

COMMUNICATION

Stronger-together: the cooperativity of aurophilic interactions

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To the memory of Prof. Hugo Torrens

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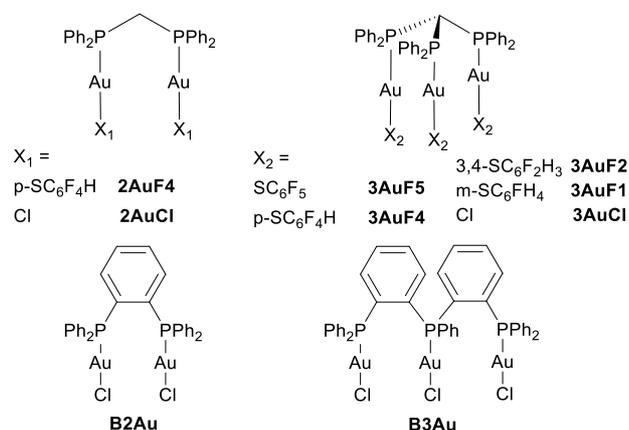
Crystallographic distances and the electron density of bi- and trinuclear gold(I) compounds reveal that the existence of multiple Au...Au interactions increases their individual strength in the order of 0.9–2.9 kcal·mol⁻¹. We observed this behaviour both experimentally and theoretically in multinuclear systems confirming a novel important cooperative character in aurophilic contacts.

Non-covalent interactions (NCIs) are the central concept of supramolecular chemistry.¹ Modern supramolecular chemistry aims to reach new levels of complexity, inspired by biological systems and processes.² In order to exploit NCIs in the construction of such complex supramolecular systems, in the so called supramolecular synthesis,² NCIs have to be fully characterised in terms of their energetic significance, directionality, and additivity.^{2–4}

Among the emerging NCIs,⁵ aurophilic interactions have attracted particular attention.^{6–8} Many interesting applications have proven the importance of these contacts,^{9–14} for example in the generation of luminescent supramolecular assemblies.^{15–17} However, much about their nature remains to be understood. Most attention has focused on their energetic relevance, which is strongly influenced by the incidence of competing interactions and geometrical constraints. These circumstances make the energetics of these interactions widely span from less than 1 to more than 15 kcal·mol⁻¹.^{18–24} Generally, the investigations concerning Au...Au contacts have only examined dimeric arrangements and neglected effects of higher-order aggregates, thereby disregarding non-additivity. Cooperative and anticooperative effects are of paramount importance in supramolecular synthesis,²⁵ and they have been studied for other NCIs, for example H-bonds.^{26–28} In the case of aurophilicity previous theoretical assessments of these effects in small model systems have

given inconclusive results.^{7,29,30} Some early experimental observations suggest an energetic advantage in the accumulation of gold-gold interactions, such as that indicated by the unusual geometries of multiaurated atoms^{31–33} and the possibility of generating high dimensionality arrangements by multiple Au-Au contacts.³⁴ However, the experimental investigation of non-additivity in aurophilic interactions has been a pending matter since the discovery of these contacts. Cooperative effects have a crucial role in the mechanisms of supramolecular assembly.³⁵ These circumstances make relevant to study non-additivity in metallophilic (e.g. aurophilic) interactions which recently have attracted much attention.^{36–40} More specifically, cooperativity is a desirable feature as it would provide more controlled assembly paths^{25,35} as demonstrated by the living supramolecular polymerisations.^{41,42} Moreover, multiple Au...Au and M-M interactions have proved to be pivotal in self-assembly processes of metallic clusters.^{43–45}

In order to determine the non-additive features of aurophilic interactions in experimental systems, we have synthesised, characterised and determined the single-crystal X-ray diffraction structures of the dinuclear compound [Au₂(p-SC₆H₄)₂(μ-dppm)], **2AuF4** (dppm = bis(diphenylphosphino)methane) and the trinuclear compounds [Au₃(SC₆F₅)₃(CP₃)], **3AuF5**; [Au₃(SC₆H₄-4)₃(CP₃)], **3AuF4**; [Au₃(SC₆H₃F₂-3,4)₃(CP₃)], **3AuF2**; [Au₃(SC₆H₄F-3)₃(CP₃)], **3AuF1**; (CP₃ = Tris(diphe-



Scheme 1. Structure of the compounds studied in this work.

