

# Effect of substituents on photocatalytic partial oxidation of aromatic alcohols assisted by polymeric C<sub>3</sub>N<sub>4</sub> photocatalysts

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**Abstract:** Photocatalysis is an environmentally-friendly and energy-efficient mean of selective oxidation of aromatic alcohols to the corresponding aldehydes. In the present work we scrutinized the effect of benzyl alcohol phenyl ring substituents on its aqueous-phase photo-oxidation driven by polymeric carbon nitride (PCN) catalyst. It has been established that for the case of benzyl alcohols, electron donating (ED) substituents in *para*- and *ortho*-position with respect to the CH<sub>2</sub>OH-group promote the reactivity of the substrate without compromising the selectivity towards benzaldehydes formation, maintaining it in the range of 84-98 %, if compared to the unsubstituted molecule. The same observation is true for *meta*-substituted benzyl alcohol with an electron withdrawing (EW) group. On the other hand, the presence of ED-group in *meta*-position or EW-group in *para*-position with respect to the benzylic carbon reduces the reactivity as well as the selectivity towards the aldehyde production, resulting in the values of selectivity ranging from 40 to 80 %. The analyses of the experimental data and quantum chemical computational studies of "substrate-catalyst" complexes have established that the reactivity is inversely proportional to the positive charge on the benzylic carbon in benzyl alcohol cation intermediate, while the selectivity correlates with a negative charge on the carbon atoms in the phenyl ring. The ED substituents in *meta*- and the EW ones in *para*-position induce a negative charge on one of the carbons in the phenyl ring, making it susceptible for an attack of electrophilic species such as photo-generated holes or <sup>•</sup>OH radicals, when the substrate is interacting with the carbon nitride non-condensed NH<sub>2</sub>-groups. The modification of the PCN photocatalyst with H<sub>2</sub>O<sub>2</sub> creates a charge recombination center or a steric hindrance on the NH<sub>2</sub>-moieties complicating the reactions of oxidative species with the phenyl ring, thus increasing the selectivity towards the corresponding aldehyde production.

## Introduction

Partial oxidation of alcohols to carbonyl compounds avoiding their overoxidation to carboxylic acids or their total oxidation to carbon oxides is a process of key importance in chemical industry allowing to obtain fragrances, pharmaceuticals and food additives.<sup>[1]</sup> This reaction is conventionally catalysed by chromic acid<sup>[2]</sup> or chromium complexes<sup>[3]</sup>. However, the use of toxic chromium-containing catalysts does not fit with the modern trends towards environmentally friendly and sustainable ways of chemical synthesis. Molecular oxygen is a perfect non-toxic oxidant for such reactions whose performance is efficiently promoted by supported metal nanoparticles<sup>[4]</sup>, vanadium phosphates<sup>[5]</sup> and heteropolyacids.<sup>[6]</sup> The possibility of application of solar energy to drive partial oxidation reactions resulted in the development of photocatalytic procedures for aromatic aldehydes production assisted by inorganic semiconductors such as TiO<sub>2</sub>, WO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub>.<sup>[7-11]</sup> In order to decrease the oxidant ability of the photocatalysts and increase

the selectivity to partial oxidation products, an appropriate strategy to decrease the presence of certain undesirable photo-generated reactive oxygen species (ROS) could be the implementation of ligand-to-metal charge transfer (LMCT) oxidation. This implies the formation of a surface substrate-metal oxide complex and its excitation under visible light, without activating an electron ejection from the valence band (VB) to the conduction band (CB) of the photocatalyst itself.<sup>[12-14]</sup>

Despite water is considered as a desirable reaction medium from the point of view of sustainability, still, the major part of selective photo-oxidation reactions is carried out in organic solvents,<sup>[15,16]</sup> not only because most of the organic molecules are insoluble or scarcely soluble in water, but also because water does not permit an easy control of the reaction pathway. In fact, the formation of highly oxidative hydroxyl radicals readily occurs on the surface of inorganic semiconductor photocatalysts having high VB potential.<sup>[17]</sup> Numerous approaches including non-metal doping<sup>[18]</sup> and using low-crystalline TiO<sub>2</sub><sup>[19]</sup> were intended to enhance the selectivity of alcohols partial oxidation. However, it was not possible to completely avoid the formation of by-products and substrate mineralisation, hence a selectivity far below 100 % was usually obtained. In this context, polymeric carbon nitride (PCN), an organic semiconductor possessing a low valence band potential insufficient to directly oxidise water molecule producing <sup>•</sup>OH,<sup>[20]</sup> was successfully used for partial heterogeneous photo-oxidation of aromatic alcohols<sup>[21-29]</sup> achieving high yields of aldehydes while using water as solvent.<sup>[30,31]</sup> Although -H, -OCH<sub>3</sub>, -CH<sub>3</sub>, -Cl, -NO<sub>2</sub> and -F substituted benzyl alcohols were converted to the corresponding aldehydes by PCN with a nearly 100 % selectivity,<sup>[31,32]</sup> the attempts with some other molecules like piperonyl alcohol and 5-hydroxymethyl furfural (HMF) showed worse results.<sup>[31,33]</sup> The non-condensed -NH and/or -NH<sub>2</sub> species in PCN were suggested to be responsible for the unselective oxidation of HMF.<sup>[33]</sup> The recently synthesised PCN-H<sub>2</sub>O<sub>2</sub> adduct<sup>[34,35]</sup> was found able to reduce the detrimental effect of the presence of these -NH<sub>x</sub> groups due to their coordination with hydrogen peroxide. The PCN-H<sub>2</sub>O<sub>2</sub> adduct resulted more selective photocatalyst for HMF to 2,5-furandicarboxaldehyde (FDC) conversion<sup>[35,36]</sup> than the pristine carbon nitride with more accessible -NH<sub>x</sub> groups. However, no clear understanding of the PCN-H<sub>2</sub>O<sub>2</sub> adduct properties determining its improved selectivity in certain photo-oxidation reactions has yet been achieved. In this work, we report the effect of substituents in the phenyl-ring of aromatic alcohols on its photo-conversion to the corresponding aromatic aldehyde. Moreover, a theoretical approach addressing the questions of interaction of each substrate with the PCN and PCN-H<sub>2</sub>O<sub>2</sub> photocatalysts will be discussed, to get the information on the mechanism of the aromatic alcohol to aldehyde conversion.

