **Thermal Characterization.** A Mettler-Toledo TGA/SDTA851^e
115 and a DSC822^e were used for the thermal analyses in an oxygen dynamic
116 atmosphere (50 mL/min) at a heating rate of 10 °C/min. In all cases, ca.
117 10 mg of powder sample was thermally treated, and blank runs were
118 performed. In TG tests, a Pfeiffer Vacuum ThermoStar GSD301T mass
119 spectrometer was used to determine the evacuated vapors. The masses
120 18 (H₂O), 44 (CO₂), and 78 (C₆H₆) were tested by using a detector
121 C-SEM, operating at 1200 V, with a time constant of 1 s.

122 **Morphological Characterization.** Micrographs and X-ray micro-
123 analysis (SEM/EDX) were recorded with a JEOL JSM-6100 electron
124 microscope operating at 20 kV coupled with an INCA Energy-200
125 energy dispersive X-ray microanalysis system (EDX) with a PentaFET
126 ultrathin window detector. SEM images show that the particles are
127 nanoplates with diameters between 200–400 nm (see Figure 1), and
128 EDX confirmed that the ratio Ln/P is ca. 1:2.

129 **Infrared Absorption Spectra.** The infrared data were collected
130 at room temperature (RT) using a FT-IR Bruker Tensor-27 spectro-
131 meter from KBr pellets. The spectra were collected over the range
132 4000–400 cm⁻¹ by averaging 15 scans at a maximum resolution
133 of 4 cm⁻¹.

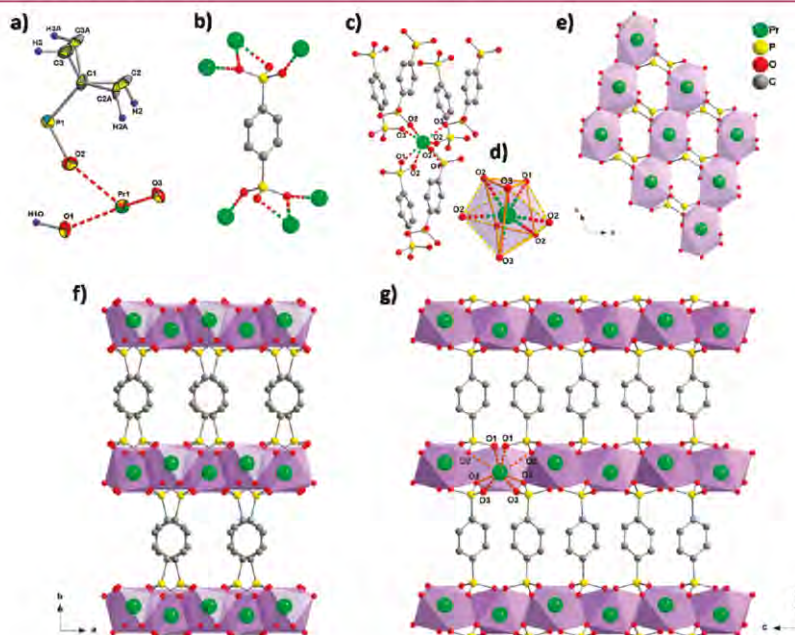


Figure 3. (a) Asymmetric unit of $[\text{Pr}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$. (b) Coordination modes of 1,4-phenylbis(phosphonate) ligand $[\mu_6 - 2(\eta^1: \eta^2: \eta^1)]$. (c, d) Perspective view of the coordination environment of Pr^{3+} . (e) Perspective view of the inorganic layer along the b -axis. (f, g) Projection of the structure along the a -axis (a) and c -axis (b), respectively.

134 **Powder X-ray Diffraction Studies.** Powder X-ray diffraction
 135 (PXRD) patterns were recorded on a Bruker D8 Advance powder X-ray
 136 diffractometer with Cu–K α radiation. The samples were gently ground
 137 in an agate mortar in order to minimize the preferred orientation.
 138 Routine XRD data were collected at room temperature over the angular
 139 2θ range 4–40° with a step of 0.009° and a counting time of 0.15 s/step.
 140 High-resolution X-ray diffraction (XRD) measurement collected at RT
 141 over the angular 2θ range 4–90° with a step of 0.013° and a counting
 142 time of 7 s. The PXRD patterns of the compounds were compared with
 F2 143 the calculated one (see Figure 2), indicating that the products have been
 144 successfully obtained as isostructural pure crystalline phases. Rietveld
 145 refinement was carried out by the FullProf program.⁴⁰ Single crystal
 146 structure of **Za1** was used as the initial model in all cases. The PXRD
 147 profiles have been modeled as a Cauchy (Lorentzian) function in the
 148 range $2\theta = 6–70^\circ$. The zero offset, the scale factor, six background
 149 terms, fwhm parameters, the unit cell, asymmetry correction for peaks
 150 below $2\theta = 20^\circ$, and the positions of Ln, O, and P atoms (excepting C
 151 and H) were refined.

152 **Powder X-ray Thermodiffraction Studies.** Powder X-ray
 153 thermodiffraction studies were performed in air. The sample was placed
 154 in an Anton Paar XRK 900 reactor chamber on a Bruker D8 Advance
 155 diffractometer with DAVINCI design, using Cu K α radiation, equipped
 156 with a LynxEye detector. Each powder pattern was recorded in the
 157 7–60° range (2θ) from RT to 900 °C with a step of 0.02° and a counting
 158 time of 0.4 s. The temperature ramp between two consecutive tempera-
 159 tures was 10 °C/min.

160 **Gas Adsorption Study.** Nitrogen adsorption data were performed
 161 volumetrically at 77 K using a Micromeritics ASAP 2020 analyzer.

162 **Luminescence and Excitation Measurements.** RT lumines-
 163 cence and excitation spectra were measured using a standard spectro-
 164 fluorometer (Jobin-Yvon Fluorolog-2). The sample was excited with a
 165 150 W Xe-lamp by an excitation monochromator and the dispersed
 166 emitted light was detected with a photomultiplier (Hamamatsu R928) at
 167 a 90° configuration to minimize direct light from the lamp. Excitation
 168 spectra were corrected for the lamp response at different wavelengths.
 169 Luminescence spectra were not corrected for the detection system
 170 response (monochromator + detector). Emission lifetimes were mea-
 171 sured in a FLSP920 fluorescence spectrometer (Edinburgh Inst.),
 172 equipped with a microsecond xenon flashlamp and a cooled R928P
 173 photomultiplier (Hamamatsu), based on the multichannel scaling tech-
 174 nique (repetition rate 50 Hz and pulse width of 1 μ s).

175 ■ RESULTS AND DISCUSSION

176 The detailed crystallographic data of and the structure refine-
 177 ment parameters of Pr-compound (**Za1**) are summarized in
 T1 178 Table 1. Selected bond distances, angles, and hydrogen bonds are
 T2 179 given in Tables 2 and 3. The asymmetric unit of **Za1** is relatively
 T3 180 simple containing half Pr³⁺ cation and half the HBDP³⁻ ligand as
 F3 181 displayed in Figure 3a. This is a consequence of the fact that Pr³⁺
 182 cation is situated on a crystallographic 2-fold axis along the
 183 *b*-direction, while HBDP³⁻ resides on an inversion center. The
 184 coordination mode of the HBDP³⁻ ligand is depicted in Figure 3b.
 185 We should mention that this coordination mode has not yet been
 186 reported. However, the same coordination mode has been
 187 reported with another similar ligand.²⁹ The Pr³⁺ cation is bonded
 188 to eight oxygen atoms that come from six phosphonate crystal-
 189 lographically equivalent groups (Figure 3c). Its coordination
 190 geometry may be described as a distorted bicapped trigonal-prism,
 191 {PrO₈} (Figure 3d), out of six phosphonate groups surrounding
 192 Pr³⁺: (i) two of them are coordinated in chelating modes via the
 193 oxygen atoms O1 and O2, (ii) the other two act as a bridge
 194 between two adjacent Pr³⁺ cations within the oxygen atom O2,
 195 (iii) and the two remaining are bonded via oxygen atom O2.

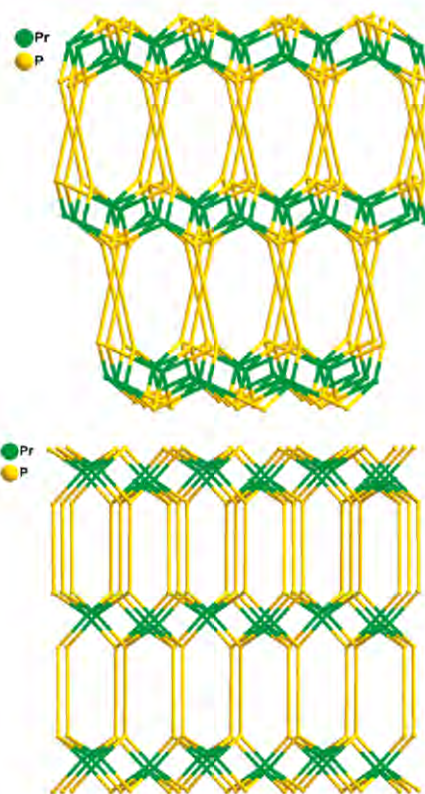


Figure 4. Topological representation of the binodal frameworks of [Ln(HBDP)]: P corresponds to 4-connected nodes and Pr is 6-connected nodes. Internodal distances: P \rightarrow P 6.44 Å; P \rightarrow Pr 3.24 Å, 3.78 Å, and 3.84 Å.

The distances Pr–O range from 2.371(9) to 2.516(9) Å, with average values of 2.44(1) Å. The Pr³⁺ polyhedra alternate in a chain edge-to-edge parallel to the [101] direction, and the distance between adjacent Pr³⁺ cations in the chain is 4.2503(6) Å. These chains are in turn connected via phosphonate groups along the [101] direction forming the inorganic layer (see Figure 3e). Connection between adjacent layers is ensured by HBDP³⁻ organic pillars leading to an alternation along *c*-axis of organic and inorganic fragments as depicted in Figure 3f,g, forming channels running along the *a*- and *c*-axis, with approximate dimensions of 6.5 \times 4.2 Å² and 6.5 \times 5.6 Å². Gas (N₂/77 K) adsorption study was performed in order to check the accessibility of channels, and the results prove they are not accessible (*S*_{BET} = 29 m²/g). Taking as network nodes the phosphorus atoms and Ln³⁺ cations, Ln-compounds can be envisaged as binodal frameworks built-up from one type of 4-(P-atom) and 6-connected (Ln³⁺ cation) nodes (Figure 4).

All the other members of the family have been obtained as microcrystalline powders. Rietveld refinement shows the isostructurality of all Ln-compounds, tuned by the influence of the Ln³⁺ cations (see Table 4). The final values obtained of figures of merit are within acceptable ranges,⁴¹ as the model used adjusts very well with the experimental data and the final Rietveld refinements plots for all compounds are shown in Figure 5.

Table 4. Refinement Indexes of Agreement, Cell Parameters (a , b , c , β , and Volume), and Distances Ln–Ln and Ln–O of the Ln-Compounds Compared with Single-Crystal Data of Za1

Ln	Pr (single-crystal)	La	Ce	Pr	Nd	Sm
$R_{\text{Shannon}}/\text{\AA}$	1.126	1.16	1.143	1.126	1.109	1.079
R_{Bragg}		2.62	4.41	3.48	4.91	3.92
R_f		2.37	3.62	2.30	3.67	3.41
a (Å)	5.6060(4)	5.6184(4)	5.5897(9)	5.5746(6)	5.555(1)	5.5196(9)
b (Å)	20.251(7)	20.149(1)	20.073(3)	20.056(2)	20.050(4)	19.973(3)
c (Å)	8.2740(6)	8.3824(5)	8.325(1)	8.2868(8)	8.244(2)	8.179(1)
β (°)	108.52(1)	108.674(3)	108.573(7)	108.588(4)	108.496(8)	108.469(7)
cell volume/Å ³	890.7(3)	898.9(1)	885.4(2)	878.2(2)	870.7(3)	855.3(2)
Ln–Ln	4.2503(6)	4.2901(5)	4.2682(9)	4.2505(8)	4.223(1)	4.1970(9)
Ln–O(1)	2.516(9)	2.621(9)	2.65(2)	2.49(1)	2.54(3)	2.53(2)
Ln–O(2)	2.435(8)	2.501(8)	2.52(1)	2.48(1)	2.59(2)	2.44(2)
Ln–O(2)	2.650(9)	2.669(9)	2.74(2)	2.66(2)	2.66(2)	2.61(2)
Ln–O(3)	2.370(9)	2.33(1)	2.32(2)	2.21(2)	2.29(3)	2.41(2)
Ln	Pr (single-crystal)	Eu	Gd	Tb	Dy	Ho
$R_{\text{Shannon}}/\text{\AA}$	1.126	1.066	1.053	1.04	1.027	1.015
R_{Bragg}		3.13	6.03	4.56	6.70	8.14
R_f		2.13	4.15	3.92	4.67	5.09
a (Å)	5.6060(4)	5.4997(7)	5.480(1)	5.4735(7)	5.4462(9)	5.4309(5)
b (Å)	20.251(7)	19.955(3)	19.943(4)	19.894(2)	19.869(3)	19.844(2)
c (Å)	8.2740(6)	8.158(1)	8.132(2)	8.116(1)	8.086(1)	8.0629(6)
β (°)	108.52(1)	108.353(5)	108.367(8)	108.323(5)	108.237(6)	108.208(3)
cell volume/Å ³	890.7(3)	849.8(2)	843.5(3)	838.9(2)	831.1(2)	825.4(1)
Ln–Ln	4.2503(6)	4.1904(9)	4.173(1)	4.1764(9)	4.169(1)	4.1512(9)
Ln–O(1)	2.516(9)	2.53(2)	2.59(3)	2.51(2)	2.48(2)	2.49(2)
Ln–O(2)	2.435(8)	2.52(2)	2.62(2)	2.47(1)	2.26(2)	2.28(1)
Ln–O(2)	2.650(9)	2.62(2)	2.69(2)	2.61(2)	2.64(2)	2.56(1)
Ln–O(3)	2.370(9)	2.27(2)	2.42(3)	2.13(2)	2.11(3)	2.06(2)

220 The variation of unit cell parameters show dependency to the
 221 Shannon's effective ionic radii,⁴² and the expected tendencies are
 222 observed: the ionic radii decrease linearly as the unit cell
 223 parameters (a , b , c , β , and volume) and distances Ln–Ln do.
 224 These tendencies are illustrated in Figure 6.