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nylphosphino)methane) (Scheme 1). Along with these newly reported compounds we have studied the previously synthesised $[\text{Au}_2\text{Cl}_2(\mu\text{-dppm})]$, **2AuCl**;⁴⁶ $[\text{Au}_3\text{Cl}_3(\text{CP}_3)]$, **3AuCl**;⁴⁷ $[\text{Au}_2\text{Cl}_2(\text{dppBz})]$, **B2Au**;⁴⁸ and $[\text{Au}_3\text{Cl}_3(\text{BPPP})]$, **B3Au**⁴⁹ (BPPP = Bis[2-(diphenylphosphino)phenyl]phenylphosphine). Additionally, these systems allowed us to investigate the electronic effects of fluorination on aurophilic interactions. We examined the chemical bonding scenario in equilibrium structures based on DFT⁵ and the Quantum Theory of Atoms in Molecules (QTAIM) calculations. In particular, the QTAIM is based on the examination of the orbital-invariant electron density, which is a quantum-mechanical observable as opposed to orbitals.⁵⁰ QTAIM descriptors allow to estimate the ionic and covalent energetic contributions of different interactions.⁵¹ We point out that the exchange correlation functionals employed in our calculations do not include Dispersion Corrections (DCs). We proceeded in this way, because we consider experimental geometries for most of the systems examined in this paper and such corrections do not alter the electron density computed via DFT used in the analyses performed herein. Most importantly, functionals which do not contain DCs do not take into account intramolecular dispersion interactions⁵² expected due to the side chains of the ligands of the compounds addressed herein. Thus, we could assess in a better way the non-additive effects of the aurophilic interactions considered in this work. In our experience with water clusters,²⁶ an overestimation of the dispersion contribution exaggerates cooperativity. We investigated the aurophilic contacts and the gold-ligand bonds in the above-mentioned compounds via this combined experimental/theoretical approach. Our results show that the electronic landscape of the Au...Au interactions is substantially influenced when an additional aurophilic interaction is formed. In all the studied cases, the individual strength of the interactions increases upon the formation of additional aurophilic contacts in no less than 0.9 and up to 2.9 kcal·mol⁻¹. Altogether, our results demonstrate the cooperative character of Au...Au interactions, and they give new useful insights for the design and understanding of supramolecular systems based on aurophilic synthons.

The five newly reported compounds were synthesised similarly to other compounds previously reported by us (See S1).¹⁹ Figure 1 shows the molecular structures of compounds **2AuF4** and **3AuF4**. Both structures have similar arrangements, and they have the same fluorination pattern in the thiolate ligand. These molecular motifs allowed the direct comparison of the effects of the increase in the nuclearity on the aurophilic contacts while keeping the electronic and steric effects due to the ligands almost unchanged. The first indication of cooperativity in these systems are shown by the 0.1 Å shortening of the Au...Au distances from 3.21 Å in **2AuF4** to 3.11 ± 0.02 Å in **3AuF4** (Table S1). There is a similar shortening in O...O distances in the comparison of (H₂O)₂ (*d*_{O...O} = 2.98 Å) with (H₂O)₃ (*d*_{O...O} = 2.88 Å), due to H-bond cooperativity.²⁸ The NCI-Index analyses⁵³ (Figure S1) revealed that the non-covalent interaction scenarios are indeed similar in **2AuF4** and **3AuF4**. In these complexes, the Au...Au interactions are the main non-covalent contact within the structure, as displayed by blue surfaces between the gold atoms in

Figure S1, which indicate in both cases strong attractive interactions. Indeed, visual examination suggests a strengthening of the Au...Au interactions upon an increase on nuclearity, observed as an intensification of the blue tonality on the surfaces associated with Au...Au contacts in the trinuclear compound. Besides, there are also some weak $\pi\cdots\pi$ and S...S interactions indicated by green surfaces in the NCI-index plot (Figure S1).