## Results and Discussion

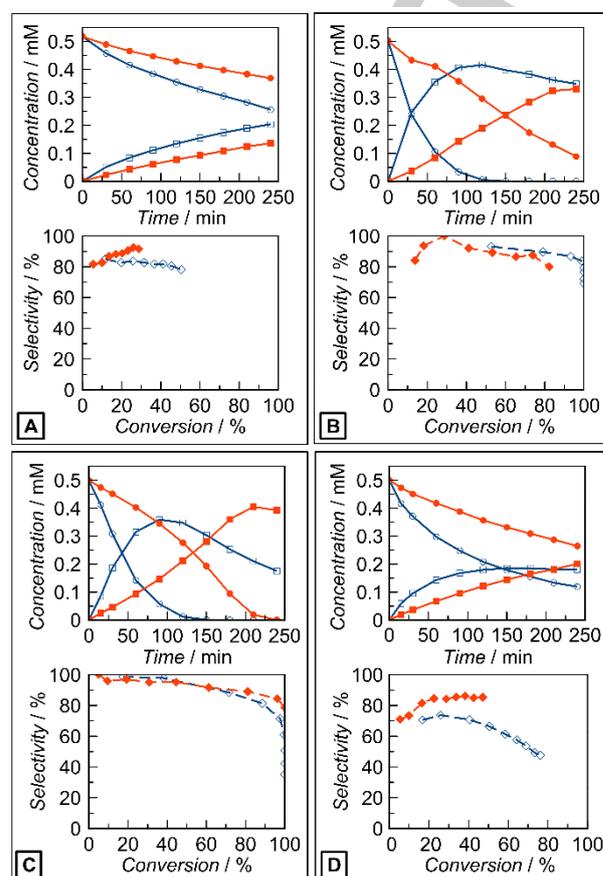
### Photocatalytic oxidation of aromatic alcohols

In several preceding works of some of us, a thorough investigation of the structural and surface properties of the used PCN and PCN-H<sub>2</sub>O<sub>2</sub> catalysts has been performed.<sup>[34-36]</sup> The applied techniques, especially XPS and solid state NMR, provided a significant insight into the features of the H<sub>2</sub>O<sub>2</sub>-modified PCN. XPS study evidenced the presence of similar type of oxygen species in the PCN-H<sub>2</sub>O<sub>2</sub> adduct and the single-crystal melamine hydrogen peroxide complex.<sup>[35]</sup> Moreover, the <sup>1</sup>H-<sup>13</sup>C CPMAS and <sup>1</sup>H, <sup>13</sup>C MAS solid state NMR data suggested the formation of hydrogen bonds between NH<sub>x</sub> moieties and H<sub>2</sub>O<sub>2</sub>, and TPD-MS measurements confirmed the evolution of molecular O<sub>2</sub> while heating the PCN-H<sub>2</sub>O<sub>2</sub> adduct in an inert atmosphere indicating on the decomposition of hydrogen peroxide contained in the sample. The EPR study reported by Marci et al.<sup>[37]</sup> showed a signal at about 2.02 g-value earlier assigned to peroxy groups in titanium silicalite,<sup>[38]</sup> additionally confirming the presence of bonded H<sub>2</sub>O<sub>2</sub> in the PCN-H<sub>2</sub>O<sub>2</sub> material. Henceforth, based on these experimental results a theoretical model demonstrating that the H<sub>2</sub>O<sub>2</sub> in TEO is bonded to the non-condensed carbon nitride species by strong hydrogen bonding was proposed.<sup>[34,35]</sup> Such strong hydrogen-bond interaction in the PCN-H<sub>2</sub>O<sub>2</sub> system makes TEO stable in solutions, up to 200 °C in air and under UV-irradiation.<sup>[35,36]</sup>

All the used substrates in the present study were photo-stable and they did not undergo any significant photolysis in water solution under UV-irradiation. The adsorption of the studied substrates on the surface of TE and TEO were negligible and did not exceed 1 % of the initial substrate concentration.

The photocatalytic reactivity in terms of reaction rate, conversion and selectivity towards the corresponding aldehydes for benzyl alcohol and the substrates with one additional ED-group (methoxy-group) are summarized in Table 1. In agreement with the previous reports,<sup>[31,36]</sup> unsubstituted BA shows relatively low reactivity by using TE as photocatalyst (Fig. 1A). Both the reaction rate and the conversion are approximately halved in the presence of TEO compared to those obtained for TE. The oxidation of BA to benzaldehyde (BAL) proceeds with high selectivity (in the range of 82-88 %) for both photocatalysts (Fig. 1A), similar to that reported in.<sup>[36]</sup> The presence of the ED group, CH<sub>3</sub>O-substituent, on phenyl ring favours the alcohol to aldehyde oxidation in all cases, but the extent of conversion of the substituted benzyl alcohols is dependent on the position of the methoxy group with respect to the alcohol one (Table 1). This is particularly evident when the -OCH<sub>3</sub> group is in the *para*- and *ortho*-positions with respect to the alcohol group, i.e. for 4MBA and 2MBA (Fig. 1B,C). The reaction rate of the methoxy-substituted benzyl alcohols by using both photocatalysts follows the order: *para*>*ortho*>*meta*, although the TE photocatalyst demonstrates a significantly higher activity than TEO. As reported in Table 1, by using TE the aromatic alcohol partial oxidation rate is more than 5 times higher for 4MBA than for BA, whereas it increases only twice while using TEO. As in the case of BA, the selectivity values for the oxidation of 4MBA and 2MBA to the respective aldehydes by using both TE and TEO are high

also for higher conversions of ca. 80%, as reported in Fig. 1B,C, showing a slight decrease when the aromatic alcohol is almost completely consumed.



**Figure 1.** UV-assisted partial photocatalytic oxidation of (A) benzyl alcohol, (B) 4-methoxybenzyl alcohol, (C) 2-methoxybenzyl alcohol, (D) 3-methoxybenzyl alcohol, to the benzaldehydes in the presence of TE (empty symbols) and TEO (full symbols) photocatalysts. Alcohol concentration (circle) and aldehyde concentration (square) versus irradiation time and selectivity versus conversion (diamond).

The photo-driven transformation of the *meta*-substituted methoxybenzyl alcohol (3MBA) results in lower reaction rates than those of 4MBA or 2MBA (Fig. 1D). The conversion extent is 76 and 47 % for the TE and TEO samples, respectively. Moreover, the selectivity of 3MBA oxidation to *meta*-methoxybenzaldehyde is also inferior to that found for 4MBA and 2MBA, reaching 72 or 85 % by using the TE or TEO catalysts, respectively. In any case, the TEO photocatalyst, although providing lower reactivity, appears to favour the selectivity to the aldehyde formation (Fig. 1D, Table 1).

Comentar algo sobre los supproductos...¿CO<sub>2</sub> o carboxilos?...los subproductos se forman a partir del alcohol o de del aldehído?...incluso en aquel caso en el que hay selectividades significativas al carboxilo, se podría incluir en la gráfica...

