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## ARTICLE

# Visible Light-Driven Simultaneous Water Oxidation and Quinone Reduction by Nano-Structured Conjugated Polymer Without Co-catalysts

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In artificial photosynthesis, chemists are aiming to borrow principles from natural photosynthesis to develop photoelectrochemical cells (PEC) for water splitting. The water plastoquinone photooxidoreductase enzyme, also known as Photosystem II, uses light to perform the four-electron, four-proton oxidation of water to dioxygen and stores reducing equivalents in reduced forms of quinones which are ultimately used in dark reactions for the synthesis of energy-rich molecules. We report a nano-structured semiconducting conjugated polymer based on poly(diphenylbutadiyne) (nano-PDPB) and its photocatalytic activities towards the water oxidation reaction under visible light irradiation when dispersed in water in the absence of any sacrificial agents or co-catalysts. Charge recovery at the nano-PDPB directly or delayed in time was exemplified by the reduction of quinone acting as a hydrogen reservoir. In the absence of quinones as electron acceptor H<sub>2</sub>O<sub>2</sub> formation was detected stemming from the partial reduction of O<sub>2</sub>.

## Introduction

Solar energy could be harnessed and stored as a fuel using water as a renewable source of electrons and protons.<sup>1</sup> Among different materials under intense investigation for this thrust, organic semiconductors have captured an immense attention for their synthetic readiness, robustness and handles to adjust the energy levels of the conduction and valence bands. Domen and Antonetti first reported the use of g-C<sub>3</sub>N<sub>4</sub> as photocatalyst for hydrogen production.<sup>2</sup> These findings triggered a vibrant research effort in the design of organic semiconductors for the photocatalytic water splitting. Unfortunately, the progress towards functional material for the overall water splitting reaction has been mitigated due to the challenging and limiting step of the four-electron water oxidation reaction.<sup>3</sup> Two strategies are currently employed to bypass this hurdle, the adjunction of a known metal-based water oxidation co-catalyst

or replacing water by sacrificial electron donors that provide the necessary electrons for the production of hydrogen. Henceforth, a great effort is needed to engineer organic photocatalytic materials that can genuinely perform the water oxidation reaction coupled to the usage of the liberated electrons and protons.<sup>4</sup> Advancement in this prolific research theme has recently been updated by Mullins with a bird eye view on the challenges ahead of chemists to reach cost-effective metal-free photocatalysts. Significant examples from Xu and co-workers demonstrated overall water splitting using only conjugated microporous polymers.<sup>5</sup> Another original approach was to develop the Z-scheme scenario mimicking the serial operation of two charge separation systems found in oxygenic photosynthesis.<sup>6, 7</sup> Heterostructures interfacing two different polymer photocatalysts for O<sub>2</sub> and H<sub>2</sub> release respectively were successfully demonstrated.<sup>6, 7</sup> Liu *et al.* also reported on a metal-free CDots/C<sub>3</sub>N<sub>4</sub> system that leads to overall water splitting with an overall conversion efficiency of ~2 % under visible light irradiation.<sup>8</sup> Beyond the photon absorption and charge separation process further challenges come from coupling the photo oxidation and reduction chemistry and separating O<sub>2</sub> and H<sub>2</sub> in the gas mixture. The inherent chemical complexity to build such systems together with the challenge to suppress short-circuit reactions between the oxidation and reduction parts also hampers the advancement in this field.<sup>8-17</sup> Therefore, decoupling the oxidative and the reductive processes in time can be an alternative way to capture and store solar energy.

