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**Dye-sensitized photocatalytic hydrogen generation: efficiency enhancement by organic photosensitizer – co-adsorbent intermolecular interaction**

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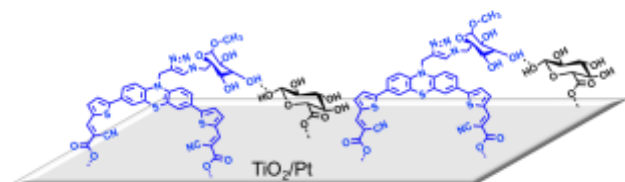
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**ABSTRACT:** The dye-sensitized photocatalytic H<sub>2</sub> generation has been investigated using a metal-free phenothiazine-based donor-acceptor sensitizer (PTZ-GLU) in combination with co-adsorbents. The co-adsorption of the PTZ-GLU dye, functionalized with a glucose end-group, in combination with a glucose-based co-adsorbent on the surface of Pt/TiO<sub>2</sub>, afforded improved photocatalytic activity compared to the absence of co-adsorbents or to the use of a conventional (chenodeoxycholic acid) co-adsorbent or by replacing the dye glucose functionality with an alkyl chain, suggesting the strategic role of directional intermolecular interactions dye – co-adsorbent on the semiconductor surface, as confirmed by accurate computational evidence, which likely suppressed detrimental recombination processes.

## TOC GRAPHICS



Hydrogen is a pivotal chemical in the industry and energy sectors, with applications in petroleum refining, power generation in turbines and fuel cells, methanol and ammonia production, and food processing. H<sub>2</sub> is mainly produced from fossil fuels reforming, since sustainable technologies are still not cost-effective despite the great advances of the last decades.<sup>1-3</sup> Photocatalysis is a green technology that could be used to produce H<sub>2</sub> by water splitting<sup>4-5</sup> or by photoreforming of renewable biomasses,<sup>6-7</sup> using suitable photocatalytic materials activated by sunlight.<sup>8-9</sup> Similarly to the natural photosynthetic process, solar-induced reactions can be obtained by dye-sensitization of a photocatalyst otherwise not active in the visible (Vis) range of the solar spectrum, such as TiO<sub>2</sub>.<sup>10-12</sup>