225 Selected IR spectra of Ln-compounds are depicted in Figure
 226 S1 (see Supporting Information). The presence of the **HBDP**³⁻
 227 ligand in the Ln-compounds is confirmed by two bands at
 228 1140 cm⁻¹ (strong) and 1046 cm⁻¹ (medium) characteristic
 229 of the stretching vibrations of the phosphonate P–O₃ groups, as
 230 well as the broad band at around 1634 cm⁻¹ characteristic of
 231 P=O stretching vibrations. The band at 1260 cm⁻¹ may
 232 attributed to P=O deformation vibration. Bands between
 233 600 cm⁻¹ and 400 cm⁻¹ main correspond to the bending modes
 234 of the PO₃ group. However, the band at 538 cm⁻¹ may be
 235 assigned to Ln–O stretching vibration. The band at 975 cm⁻¹ is
 236 characteristic of P–C stretching vibrations. Bands at 1385 cm⁻¹
 237 and 663 cm⁻¹ are, respectively, characteristic of C–C stretching
 238 vibrations of the phenylene group and in-plane deformation
 239 vibrations of para-disubstituted aromatic ring with identical
 240 groups. Bands at 836 cm⁻¹ and 819 cm⁻¹ are attributed to the
 241 C–H out-of-plane vibrations for para-disubstituted phenylene
 242 rings. The broad bands around 3600 and 3000 cm⁻¹, arising from
 243 the O–H stretching vibrations of the protonated phosphonate
 244 oxygens O(1), suggest that extensive hydrogen bonds are present
 245 in the Ln-compounds because of the absence of O–H deformation

band around 1568 cm⁻¹, as they do not contain either coordinated
 or lattice water molecules.^{10,11,45–46}

The thermal stability in air of Ln-compounds was investigated.
 The TG curves, and some typical mass spectrometry analysis
 curves, are depicted in Figure S2a,b (see Supporting In-
 formation). According to the difference in their thermal stability,
 TG curves may be divided into two groups named **hs** (high
 stability) and **ms** (medium stability). TG curves of Ln-com-
 pounds reveal the observed total mass losses, presented in the
 Table 5, from room temperature up to 1200 °C, and a 1:1
 mixture of LnPO₄ and Ln(PO₃)₃ as the final product. The TG
 curves of Ln-compounds very closely resemble each other and
 show that this series of compounds is characterized by high
 thermal stability. A noticeable increase in thermal stability has
 been observed in the case of Dy- and Ho-compounds. From
 room temperature to ca. 600 °C in the case of **hs**, and to ca.
 500 °C in the case of **ms**, no noticeable mass loss (or a slight mass
 loss of ca. 3%) was detected. Between ca. 600 and 1100 °C in the
 case of **hs**, and between ca. 500 and 1000 °C in the case of **ms**, the
 mass loss proceeds in continuous and overlapping stages and
 corresponds to the loss of the phenyl group. The associated mass
 spectrometry m/z 18 (H₂O), 44 (CO₂), and 78 (C₆H₆) curves
 are in a good agreement with TG curves. The very slight mass
 loss below 600 and 500 °C for **hs** and **ms**, respectively, is
 explained by the m/z 78 curve which shows the desorption
 of the phenyl group in the ranges 500–750 °C (**hs**) and

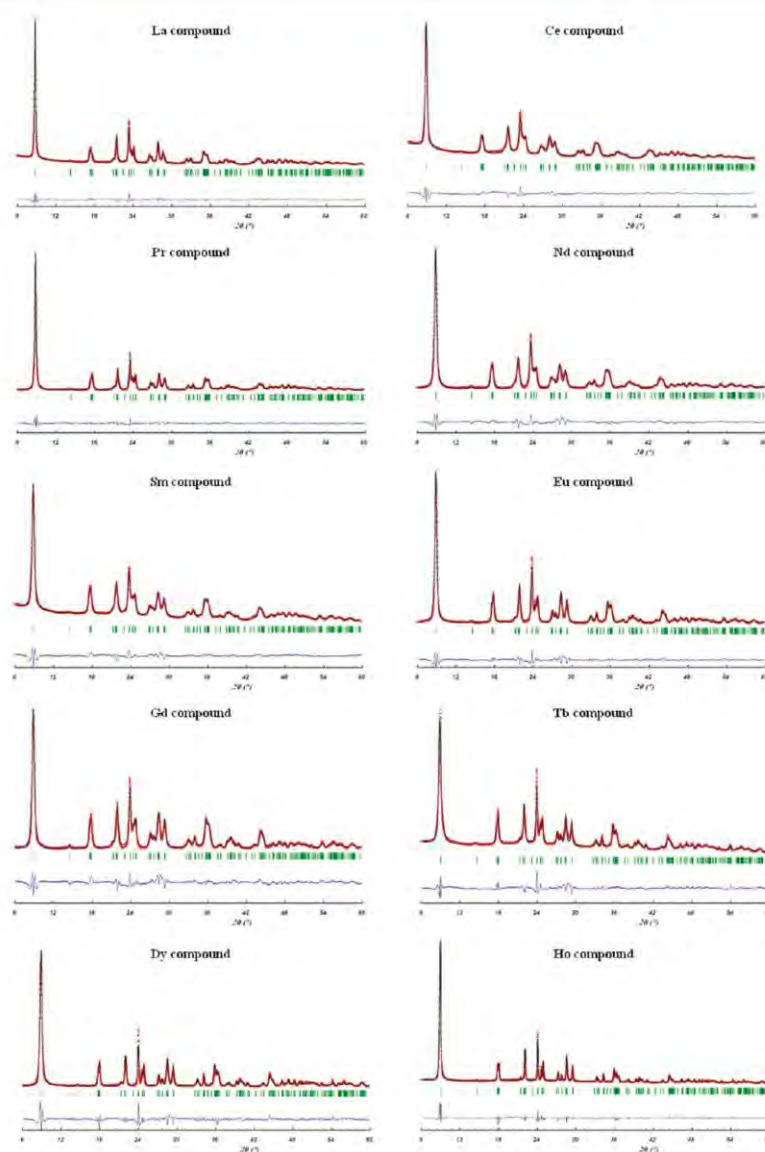


Figure 5. Observed (red) and calculated (black) profiles for the final Rietveld refinement of $[\text{Ln}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$ compounds (Ln = La, Ce, Pr, Nd, Eu, Dy, Ho). The difference plot (blue) is on the same intensity scale.

272 400–700 °C (ms), with first maxima at around 560 °C (hs)
 273 and 528 °C (ms). After 600 °C (hs) or 500 °C (ms), the
 274 mass loss increases rapidly due to the combustion of phenyl
 275 groups and that is manifested by a series of bands on the m/z
 276 18 and 44 curves in the ranges of 600–1100 °C (hs) and
 277 500–1000 °C (ms).

278 The X-ray thermodiffraction analysis of the Ho-compound
 F7 279 carried out under air heating up to 900 °C (Figure 7) has
 280 confirmed that no significant structural change occurs up
 281 600 °C. At 650 °C, a noticeable diffraction intensities drop is
 282 observed and peak broadening is observed, and continues
 283 decreasing and broadening until 850 °C. At 900 °C, practically

no diffraction peaks have been observed. Nevertheless, by main-
 284 taining the temperature at 900 °C for a longer time as well as after
 285 cooling down to 30 °C, two new phases have been formed
 286 characterized by a series of broad diffraction peaks correspond-
 287 ing to the formation of HoPO_4 and $\text{Ho}(\text{PO}_3)_3$.^{47,48} The X-ray thermo-
 288 diffraction study is consistent with TG analysis and confirms
 289 the very high thermal stability of the Ln-compounds reported in
 290 this paper.

The RT luminescence and excitation spectra of the Eu- and
 292 Tb-compounds as powders are shown in Figure 8a,b. The
 293 emission peaks in the luminescence spectra are assigned to the
 294 electronic transitions from the $^5\text{D}_0$ and $^5\text{D}_4$ multiplet to lower
 295

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energy states 7F_J of Eu^{3+} and Tb^{3+} , respectively. The excitation spectra correspond to transitions from the ground states — 7F_0 and 7F_6 of Eu^{3+} and Tb^{3+} , respectively — to excited states according to the Dieke's diagram (see insets of Figure 8a,b).⁴⁹ In addition to these f–f transitions, the excitation spectra show strong bands at wavelengths smaller than 340 nm, which are tentatively assigned to an energy transfer process from the ligand. The presence of

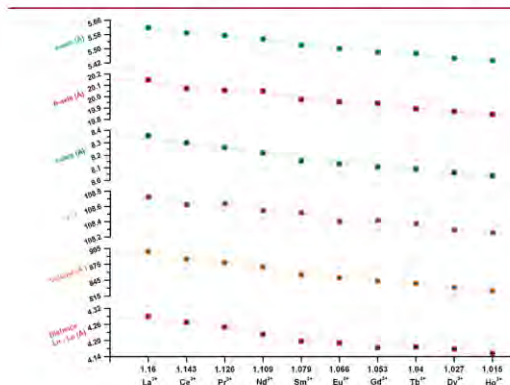


Figure 6. Variation of cell parameters (a , b , c , and β), volume, and distance Ln–Ln versus Shannon's ionic radii (\AA) of Ln^{3+} cations in the isostructural Ln-compounds.

organic ligands usually leads to an absence of luminescence due to the strong competition with nonradiative relaxation processes induced by high energy ligand vibrations. Moreover, it is well-known that a strong quenching of luminescence occurs for high concentration of lanthanide ions due to energy migration of the excitation to quenching impurities (killer traps).⁵⁰ This is especially relevant for two- or three-dimensional lattices. Therefore, the observation of visible luminescence in a solid form in concentrated lanthanide compounds at room temperature is an outstanding result itself. Additionally, the sharp lines observed in luminescence and excitation spectra are a clear demonstration of the good crystalline quality of the samples. The absence of emission from the excited state 5D_1 and 5D_3 to the ground state in Eu^{3+} and Tb^{3+} , respectively, can be explained by the energy gap's law taking into account the maximum phonon energy of the lattice or by resonant energy transfer processes between adjacent Eu^{3+} or Tb^{3+} ions. In this process the excited electron in 5D_1 can relax to 5D_0 multiplet and excites the ground state 7F_0 electron to the 7F_3 state in a neighboring Eu^{3+} ion since the energy difference between these states is the same. In the same manner, a Tb^{3+} ion can relax from the 5D_3 level to the 5D_4 and excites a near neighbor Tb^{3+} from the 7F_6 to the ${}^7F_{1,0}$.⁵¹ The same process can be responsible for the lack of visible emission in all the other members of the series. Temporal dependence of Tb^{3+} and Eu^{3+} luminescence, corresponding to transitions from the 5D_4 and 5D_0 to lower energy levels, shows a single exponential behavior

Table 5. Calculated and Found Percentages of C–H and Total Mass Losses of $[\text{Ln}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$ Compounds

compound	M_r (g/mol)	calculated			experimental		
		C (%)	H (%)	weight loss (%)	C (%)	H (%)	weight loss (%)
$\text{La}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	373.95	19.25	1.34	20.62	19.1	1.2	21.8
$\text{Ce}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	375.16	19.19	1.33	20.55	19.4	1.1	21.2
$\text{Pr}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	375.95	19.15	1.33	20.51	18.7	1.4	21.3
$\text{Nd}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	379.29	18.98	1.32	20.33	19.2	1.3	20.8
$\text{Sm}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	385.41	18.86	1.30	20.01	18.7	1.2	21.0
$\text{Eu}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	387.01	18.60	1.29	19.92	18.9	1.1	20.4
$\text{Gd}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	392.30	18.35	1.27	19.65	18.1	1.3	20.2
$\text{Tb}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	393.97	18.27	1.27	19.57	18.6	1.2	20.4
$\text{Dy}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	397.55	18.11	1.26	19.40	18.2	1.3	19.6
$\text{Ho}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$	399.98	18.00	1.25	19.28	18.1	1.2	18.7

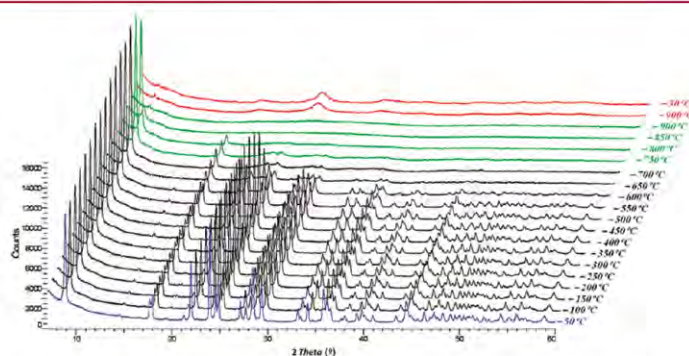


Figure 7. X-ray thermodiffractogram of Ho-compound recorded in air heating up from 50 to 900 °C. Color code corresponding to the structural changes.