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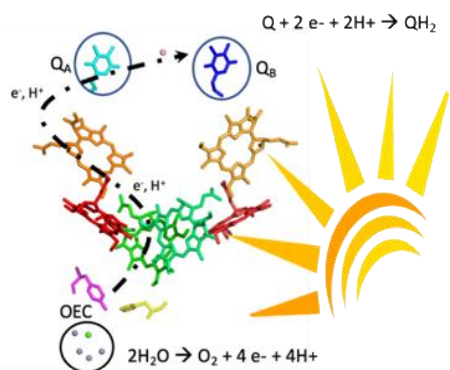
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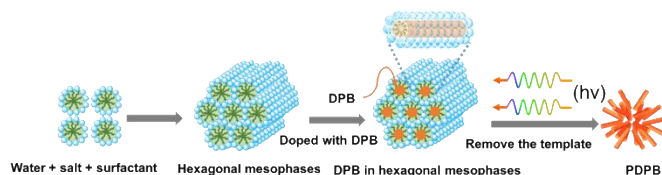
Here we report that visible light irradiation of a suspension of nano-structured conjugated polymers based on PolyDiPhenylButadiyne (nano-PDPB herein) in water leads to O<sub>2</sub> evolution. Intriguingly, no H<sub>2</sub> was detected. Instead we evidenced that the electrons and protons from water oxidation are stored on the nanostructured semiconductor and could be recovered as reduced form of quinone paralleling the functions of Photosystem II (Scheme 1).



Scheme 1: Map of the main cofactors of Water Plastoquinone Photo-oxidoreductase (PSII) and reactions for water oxidation at the oxygen evolving complex (OEC) and reduction of quinones  $\text{Q}_A$  and  $\text{Q}_B$  under sunlight irradiation

## Results and discussion

As a short summary of our previous report, nano-PDPB was obtained from the controlled polymerization of diphenylbutadiyne in confined domain of a hexagonal mesophase used as a soft template by radiolysis as we described (Scheme 2).<sup>18</sup>



Scheme 2: Soft template photopolymerization of diphenylbutadiyne

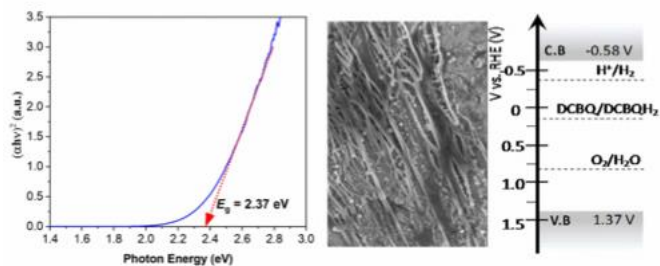


Figure 1. Left: Tauc plot; middle: TEM image of nano-PDPB; right: energy diagram representing the evaluated valence band (V.B.) and conduction band (C.B.) levels of PDPB polymer with regard to the water splitting reactions.

Transmission Electron Microscopy (TEM) images of nano-PDPB indicate nanofibers of diameters  $\sim 20$  nm and some tens of micrometers long (Figure 1). The molar mass of nano-PDPB was estimated around 1,625 g/mol by Gel permeation chromatography. This corresponds to short-chain oligomers with mainly a degree of polymerization of 8 diphenylbutadiyne units. The fragmentation patterns obtained from MALDI-TOF mass spectrometry technique also support this chemical formulation (see ESI Fig. S2). The nano-PDPB in the solid state presents a broad absorption band covering most of the visible region. The Kubelka-Munk and Tauc plot analyses (see ESI Fig. S3, Figure 1, left) give a direct band-gap value of 2.37 eV. This value is in good agreement with the maximum of the photoemission band detected at 530 nm after laser flash excitation of an acetonitrile solution of nano-PDPB (see ESI Fig. S4) corresponding to a HOMO-LUMO gap of *ca.* 2.34 eV. From the cyclic voltammetry studies, the conduction band minimum and valence band maximum of the nano-PDPB were poised within the potential window of -0.6 V and 1.4 V (vs. NHE) respectively.<sup>18</sup> These band positions suggest that from a thermodynamic point of view nano-PDPB could act as a photocatalyst for the water splitting reaction (Figure 1, right).