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3 The rational design of molecular and supramolecular dye-sensitizers is the foremost strategy to  
4 increase performances and stability of sensitized photocatalytic system.<sup>13-22</sup>  
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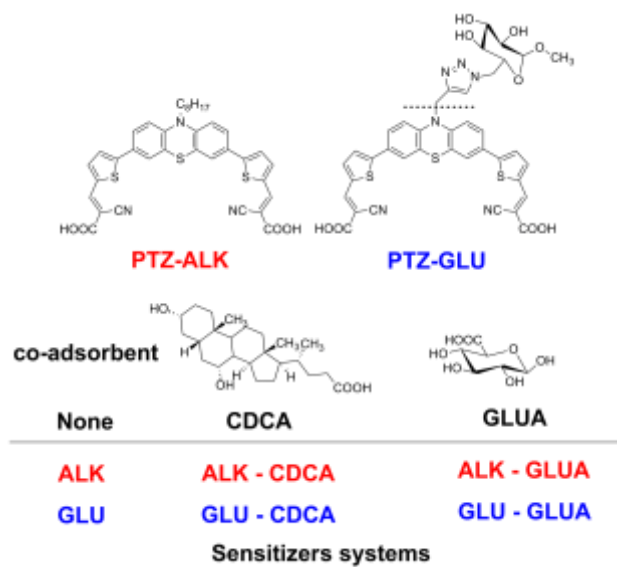
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8 Herein we report the first example of induced intermolecular interactions between dyes and co-  
9 adsorbents on the surface of a semiconductor catalyst to yield enhanced photocatalytic hydrogen  
10 generation efficiencies by suppressing detrimental intermolecular interactions. We have recently  
11 reported a new series of donor-acceptor thiophene-based phenothiazine sensitizers (**PTZ**) showing  
12 that careful molecular design can afford improved long-term H<sub>2</sub> production rates and stability under  
13 irradiation.<sup>23</sup> The **PTZ** series is characterized by the presence of a phenothiazine core, a very  
14 convenient scaffold with appropriate electronic properties which can be easily functionalized to  
15 obtain tailor-made derivatives. More recently, we have designed a glucose functionalized sensitizer  
16 **PTZ-GLU** (Figure 1) with hydroxyl groups. By promoting affinity to water and efficient interfacial  
17 interaction between the different components of the photocatalytic system, the glucose sensitizer  
18 afforded improved H<sub>2</sub> photogeneration over Pt/TiO<sub>2</sub> compared to conventional hydrophilic dyes.<sup>24</sup>  
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34 One of the most critical issues of dye-sensitized systems is the tendency of the quasi-planar  $\pi$ -  
35 conjugated organic dyes to aggregate on the surface of the n-type semiconductor (typically, TiO<sub>2</sub>)  
36 causing self-quenching of the photoexcited state and, accordingly, a partial or total deactivation.<sup>25</sup>  
37 For this reason, co-adsorbents, such as chenodeoxycholic acid (**CDCA**, Figure 1), are commonly  
38 added to the dye solutions,<sup>26</sup> thus competing with dye adsorption and suppressing intermolecular dye-  
39 dye interaction, helping charge separation.<sup>27</sup> However, this effect is random, since no directional  
40 intermolecular interaction is operating between the dye and **CDCA**, limiting beneficial effects.  
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50 In this work we exploit the rigid geometry of the sensitizer **PTZ-GLU** in order to promote more  
51 directional and specific intermolecular interactions with a proper co-adsorbent. The glucose ring is  
52 optimal for this scope because of its rigid nature and because of the presence of the terminal –OH  
53 groups. We have selected glucuronic acid (**GLUA**, Figure 1) as a co-adsorbent since its **pyranose**  
54 scaffold should efficiently promote strong co-adsorbent/dye intermolecular hydrogen bonds.  
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Though more sophisticated systems could be envisaged, **GLUA** has been preferred in reason of its

simple structure, low cost, wide availability from natural sources,<sup>28-32</sup> and the presence of a carboxylic functionality able to anchor the molecule on the TiO<sub>2</sub> surface.



**Figure 1.** Top: structure of sensitizers used in this study: the glucose-derivative **PTZ-GLU** and the alkyl-derivative **PTZ-ALK** as a reference. Middle: co-adsorbent agents used in this study. Bottom: sensitizer systems tested in dye sensitized photocatalytic hydrogen production in this work.

We show that the production of H<sub>2</sub> sensitized by **PTZ-GLU** in the presence of **GLUA** as co-adsorbent is significantly enhanced with respect to the experiment without co-adsorbent or with conventional **CDCA** as a co-adsorbent. In contrast, when the hydrophobic **PTZ-ALK** sensitizer is used in place of **PTZ-GLU**, *i.e.* if the glucose functionality of **PTZ-GLU** is replaced by a linear alkyl chain in **PTZ-ALK**, the effects of **GLUA** and **CDCA** co-adsorbents for the alkyl-chain-sensitizer did not differ from each other. Accurate computational studies confirmed the occurrence of directional intermolecular bonds on the semiconductor surface.

The dye-sensitizer/co-adsorbent pairs listed in Figure 1 were investigated as sensitizer systems. In order to focus the attention on the reduction photocatalytic system, the overall water splitting reaction has not been considered and the photocatalytic experiments were carried out in presence of a sacrificial electron donor, which allows back-regeneration of the neutral dye following dye excitation

and electron donation to the n-type semiconductor. The commonly used triethanolamine (TEOA) (see Figure 2) was selected as sacrificial electron donor.