**Table 1.** Initial reaction rate of methoxy-substituted alcohols to aldehydes, conversion of the reaction after 4 hours of irradiation and selectivity at 20% of conversion in the presence of the TE and TEO photocatalysts

Substrate	Product	Initial reaction rate · 10 <sup>4</sup> / mM min <sup>-1</sup>		Conversion / %		Selectivity / %	
		TE	TEO	TE	TEO	TE	TEO
		16	8	50	29	82	88
		91	19	100	82	90 <sup>a</sup>	89 <sup>a</sup>
		77	18	100	100	98	96
		30	13	76	47	72	85

[a] Selectivity at 60% of conversion

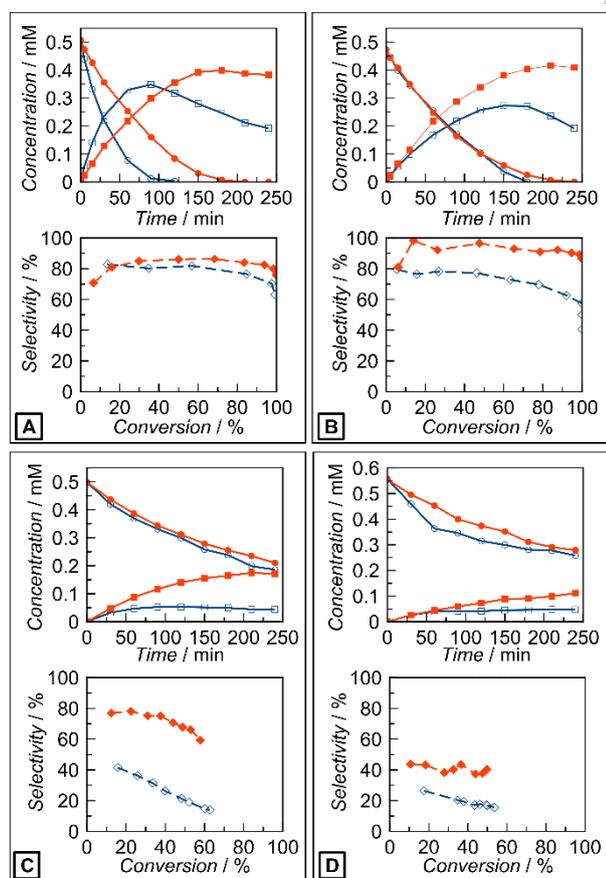
Various researchers suggest that superoxide radical is the main oxidative species for these reactions occurring in irradiated suspensions of carbon nitrides.<sup>[22,39]</sup> This mild oxidant species promotes the transformation of alcohols to aldehydes avoiding the overoxidation of the latter. Moreover, the presence of <sup>•</sup>O<sub>2</sub><sup>-</sup> as the principal oxidative species in irradiated suspensions of PCN can be evidenced by the fact that during the alcohol degradation the concurrent formation of the corresponding aldehyde and of H<sub>2</sub>O<sub>2</sub> in stoichiometric amount was observed<sup>[36,40]</sup> by following the reaction scheme hypothesized by Su et al.<sup>[22]</sup> Consequently, it appears clear that the oxidation mechanism in the presence of PCN is different from that occurring when TiO<sub>2</sub> is used as photocatalyst.<sup>[41,42]</sup> It is important to emphasize the different performances of PCN and TiO<sub>2</sub> in selective photo-oxidation reactions. Yurdakal et al. while studying the photocatalytic conversion of methoxybenzyl alcohols in water under UV-irradiation observed somewhat a different reactivity order: *ortho*>*para*>*meta*.<sup>[43]</sup> This can be explained by the presence on the TiO<sub>2</sub> surface of alternative photo-generated reactive oxygen species (ROS) than superoxide radical, which would oxidise the substrate unselectively. Higashimoto et al. studied the

methoxybenzyl alcohols oxidation promoted by TiO<sub>2</sub> in water-free medium. The dependency of the substituent effect on the reactivity i.e. *meta*>*para*>*ortho*, was different to that observed in the present research, and this can be ascribed to the LMCT mechanism of the alcohols oxidation on TiO<sub>2</sub> under visible light.<sup>[14]</sup> This observation supports the opinion that the type of photocatalyst and the reacting medium could influence the type of ROS formed during the photocatalytic oxidation, and consequently reaction rate and selectivity of the benzyl alcohols oxidation reaction are different.

By studying the photocatalytic reactivity of unsubstituted BA it is evident that the most reactive position is the carbon of the alcohol group as it was already demonstrated by Fristrup et al.<sup>[44]</sup> When an ED group is inserted in the ring, an increase of the alcohol conversion is observed because the ED group activates the ring modifying the charge distribution on the -CH<sub>2</sub>OH group. Moreover, when the alcohol group is present in *ortho*- or *para*-position with respect to the -OCH<sub>3</sub> group (2MBA and 4MBA, respectively) the selectivity towards the corresponding aldehyde increases, probably because the methoxy group is *ortho-para* orienting. On the contrary, when the alcohol group is found in *meta*-position with respect to the -OCH<sub>3</sub> (3MBA), the selectivity decreases, because other positions of the ring (*ortho*- and *para*- with respect to the methoxy group) become more reactive. According to Higashimoto et al.,<sup>[14]</sup> the resonance effect favours the stabilization of a partially deprotonated benzylic carbon when the ED group is *ortho*- or *para*-positioned, while it does not occur for the case of 3MBA. Such resonance effect of the ED methoxy group greatly promotes the reaction rate of photo-oxidation of 4MBA and 2MBA to 4-methoxybenzaldehyde (4MBAL) and 2-methoxybenzaldehyde (2MBAL), respectively. Despite this effect is not observed in the case of 3MBA, still this compound demonstrates higher reactivity than BA, which is probably due to the increased charge on the phenyl-ring and the consequent activation of the benzylic carbon position. The reactivity in the present case does not follow the Hammett rule, neither it shows an apparent dependency from the oxidative potentials of methoxy-substituted molecules which are 1.66, 1.80, 1.76 V vs SCE for *para*-, *ortho*- and *meta*-substituted methoxybenzyl alcohols, respectively.<sup>[14]</sup>