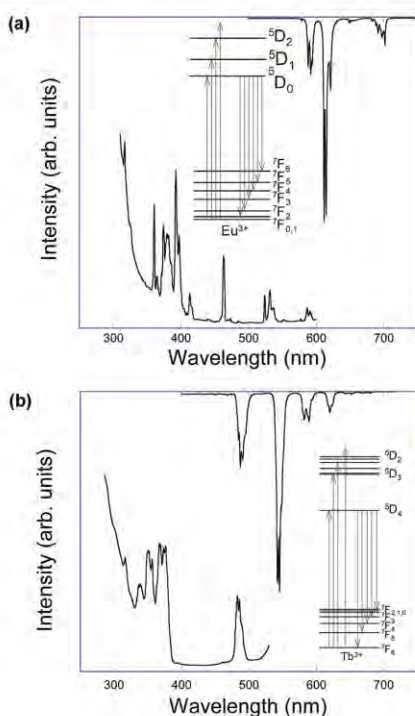


Figure 8. RT emission (up) and excitation (down) spectra of (a) Eu- and (b) Tb-compounds. Emission spectrum was obtained upon excitation at 464 and 376 nm, while excitation spectrum was performed detecting luminescence at 615 and 545 nm, for Eu- and Tb-compounds, respectively. Energy level scheme of Eu^{3+} and Tb^{3+} ion with the transitions responsible for the luminescence and excitation spectra are depicted in the inset.

(Figure S3, see Supporting Information) with lifetimes of 1.89 ± 0.02 ms and 1.397 ± 0.015 ms, respectively.

CONCLUSIONS

The hydrothermal synthesis and the structural characterization of a series of novel isostructural metal–organic hybrids based on lanthanide and 1,4-phenylenebis(phosphonate) $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H}]$ (where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}$ and Ho) have been reported. These compounds have been obtained as single phases and exhibit very high thermal stability, and their photoluminescence properties are also discussed. Currently, our work is focused on using the extended analogue 1,4-biphenylenebis(phosphonate) and spacer molecules as a second ligand, such as phosphorus or phosphoric acid, to create porous structures, as these may be promising materials in the fields of gas storage and photoluminescence.

ASSOCIATED CONTENT

S Supporting Information. IR spectra of $[\text{Ln}(\text{HO}_2\text{P}_2\text{C}_6\text{H}_4)]$ compounds, $[\text{Ln}(\text{HO}_2\text{P}_2\text{C}_6\text{H}_4)]$ TG curves; representative MS curves for Ho-compound and La-compound, room temperature of Eu^{3+} emission decay curve, and X-ray crystallographic

information (CIF files) for the $\text{Ln}(\text{HBDP})$ compounds can be obtained free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420.
- (2) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268.
- (3) Clearfield, A. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons, Inc.: New York, 1998; Vol. 47, pp 371–510.
- (4) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 495.
- (5) Maeda, K. *Microporous Mesoporous Mater.* **2004**, *73*, 47.
- (6) Clearfield, A. *In Design of New Materials*; Cocke, D. L., Clearfield, A., Eds.; Plenum: New York, 1986.
- (7) Gómez-Alcántara, M. M.; Cabeza, A.; Moreno-Real, L.; Aranda, M. A. G.; Clearfield, A. *Microporous Mesoporous Mater.* **2006**, *88*, 293.
- (8) Wang, Z.; Heising, J. M.; Clearfield, A. *J. Am. Chem. Soc.* **2003**, *125*, 10375.
- (9) Clearfield, A.; Wang, Z.; Bellinghausen, P. *J. Solid State Chem.* **2002**, *167*, 376.
- (10) Poojary, D. M.; Zhang, B.; Bellinghausen, P.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 4942.
- (11) Poojary, D. M.; Zhang, B.; Bellinghausen, P.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5254.
- (12) Poojary, D. M.; Zhang, B.; Clearfield, A. *An. Quim.-Int. Ed.* **1998**, *94*, 401.
- (13) Clearfield, A.; Wang, J. D.; Tian, Y.; Campbell, F. L., III; Peng, G. Z. In Perry, D., Ed.; *Materials Synthesis and Characterization*; Plenum: New York, 1997.
- (14) Clearfield, A.; Wang, Z. *J. Chem. Soc., Dalton Trans.* **2002**, *15*, 2937.
- (15) Distler, A.; Sevov, S. C. *Chem. Commun.* **1998**, 959.
- (16) Fredoueil, F.; Massiot, D.; Poojary, D. M.; Bujoli-Doeuff, M.; Clearfield, A.; Bujoli, B. *Chem. Commun.* **1998**, 175.
- (17) Burwell, D. A.; Thompson, M. E. *Chem. Mater.* **1991**, *3*, 14.
- (18) Silvestre, J. P.; El Messbahi, N.; Rochdaoui, R.; Dao, N. Q.; Lee, M. R.; Neuman, A. *Acta Crystallogr.* **1990**, *C46*, 986.
- (19) Poojary, D. M.; Zhang, B.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *J. Mater. Chem.* **1996**, *6*, 639.
- (20) Soghomonian, V.; Chen, R.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 223.
- (21) Maeda, K.; Akimoto, J.; Kiyozumi, Y.; Mizukami, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1199.
- (22) Finn, R. C.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 1821.
- (23) Serre, C.; Ferey, G. *Inorg. Chem.* **1999**, *38*, 5370.
- (24) Loshe, D. L.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1619.
- (25) Wharmby, M. T.; Mowat, J. P. S.; Thompson, S. P.; Wright, P. A. *J. Am. Chem. Soc.* **2011**, *133*, 1266.
- (26) Rocha, J.; Almeida Paz, F. A.; Shi, F. N.; Ananias, D.; Silva, N. J. O.; Carlos, L. D.; Trindade, T. *Eur. J. Inorg. Chem.* **2011**, *13*, 2035.
- (27) Vivani, R.; Alberti, G.; Costantino, F.; Nocchetti, M. *Microporous Mesoporous Mater.* **2008**, *107*, 58.
- (28) Mao, J. G. *Coord. Chem. Rev.* **2007**, *251*, 1493.
- (29) Shi, F. N.; Trindade, T.; Rocha, J.; Almeida Paz, F. A. *Cryst. Growth Des.* **2008**, *8*, 3917.

- 412 (30) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2009**, *48*, 2732.
413 (31) Diwu, J.; Nelson, A. G. D.; Wang, S.; Campana, C. F.; Albrecht-
414 Schmitt, T. E. *Inorg. Chem.* **2010**, *49*, 3337.
415 (32) Wang, R. C.; Zhang, Y.; Hu, H.; Frausto, R. R.; Clearfield, A.
416 *Chem. Mater.* **1992**, *4*, 864.
417 (33) Song, S. Y.; Ma, J. F.; Yang, J.; Cao, M. H.; Zhang, H. J.; Wang,
418 H. S.; Yang, K. Y. *Inorg. Chem.* **2006**, *45*, 1201.
419 (34) APEX2 and SAINT; Bruker AXS Inc.: Madison, Wisconsin,
420 2007.
421 (35) Sheldrick, G. M. SADABS, *Program for Absorption Correction of*
422 *Area Detector Frames*, Bruker AXS, Inc., Madison, WI.
423 (36) Sheldrick, G. M. SHELXL-97, *Program for Refinement of Crystal*
424 *Structures*; University of Göttingen: Germany, 1997.
425 (37) Parkin, S.; Moezzi, B.; Hope, H. J. *Appl. Crystallogr.* **1995**,
426 *28*, 53.
427 (38) PLATON/PLUTON: (a) Spek, A. L. *Acta Crystallogr., Sect. A*
428 **1990**, *46*, C34. (b) Spek, A. L. *PLATON: A Multipurpose Crystallographic*
429 *Tool*; Utrecht University: Utrecht, The Netherlands, 1998.
430 (39) Brandenburg, K. DIAMOND, Version 3.1; Crystal Impact
431 GbR: Bonn, Germany, 2007.
432 (40) Rodríguez-Carvajal, J. *Physica B* **1993**, *192*, 55.
433 (41) Toby, B. H. *Powder Diffr.* **2006**, *21*, 67.
434 (42) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
435 (43) Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*, 3rd
436 ed; Chapman and Hall: London, 1975.
437 (44) Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley:
438 New York, 1994.
439 (45) Abdel Kerim, F. M.; Aly, H. F.; El-Agramy, A. *Proc. Indian Acad.*
440 *Sci.* **1977**, *85*, 559.
441 (46) Amicangelo, J. C.; Leenstra, W. R. *Inorg. Chem.* **2005**, *44*, 2067.
442 (47) Milligan, W. O.; Mullica, D. F.; Beall, G. W.; Boatner, L. A.
443 *Inorg. Chim. Acta* **1983**, *70*, 133.
444 (48) Hoeppe, H. A. J. *Solid State Chem.* **2009**, *182*, 1786.
445 (49) Dieke, G. H. In *Spectra and Energy Levels of Rare Earth Ions in*
446 *Crystals*; Wiley Interscience: New York, 1968.
447 (50) Berdowski, P. A. M.; Blasse, G. J. *Lumin.* **1984**, *29*, 243.
448 (51) Hayakawa, T.; Kamata, N.; Yamada, K. J. *Lumin.* **1996**, *68*, 179.

Organic-inorganic hybrids assembled from lanthanide and 1,4-phenylenebis(phosphonate)

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Electronic Supplementary Information

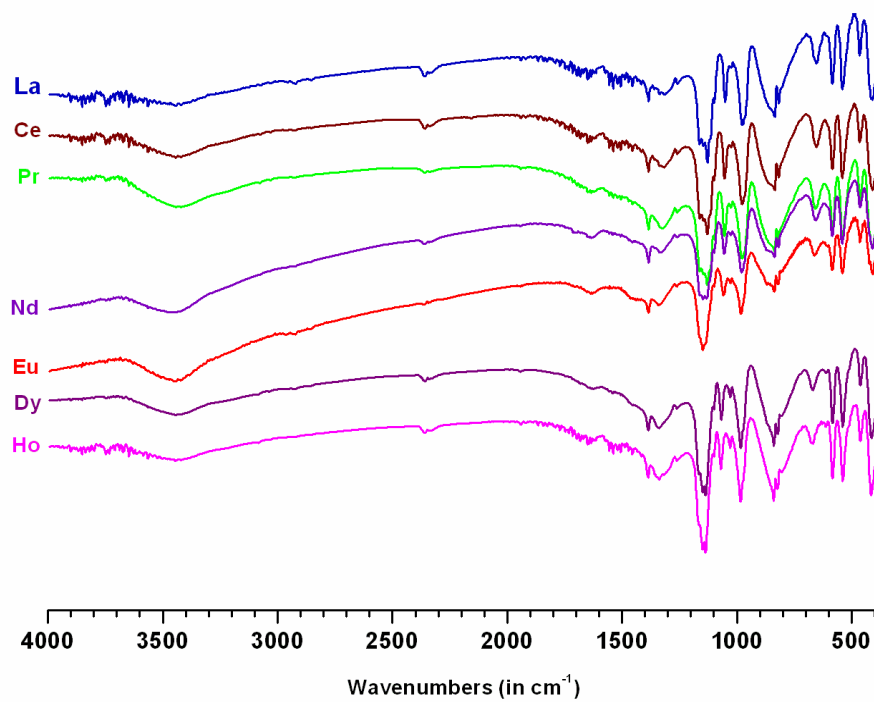


Figure S1. IR spectra of $[\text{Ln}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$ compounds (Ln = La, Ce, Pr, Nd, Eu, Dy, Ho).