A Pt(1 wt.)/TiO<sub>2</sub> photocatalysts has been used as a benchmark material to compare the sensitization ability of the dye/co-adsorbent pairs in H<sub>2</sub> production under irradiation with visible light ( $\lambda > 420$  nm) from TEOA/HCl aqueous buffer solution at pH = 7.0. The Pt/TiO<sub>2</sub> material was prepared by photodeposition of Pt nanoparticles (mean diameter 2.5 nm) on the surface of TiO<sub>2</sub> P25, an anatase/rutile mixture (~70/30 by weight) with mean crystallite sizes of 20 nm for both phases.<sup>24</sup> Textural analysis revealed a surface area of 55 m<sup>2</sup> g<sup>-1</sup> with pores diameters around 48 nm and a pore volume of 0.242 mL g<sup>-1</sup>. In all cases, the remarkable stability previously observed for these **PTZ**-based dyes was maintained, even when a co-adsorbent was present.<sup>23</sup>

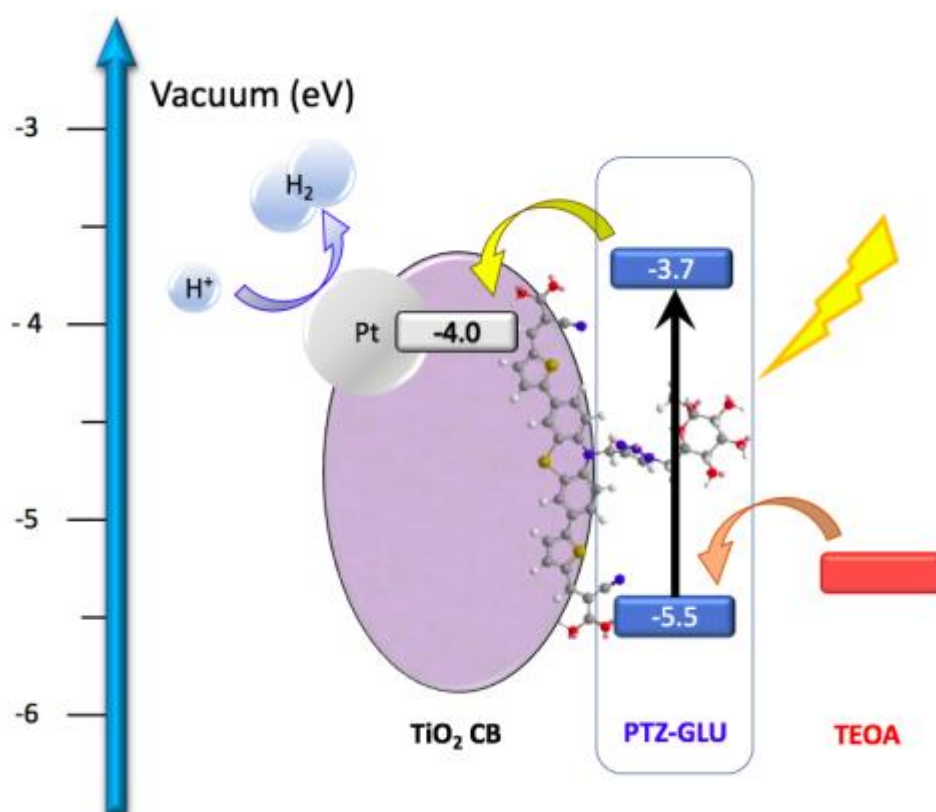
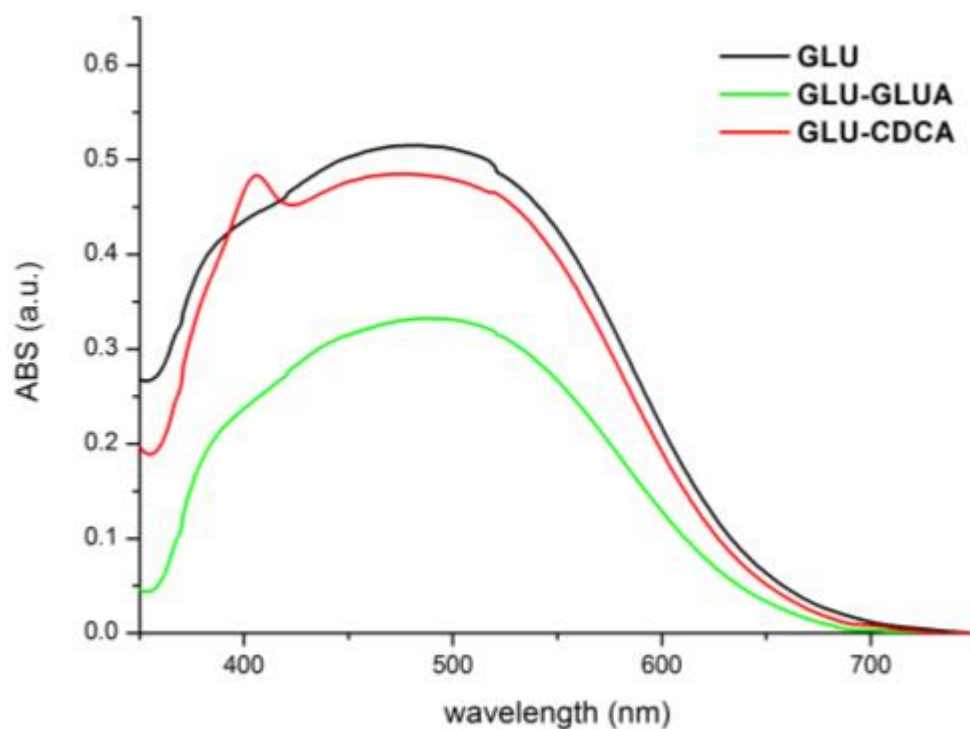