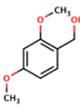
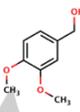
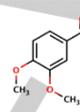
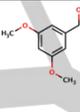
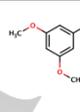
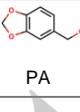
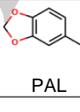
The photocatalytic partial oxidation results obtained in the presence of TE and TEO by using di-substituted methoxybenzyl alcohols as substrates are reported in Table 2. As it is expected from the discussed reactivity data for the mono-substituted methoxybenzyl alcohols, two -OCH<sub>3</sub> substituents in *para*- and *ortho*-positions with respect to the benzylic carbon, such is the case of 2,4DMBA, lead to the highest reaction rates (Fig. 2A). Both photocatalysts are able to completely oxidize the substrate within the reaction time with good selectivity to 2,4-dimethoxybenzaldehyde (2,4DMBAL) of ca. 84-89 %; figures similar to that are observed for the unsubstituted BA, which, however, shows much lower conversion (Table 1). In contrast, the performance of the TE photocatalyst changes when the substrate molecule contains two -OCH<sub>3</sub> substituents in *para*- and *meta*-positions with respect to the benzylic alcohol (3,4DMBA). In this case, the oxidation rate is still high, providing complete disappearance of 3,4DMBA in less than 4 h, although it is

inferior (ca. halved) to that obtained for 2,4DMBA (Fig. 2B, Table 2). The selectivity towards the 3,4-dimethoxybenzaldehyde (3,4DMBAL) formation, in the presence of the TE sample, is slightly lower than in the case of 2,4DMBA oxidation to 2,4DMBAL and results in ca. 80 % at 20 % of the substrate conversion (Fig. 2B, Table 2). On the other hand, the TEO photocatalyst, differently from the above showed for the other substrates, is as active as the TE sample in this particular reaction (oxidation of 3,4DMBA). It is also important to note that in the presence of the TEO catalyst the selectivity towards the aldehyde formation does not suffer any reduction, being ca. 92 % at 20 % of 3,4DMBA conversion (Fig. 2, Table 2). When both methoxy-substituents are *meta*-positioned with respect to the benzylic carbon, their significant inhibiting effect on the oxidation rate of 3,5DMBA is observed (Fig. 2C, Table 2). Similar to the case of 3,4DMBA, both of the used catalysts show almost identical reactivity (Fig. 2C, Table 2). However, the difference in the selectivity towards the 3,5DMBAL formation demonstrated by TE and TEO is dramatic. While TE achieves only 40 % of selectivity, TEO reaches 78 % at 20 % of the substrate conversion (Table 2). In order to explain both reactivity and the selectivity showed for the three di-substituted methoxybenzyl alcohols, similar considerations can be done as in the case of the mono-substituted ones. Indeed, the reactivity follows the order *ortho*, *para*>*para*, *meta*>*meta*, *meta* (Table 2).



**Figure 2.** UV-assisted partial photocatalytic oxidation of (A) 2,4-dimethoxybenzyl alcohol, (B) 3,4-dimethoxybenzyl alcohol, (C) 3,5-dimethoxybenzyl alcohol, (D) piperonyl alcohol to the respective aldehydes in the presence of TE (empty symbols) and TEO (full symbols) photocatalysts. Substrate concentration (circle) and product concentration (square) versus irradiation time and selectivity versus conversion (diamond).

**Table 2.** Initial reaction rate of dimethoxy-substituted alcohols to aldehydes, conversion of the reaction after 4 hours of irradiation and selectivity at 20% of conversion in the presence of the TE and TEO photocatalysts

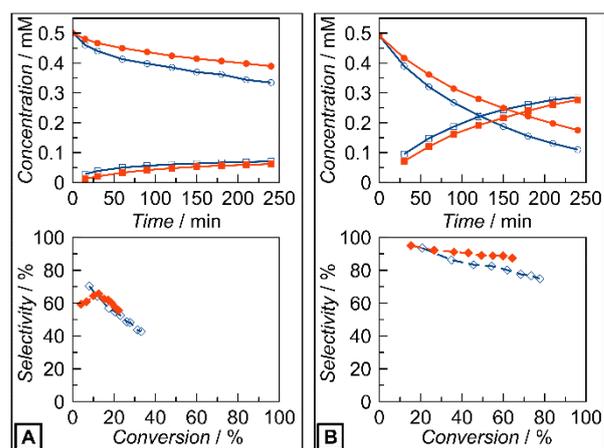
Substrate	Product	Initial reaction rate · 10 <sup>4</sup> / mM min <sup>-1</sup>		Conversion / %		Selectivity / %	
		TE	TEO	TE	TEO	TE	TEO
		109	48	100	100	84	89
2,4DMBA	2,4DMBAL						
		40	41	100	100	80	92
3,4DMBA	3,4DMBAL						
		20	19	63	58	40	78
3,5DMBA	3,5DMBAL						
		27	19	54	50	25	46
PA	PAL						

The experimental results can be explained by considering the resonance effect induced by the two -OCH<sub>3</sub> groups in different positions; i.e. the *ortho*-, *para*- di-substituted methoxybenzyl alcohol (2,4DMBA) showing the highest conversion rate probably because of the presence of two ED *ortho*-, *para*-orienting groups, which favour the reactivity of the benzylic carbon. This fact gives rise to an increase of the reactivity, but at the same time the selectivity towards the aldehyde formation remains high. In the case of the *para*-, *meta*- di-substituted methoxybenzyl alcohol (3,4DMBA), its reactivity is higher with respect to that of BA, but it is lower if compared with that of the 2,4DMBA, particularly in the presence of the TE photocatalyst. This can be explained by the relative position of the two *meta*-, *para*- orienting groups donating the electron density to the different carbon sites of the phenyl ring. One can relate a slight decrease of the selectivity of the 3,4DMBA to 3,4DMBAL oxidation demonstrated by TE with respect to that of TEO to the same effect of the *meta*-substituent manifested for 3MBA (Tables 1, 2). The *meta*-, *meta*- di-substituted methoxybenzyl alcohol (3,5DMBA) is the least reactive molecule of the three di-substituted benzyl alcohols, although its reactivity is still higher with respect to that showed by BA. In this case, the positions 2,

4, 6 with respect to the alcohol group become activated. The activated positions on phenyl ring might be a target for photo-generated electrophilic species such as holes or hydroxyl radicals, thus open-ring products could be formed drastically decreasing the selectivity to the corresponding benzaldehyde.

The last benzyl alcohol bearing an ED substituent tested in this work is piperonyl alcohol, whose selective photo-oxidation in water medium is a serious challenge.<sup>[31,45]</sup> The TE photocatalyst, despite showing a reasonable activity and converting 54 % of the substrate, shows a poor selectivity towards the piperonal production accounting only for 25 % (Fig. 2D, Table 2). The use of the TEO photocatalyst for this reaction not only enhances the selectivity up to 46 %, but also it does not compromise the oxidation rate of piperonyl alcohol, indeed, still a ca. 50 % of the substrate is converted after 4 h of UV-irradiation, (Fig. 2D, Table 2). In order to explain the reactivity of piperonyl alcohol and the selectivity towards the piperonal formation demonstrated by the two photocatalysts, the same considerations can be made as for the case of 3,4DMBA. Indeed, the two methoxy- groups of the latter are in the same positions to those occupied by the dioxole group present in the piperonyl alcohol. The very low selectivity observed towards the piperonal formation can be due to the possible  $\cdot\text{O}_2^-$  attack on the carbon of both the alcohol and the dioxole groups.