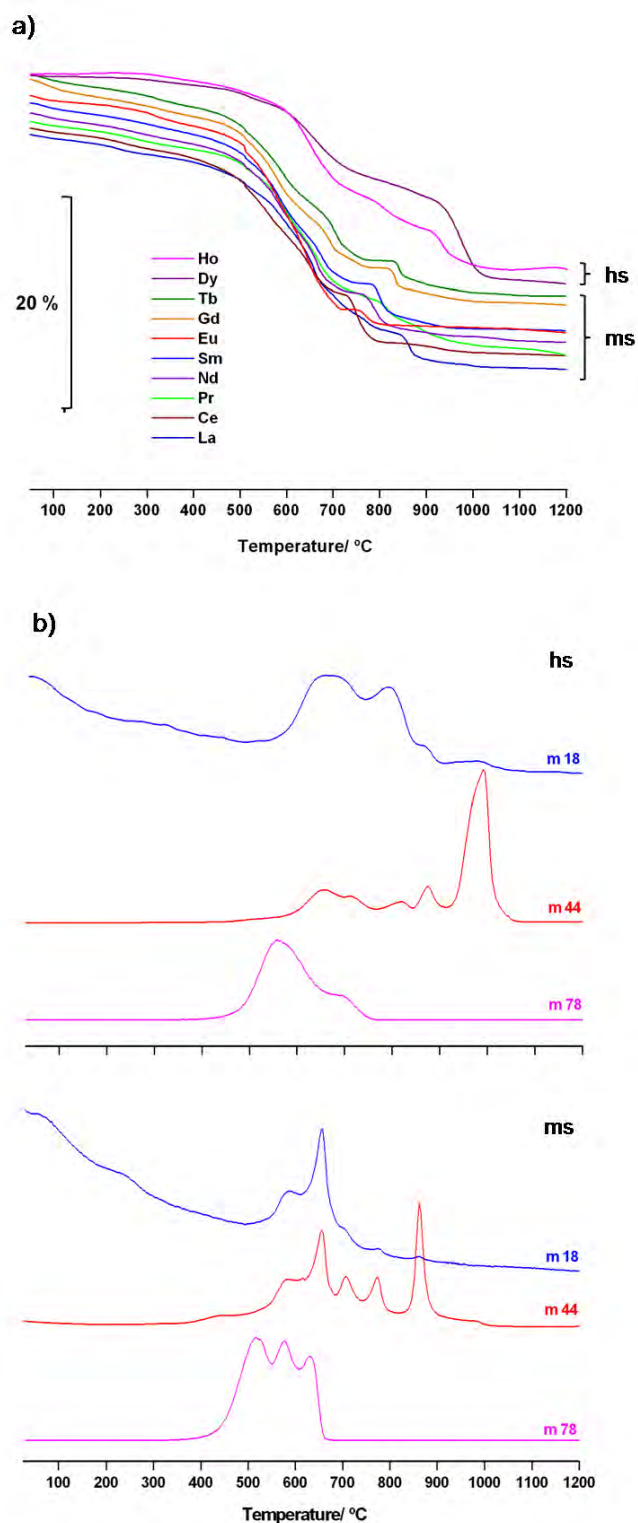


Figure S2. (a) $[\text{Ln}(\text{HO}_6\text{P}_2\text{C}_6\text{H}_4)]$ TG-curves classified as a function of the compound's thermal stability: high (hs) and medium (ms). (b) Representative MS-curves for Ho-compound (hs) and La-compound (ms).

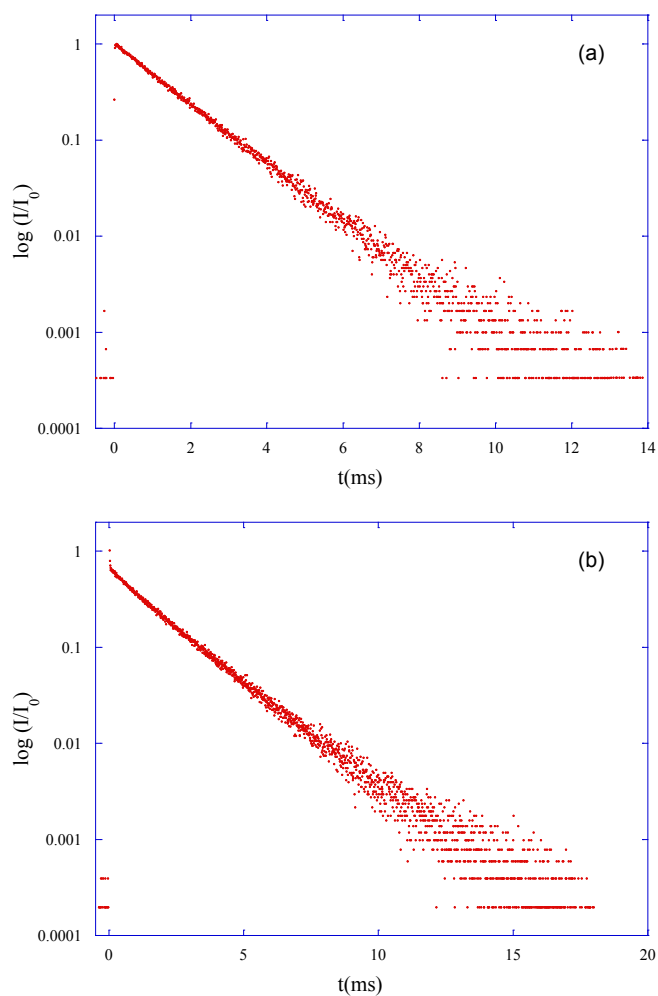


Figure S3. (a) Room temperature (RT) of Eu^{3+} emission decay curve detected at 612 nm after 393 nm excitation wavelength in semilog scale. (b) RT Tb^{3+} emission decay curve detected at 545 nm after 484 nm excitation wavelength in semilog scale. The least square fitting to eq. $I = A + I_0 \cdot \exp(-t/\tau)$ gives lifetimes of $\tau = 1.397 \pm 0.015$ ms and $\tau = 1.89 \pm 0.02$ ms for Eu^{3+} and Tb^{3+} , respectively. Note the different scale of the x-axis.

3.7. Fosfatos de lantánidos a nanoescala.

Artículo VI

Artículo en trámite de publicación en la revista *Journal of Alloys and Compounds*, con el título “Nanoscale Lanthanide Phosphonates: Synthesis, Thermal Stability and Magnetic Properties”.

Resumen

El objetivo del trabajo presentado en este artículo fue la síntesis y caracterización estructural del resto de los miembros de la familia de fosfonatos de lantánidos descritos en el capítulo anterior, culminando con la descripción de sus propiedades magnéticas.

Se describe aquí la síntesis y caracterización estructural de los compuestos basados en un ligando de vinculación bidentado rígido, el 1,4-fenilbis(fosfonato), y elementos lantánidos (itrio, erbio, tulio, iterbio, y lutecio), completando así la serie de los fosfonatos de lantánidos previamente descritos y discutidos en el capítulo anterior. Su caracterización mediante difracción de rayos X de polvo cristalino, microscopía electrónica de transmisión (TEM) y barrido (SEM/EDX), espectroscopia infrarroja y análisis térmico (TG-MS/SDTA y DSC) se completó con el estudio de las propiedades magnéticas de los compuestos basados en gadolinio, disprosio, holmio, erbio, tulio, e iterbio.

Se ha obtenido la serie completa de nuevos híbridos organo-inorgánicos basados en elementos lantánidos trivalentes ($\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$) y el ligando de vinculación 1,4-phenylbis(fosfonato) en condiciones hidrotermales, usando calefacción convencional, o asistida por microondas, en este último caso con tiempos de síntesis muy cortos. Los compuestos basados en La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, y Ho se obtuvieron bajo condiciones hidrotermales como fases anhidras isoestructurales de fórmula $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$, independientemente del método de calentamiento (convencional o asistido por microondas), la duración de la síntesis y la concentración de reactivos. Sin embargo, los compuestos basados en Y, Er, Tm, Yb, Lu, se obtuvieron bajo condiciones hidrotermales convencionales, en la mayoría de los casos como fases hidratadas desconocidas, con un producto final que es función de las condiciones de síntesis. En el caso del compuesto basado en Y^{3+} , que tiene un radio iónico similar a Ho^{3+} , y en función de las condiciones de síntesis, la fase puede variar de anhidra (180 °C, 3-5 días, calefacción convencional) a hidratada (120 °C, 3 horas, microondas) (véanse los diagramas de difracción de rayos X en la Figura 3.7.1 y las correspondientes curvas TG en la Figura 3.7.2). La fase anhidra, $\text{Y}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$, isoestructural a las fases basadas en La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, y Ho, cristaliza en el sistema monoclinico ($C2/c$), con los siguientes parámetros de celdilla: $a = 5.4339(7) \text{ \AA}$, $b = 19.842(3) \text{ \AA}$, $c = 8.0688(9) \text{ \AA}$, $\beta = 108.233(7)^\circ$. Sin embargo, hasta el momento, se desconoce la estructura de la fase hidratada. Su análisis mediante TG-MS sugiere que contiene una molécula de agua, probablemente coordinada, que abandona el sólido a 200-300 °C (Figura 3.7.2), lo que se traduce en una pérdida de masa del 5.4% (calc. 5.3%). El proceso de descomposición continúa hasta alcanzar una pérdida de masa total del 26.7% (calc. 25.5%, para $\text{Y}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}(\text{H}_2\text{O})]$). El diagrama de difracción de rayos X de polvo cristalino (Figura 3.7.1) sugiere que esta nueva fase hidratada posee estructura laminar, con un espaciado basal de $\sim 9.8 \text{ \AA}$ (véase el detalle insertado de la Figura 3.7.1) similar al de su fase anhidra. Estos resultados sugieren que, de la fase anhidra a la hidratada, la coordinación del Y^{3+} ha pasado de 8 a 9 por la incorporación de una molécula de agua en su esfera de coordinación. Cuando el radio iónico del catión lantánido disminuye hasta el del Er^{3+} , se obtuvo únicamente la fase hidratada (véanse las Figuras 3.7.1 y 3.7.2).

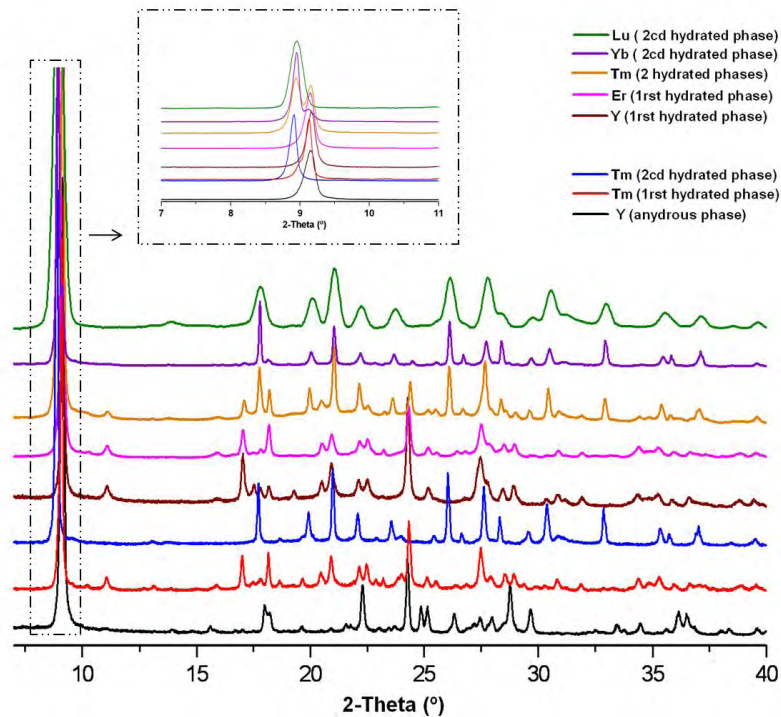


Figura 3.7.1. Diagramas de difracción de rayos X de polvo cristalino de los compuestos basados en Y, Er, Tm, Yb, y Lu.