From a kinetic point of view, the transient absorption data indicate that the emissive singlet excited state is evolving to a long-lived charge separated state (see ESI Fig. S4). Irradiating a solution of PDPB in acetonitrile with visible light in presence of a sacrificial electron donor such as triethanolamine (TEOA) and methyl viologen ( $\text{MV}^{2+}$ ) as an electron acceptor leads to the formation of a persistent blue solution, characteristic of the formation of methyl viologen radical  $\text{MV}^{\bullet+}$  (Figure 2a). Considering the potentials of TEOA (0.84-1.14 V/NHE)<sup>19</sup> and  $\text{MV}^{2+}$  (-0.45 V/NHE)<sup>20</sup> this result is consistent with the estimated band positions.

The photocatalytic activity of nano-PDPB was tested by suspending 2 mg of the orange solid heterogeneously in 2 mL of pure water (without the presence of any co-catalyst or sacrificial agents) in a water-cooled Clark electrode maintained at 20°C and subjected to visible light irradiation ( $\lambda \geq 435$  nm) under stirring (see Supporting Information). The time course of evolution of O<sub>2</sub> is represented in Figure 2b.

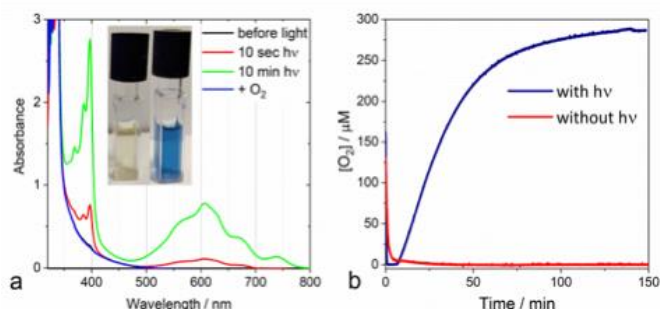


Figure 2. a) Spectral changes induced in an Ar-purged solution of nano-PDPB, 100 μM  $\text{MV}^{2+}$ , 10% TEOA in MeCN by illumination with blue light and after aeration (inset: formation of the blue  $\text{MV}^{\bullet+}$  radical). b) Time courses of oxygen evolution from water measured by a Clark Electrode. Blue curve: with nano-PDPB (synthesized in mesophases), Red curve: no irradiation.

After a time lag of a couple of minutes, the evolution of O<sub>2</sub> follows a sigmoid curve that levels off at a concentration of around 250 μM (saturated solution of O<sub>2</sub> in water) after irradiation for roughly one hour. The evolved O<sub>2</sub> was detected and quantified by GC-MS and Clark electrode respectively.<sup>21</sup> No O<sub>2</sub> production was observed in control experiments without nano-PDPB (see ESI Fig. S5) or when the nano-PDPB suspension was left in the dark (Fig. 2b). Importantly, photocatalysis with H<sub>2</sub><sup>18</sup>O indicates the formation of <sup>36</sup>O<sub>2</sub> detected by GC-MS, bringing a clear proof that the O<sub>2</sub> comes from the genuine oxidation of water (see ESI Fig. S6). We also found that the O<sub>2</sub> evolution was function of the intensity of the irradiation and the spectral window (see ESI Fig. S7). An important checkpoint before validating the intrinsic photocatalytic activity of organic material as photocatalysts resides in the insidious participation of traces of metal ions used during the synthetic process. We excluded the presence of metal ions upon examination by EDX method (see ESI Fig. S1). To ascertain this result, inductive coupled plasma mass spectrometry (ICP-MS) was used to evaluate the presence of metal ions, more specifically of copper or palladium. These salts are commonly used in the coupling of terminal alkyne groups. No trace of copper was found within the limit of detection. In a control photocatalytic experiment we deliberately added a copper(II) salt and we found a longer time delay and weaker photocatalytic activity for O<sub>2</sub> release (see ESI Fig S8). This can be supported by a similar quenching mechanism as proposed for g-C<sub>3</sub>N<sub>4</sub> material.<sup>22</sup> It has to be noted that no significant activity was obtained with bulk-PDPB (see ESI Fig. S9) pointing out that the nano-structuration of the conjugated polymers is crucial for photocatalytic activity. A rough estimation of the internal quantum yield (photon-to-electron) in the wavelength interval 450-700 nm yielded a value of 12% (see ESI for details). Surprisingly, no H<sub>2</sub> gas could be detected under our experimental conditions (see ESI Fig. S10). This can appear intriguing as the band-gap structure diagram suggests that the reduction potential for the H<sup>+</sup>/H<sub>2</sub> couple is indeed below the level of the conduction band of nano-PDPB. Such an observation can be assigned to kinetics issues for the formation of H<sub>2</sub> at the surface of the nano-structured polymeric material. An archetypal example is bare TiO<sub>2</sub>, where H<sub>2</sub> production under UV irradiation is very low and catalytic nanoparticles are needed for the formation of the H-H bond.<sup>23-25</sup> As already pointed out in the literature, the presence of traces of palladium coming from the synthesis of the material is often involved as the catalytic species responsible for H<sub>2</sub> production. In our case no H<sub>2</sub> formation was observed and ICP-MS also rules out the presence of Pd (see ESI Table S1).