In order to get a more profound understanding of the processes underlying the studied photocatalytic oxidation reaction, it is crucial to investigate the conversion of benzyl alcohols bearing an electron withdrawing (EW) substituent. The rate of the photocatalytic oxidation of 4NBA bearing an EW nitro-group in *para*-position is reduced with respect to that of BA for both photocatalysts (Fig. 3A, Table 3). The selectivity towards the 4-nitrobenzaldehyde (4NBAL) formation is also lower than that found for BA to BAL, independently from the choice of the photocatalyst (Fig. 3A, Table 3). On the contrary, the presence of a *meta*-substituent in 3NBA promoted the photo-oxidation reaction as evidenced by the rate of oxidation and conversion extent values of 78 and 64 % for TE and TEO, respectively (Fig. 3B, Table 3). The obvious improvement of the reaction selectivity towards the aldehyde production is also worth mentioning and the values obtained by both TE and TEO are almost equal to ca. 94 % at 20 % of alcohol conversion (Fig. 3B, Table 3).



**Figure 3.** UV-assisted partial photocatalytic oxidation of (A) 4-nitrobenzyl alcohol, (B) 3-nitrobenzyl alcohol and (C) 1-phenyl ethanol to the respective aldehydes in the presence of TE (empty symbols) and TEO (full symbols) photocatalysts. Substrate concentration (circle) and product concentration (square) versus irradiation time and selectivity versus conversion (diamond).  
¿FALTA UNA GRÁFICA?

**Table 3.** Initial reaction rate of nitro-substituted alcohols to aldehydes, conversion of the reaction after 4 hours of irradiation and selectivity at 20% of conversion in the presence of the TE and TEO photocatalysts

Substrate	Product	Initial reaction rate · 10 <sup>4</sup> / mM min <sup>-1</sup>		Conversion / %		Selectivity / %	
		TE	TEO	TE	TEO	TE	TEO
		11	7	33	22	55	58
4NBA	4NBAL						
		28	22	78	64	94	94
3NBA	3NBAL						

To explain these findings, it must be considered that, as in the case of BA, the carbon of the alcohol group is the most reactive one of the molecule. Moreover, the nitro-group is a deactivating one affecting in particular the reactivity in *ortho*- and *para*-position (it is *meta*-orienting) by retrieving the electron density from them. Consequently, when the  $-\text{CH}_2\text{OH}$  group is in *para*-position with respect to the  $-\text{NO}_2$ , as occurs in 4NBA, the substituted benzyl alcohol becomes less reactive than BA and both the conversion and the selectivity towards 4NBAL decrease. On the contrary, when the  $-\text{CH}_2\text{OH}$  group is in *meta*-position with respect to the  $-\text{NO}_2$  (3NBA), this substrate results more reactive than the unsubstituted BA and both the conversion and the selectivity versus 3NBAL increase.

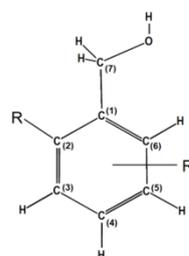
In order to obtain a more complete picture of the PCN-driven alcohol to aldehyde photo-oxidation, the aromatic alcohol 1-phenylethanol (1-PE) where the OH-group is bonded to a secondary carbon has been included in the present study. 1-PE is the least reactive compound among all the studied substrates in the present research as only 29 % and 20 % of it are converted after 4 h in the presence of TE and TEO, respectively (Fig. S2). The selectivity towards the acetophenone formation is good for the both photocatalysts (Fig. S2).

The low reaction rate of the oxidation of the alcohol group belonging to the secondary benzylic carbon observed in the case of 1-PE can be attributed to the smaller formal charge on this carbon atom or to a sort of shielding effect generated by the presence of the  $-CH_3$  group bonded to it.

### Computational study and correlation with the experimental data

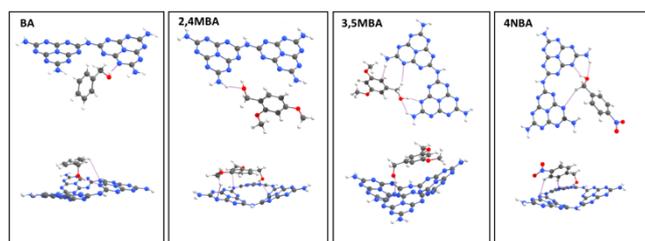
In order to uncover certain dependencies and correlations between steric and electronic effects and the performance of the PCN photocatalysts in aromatic alcohols partial oxidation reactions, the modelling of molecular complexes of  $CH_3O$ - and  $NO_2$ -substituted substrates with dimelem and polyheptazine (melon) fragments has been performed. The substrates such as 1-phenylethanol and piperonyl alcohol were excluded from the theoretical investigation, due to their significantly different properties to the selection of substituted benzyl alcohols, which complicates establishing correlations. Some representative examples of the substrate complexes with the pristine carbon nitride fragments are shown in Figure 4A (for the other models see Supplementary Information Fig. 1S). For the estimation of the effect of modification of the PCN catalyst with hydrogen peroxide, three-component complexes have been considered, where the  $H_2O_2$  molecule hydrogen-bonded to dimelem or polyheptazine fragments is oriented near the substrate's  $CH_2OH$  group (Fig. 4B).

**Figure 4.** (A) Models of molecular complexes of  $CH_3O$ - and  $NO_2$ -substituted substrates with fragments of dimelem and melon. (B) Models of molecular complexes of  $CH_3O$ - and  $NO_2$ -substituted substrates with fragments of dimelem and melon modify by  $H_2O_2$ .

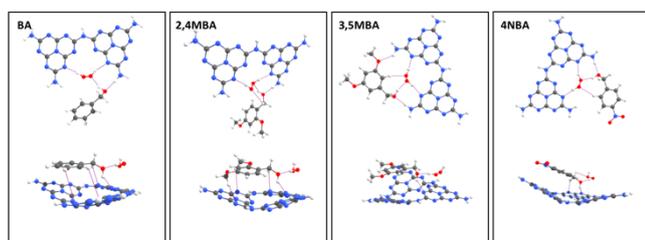


**Scheme 1.** Numbering of carbon atoms in aromatic alcohols

Considering the steric aspects of the interaction of aromatic alcohols with the PCN fragments for the “substrate –dimelem” complexes, one can state that if the interaction occurs in the dimelem cavity, the substrate's  $CH_2OH$ -group always participates in the H-bonding ( $O-H \dots N_{Ar}$ ) with the heterocyclic  $N_{Ar}$  of a dimelem species (Fig. 4A). The bonding of aromatic alcohols in the dimelem cavity is reinforced by an additional H-bonding ( $O \dots H-N$ ) between the hydroxyl and amino group. Noteworthy, hydrogen atoms of the benzylic carbon in  $CH_2OH$ -group of only certain molecules (4MBA, 3MBA, 3,4DMBA, 3,5DMBA, 3NBA) participate in the bonding with the carbon nitride moieties, thus, probably, remaining accessible for the reaction with photo-generated radicals leading to aromatic alcohol deprotonation (Fig. 4A). In the case of the modified PCN- $H_2O_2$  photocatalyst,  $H_2O_2$  molecules always participates in the interaction with the  $CH_2OH$ -group, but unlike for pristine PCN one of the H atoms becomes almost orthogonally oriented with respect to the carbon nitride surface (Fig. 5B).