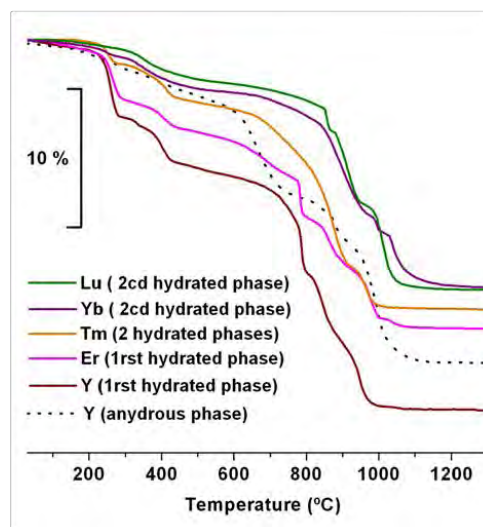


Figura 3.7.2. Curvas TG de los compuestos basados en Y, Er, Tm, Yb, y Lu.

Por otro lado, cuando el radio iónico disminuye hasta el del Tm^{3+} , en adición a la fase hidratada descrita en el párrafo anterior, se observa la una segunda fase hidratada (Figura 3.7.1 y 3.7.2), que presenta un espacios interlaminaar ligeramente superior ($\sim 10.0 \text{ \AA}$ frente a $\sim 9,8 \text{ \AA}$), como puede apreciarse en el cuadro insertado en la Figura 3.7.1. Estas dos fases hidratadas han podido ser aisladas cambiando ligeramente las

condiciones de síntesis (usando microondas como medio de calefacción, a 180 °C durante 1 h, se obtiene la primera fase hidratada si se adiciona 1 mL de agua, mientras que se alcanza la segunda si se añaden 3 mL).

Cuando se utilizan otros cationes lantánidos, la proporción de la primera fase hidratada disminuye al hacerlo el radio catiónico (es el caso del compuesto basado en Yb^{3+}) hasta que la única fase hidratada que se obtiene es la descrita en segundo lugar, como es el caso del compuesto basado en Lu^{3+} (véase el cuadro insertado de la Figura 3.7.1).

Los estudios morfológicos realizados a todos los materiales de esta familia, utilizando microscopía electrónica de transmisión (TEM) y barrido (SEM/EDX), desvelaron un tamaño de partícula muy variable, que abarca de aproximadamente 20 nm a 1-5 micras (Figura 3.7.3). Aparentemente, las características del catión lantánido influyen en el tamaño de partícula, que aumenta desde 20-50 nm (Ce, Nd, Sm, Eu, y Gd) a 400-500 nm (en el caso de Dy y Ho) llegando a unas pocas micras (Lu) al avanzar en el periodo.

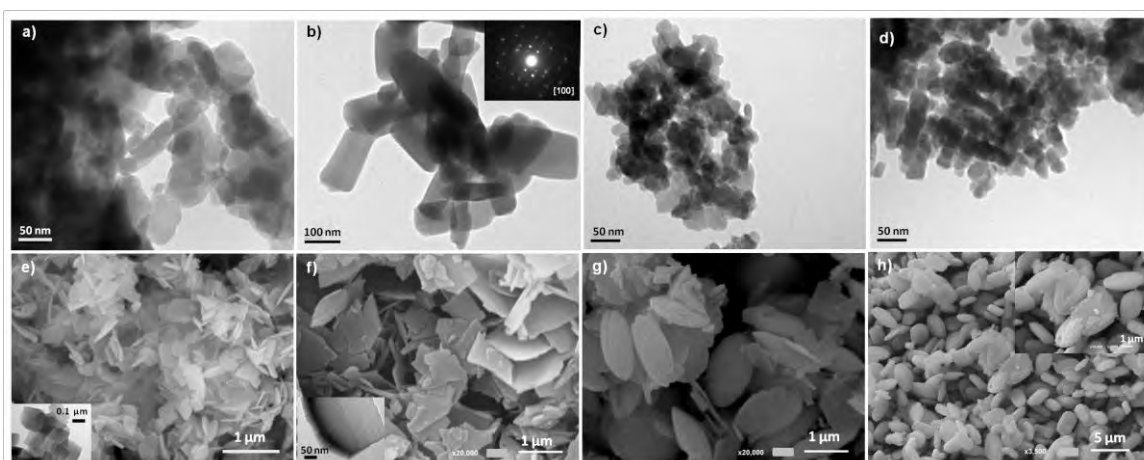


Figura 3.7.3. Imágenes TEM y SEM de los compuestos basados en Ce (a), Pr (b), Sm (c), Eu (d), Ho (e), Y (f), Tm (g), and Lu (h).

Finalmente, se han estudiado las propiedades magnéticas de los compuestos basados en gadolinio, disprosio, holmio, erbio, tulio, e iterbio. En todos los casos, se ha observado comportamiento paramagnético, con la susceptibilidad magnética siguiendo la ley de Curie-Weiss y momentos paramagnéticos efectivos en buen acuerdo con los esperados para los iones lantánidos libres.

Artículo VI

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Abstract: Series of novel organic-inorganic hybrids materials based on trivalent metal (metal = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and 1,4-phenylbis(phosphonate) obtained under hydrothermal conditions either by oven heat or microwave irradiation. Compounds containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, are isostructural. However, the compounds based on Y, Er, Tm, Yb, and Lu are hydrated and their structures have not yet been solved. The series of compounds are characterized by PXRD, TEM, SEM-EDX and thermal analyses (TG-MS and DSC). TEM study show a variable particles size with a minimum size of ca. 20 nm. This compounds exhibit unusual very high thermal stability. The size of particles and the thermal stability are depending on metal(III) cation features. All the investigated materials show paramagnetic behaviour. The magnetic susceptibility data follow a Curie-Weiss laws with paramagnetic effective moments in good agreement with those expected for Ln³⁺ free ions.

Nanoscale Lanthanide Phosphonates: Synthesis, Thermal Stability and Magnetic Properties

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Abstract

Series of novel organic-inorganic hybrids materials based on trivalent metal (metal = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and 1,4-phenylbis(phosphonate) obtained under hydrothermal conditions either by oven heat or microwave irradiation. Compounds containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, are isostructural. However, the compounds based on Y, Er, Tm, Yb, and Lu are hydrated and their structures have not yet been solved. The series of compounds are characterized by PXRD, TEM, SEM-EDX and thermal analyses (TG-MS and DSC). TEM study show a variable particles size with a minimum size of *ca.* 20 nm. This compounds exhibit unusual very high thermal stability. The size of particles and the thermal stability are depending on metal(III) cation features. All the investigated materials show paramagnetic behaviour. The magnetic susceptibility data

follow a Curie-Weiss laws with paramagnetic effective moments in good agreement with those expected for Ln^{3+} free ions.

PACS codes: 81.07.Pr, 81.05.Lg, 81.16.Dn, 81.70.Pg, 75.30.Cr

Keywords: Lanthanides, phosphonate, hydrothermal synthesis, microwave, thermal behaviour, magnetic susceptibility.

1. Introduction

The research field on metal phosphonates has been deeply explored during the last two decades because of the great variety of building block available for the preparation of functional materials useful in the field of molecular recognition, gas storage, intercalation chemistry and for their optical and magnetic properties [1-6]. The wide choice of metals (mono-, di-, tri-, tetra-, penta-, and hexavalent) and the variety of organic ligands that can be utilized to prepare the metal phosphonate, has made the scientific literature on this field more and more rich and still today the research for new functional phosphonates is far from being exhausted. Recently, investigations of di-, tri-, and tetra-valent metal phosphonates have yielded exciting structural diversity with interesting chemistries and applications [7-15], including open framework structures [15] and porous pillared layered structures [10,11]. The synthesis of lanthanide phosphonates has drawn the scientist's attention for their possible optical and magnetic properties. However, reports on lanthanide phosphonates are rather limited [12], due to the fact that lanthanide phosphonates normally have low solubility in water and organic solvents, hence it is difficult to obtain single crystals suitable for X-ray structural analysis.

The topic of this communication is the preparation, either by conventional or microwave-assisted hydrothermal synthesis, characterization of trivalent lanthanides 1,4-phenylbis(phosphonate) compounds

mainly those based on Y, Er, Tm, Yb, and Lu, and finally the study of magnetic properties of those based on Gd, Dy, Ho, Er, Tm, and Yb.

2. Experimental procedures

1,4-Phenylenebis(phosphonic acid) (H₄BDP) was prepared according to the reported procedure [7]. Lanthanide(III) 1,4-phenylenebis(phosphonates) were prepared by mixing 0.2 mmol of 1,4-phenylenebis(phosphonic acid), 0.2 mmol of Ln(NO₃)₃·xH₂O (x = 5, 6) or LnCl₃·6H₂O (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and 6 mL of distilled water. The reaction mixture was stirred and sealed in a PTFE-lined stainless steel autoclave with an internal volume of 15 mL and heated at 180 °C for 5 days under autogenous pressure. After cooling, the resulting products were filtered off, washed with water, and dried. The same procedure was followed and the only difference is the amount of water added was reduced to 3 mL or less and the conventional hydrothermal process was substituted by microwave-assisted hydrothermal synthesis carried out in CEM Explorer-12 Microwave at 120 °C or 180 °C for different reaction times (30 min, 1 h, 3 h, or 7 h).

Micrographs were recorded with a JEOL 2000EX-II transmission electron microscope, operating at 120-200 kV. Micrographs and X-ray microanalysis (SEM/EDX) were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV coupled with an INCA Energy-200 energy dispersive X-ray microanalysis system (EDX).

X-ray powder diffraction data were recorded on a Bruker D8 Advance powder X-ray diffractometer with CuK α radiation. The samples were gently ground in an agate mortar in order to minimize the preferred orientation. Room temperature data were collected over the angular 2 θ range 4-40° with a step of 0.009° and a counting time of 0.15 s/step.

A Mettler-Toledo TGA/SDTA851° were used for the thermal analyses in oxygen dynamic atmosphere (50 mL/min) at a heating rate of 10 °C/min. In all cases, *ca.* 10 mg of powder sample was thermally treated, and blank runs were performed. A Pfeiffer Vacuum ThermoStar™ GSD301T mass

spectrometer was used to determine the evacuated vapours. The masses 18 (H₂O), 44 (CO₂), and 78 (C₆H₆) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

DC magnetic susceptibility measurements of powdered samples were performed using Quantum Design PPMS magnetometer whilst heating from 2 to 300 K under an applied magnetic field of strength 1 kOe. Magnetization as a function of field (H) was measured using the same magnetometer in the $-85 \leq H/kOe \leq 85$ at 2 K after cooling the sample in zero field.

3. Results and Discussion

Complete series of novel organic-inorganic hybrids based on trivalent metal (metal = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and 1,4-phenylbis(phosphonate) have been obtained under hydrothermal conditions either by oven heat or microwave irradiation. Compounds based on La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho were obtained under hydrothermal conditions as anhydrous phases, with formula $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$, independently of the method of heat (oven heat or microwave irradiation), reaction time, and reagent concentration. However, when the ionic radius of Ln^{3+} decreases up to Y^{3+} , having ionic radius similar to Ho^{3+} , and depending on the synthesis conditions, the structure of Y^{3+} based compound can vary from anhydrous (180 °C, 3-5 days, oven) to hydrated phase (120 °C, 3 hours, microwave) (see black/brown X-ray patterns in Fig. 2 and dash/brown TG curves in Fig. 3). The anhydrous phase $\text{Y}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$, isostructural to those based on La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, crystallizes in the monoclinic space group, $C2/c$, with $a = 5.4339(7)$ Å, $b = 19.842(3)$ Å, $c = 8.0688(9)$ Å, $\beta = 108.233(7)^\circ$. The crystal structure is illustrated in Figure 1. However, the structure of hydrated phase (1st hydrated phase) is unknown as yet (red pattern, Fig. 2). TG-MS analyses confirm that the structure of the new hydrated phase contains coordinated water molecule through the first mass loss of 5.4% (calcd. 5.3%) between 200-300 °C (brown TG-curve, Fig. 3), and the total mass loss of 26.7% (calcd. 25.5%) which suggest the formula

$\text{Y}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}(\text{H}_2\text{O})]$. In addition, X-ray powder pattern (brown pattern, Fig. 2) indicates that the interlayer space of *ca.* 9.8 Å of the new hydrated phase is similar to the anhydrous one (see the inset in Fig. 2). These results suggest that the coordination number of Y^{3+} change from 8 to 9 by incorporating one water molecule into the coordination sphere. When ionic radius decreasing up to Er^{3+} , the only phase obtained was the hydrated (see pink pattern in Fig. 2 and pink TG curve in Fig. 3). However, when ionic radius decreases up to Tm^{3+} , two hydrated phases appear: the pervious hydrated phase and second new hydrated phase (see orange pattern and TG-MS curves in Figs. 2 and 3, respectively), which have two different interlayer space of *ca.* 10.0 Å and *ca.* 9.8 Å (see inset in Fig. 2). These two phases have been successfully isolated separately (see red/blue powder patterns in Fig. 2) by changing the reaction conditions (180 °C, 1 h, microwave, in 1 mL of H_2O to obtain 1st hydrated phase, and in 3 mL to obtain 2nd hydrated phase). As the ionic radius decreases, the 1st hydrated phase decreases and the 2nd increases, case of Yb^{3+} based compound, until the 2nd hydrated phase is the only phase obtained, case of Lu^{3+} compound (purple and green patterns and the inset in Fig. 2).