Inspired by the functions of PS II, we added a quinone derivative, the dichlorobenzoquinone (DCBQ), to the mixture at different oxygen concentrations upon photocatalysis till reaching the plateau for O<sub>2</sub> evolution. A rapid change in color of the solution from colorless to purple was observed with an intensity increasing with the concentration of O<sub>2</sub> produced (Figure 3a, ESI Fig. S11). This purple solution presents an absorption band with a maximum at 530 nm. This absorption feature is characteristic of the formation of a quinhydrone complex exhibiting a charge transfer band between reduced

hydroquinone and the quinone.<sup>26-30</sup> The formation of such a redox pair brings unambiguous support for the charge accumulation on the nano-PDPB upon the water photo-oxidation reaction. The storage of electrons and protons on metal oxides semiconductors such as TiO<sub>2</sub> for instance has recently opened new perspectives in solar energy conversion.<sup>31</sup> This finding is of major interest, as the nano-PDPB can be considered as a photocatalytic material where light-driven oxidation of water and the dark phase chemical energy storage can be delayed in time.<sup>32-35</sup> In a complementary test, we added silver nitrate to the nano-PDPB suspension in water when the plateau of O<sub>2</sub> evolution was reached and the irradiation was ceased. Silver nano-particles were found to decorate the nano-PDPB fibers, as confirmed by TEM images (Figure 3b). This result further confirmed that the nano-PDPB is acting as the sieve for the charge accumulation upon photooxidation of water.

With these findings, we reasoned that adding an exogenous electron acceptor may help to evacuate the built-up charges on the nano-PDPB and thereby would enhance the photocatalytic water oxidation reaction. In a first attempt, we added an excess of DCBQ at the beginning of the photocatalytic run. Accordingly, we evidenced a noticeable improvement in the photocatalytic O<sub>2</sub> evolution (Figure 4a). When an excess of sodium persulfate, an irreversible electron acceptor, was added followed by irradiation, we noticed a vertiginous increase in the O<sub>2</sub> production (Figure 4a). With this very efficient electron acceptor the concentration of dissolved O<sub>2</sub> increases to levels far above the 250 μM expected for an air-equilibrated solution within some minutes. This fast rate of production does not allow establishment of equilibrium between dissolved O<sub>2</sub> and the head space volume (see ESI Fig. S12). A control experiment with alternate periods of dark and illumination in presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> was carried out to dismiss the decomposition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> with release of O<sub>2</sub> pathway (see ESI Fig. S13). The time-course of the O<sub>2</sub> evolution curve clearly indicates that O<sub>2</sub> is generated only in the light excitation phase while no O<sub>2</sub> is released in the dark condition thus confirming that the liberated O<sub>2</sub> comes from the light-driven oxidation of water. Control experiments with persulfate in the dark or irradiating the electron acceptor in the absence of nano-PDPB did not indicate the formation of any trace of O<sub>2</sub> (see ESI Figure S14). Noteworthy, in weakly buffered water we registered a noticeable drop in the pH of the solution from 7 to 2.5 upon the evolution of O<sub>2</sub> in presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions pertaining the occurrence of water oxidation with the release of protons. In contrast, no marked pH change were monitored when quinone was present, indicating the consumption of the protons upon reduction of the quinone, as expected. Also in absence of an exogenous electron acceptor, no marked variation of the pH was evidenced, thus bringing more support to the fact that protons are being stored at the nano-PDPB. In an attempt to obtain more information on such a hypothetical storage of reducing equivalents on the PDPB we measured changes in the FTIR spectra during illumination in presence of H<sub>2</sub>O or D<sub>2</sub>O (see ESI Fig. S15). These data clearly point to noticeable changes in the spectral window of the C-C aromatic ring stretch region with bands appearing at 1350 and 1525 cm<sup>-1</sup> attributed to π-conjugated eneyne and aromatic rings. The