**A**



**B**

**Table 4.** Binding energy in the “substrate-catalyst” complexes and Mulliken charges on C(7) and C(2) carbon atoms in the substrates

Substrates	Binding energy / kcal mol <sup>-1</sup>					Charges			
	Eb <sub>-D</sub>	Eb <sub>-DM</sub>	Eb <sub>-T</sub>	Eb <sub>-TM</sub>	qC <sup>o</sup> <sub>(7)</sub>	qC <sup>Kt</sup> <sub>(7)</sub>	qC <sup>o</sup> <sub>(2)</sub>	qC <sup>D</sup> <sub>(2)</sub>	qC <sup>DM</sup> <sub>(2)</sub>
BA	-17.4	-18.8	-12.3	-19.0	0.03	0.19	-0.06	-0.06	-0.07
4MBA	-17.2	-19.3	-13.4	-21.2	0.02	0.09	-0.05	-0.05	-0.06
2MBA	-16.5	-18.7	-11.9	-19.3	0.01	0.14	0.17	0.15	0.21
3MBA	-17.6	-24.0	-13.1	-19.8	0.06	0.19	-0.10	-0.07	-0.08
2,4DMBA	-16.4	-18.5	-12.7	-20.3	0.00	0.08	0.17	-0.07	0.22
3,4DMBA	-17.5	-25.1	-12.7	-20.6	0.02	0.16	-0.10	-0.05	-0.05
3,5DMBA	-18.0	-22.9	-13.5	-21.4	0.06	0.18	-0.11	-0.25	-0.11
4NBA	-17.5	-21.5	-15.3	-23.2	0.05	0.27	-0.09	-0.15	-0.08
3NBA	-17.2	-26.5	-13.4	-20.0	0.06	0.21	-0.07	-0.04	-0.05

[D] for complexes of “substrate – dimelem”;

[DM] for complexes of “substrate – dimelem – H<sub>2</sub>O<sub>2</sub>”;

[T] for complexes of “substrate – melon”;

[TM] for complexes of “substrate – melon – H<sub>2</sub>O<sub>2</sub>”.

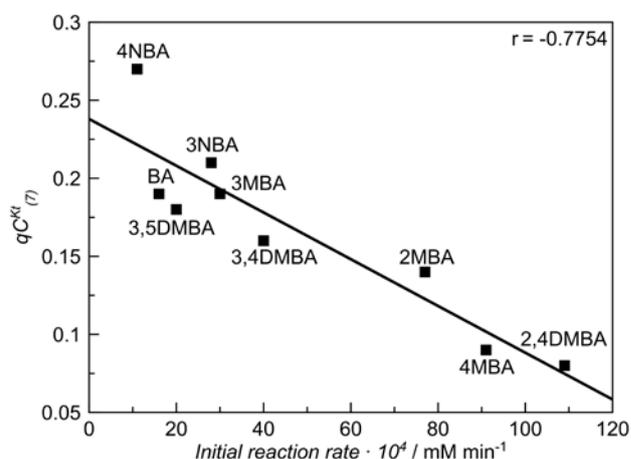
[o] for isolated molecules;

[Kt] for cations of substrates

The estimation of non-covalent interactions in the “substrate – dimelem”, “substrate – melon” complexes demonstrates that the bonding of aromatic alcohol molecules in the dimelem cavity is stronger than it is on the polyheptazine surface for all studied substrates (see Tables 4 and 1S). The numbering of carbon atoms in substrates, as reported in Table 4, was made according to Scheme 1. According to the calculated energies of interaction in the complexes “substrate – dimelem – H<sub>2</sub>O<sub>2</sub>”, “substrate – melon – H<sub>2</sub>O<sub>2</sub>”, the photocatalysts modification with hydrogen peroxide always leads to a stronger substrate bonding on the carbon nitride surface, which is especially evident considering the difference of the energies of interaction of the substrates with the polyheptazine surface of the pristine and modified carbon nitrides (Tables 4 and 1S).

The Mulliken atomic charges have been determined for the isolated substrates, substrate benzyl radicals, substrate cations and for the substrates complexes with dimelem and polyheptazine fragments from the obtained models (Table 4, see also Supplementary Information Table 2S). One can see that C<sub>(7)</sub> has a significant positive charge if the substrate molecules are considered independently from their interactions with the photocatalysts surface. Homolytic as well as heterolytic cleavage of the C–H bond in the CH<sub>2</sub>OH-group increases even more the positive charge on the benzylic carbon (Table 4), while the non-covalent interactions of aromatic alcohols with the carbon nitride functional groups in the complexes “substrate – dimelem”, “substrate – melon” causes the charge of C<sub>(7)</sub> to decrease (Table 4).

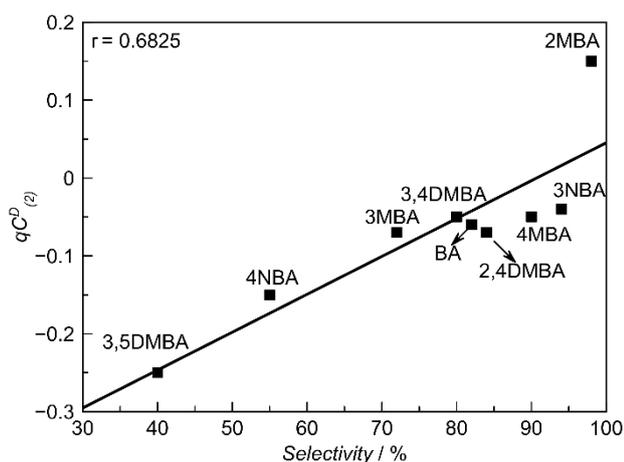
Considering strong ED and EW nature of the studied substituents, one might expect that the reactivity of the PCN photocatalysts towards different substrates would depend on the charge of the carbon in CH<sub>2</sub>OH-group. Indeed, the analysis of the electronic effects of the substituents shows that the Mulliken charges might be informative for the explanation of both the reaction rate and the selectivity of benzyl alcohols to benzaldehydes oxidation. It has been found that the reaction rate of benzyl alcohols oxidation on TE is inversely proportional to the charge on C<sub>(7)</sub> of benzyl alcohol cation, qC<sup>Kt</sup><sub>(7)</sub>, which among the all other parameters shows the best correlation coefficient (Fig. 5). Although this correlation suggests the formation of benzyl alcohol cations via the reaction with h<sup>+</sup>, the explanation of the inverse dependency of the reactivity from the C<sub>(7)</sub> charge is counterintuitive, since ‘O<sub>2</sub>’ is known to act as a nucleophile. It is reasonable to suppose that a high positive charge on the C<sub>(7)</sub> might complicate further alcohol deprotonation.