QTAIM analyses of the electron density (Table S2) confirm the occurrence of cooperativity in the investigated aurophilic contacts. The descriptors which characterise the aurophilic contact in **2AuF4**, indicate weaker interactions than those in the three Au...Au contacts within **3AuF4**. For instance, the electron density at the bond critical point ($\rho(\mathbf{r}_{\text{bcp}})$), an indicator of bond strength,^{54,55} increases roughly 20% when the third gold centre is added from 0.0223 to 0.0271 ± 0.001 a.u. (Table S2). Such increment in the electron density indicates a rise in the strength of the individual interactions upon the addition of a third Au centre.²⁵ Interestingly, this increase in the bond strength is not reflected on the delocalisation index (DI), a measure of the electron pairs shared between two atoms, as it remains unchanged after the inclusion of the third Au atom (0.270 and 0.269 ± 0.016 a.u. for **2AuF4** and **3AuF4**, respectively). The partition of the

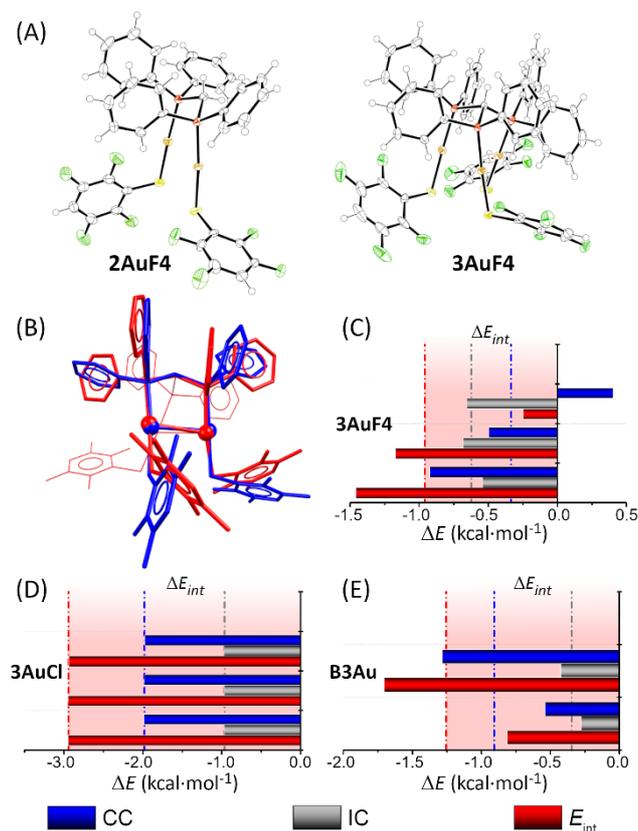


Figure 1. (A) ORTEP diagrams at a 50% probability level of the single crystal X-ray diffraction structures of compounds **2AuF4** and **3AuF4**. Color code for the elements: C, white; F, lime; S, yellow; P, orange; Au, golden (B) Overlay view of the structures of **2AuF4** (blue) and **3AuF4** (red). (C), (D) and (E) Plots of the change in the energy contributions for the different aurophilic interactions in the trinuclear compounds **3AuF4**, **3AuCl** and **B3Au**, when compared with the single aurophilic interaction in the dinuclear compounds **2AuF4**, **2AuCl** and **B2Au**, respectively. The dashed lines represent the mean values from the different interactions in the trinuclear compounds for the ionic (grey) covalent (blue) and total energy (red). The red areas indicate the mean interaction energy differences due to the cooperativity of the aurophilic contacts.

electronic energy put forward by Martín Pendás et al.,^{51,56} allows to assess the ionic (IC) and covalent (CC) contributions to the chemical bond energies ($E_{\text{int}} = \text{IC} + \text{CC}$). This analysis reveals that the energetic difference among the aurophilic interactions within both compounds are principally due to a decrease in the electrostatic repulsion between Au centres upon increase of the nuclearity. These effects account for 0.62 kcal·mol⁻¹ from the total 0.96 kcal·mol⁻¹ gained in average per interaction in the comparison of **2AuF4** with **3AuF4** as revealed by the dashed lines in Figure 1C.