H/D isotopic effect can be tentatively related to the changes in the electron density together with the accumulations of protons/deuterons at the nano-PDPB. Interestingly, we also found that the presence of an electron acceptor from the start of the photocatalysis led to the disappearance of the lag period before detection of O<sub>2</sub> (Fig. 4). We attribute this observation to the more efficient accumulation of holes in the valence band upon rapid evacuation of the electrons from the conduction band resulting in reduced charge recombination.

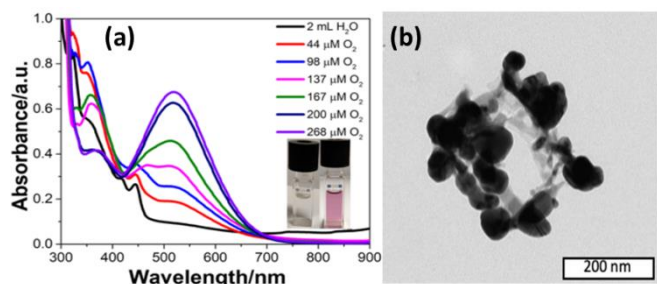


Figure 3. a) UV-visible spectra of 1 mM DCBQ in 2 mL photo catalytic solution at different concentrations of the evolved oxygen (inset: visible colour change upon formation of quinhydrone) b) TEM image of NPs of Ag decorating PDPB nano fibers after addition of AgNO<sub>3</sub> ions in the dark after a photocatalytic run.

Another important observation comes from the monitoring of the oxygen production when irradiation was ceased (in the absence of external electron acceptors). We consistently observed a small consumption of O<sub>2</sub> (see ESI Fig. S16) while the temperature of the mixture was controlled. Actually, any drop in temperature upon stopping the irradiation would have led to a small increase in O<sub>2</sub> in the aqueous phase. We assign this consumption to the partial reduction of dioxygen at the surface of the nano-PDPB by the accumulated photogenerated charges to form reduced oxygen species such as O<sub>2</sub><sup>•-</sup>. It is important to notice that detection of sustained production of O<sub>2</sub> in our system supports the fact that O<sub>2</sub> release from oxidation of water largely outcompetes the partial O<sub>2</sub> consumption due to its reduction to O<sub>2</sub><sup>•-</sup>. Such reduced oxygen species are quite short-lived and are expected to undergo dismutation to form H<sub>2</sub>O<sub>2</sub>.<sup>36</sup> We thus checked the presence of H<sub>2</sub>O<sub>2</sub> by titration of the reaction solution with KMnO<sub>4</sub>.<sup>37</sup> Interestingly, titration at the beginning of the photocatalytic experiment revealed only negligible formation of H<sub>2</sub>O<sub>2</sub>. However, a titration realized during the O<sub>2</sub> evolution time course clearly attests the presence of H<sub>2</sub>O<sub>2</sub> by the fading of the prominent violet permanganate color as shown in Figure 4b (see also ESI Figs. S17 and S18). Further support for this attribution comes from the experiment with sacrificial electron acceptor where no lag time for O<sub>2</sub> production was found and no trace of H<sub>2</sub>O<sub>2</sub> was detected after photocatalysis. These observations and the time course of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> production (see ESI Figs S18, S13) suggest that the two-electron oxidation of H<sub>2</sub>O to H<sub>2</sub>O<sub>2</sub>, unfavorable also from an energetic point of view, can be discarded. With the focus to access the recyclability of the nano-PDPB, we isolated the nano-PDPB after photocatalysis in absence of electron acceptor, air dried it and reused it in fresh N<sub>2</sub> degassed water. As we can notice in (see ESI Fig S19) for the same time lapses, the amount