**Figure 5.** Correlation of calculated Mulliken charges on C<sub>(7)</sub> atom of the benzylic alcohols with the initial reaction rate of their photo-oxidation.

As a rule, the reaction rates of benzyl alcohols oxidation are much lower for the TEO catalyst due to its lower specific surface area and the presence of bonded H<sub>2</sub>O<sub>2</sub> creating a charge recombination center, which is manifested by the appearance of a new photoluminescence band centred at about 550 nm.<sup>[35]</sup> Interestingly, this does not apply to the 3,4DMBA and 3,5DMBA photo-oxidation reactions, where both catalysts demonstrate almost the same activity (Tables 1 and 2). One can see that these substrates form one of the strongest complexes with dimelem fragments (Table 4, Fig. 4). Indeed, for this cases the formation of hydrogen bonds (H...N<sub>Ar</sub>) involving one of the H atoms of the benzylic carbon is observed (Fig. 4). This suggests that such arrangement creates a steric hindrance for the deprotonation of the CH<sub>2</sub>OH-group in the proximity of the NH<sub>2</sub>-containing sites of PCN.

The apparent reasons for low selectivity in partial photo-oxidation reactions might be over-oxidation of benzyl alcohols to

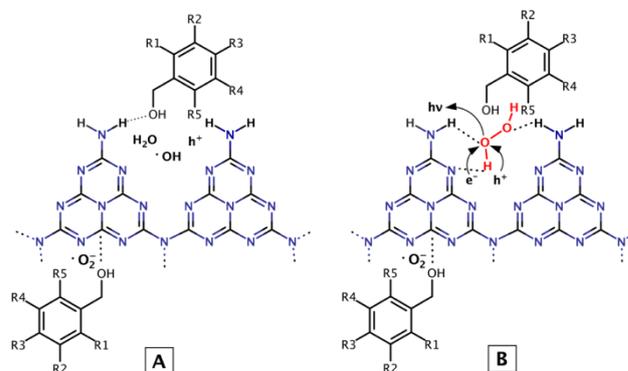
benzoic acids or competitive reactions might take place. For all the substrates the formation of only negligible quantities of benzoic acids was observed, with the exception of 4NBA, for which the selectivity towards 4-nitrobenzoic acid production was 15 % after 4 h of irradiation (Fig. S2), which correlates with the high  $C_{(7)}^{Kt}$  charge (Table 4, Table S2). The occurrence of the competitive reactions leading to ring-opening is likely to depend on the electronic effect of the substituents inducing negative charge on carbon atoms in phenyl ring making them target for electrophilic species such as  $h^+$  and  $\cdot OH$ . For the pristine TE photocatalyst a correlation between the selectivity towards benzaldehyde production and the charge on  $C_{(2)}$  of benzyl alcohol in the complexes with dimelem fragment ( $qC_{(2)}^D$ ) is established (Table 4, Fig. 6). Thus, the  $C_{(2)}$  is the most likely position in the substrates for an electrophilic attack of the photo-generated species. Although the VB oxidation potential of PCN is not sufficient to directly oxidize water and produce hydroxyl radicals, the photocatalytic formation of hydroxyterephthalic acid from terephthalic acid in the presence of carbon nitride was earlier reported.<sup>[35,46]</sup> This can occur either via the formation of  $\cdot OH$  radicals on the uncondensed PCN species,<sup>[35]</sup> or by the oxidation of organic substrate by  $h^+$  with the consecutive addition of  $H_2O$ .<sup>[47,48]</sup>



**Figure 6.** Correlation of calculated Mulliken charges on  $C_{(2)}$  atom of the benzylic alcohols with the selectivity towards benzaldehydes formation.

The modification of the photocatalyst with hydrogen peroxide results in the increased selectivity towards the oxidation of  $CH_2OH$ -group avoiding competitive reactions. According to the obtained models of the PCN- $H_2O_2$  interactions,  $H_2O_2$  molecule occupies the dimelem cavity (Fig. 7B), however the modified site still participate in non-covalent bonding with the  $CH_2OH$ -group of the substrates. Nonetheless, such modification may cause a steric hindrance for the direct interaction of the substrate with uncondensed carbon nitride species complicating its reaction with  $h^+$ ,  $\cdot OH$  or adsorbed on amino-groups  $H_2O$ . The presence of bonded  $H_2O_2$  is also responsible for the appearance of an

additional photoluminescence band (not present in the pristine PCN),<sup>[35]</sup> which suggests that a radiative recombination of the charge carriers might take place on this site hindering the production of the above mentioned reactive species (Fig. 7).



**Figure 7.** Proposed mechanism of partial benzyl alcohol photo-oxidation (A) on pristine PCN and (B) on highly selective PCN- $H_2O_2$ .

## Conclusions

A clear effect of substituents in the phenyl ring of the benzyl alcohol on their photo-oxidation in the presence of polymeric carbon nitride (PCN) photocatalyst in aqueous medium has been observed. The photocatalytic reactivity of the aromatic alcohol largely depends on the presence of electron-donating or electron-withdrawing groups on the phenyl ring and their respective positions to the  $CH_2OH$ -group. Thus, the *para*- and *ortho*-positioned ED substituents produce a resonance effect favouring higher reactivity of the aromatic alcohol oxidation to the corresponding carbonyl than that of the unsubstituted BA, while maintaining high selectivity values in the range of 84-98 %. The *meta*-substituted benzyl alcohols, although being somewhat more reactive than their unsubstituted counterpart, demonstrate reduced selectivity to the corresponding benzaldehydes, ranging from 40 to 80 %, when the pristine PCN photocatalyst is used. The opposite dependence is observed for the EW substituent,  $NO_2$ -group. *p*-Nitrobenzyl alcohol shows both low reaction rate and selectivity towards *p*-nitrobenzaldehyde production, while *m*-nitrobenzyl alcohol gives rise to an excellent selectivity to the respective benzaldehyde formation and high conversion rate in the presence of TE. The theoretical calculations performed on the substrate molecules and their complexes with the PCN photocatalyst surfaces have allowed to draw a correlation between the charge on the benzylic carbon of the substrate cation, one of the possible oxidation intermediates, and the photo-oxidation reaction rate showing an inversely proportional dependency. According to the established correlation between the experimental data and calculated Mulliken charges for the "substrate-dimelem" complexes, the principal factor responsible for the lower selectivity of photo-oxidation of all *meta*-substituted aromatic alcohols is a competitive reaction occurring by the action of electrophilic photo-generated species on negatively