Figure 2. Energy band structure diagram of heterostructure between TiO<sub>2</sub>/Pt and **PTZ-GLU**, using TEOA as a sacrificial electron donor and proposed photocatalytic mechanism.

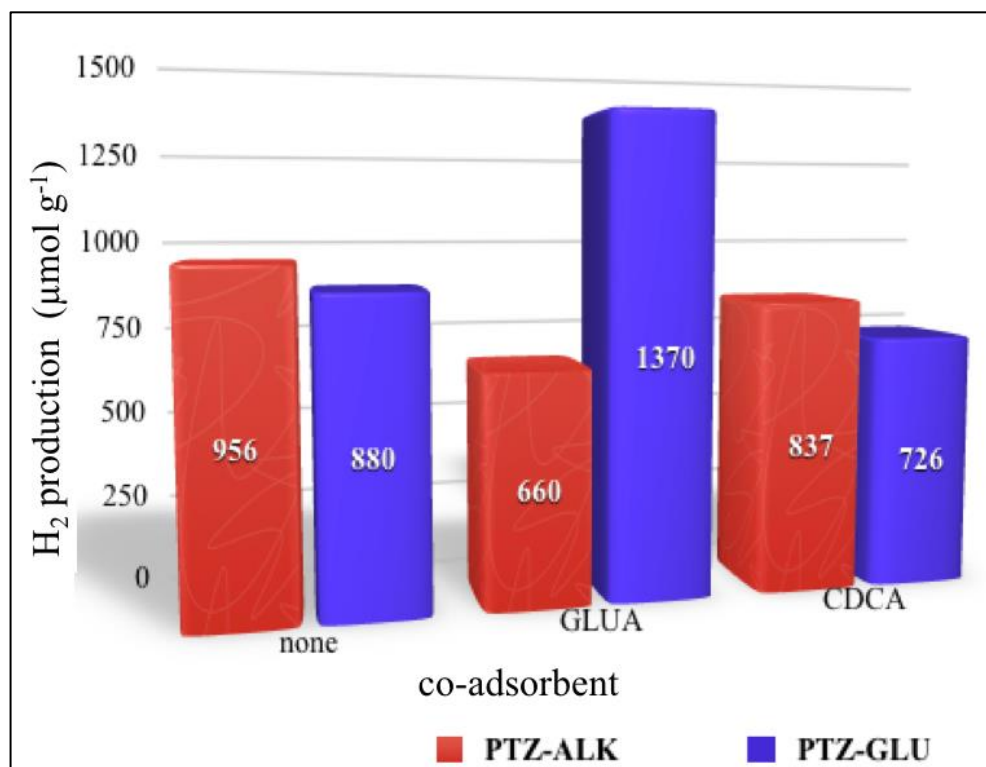
The UV-vis absorption of the **PTZ-GLU** itself and in presence of **GLUA** or **CDCA**, adsorbed on a 2.5  $\mu$ m transparent TiO<sub>2</sub> film, are shown in Figure 3. The presence of different co-adsorbents did