On the other hand, the introduction of a third gold atom and the formation of the triangular Au₃ moiety causes a weakening of the Au-ligand bonds as evidenced by a decrease on the values of $\rho(r_{\text{bcp}})$ and DI of the Au-S and Au-P bonds. The reductions in the corresponding interactions energies are in the range of 3–10 kcal·mol⁻¹ (Table S2 and Figure S2). This effect is concomitant with the increase of the Au...Au bonding character upon the addition of gold interacting units.

We considered a set of fluorinated ligands to study the effect of the thiolate fluorination on the chemical bonding scenario. We observed that a decrease in the fluorination degree strengthens the Au-P and Au-S bonds (Table S2, Figures S3 and S4). The effect is more pronounced in the Au-P bonds for which the interaction energies decrease about 5 kcal·mol⁻¹ from **3AuF1** and **3AuF2** to **3AuF4** and **3AuF5** (Figure S4). On the other hand, the strength of the aurophilic contacts, changes in the opposite way. These results indicate an interplay between the strength of aurophilic and Au-L bonds, i.e., when the Au...Au contact strengthens the Au-L bonds are weakened and vice versa.

We also considered separately the effects of the thiolate ligands from the observed cooperative nature of aurophilic contacts. For that purpose, we performed the same analysis in the previously reported experimental structures [Au₂Cl₂(μ -dppm)](**2AuCl**)⁴⁶ and [Au₃Cl₃(CP₃)](**3AuCl**)⁴⁷ that contain chloride as an anionic ligand (Scheme 1). Being chloride the most common anionic ligand in gold compounds, the analysis of these compounds results most convenient to extrapolate the observed results to many other reported systems. In these systems, the Au-Au distance decreases around 0.14 Å when increasing the nuclearity (Table S1) and the increase in the internuclear electron density of the Au...Au interactions is clearer than that observed in the thiolate derivatives (Table S3). The values of the electron density at the Au...Au interactions are $\rho(r_{\text{bcp}}) = 0.019$ a.u. in **2AuCl** and 0.023 a.u. in **3AuCl** whereas the DI(Au|Au) values are 0.20 a.u. and 0.23 a.u., respectively. These indicators are associated with an energetic difference of 2.94 kcal·mol⁻¹ (Figure 1D). This enhanced stabilisation is due to the conjunction of two factors. First, the stabilisation via the IC contribution which is even larger in the **3AuCl/2AuCl** pair than it is for **2AuF4/3AuF4** (Figure 1). The gold atoms in **3AuCl** have the smallest negative charge among **2AuF4**, **3AuF4**, **2AuCl** and **3AuCl** (Tables S4, S6, S9 and S10) and therefore this complex presents the weakest electrostatic repulsion between Au centres. And second, the number of shared electrons between the gold atoms rises more than 10% when we move from **2AuCl** to **3AuCl** as opposed to the virtually constant values of DI among Au atoms in **2AuF4** and **3AuF4**. Thus, CC is also an important

contribution to cooperativity of Au...Au contacts in **3AuCl**, even to the extent that it is more relevant than IC as shown in Figure 1D.

We now consider the fact that the triphosphine CP₃ promotes the formation of triangular arrangements observed until now for trimetallic compounds. We conjectured that these cyclic interactions could be responsible of the strengthening of aurophilic contacts. Thus, we also studied systems in which this trigonal arrangement is not ligand-imposed. We selected the related compounds **B2Au**⁴⁸ and **B3Au**⁴⁹ which have been characterised experimentally (Scheme 1) and whose aurophilic interactions display an open arrangement. In the same way than the previously presented examples, the decrease in the interatomic distances (Table S1) and the QTAIM indicators (Table S3) support a cooperative character among the Au...Au contacts, that in this case accounts for an increase of 1.25 kcal·mol⁻¹ in the individual Au...Au interaction energies (Figure 1E).