charged carbon atoms in the phenyl ring, leading to the ring-opening. The experimental results and theoretical studies converge suggesting that the reasons behind the enhanced selectivity of the PCN-H<sub>2</sub>O<sub>2</sub> catalyst towards the oxidation of *meta*-substituted aromatic alcohols to benzaldehydes is the blocking of the dimelem adsorption sites by H<sub>2</sub>O<sub>2</sub> molecule. This interaction creates either a charge recombination center or a steric hindrance for the direct interaction of substrates with h<sup>+</sup> or <sup>•</sup>OH. The exclusion of the attack of photo-produced oxidants on the phenyl ring increases the selectivity, although reducing the reaction rate.

## Experimental Section

### Materials and methods

Melamine (99% Aldrich) and aqueous solution of hydrogen peroxide (30% VWR chemicals) were used for the photocatalysts preparation. The series of substrates (structures reported in Tables 1 to 3) chosen to carry out the photocatalytic experiments were: benzyl alcohol (BA) and three substrates with an electron donating group (ED): the methoxy-group substituent, in position 2-, 3- or 4- with respect to the benzylic carbon; i.e. *o*-methoxybenzyl alcohol (2MBA), *m*-methoxybenzyl alcohol (3MBA) and *p*-methoxybenzyl alcohol (4MBA). Additionally, three more substrates containing two methoxy-groups, apart from the benzyl alcohol one, were used: 2,4-dimethoxybenzyl alcohol (2,4DMBA); 3,4-dimethoxybenzyl alcohol (3,4DMBA) and 3,5-dimethoxybenzyl alcohol (3,5DMBA). Also, piperonyl alcohol (PA) was tested as substrate. Furthermore, two more substrates possessing a nitro group, which is an electron withdrawing group (EW), were selected for the oxidation reaction. The -NO<sub>2</sub> group was located in 3 or 4- position with respect to the benzyl alcohol, i.e. *m*-nitrobenzyl alcohol (3NBA), *p*-nitrobenzyl alcohol (4NBA). Additionally, 1-phenyl ethanol (PE) was also used as model substrate to be partially oxidised. For the reactivity studies all the alcohols above mentioned, along with their corresponding aldehydes, reported in Tables 1-3, were purchased from Aldrich and had a >99% purity.

### Photocatalysts preparation

Thermally etched PCN and the material treated with H<sub>2</sub>O<sub>2</sub>, PCN-H<sub>2</sub>O<sub>2</sub>, labelled as TE and TEO, respectively, were prepared as reported elsewhere.<sup>[36]</sup> Briefly, TE was prepared by thermal etching of bulk PCN prepared by melamine condensation heating it at 3 °C min<sup>-1</sup> and subsequently leaving the material for 7 h at 520 °C. The obtained TE material was used to prepare TEO by suspending it in aqueous 30 wt% H<sub>2</sub>O<sub>2</sub> while heating at 70 °C and stirring until complete evaporation of the liquid. The formed TEO was thoroughly washed with deionized water and dried at 80 °C for 24 h.

### Photocatalytic study

The partial photocatalytic oxidation of the aromatic alcohols to the corresponding aldehydes under UV-light was carried out by using the set-up described elsewhere.<sup>[33]</sup> A water-cooled Pyrex reactor containing 150 mL of aqueous suspension was irradiated by six Actinic BL TL MINI 15 W/10 Philips fluorescent lamps having an irradiation maximum at 365 nm. The initial substrates concentration was 0.5 mM at the natural pH. The amount of solid photocatalyst used for the experiments was 100 mg; in this way, all the entering photons were virtually absorbed by the suspension. The impinging radiation energy in the range 315-400 nm

was measured by a radiometer Delta Ohm DO9721 with an UVA probe and its average value was 3.9 W·m<sup>-2</sup>. Samples of the irradiated solution were withdrawn at fixed time intervals and immediately filtered through 0.25 μm membranes (polypropylene, VWR) to separate the photocatalyst particles. Liquid aliquots were analyzed by liquid chromatography using Agilent 1200 or a Beckman coulter HPLC apparatus equipped with a Diode Array detector. The column was a Phenomenex KINETEK 5 μm C18 and the eluent (0.8 mL min<sup>-1</sup>) consisted of a mixture of acetonitrile and 13 mM trifluoroacetic acid (20:80 v:v). Standards purchased from Sigma-Aldrich with a purity > 99% were used to identify the products and to obtain the calibration curves.

### Calculations

The features of structure, intermolecular interaction energy and electronic properties were analyzed for the following types of molecular complexes "substrate – dimelem", "substrate – polyheptazine (melon)", "substrate – dimelem – H<sub>2</sub>O<sub>2</sub>", "substrate – melon – H<sub>2</sub>O<sub>2</sub>". The equilibrium geometry location for all types of complexes and for isolated molecules, radicals and cations of substrates were carried out on the level of B3LYP/6-311+G(d,p) using Firefly 8.0.1 program.<sup>[49]</sup> The absence of imaginary vibration frequencies was controlled in all cases. The interaction energy between substrates and polyheptazine fragments in complexes were calculated with BSSE correction:  $E_{\text{int}} = E_{\text{com}} - (E_{\text{s}} + E_{\text{frag}}) - E_{\text{BSSE}}$ , where  $E_{\text{com}}$ ,  $E_{\text{s}}$ ,  $E_{\text{frag}}$  are the total energy of complex, substrate and polyheptazine fragments, correspondently. Atomic Milliken charges for substrates in complexes were compared with that in isolated molecules, radicals and cations. The visualization of structures were performed using Chemcraft package.<sup>[50]</sup>

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**Keywords:** carbon nitride • photocatalysis • selective oxidation • benzyl alcohol • substituent effect

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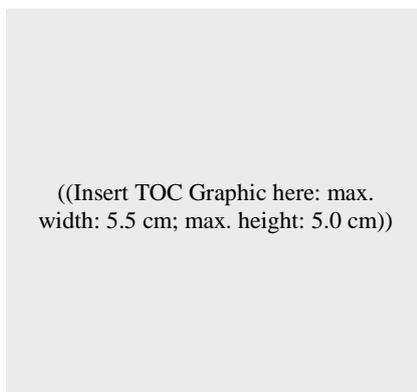
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