not affect the shape of the absorption spectra. However, using the same concentration of the staining solutions and the same equimolar ratio dye:co-adsorbent, the measured intensity was significantly different. In particular, the spectrum in presence of GLUA showed much lower intensity, suggesting a competitive adsorption.



**Figure 3.** UV-Vis absorption spectra of PTZ-GLU adsorbed onto a 2,5  $\mu\text{m}$  transparent  $\text{TiO}_2$  film, and in presence of GLUA or CDCA 1:1 molar ratio.

The scheme of the principle of action of the photocatalysts with relevant energy levels and standard potentials for the hydrogen evolution reaction and oxidation of the sacrificial electron donor is shown in Figure 2. The photocatalytic  $\text{H}_2$  generation performance of the glucose- and alkyl-functionalized sensitizers in presence of the two different GLUA and CDCA co-adsorbents is summarized in Figure 4, which depicts the hydrogen generation evolution from 0 to 20 h under irradiation. Amount of produced  $\text{H}_2$ , TON, TOF values, Apparent Quantum Yield (AQY) and Light-to-Fuel Efficiencies (LFE<sub>20</sub>) calculated at 20 h are listed in Table 1.



**Figure 4.** H<sub>2</sub> production (μmol g<sup>-1</sup>) from TEOA 10% v/v solution at pH = 7.0 after 20 h irradiation with Vis light ( $\lambda > 420$  nm) over Pt/TiO<sub>2</sub> materials sensitized with **PTZ-GLU** and **PTZ-ALK** in the presence of co-adsorbents **GLUA** or **CDCA** (1:1 molar with respect to the dye).

The effect of the co-adsorbent on the H<sub>2</sub> production rate was notable and dependent on the type of dye/co-adsorbent photosensitizer system. The H<sub>2</sub> production over **PTZ-GLU** sensitized systems was significantly enhanced (56%) by addition of the **GLUA** co-adsorbent. In contrast, gas generation was almost unvaried, or even slightly hindered, by addition of the **CDCA** co-adsorbent (Figure S1). In particular, the **GLU-GLUA** system is almost twice more efficient than the **GLU-CDCA** pair (see **TON**, **TOF**, and **LFE<sub>20</sub>** in Table 1).

To properly distinguish the effect of the presence of the peripheral glucose functionality of **PTZ-GLU** in the process, the **PTZ-ALK** dye was used as a control sensitizer. The photocatalytic activity of **PTZ-ALK** coupled with the same co-adsorbents **GLUA** and **CDCA** was investigated and compared with that of **PTZ-GLU** (Figure 4 and Table 1). The H<sub>2</sub> generation activity of **PTZ-ALK** is actually similar to that of **PTZ-GLU**, as expected by the same  $\pi$  architecture **PTZ**, but the effect



of the co-adsorbents was significantly different from the case of the **PTZ-GLU dye**. Indeed, neither the presence of **GLUA** nor the presence of **CDCA** was able to induce any particular enhancement of the photocatalytic activity, with the effects of the two different co-adsorbents being similar to each other (Figure S1).