TEM and SEM micrographs (see Fig. 4) show variable particles size with a minimum size of *ca.* 20 nm and maximum of *ca.* 1-5 µm, which is tuning by the ionic radii of Ln^{3+} cations. The particles size vary from *ca.* 20-50 nm (Ce, Nd, Sm, Eu, Gd) to *ca.* 400-500 nm (Dy and Ho) until reaching few micrometers (Lu).

The magnetic susceptibility of all the studied compounds is characterized by exhibiting a paramagnetic behavior over the whole temperature range (2-300 K). At temperatures higher than 20 K, the magnetic susceptibility data follow a Curie-Weiss laws with paramagnetic effective moments (μ_{eff}) of 7.96, 10.25, 10.42, 9.57, 7.38 and 4.66 μ_{B} and paramagnetic Curie temperatures (θ) of -1.1, -2.8, -5.4, -5.0, -13.7 and 0.1 K for organic-inorganic hybrids materials based on Gd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} and Yb^{3+} ions, respectively. Magnetization curves as a function of field (H) at 2 K are shown in Fig. 5, and its general shape is also consistent with a paramagnetic behavior. In particular, the curves do not show any irreversibility, as can be observed in the inset of Fig. 5, proving the absence of ferromagnetic

ordering. In addition, the measured magnetic moments at 85 kOe is lower than the theoretical saturation value for the Ln^{+3} ions, except of the Gd^{+3} phosphonate, where the magnetization tent to saturate and its value, $m \approx 6.9 \mu\text{B}/\text{Gd ion}$, is closed to the theoretical value ($7 \mu\text{B}/\text{Gd}$). This behavior is due to the low magnetocrystalline anisotropy of Gd^{+3} ion, associated with the spherical symmetry of its angular moment ($L=0$).

4. Conclusion

Under conventional hydrothermal synthesis or microwave-assisted hydrothermal synthesis complete series of lanthanide 1,4-phenylbis(phosphonate) compounds have been obtained and exhibiting unusual very high thermal stability. Cation size was the tuning factor (key factor) for the structural variations, and therefore, thermal behaviour and particles size variations from nano to microplate crystals. The crystal structures of anhydrous compounds (based on La, Ce, Pr Nd, Sm, Eu, Gd, Tb, Dy, and Ho) have been solved and confirmed to be isostructural. However, those of hydrated compounds (based on Y, Er, Tm, Yb, Lu) are unsolved as yet and may differ. The magnetic susceptibility of investigated compounds follows a Curie-Weiss type behaviour.

Acknowledgments

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References

- [1] G. Cao, H. Hong, T. E. Mallouk, *Acc. Chem. Res.* 25 (1992) 420.
- [2] A. Clearfield, *Curr. Opin. Solid State Mater. Sci.* 1 (1996) 268.

- [3] A. Clearfield, A. *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley & Sons, Inc., New York, 47 (1998) 371–510.
- [4] A. Clearfield, *Curr. Opin. Solid State Mater. Sci.* 6 (2002) 495.
- [5] K. Maeda, *Micropor. Mesopor. Mater.* 73 (2004) 47.
- [6] A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem., Int. Ed.* 38 (1999) 3268
- [7] D. M. Poojary, B. Zhang, P. Bellinghausen, A. Clearfield, *Inorg. Chem.* 35 (1996) 4942.
- [8] A. Clearfield, J. D. Wang, Y. Tian, F. L. Campbell III, G. Z. Peng, *Materials Synthesis and Characterization*, ed. D. Perry, Plenum Press, New York, 1997.
- [9] A. Clearfield, Z. Wang, P. Bellinghausen, *J. Solid State Chem.* 167 (2002) 376.
- [10] Z. Wang, J. M. Heising, A. Clearfield, *J. Am. Chem. Soc.* 125 (2003) 10375.
- [11] M. M. Gómez-Alcántara, A. Cabeza, L. Moreno-Real, M. A. G. Aranda, A. Clearfield, *Micropor. Mesopor. Mater.* 88 (2006) 293.
- [12] J. G. Mao, *Coord. Chem. Rev.* 251 (2007) 1493.
- [13] R. Vivani, G. Alberti, F. Costantino, M. Nocchetti, *Micropor. Mesopor. Mater.* 107 (2008) 58.
- [14] F. N. Shi, T. Trindade, J. Rocha, F. A. Almeida Paz, *Cryst. Growth Des.* 8 (2008) 3917.
- [15] M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, P. A. Wright, *J. Am. Chem. Soc.*, 133 (2011) 1266.

FIGURE CAPTIONS

Figure 1. Structure of Y-based compound view along the a-axis.

Figure 2. Powder X-ray diffraction pattern of compounds based on Y, Er, Tm, Yb, and Lu.

Figure 3. TG curve of compounds based on Y, Er, Tm, Yb, and Lu (a), and representative MS-curves for Tm-compound (b)

Figure 4. TEM or SEM images of compounds containing: Ce (a), Pr (b), Sm (c), Eu (d), Ho (e), Y (f), Tm (g), or Lu (h).

Figure 5. Magnetization vs. applied magnetic field at 2 K for phosphonate compounds based on Gd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} and Yb^{3+} ions. The insets show an enhance of low magnetic field.