Finally, in order to reduce the geometrical constraints imposed by the bridge phosphine ligands and to study the effects of a larger increase in nuclearity, we examined the model systems [AuCl(PH₃)]_n (n = 2, **Au2**; 3, **Au3**; 4, **Au4**). The optimised structures analysed by QTAIM are shown in Figure 2. There is a clear strengthening of the aurophilic interactions upon the increase in the nuclearity of the aggregates. In particular, the values of DI(Au|Au) for the aurophilic interactions are 0.37, 0.33 and 0.29 a.u. for **Au4**, **Au3** and **Au2**, respectively (Table S4 and Figure S3). These changes account for the increase of 2.8 and 2.5 kcal·mol⁻¹ in the interaction energy after the addition of the second and third aurophilic interactions, respectively (Figure 2a). These increments are related to a considerable rise in the covalent contribution of the Au...Au contact. Likewise the previously discussed experimental systems, the increase in the number of aurophilic contacts weakens the L-Au bonds. In particular, the DI(Au|Cl) decreases from 1.05 a.u. when the gold

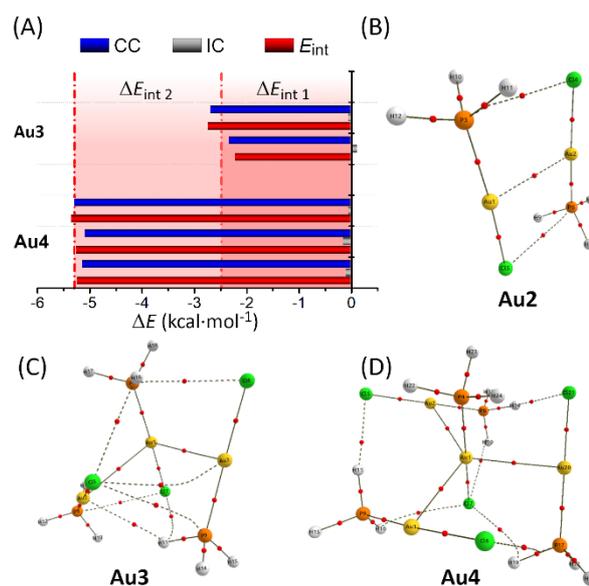


Figure 2. (A) Plot of the change in the energy contributions for the aurophilic interactions in the model oligomers **Au3** and **Au4** compared with the single Au...Au contact in the dimer **Au2**. The red areas indicate the mean energy gains due to the increase in nuclearity. (B), (C) and (D) Molecular graphs of the model systems **Au2**, **Au3** and **Au4**, respectively. Color code: H, white; Cl, green; P, orange; Au, golden; the red dots correspond to bond critical points.

atom has only one aurophilic contact to 0.91 a.u. when the parent gold presents three Au...Au interactions. This reduction in the number of shared electrons represents a change of about 8 kcal·mol⁻¹ in the Au-Cl bonds between **Au2** and **Au4** (Table S4, Figure S5 and S6). The change in the Au-P bond is even more notorious decreasing 15 kcal·mol⁻¹ from **Au2** with one single aurophilic contact to **Au4** in which the gold atom has three aurophilic bonds. The electron densities at the Au-L bcps follow the same trend as the DI in **Au2-Au4** (Tables S2).

All in all, using our combined experimental and theoretical approach, we have shown that aurophilic interactions exhibit cooperative behaviour. This effect is characterized by increments in the values of $\rho(r_{\text{bcps}})$ and DI(Au|Au) of the individual Au...Au interactions which account for rises in the interaction energy in the range from 0.9 to 2.9 kcal·mol⁻¹. This determination of the cooperative nature of aurophilic interactions provides new useful insights for the design of aurophilic supramolecular materials. Additionally, our results set the basis for further understanding non-additive mechanisms which drive supramolecular polymerisation in metallophilic-based aggregates.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ For the experimental systems the electron density was calculated using the experimental crystallographic geometries using PBE⁵⁷/TVZ-ZORA⁵⁸ as implemented in Orca.⁵⁹ The geometry of the model systems was optimised using the same methods. The effect of the functional over the results was tested as explained in the Supporting Information. The QTAIM analyses were performed using the program AIMAll.⁶⁰

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