**Table 1.** Hydrogen amount, TON and TOF values, LFE<sub>20</sub> and AQY for the studied Pt/TiO<sub>2</sub> catalysts sensitized with the various dye/co-adsorbent systems.

Sensitizer system	H <sub>2</sub> amount ( $\mu\text{mol g}^{-1}$ at 20 h)	TON ( $\mu\text{mol(H}_2\text{)}$ $\mu\text{mol(dye)}^{-1}$ at 20 h)	TOF ( $\mu\text{mol(H}_2\text{)}$ $\mu\text{mol(dye)}^{-1}\text{s}^{-1}\times$ $10^{-4}$ )	LFE <sub>20</sub> (%)	AQY (%)
<b>GLU</b>	880	59	8.2	0.024	0.071
<b>GLU-GLUA (1:1)</b>	1370	91	12.6	0.037	0.139
<b>GLU-GLUA (1:10)</b>	1213	87	12.1	0.033	-
<b>GLU-CDCA (1:1)</b>	726	48	6.7	0.020	0.077
<b>GLU-CDCA (1:10)</b>	728	49	6.8	0.020	-
<b>ALK</b>	956	64	8.9	0.026	0.081
<b>ALK-GLUA (1:1)</b>	660	44	6.1	0.018	0.062
<b>ALK-GLUA (1:10)</b>	1215	84	11.7	0.033	-
<b>ALK-CDCA (1:1)</b>	837	56	7.8	0.023	0.073
<b>ALK-CDCA (1:10)</b>	1212	83	11.5	0.033	-

The results show that enhancement of the photocatalytic activity is only observed for the **GLU-GLUA** sensitizer system, when the pyranose-based dye and the pyranose-based co-adsorbent are combined. This suggests that such enhancement likely originates by **PTZ-GLU/GLUA** supramolecular interactions which somewhat disaggregate the dye molecules suppressing detrimental dye-dye interactions. In contrast, the addition of **CDCA** to the **PTZ-GLU** sensitized catalyst, or the use of the **PTZ-ALK** dye, did not induce any specific intermolecular interaction and, in turn, unvaried

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3 **H<sub>2</sub> generation**. Actually, data suggest that the presence of **CDCA** promotes the tendency of  
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6 agglomeration of the dyes in segregated domains, thus affording poorer catalytic performances.