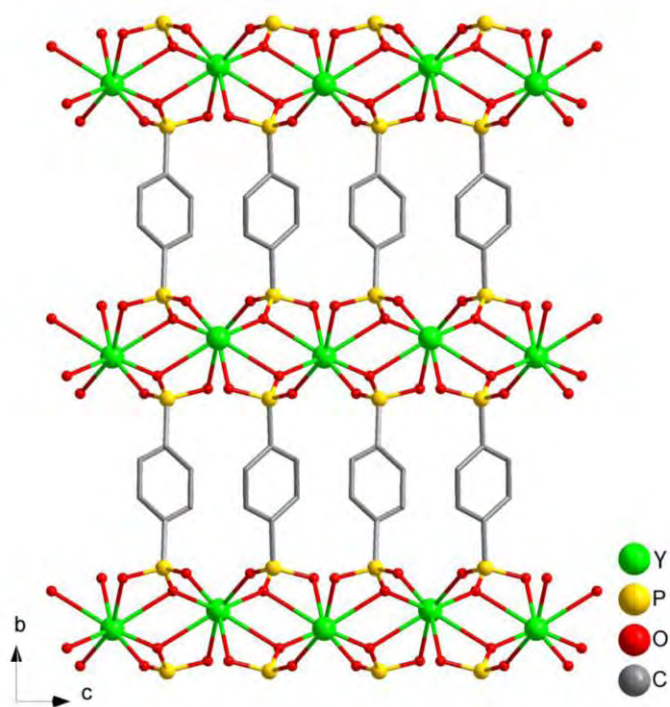


FIGURE 1

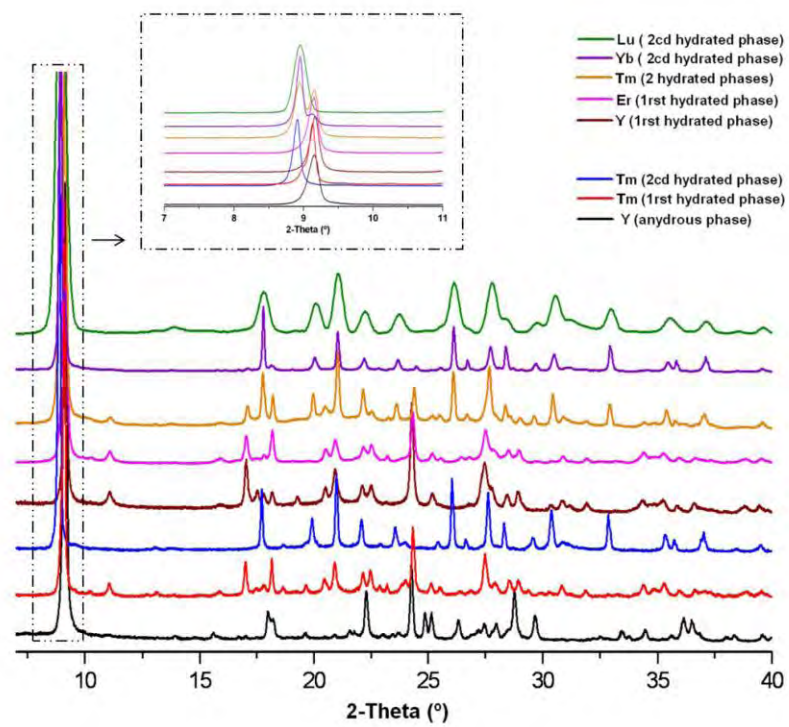


FIGURE 2

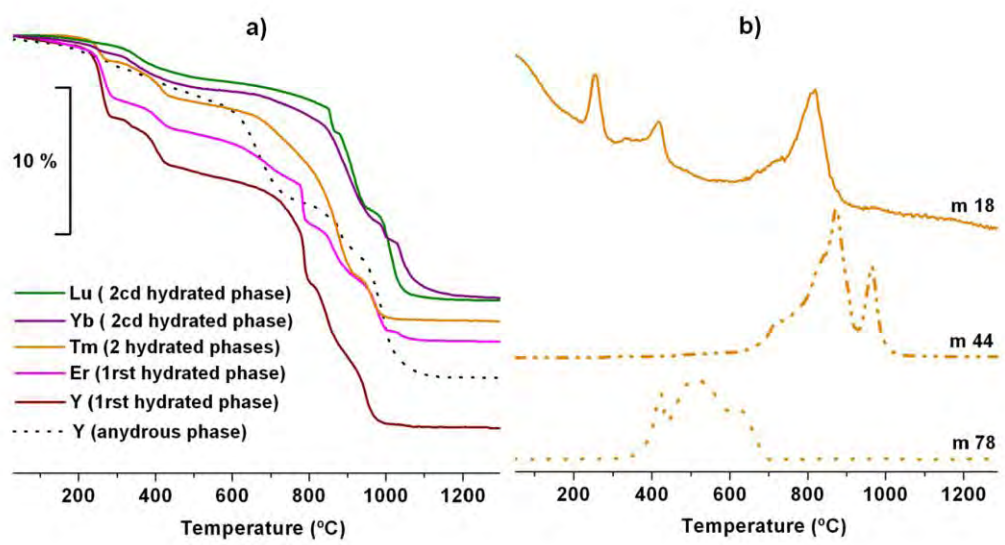


FIGURE 3

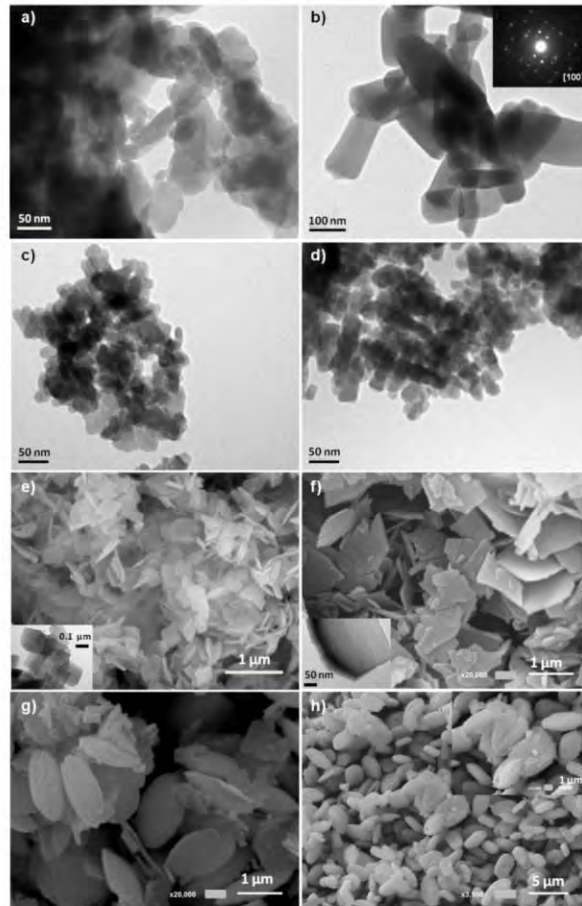


FIGURE 4

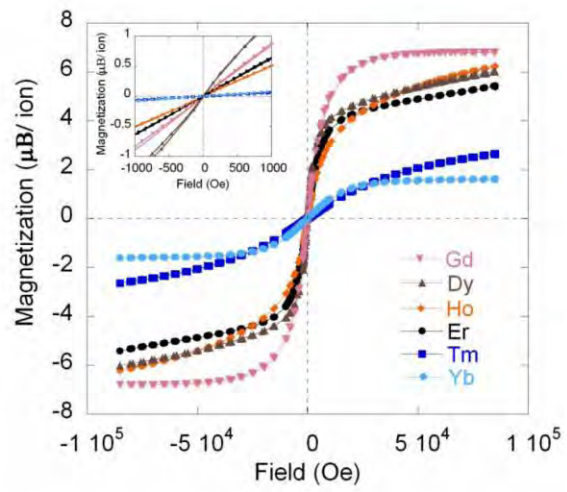


FIGURE 5

Bibliografía

4. Bibliografía

- (1) L. Pauling, Gates Chemical Laboratory, California Institute of Technology, *Proceedings of the National Academy of Sciences of the United States of America*, 1930, **16**, 578-582.
- (2) L. Pauling, *Proceedings of the National Academy of Sciences of the United States of America*, 1930, **16**, 123-129.
- (3) L. Pauling, L., *Proceedings of the National Academy of Sciences of the United States of America*, 1930, **16**, 453-459.
- (4) A. F. Cronstedt, *Natural Zeolite and Minerals*, Akad. Handl. Stockholm., 1756, **17**, 120.
- (5) R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, New York, 1982.
- (6) W. M. Meier, D. H. Oslen, C. Baerlocher, *Atlas of Zeolite Structure Types*, Elsevier, London, 2001.
- (7) R. P. Townsend, R. Harjula, *Molecular Sieves, V. 3, Post synthesis modification I*, 2002.
- (8) A. Corma, *Chemical Reviews*, 1997, **97**, 2373- 2419.
- (9) A. Corma, *Journal of Catalysis*, 2003, **216**, 298- 312.
- (10) M. E. Davis, *Nature*, 2002, **417**, 813-821.
- (11) J. M. Thomas, *Scientific American*, 1992, **266**, 112-118.
- (12) A. K. Cheetham, G. Férey, T. Loiseau, *Angewandte Chemie International Edition*, 1999, **38**, 3268-3292.
- (13) C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj, A. A. Ayi, *Accounts of Chemical Research*, 2001, **34**, 80-87.

- (14) L. Roces, J. R. García, *Recent Research Developments in Inorganic Chemistry*, 2003, **3**, 1-18.
- (15) R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja, C. N. R. Rao. *Chemical Reviews*, 2008, **108**, 3549-3655.
- (16) C. N. R. Rao, J. N. Behera, M. Dan, *Chemical Society Reviews*, 2006, **35**, 375-387.
- (17) A. P. Cote', A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science*, 2005, **310**, 1166-1170.
- (18) G. R. Desiraju, *Angewandte Chemie International Edition in English*, 1995, **34**, 2311-2377.
- (19) G. Alberti, U. Constantino, S. Allulli, N. Tomassini, *Journal of Inorganic and Nuclear Chemistry*, 1978, **40**, 1113-1117.
- (20) M. D. Poojary, H. -L. Hu, F. L. Campbell III, A. Clearfield, *Acta Crystallographica Section B*, 1993, **49**, 996-1001.
- (21) B. F. Hoskins, R. Robson, *Journal of the American Chemical Society*, 1990, **112**, 1546-1554.
- (22) R. Robson, *Dalton Transactions*, 2000, 3735-3744.
- (23) B. Moulton, M. J. Zaworotko, *Chemical Reviews*, 2001, **101**, 1629-1658.
- (24) B. Moulton, M. J. Zaworotko, *Current Opinion in Solid State and Materials Science*, 2002, **6**, 117-123.
- (25) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature*, 2003, **423**, 705-714.
- (26) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O. M. Yaghi, *Journal of Solid State Chemistry*, 2000, **152**, 3-20.
- (27) S. L. James, *Chemical Society Reviews*, 2003, **32**, 276-288.
- (28) J. L. C. Rowsell, O. M. Yaghi, *Microporous and Mesoporous Materials*, 2004, **73**, 3-14.
- (29) M. J. Rosseinsky, *Microporous and Mesoporous Materials*. 2004, **73**, 15-30.
- (30) C. N. R. Rao, S. Natarajan, R. Vaidhayanathan, *Angewandte Chemie International Edition*, 2004, **43**, 1466-1496.
- (31) C. Serre, F. Millange, S. Surblé, G. Férey. *Angewandte Chemie International Edition*, 2004, **43**, 6286-6289.
- (32) D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe, O. M. Yaghi, *Chemical Society Reviews*, 2009, **38**, 1257-1283.
- (33) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim, O. M. Yaghi, *Science*, 2010, **329**, 424-428.

- (34) A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chemical Communications*, 2006, 4780-4795.
- (35) A. Sudik, J. Yang, D. Halliday, C. Wolverton. *Journal of Physical Chemistry. C*, 2008, **112**, 4384-4390.
- (36) A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill, M. R. Hill, *Journal of the American Chemical Society*, 2009, **131**, 10662-10669.
- (37) A. Clearfield, *Current Opinion in Solid State and Materials Science*, 2002, **6**, 495-506.
- (38) G. Férey. *Chemical Society Reviews*, 2008, **37**, 191-214.
- (39) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, *Journal of the American Chemical Society*, 2004, **126**, 32-33.
- (40) J. Y. Guo, T. L. Zhang, J. G. Zhang, *Chinese Journal of Chemistry*, 2006, **24**, 745-749.
- (41) Z. X. Li, J. P. Zhao, E. C. Sanudo, H. Ma, Z. D. Pan, Y. F. Zeng, X. H. Bu, *Inorganic Chemistry*, 2009, **48**, 11601-11607.
- (42) F. J. Martínez Casado, M. Ramos Riesco, M. I. Redondo, D. Choquesillo-Lazarte, S. López-Andrés, J. A. Rodríguez Cheda, *Crystal Growth & Design*, **2011**, **11**, 1021-1032.
- (43) Y. F. Zhou, F. L. Jiang, D. Q. Yuan, B. L. Wu, M. C. Hong, *Journal of Molecular Structure*, 2005, **743**, 21-27.
- (44) G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Advanced Materials*, 1996, **8**, 291-303.
- (45) J. G. Mao, *Coordination Chemistry Reviews*, 2007, **251**, 1493-1520.
- (46) R. Vivani, G. Alberti, F. Costantino, M. Nocchetti, *Microporous and Mesoporous Materials*, 2008, **107**, 58-70.
- (47) J. X. Li, Z. X. Du, H. Q. An, J. X. Dong, X. J. Hu, W. P. Huang, *Zeitschrift für anorganische und allgemeine Chemie*, 2010, **636**, 1635-1640.
- (48) Y. Inubushi, S. Horike, T. Fukushima, G. Akiyama, R. Matsuda, S. Kitagawa, *Chemical Communications*, 2010, **46**, 9229-9231.
- (49) S. Kuke, B. Marmodée, S. Eidner, U. Schilde, M.U. Kumke. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2010, **75**, 1333-1340.
- (50) M. Dan, A. K. Cheetham, C. N. R. Rao, *Inorganic Chemistry*, **45**, **2006**, 8227-8238.
- (51) J. P. Costes, J. M. Clemente-Juan, F. Dahan, F. Nicodème, *Dalton Transactions*, 2003, 1272-1275.

- (52) K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proceedings of the National Academy of Sciences of the United States of America*, 2006, **103**, 10186-10191.
- (53) H. Hayashi, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature Materials*, 2007, **6**, 501-506.
- (54) B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature*, 2008, **453**, 207-221.
- (55) S. I. Noro, S. Kitagawa, T. Akutagawa, T. Nakamura, *Progress in Polymer Science*, 2009, **34**, 240-279.
- (56) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature*, 1999, **402**, 276-279.
- (57) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *Crystal Engineering Communications*, 2002, **4**, 401-404.
- (58) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science*, 2002, **295**, 469-472.
- (59) J. L. C. Rowsell, O. M. Yaghi, *Angewandte Chemie International Edition*, 2005, **44**, 4670-4679.
- (60) J. L. C. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, *Journal of the American Chemical Society*, 2004, **126**, 5666-5667.
- (61) T. Duren, L. Sarkisov, O. M. Yaghi and R. Q. Snurr, *Langmuir*, 2004, **20**, 2683-2689.
- (62) E. C. Spencer, J. A. K. Howard, G. J. McIntyre, J. L. C. Rowsell and O. M. Yaghi, *Chemical Communications*, 2006, 278-280.
- (63) J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science*, 2005, **309**, 1350-1354.
- (64) Q. R. Fang, G. S. Zhu, J. Y. Sun, Y. Wei, S. L. Qiu, R. R. Xu, *Angew. Chem., Int. Ed.*, 2005, **44**, 3845-3848.
- (65) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun and S. L. Qiu, *Dalton Transactions*, 2006, 2399-2402.
- (66) Y. L. Liu, V. C. Kravtsov, R. Larsen, M. Eddaoudi, *Chemical Communications*, 2006, 1488-1490.
- (67) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolake, *Science*, 2005, **309**, 2040-2042.
- (68) C. Mellot-Draznieks, J. Dutour, G. Férey, *Angewandte Chemie International Edition*, 2004, **43**, 6290-6301.
- (69) T. M. Reineke, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Angewandte Chemie International Edition*. 1999, **38**, 2590-2594.

- (70) T. K. Maji, G. Mostafa, H. C. Chang, S. Kitagawa, *Chemical Communications*, 2005, 2436-2438.
- (71) X. Li, H. L. Sun, X. S. Wu, X. Qiu, M. Du, *Inorganic Chemistry*, 2010, **49**, 1865-1871.
- (72) H. Andraud, O. Maury, *European Journal of Inorganic Chemistry*. 2009, 4357-4371.
- (73) K. Müller-Buschbaum. *Z. Naturforsch., B: Chem. Sci. Zeitschrift für Naturforschung Section B-A journal of Chemical Sciences*, 2006, **61**, 792-798.
- (74) K. Müller-Buschbaum, S. Gomez-Torres, P. Larsen, C. Wickleder. *Chemistry of Materials*, 2007, **19**, 655-659.
- (75) C. J. Höller, M. Mai, C. Feldmann, K. Müller-Buschbaum, *Dalton Transactions*, 2010, **39**, 461-468.
- (76) C. J. Höller, P. Matthes, J. Beckmann, K. Müller-Buschbaum, *Zeitschrift für Anorganische und Allgemeine Chemie*, 2010, **636**, 395-399.
- (77) A. Zurawski, M. Mai, D. Baumann, C. Feldmann, K. Müller-Buschbaum, *Chemical Communications*, 2011, **47**, 496-498.
- (78) F. Hohn, H. Billetter, I. Pantenburg, U. Ruschewitz, *Zeitschrift für Naturforschung Section B-A journal of Chemical Sciences*, 2002, **57**, 1375-1381.
- (79) L. Liu, S. Duraj, P. E. Fanwick, M. T. Andras, A. F. Hepp, *Journal of Coordination Chemistry*, 2003, **56**, 647-653.
- (80) Y. Q. Zheng, Z. P. Kong, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, 2003, **629**, 1469-1471.
- (81) Q. Fang, G. Zhu, M. Xue, J. Sun, G. Tian, G. Wu, S. Qiu, *Dalton Transactions*, 2004, 2202-2207.
- (82) J. Jin, M. J. Jia, Y. C. Wang, J. H. Yu, Q. F. Yang, J. Q. Xu, *Inorganic Chemistry Communications*, 2011, **14**, 1681-1684.
- (83) H. Zhou, K. C. Strates, M. A. Munoz, K. J. Little, D. M. Pajerowski, M. W. Meisel, D. R. Talham, A. Lachgar, *Chemistry of Materials*. 2007, **19**, 2238-2246.
- (84) Y. H. Wang, K. L. Chu, H. C. Chen, C. W. Yeh, Z. K. Chan, M. C. Suen, J. D. Chen, J. C. Wang, *CrystEngComm*, 2006, **8**, 84-93.
- (85) V. P. Fedin, A. V. Virovets, I. V. Kalinina, V. N. Ikorskii, M. R. J. Elsegood, W. Clegg, *European Journal of Inorganic Chemistry*, 2000, 2341-2343.
- (86) O. S. Jung, Y. J. Kim, Y. A. Lee, J. K. Lee, K. H. Yoo, *Bulletin of the Korean Chemical Society*, 2000, **21**, 39-43.
- (87) Z. Ni, R. I. Masel, *Journal of the American Chemical Society*, 2006, **128**, 12394-12395.