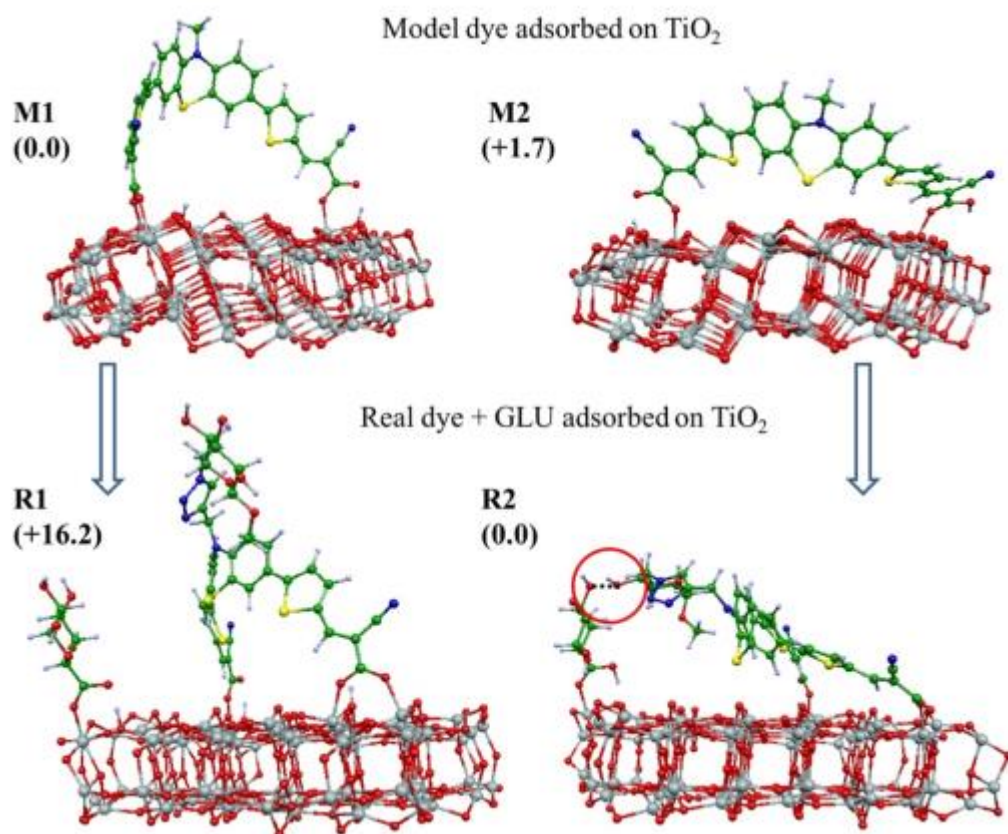
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8 We have also tested the effect of adding a strong excess of the co-adsorbents **GLUA** and **CDCA**  
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10 (nominal dye:co-adsorbent molar ratio 1:10), both in the case of **PTZ-GLU** and **PTZ-ALK** sensitized  
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12 catalysts (**Table 1 and Figures S3 and S4**). Whereas the response for the **PTZ-GLU** sensitized catalyst  
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14 was similar to the case of the lower molar ratio, an increase of H<sub>2</sub> photogeneration was observed for  
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16 **PTZ-ALK** but with no different response on the basis of the used co-adsorbent (**GLUA** or **CDCA**).  
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18 These results confirm that no specific supramolecular interaction takes place between the alkyl dye  
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20 and the co-adsorbents. In this case, we conclude that the increased H<sub>2</sub> production is simply due to the  
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22 separation of the dye molecules by a mass effect.  
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27 To validate the formation of specific supramolecular interactions as origin of the enhancement is  
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29 H<sub>2</sub> production, we modelled the TiO<sub>2</sub>-co-adsorbed dye and **GLUA** species (**GLU-GLUA** sensitizer  
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31 system) by first principles DFT calculations. TiO<sub>2</sub> was modelled by a (TiO<sub>2</sub>)<sub>82</sub> anatase cluster of ca.  
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33 2x2x1 nm dimensions exposing the majority (101) surfaces, which was previously shown to fairly  
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35 match the electronic properties of periodically replicated semiconductor surfaces.<sup>33</sup>  
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39 We started by investigating the dye adsorption modes on TiO<sub>2</sub> by means of a reduced dye model,  
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41 in which we only retained the carboxy-phenothiazine core (structure below dashed line in Figure 1)  
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43 replacing the neglected substituent by a hydrogen atom. This allows to effectively explore the  
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45 conformation space of the adsorbed dye at a reduced computational cost; **and to directly quantify the**  
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47 **impact of the PTZ-GLU/GLUA supramolecular interactions by comparing the energetics of these**  
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49 **model systems and of the real dyes, see below. Since the dye interactions with TiO<sub>2</sub> take mainly**  
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51 **place via the anchoring carboxylic groups (and to some extent the PTZ sulphur atom), which are**  
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53 **unchanged in the model and real systems, we expect the model dye adsorption modes to be effectively**  
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55 **representative of the real system.**  
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60 We found two dominant adsorption modes, **M1** and **M2** in Figure 5, characterized by a different  
coordination of the dye carboxylic groups to TiO<sub>2</sub>. **M1**, corresponding to the typical “vertical” dye

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3 adsorption mode, is calculated to be slightly more stable than **M2**, in which the dye lays almost flat  
4 on the TiO<sub>2</sub> surface, exploiting the interaction between the PTZ sulphur atom and under-coordinated  
5 Ti atoms. Despite the drastically different dye arrangements, **M1** and **M2** are calculated to lie within  
6 2 kcal mol<sup>-1</sup>. This attests the flexibility of carboxylic anchoring groups, which can bind to TiO<sub>2</sub> in  
7 different adsorption modes of comparable energy. Starting from the dye models, we then moved to  
8 simulate the supramolecular system composed by co-adsorbed **GLUA** and the real dye. **M1** and **M2**  
9 give rise to different interactions with the adsorbed **GLUA** species, **R1** and **R2** in Figure 5. **R1**, with  
10 the dye orthogonal to the TiO<sub>2</sub> surface, is essentially decoupled from the adsorbed **GLUA**, while in  
11 **R2** a sizable hydrogen-bonding interaction exists between the adsorbed dye and **GLUA** species. Most  
12 notably, such interaction significantly stabilizes **R2**, which is now calculated 16 kcal mol<sup>-1</sup> more  
13 stable than **R1**. Thus, the system will most likely adopt the **R2** adsorption mode while, in absence of  
14 such interaction, no strong energetic preference for a specific adsorption mode is calculated, as clearly  
15 indicated by the difference in the model and real dye energetics. The calculated stabilization is  
16 comparable to that previously proposed to stabilize supramolecular interactions in DSSC models.<sup>34</sup>



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3 Figure 5. Top: Model dye adsorption modes M1 and M2 with their relative stability (kcal mol<sup>-1</sup>).  
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5 Bottom: Real dye + **GLUA** co-adsorption modes R1 and R2 with their relative stability (kcal mol<sup>-1</sup>).  
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8 A red circle marks the hydrogen-bond between the adsorbed dye and **GLUA** in R2.  
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11 We have demonstrated that the combined use of the glucose-based dye (**PTZ-GLU**) and glucose-  
12 based co-adsorbent (**GLUA**) afforded enhanced photocatalytic activity (in terms of hydrogen  
13 generation, TON, **TOF**, and LFE) compared to the absence of co-adsorbents or to the presence of a  
14 conventional co-adsorbent less capable to establish specific directional intermolecular bonds  
15 (**CDCA**). Furthermore, the experiment with a conventional alkyl-functionalized sensitizer analog  
16 (**PTZ-ALK**) showed that no enhancement could be observed by adding any of the two co-adsorbents  
17 compared to the bare dye. In this case, the enhancement was only observed in presence of higher co-  
18 adsorbent/dye ratios (mass effect) for both co-adsorbents. **The control experiment using the alkyl-**  
19 **functionalized sensitizer validated the rationale for the enhanced activity of the **GLU-GLUA** system.**  
20 **DFT simulations on the investigated dye/co-adsorbents systems on the TiO<sub>2</sub> surface are fully**  
21 **consistent with the overall picture supporting the hypothesis that directional and selective interactions**  
22 **between the **PTZ-GLU** dye and the **GLUA** co-adsorbent take place on the semiconductor surface.**  
23 **This in turn likely suppressed detrimental dye-dye interactions and afforded, eventually, improved**  
24 **photocatalytic performances.**  
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44 Summarizing, we showed that it is possible to enhance photocatalytic H<sub>2</sub> production by modulating  
45 the intermolecular arrangement of organic dyes sensitizers and co-adsorbents on the photocatalyst  
46 surface, in particular by tuning their structure and using appropriate spacers.  
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## 51 ASSOCIATED CONTENT

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54 The supporting information contains experimental procedures, overall activity results, and  
55 computational details. The Supporting Information is available free of charge on the ACS  
56 Publications website.  
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8 **Notes**

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10 The authors declare no competing financial interest.

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