- (88) M. Schlesinger, S. Schulze, M. Hietschold, M. Mehring, *Microporous and Mesoporous Materials*, 2010, **132**, 121-127.
- (89) J. Klinowski, F. A. Almeida-Paz, P. Silva, J. Rocha, *Dalton Transactions*, 2011, **40**, 321-330.
- (90) E. Haque, N. A. Khan, C. M. Kim, S. H. Jung, *Crystal Growth & Design*, 2011, **11**, 4413-4421.
- (91) N. A. Khan, I. J. Kang, H. Y. Seok, S. H. Jung, *Chemical Engineering Journal*, 2011, **166**, 1152-1157.
- (92) S.H. Jung, T. Jin, Y.K. Hwang, J. S. Chang, *Chemistry-A European Journal*, 2007, **13**, 4410-4417.
- (93) D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa, S. Kitagawa, J. Groll, *Nature chemistry*, 2010, **5**, 410-416.
- (94) G. Park, H. Yang, T. H. Kim, J. Kim, *Inorganic Chemistry*, 2011, **50**, 961-968.
- (95) E. R. Parnham, R. E. Morris, *Accounts of Chemical Research*, 2007, **40**, 1005-1013.
- (96) R. E. Morris, *Studies in Surface Science and Catalysis*, 2008, **174**, 33-42.
- (97) L. Han, S. Zhang, Y. Wang, X. Yan, X. Lu, *Inorganic Chemistry*, 2009, **48**, 786-788.
- (98) L. Xu, S. Yan, E. Y. Choi, J. Y. Lee, Y. U. Kwon, *Chemical Communications*, 2009, 3431-3433.
- (99) J. Perles, M. Iglesias, C. Ruiz-Valero, N. Snejko, *Journal of Materials Chemistry*, 2004, **14**, 2683-2689.

Capítulo 5

Conclusiones

5.1. Conclusiones

1. Se han sintetizado y caracterizado 33 nuevos polímeros de coordinación, encuadrados en 6 tipos estructurales distintos, basados en elementos lantánidos y diferentes tipos de ligandos de vinculación bidentados, flexibles, rígidos, o mezclas rígido-flexible.
2. En la síntesis y caracterización de nuevos polímeros de coordinación basados en itrio y un ligando de vinculación bidentado flexible de tipo carboxílico (ácido succínico) destacan los siguientes resultados:
 - a). Se han sintetizado en condiciones hidrotermales dos nuevos succinatos de itrio, uno de ellos laminar $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ y otro tridimensional $Y_2(C_4H_4O_4)_3(H_2O)_2$.
 - b). Sus estructuras cristalinas fueron resueltas a partir de datos de difracción de rayos X de monocristal y se discutieron a la luz de la del compuesto $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$.
 - c). El estudio del comportamiento térmico de estos tres compuestos fue posible como consecuencia de su obtención como fases individuales de elevada pureza, mientras el conocimiento de sus peculiaridades estructurales permitió comprender los factores causantes de su estabilidad térmica.
 - d). La diversidad estructural de este sistema está ligada a los diferentes modos de coordinación y la flexibilidad conformacional del ligando succinato que, condicionada por la composición del medio de reacción, dirige la síntesis hacia el producto deseado.

3. En la síntesis y caracterización de nuevos polímeros de coordinación basados en itrio y ligandos mixtos de tipo dicarboxílico, destacan los siguientes resultados:
 - a). Se han sintetizado en condiciones hidrotermales dos nuevos compuestos cristalinos, $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$, obtenidos como fases puras, que son el primer ejemplo conocido de polímeros de coordinación heteronucleares con ligandos de vinculación mixtos.
 - b). Sus estructuras cristalinas han sido resueltas utilizando datos de difracción de rayos X de monocristal, revelando que ambos son compuestos quirales bidimensionales de simetría ortorrómbica, que cristalizan en el grupo espacial $C222_1$.
 - c). Los estudios de termodifracción de rayos X de polvo cristalino revelaron que ambos compuestos presentan cinéticas de rehidratación diferentes en los procesos de deshidratación/rehidratación térmica en atmósfera de aire.
 - d). Se evaluó la actividad de ambos compuestos como catalizadores heterogéneos, mostrando un comportamiento muy similar, con actividades en exceso positivas, aunque modestas.

4. En la caracterización de las fases anhidras de nuevos polímeros de coordinación basados en itrio y ligandos mixtos de tipo dicarboxílico, destacan los siguientes resultados:
 - a). $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ sufren una transformación de fase que acompaña al proceso de descomposición causado por la pérdida de las moléculas de agua coordinadas. Tras la deshidratación, ambas estructuras se contraen a lo largo del eje *b* (5.6% y 3.0%, respectivamente) con disminución de sus volúmenes de celdilla (aprox. 10% y 5%, respectivamente).
 - b). Los modelos estructurales de las fases anhidras fueron obtenidos mediante cálculos teóricos utilizando el método DFT en su aproximación de densidad local (LDA), obteniendo los datos finales mediante refinamiento *Rietveld* en los grupos espaciales *P1* (triclínico) y *P2* (monoclínico), respectivamente para $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)$ y $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)$.

5. En la síntesis y caracterización de nuevos polímeros de coordinación basados en lantánidos, sodio, y ligandos mixtos de tipo dicarboxílico, destacan los siguientes resultados:
 - a). Se han sintetizado en condiciones hidrotermales dos nuevas series formadas por 16 compuestos de composición análoga, $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ (**S1**) y $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ (**S2**) ($\text{Ln} = \text{Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb}$), obtenidos como fases puras cristalinas.
 - b). El análisis estructural mediante de difracción de rayos X de monocristal revela que los compuestos de cada serie son isoestructurales, cristalizando en el grupo espacial ortorrómbico $C222_1$. Los parámetros de celda, así como las distancias Ln-Na, varían en una función de los radios iónicos efectivos de los cationes lantánidos, disminuyendo linealmente a medida que desciende el tamaño de los cationes lantánidos al avanzar en el período.
 - c). Todos los compuestos de las series **S1** y **S2** presentan perfiles de descomposición térmica muy similar.
 - d). Se evaluó la actividad de los compuestos basados en erbio e iterbio de la serie **S1** como catalizadores ácidos de Lewis en la acetalización del benzaldehído. Como consecuencia del aumento del carácter ácido de los centros activos al disminuir el radio iónico del catión lantánido, los resultados son más favorables que cuando la estructura contiene itrio.
 - e). Las propiedades fotoluminiscentes de algunos de estos compuestos son destacables, ya que presentan emisión sintonizable de luz UV-VIS-IR mediante una efectiva sensibilización de los cationes lantánidos trivalentes a través de los ligandos aromáticos.

6. En la síntesis y caracterización de nuevos polímeros de coordinación basados en lantánidos y un ligando rígido tipo difosfonato, destacan los siguientes resultados:
 - a). Se sintetizó una serie completa de nuevos híbridos organo-inorgánicos basados en elementos lantánidos ($\text{Ln} = \text{Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) y el ligando de vinculación 1,4-fenilbis(fosfonato) en condiciones hidrotermales, usando calefacción convencional, o asistida por microondas.

- b).* Los compuestos basados en La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, y Ho se obtuvieron como fases anhidras isoestructurales (simetría monoclinica, grupo espacial $C2/c$) de fórmula $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$. Sus estructuras cristalinas se determinaron a partir de datos difracción de rayos X de monocristal para el compuesto de Pr y refinamiento Rietveld de los datos de difracción de rayos X de polvo cristalino del resto de los miembros de la serie.
- c).* Los compuestos basados en Y, Er, Tm, Yb, Lu, se obtuvieron como fases hidratadas de estructura desconocida.
- d).* El tamaño de partícula de los materiales sintetizados (de 20 nm a 5 μm) es función del catión lantánido involucrado en la síntesis, y no influye perceptiblemente en la alta estabilidad térmica de las fases anhidras de estos compuestos.
- e).* Los compuestos basados en Gd, Dy, Ho, Er, Tm, e Yb son paramagnéticos.
- f).* Los compuestos basados en Eu y Tb presentan interesante comportamiento fotoluminiscente, con una fuertes emisiones de luz en el visible (rojo y verde, respectivamente).

5.2. Conclusions

1. 33 new coordination polymers have been synthesized and characterized, belonging to 6 different structural types, based on lanthanide elements and different bidentate ligands, flexible, rigid, or mixtures rigid-flexible.
2. In the synthesis and characterization of new coordination polymers based on yttrium and a flexible dicarboxylate ligand (succinic acid), the relevant results are the following:
 - a). Two new yttrium-succinates, formulated as $Y_2(C_4H_4O_4)_3(H_2O)_4 \cdot 6H_2O$ and $Y_2(C_4H_4O_4)_3(H_2O)_2$, have been synthesized under hydrothermal conditions.
 - b). Their crystal structures have been solved using single-crystal X-ray diffraction data and compared with that of $Y_2(C_4H_4O_4)_3(H_2O)_2 \cdot H_2O$.
 - c). The study of the thermal behavior of these three compounds was possible as a result of obtaining pure crystalline phases, while the knowledge of their structural peculiarities allowed us to understand the factors responsible for the thermal stability.
 - d). The results suggest that the structural diversity obtained, in this system, is related to the coordination diversity and the conformational flexibility of the succinate ligand, which in turn depend on the synthesis conditions that play an important role in directing to one compound or another.
3. In the synthesis and characterization of new coordination polymers based on yttrium and mixed dicarboxylate ligands, we highlight the following results:
 - a). Two new compounds $NaY(C_4H_4O_6)(C_8H_4O_4)(H_2O)_2$ (**1**) and $NaY(C_4H_4O_6)(C_{14}H_8O_4)(H_2O)_2$ (**2**), have been synthesized under hydrothermal conditions

- and obtained as pure crystalline phases, which are the first example of heteronuclear coordination polymers containing mixed flexible-rigid ligands.
- b). Their crystal structures have been solved by single-crystal X-ray diffraction, revealing that both are layered coordination polymers and crystallize in the orthorhombic chiral space group $C222_1$.
 - c). The X-ray thermodiffraction studies reveal that both compounds are involved in spontaneous rehydration process characterized by different kinetics, fast in the case of **1** and slow for **2**.
 - d). Catalytic activity, evaluated for both compounds as heterogeneous catalysts, show a very similar behavior with modest positive activities.
4. In the characterization of the anhydrous phases of coordination polymers based on yttrium and mixed dicarboxylate ligands, the concluded results are:
- a). $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ and $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ undergo a phase transformation caused by loss of coordinated water molecules. After dehydration, both structures contract along the *b*-axis (of *ca.* 5.6% and 3.0%, respectively) with the unit cell volume decreases (*ca.* 10% and 5%, respectively).
 - b). Structural models of the anhydrous phases have been obtained using DFT calculations within local-density approximation (LDA), obtaining the final results by *Rietveld* refinement in triclinic space group *P1* and monoclinic *P2*, for $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)$ and $\text{NaY}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)$, respectively.
5. In the synthesis and characterization of new coordination polymers based on lanthanides and mixed dicarboxylate ligands, the concluded results are:
- a). Two Series of isorecticular chiral lanthanide-organic frameworks. $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_8\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2$ (**S1**) and $\text{NaLn}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_{14}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ (**S2**) (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), have been obtained as single phases under hydrothermal conditions
 - b). Structural analysis by single-crystal X-ray diffraction reveals that the compounds of each series are isostructural, crystallizing in the orthorhombic space group $C222_1$. The unit cell parameters as well as Ln-Na distances are

- function of the effective ionic radii of lanthanide cations, with linearly decreasing trend when the size of lanthanide cations decreases.
- c). All compounds in the series **S1** and **S2** have similar thermal decomposition profiles.
 - d). Catalytic activity has been evaluated for erbium and ytterbium based compounds of **S1** to behave as Lewis acid catalysts in acetalization of benzaldehyde. The results show an improved catalytic activity, may be explained in terms of more acidic character when the ionic radii decrease.
 - e). The photoluminescence properties of selected compounds have been investigated, exhibiting room temperature tunable UV-VIS-IR light emission through an effective lanthanide cations sensitization via aromatic ligands.
6. The synthesis and characterization of new coordination polymers based on lanthanide and rigid diphosphonate ligand, highlights the following results:
- a). Complete series of novel organic-inorganic hybrids materials assembled from lanthanide ($\text{Ln} = \text{Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) and 1,4-phenylbis(phosphonate) has been obtained under hydrothermal conditions either by oven heat or microwave irradiation.
 - b). Compounds based on La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho were obtained as isostructural anhydrous phases (monoclinic space group $C2/c$), with formula $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$. Their crystal structures have been solved from single-crystal X-ray diffraction data of Pr-compound and using *Rietveld* refinement of X-ray powder diffraction data for the other members of the series.
 - c). Compounds based on Y, Er, Tm, Yb, and Lu, were obtained as hydrated phases of unknown structure.
 - d). The particle size of the synthesized materials (ranges from 20 nm to 5 μm) is a function of the ionic radii of lanthanide cations, which do not influence significantly the high thermal stability of the anhydrous phases.
 - e). Compounds based on Gd, Dy, Ho, Er, Tm, e Yb show paramagnetic behavior.
 - f). Eu- and Tb-based compounds exhibit strong red and green luminescence, respectively.