of O<sub>2</sub> produced stays almost constant. These experiments suggest that nano-PDPB can efficiently be reused for repeated cycles without appreciable loss of activity. A crucial concern for all materials that can perform the water oxidation reaction resides in their chemical alteration during the photocatalytic reaction. In this study, the mineralization of the nano-PDPB to CO or CO<sub>2</sub> was excluded as none of these components was detected by gas chromatography (see ESI Fig S10). All gathered spectroscopic data, FTIR (see ESI Figure S20), <sup>1</sup>H and <sup>13</sup>C NMR (see ESI Figure S21, S22) as well as Maldi-TOF analysis (see ESI Fig. S2), SEM images (see ESI Figure S23) before and after completion of a photocatalytic cycle did not indicate marked changes thereby attesting that nano-PDPB conserves the same chemical formulation and morphology.

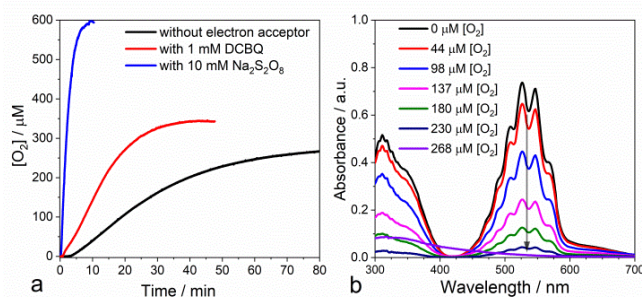


Figure 4. a) Time courses of oxygen evolution from water measured by a platinum Clark Electrode in absence of electron acceptor (black), in presence of DCBQ (red), and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> as electron acceptors (blue). b) Titration of H<sub>2</sub>O<sub>2</sub> with KMnO<sub>4</sub> at different concentrations of photoproducted O<sub>2</sub> in the absence of electron acceptor.

## Conclusions

In summary, we found that nano-PDPB, a nanostructured semiconducting conjugated polymer, can replicate the processes undergoing in Photosystem II, by oxidizing water to O<sub>2</sub> under visible light irradiation and accumulating the electrons on the nanostructured material recoverable deferred in time to reduce quinone.

Photosystem II upon excitation by light splits water producing molecular dioxygen (2H<sub>2</sub>O → O<sub>2</sub> + 4H<sup>+</sup> + 4e<sup>-</sup>) on one side of the membrane and stores the electrons and protons by the reduction of plastoquinone to plastoquinol (PQ + 2e<sup>-</sup> + 2H<sup>+</sup> → PQH<sub>2</sub>) on the other. The plastoquinol then escapes the enzyme transporting electrons and protons to a chain of electron transfer proteins to be ultimately fixed on carbon dioxide (Scheme 1).<sup>38</sup> Even after decades of effort, bioinspired molecular models of this enzyme have not yet replicated all these functions in one system. However, much has been accomplished with great success to model the separate parts of this multi-cofactor biological system.<sup>39, 40</sup>

Of particular interest, nano-PDPB can realize these reactions without the need of a co-catalyst, and in absence of sacrificial reagents.<sup>41</sup> The formation of H<sub>2</sub>O<sub>2</sub> can be assigned to the partial reduction of O<sub>2</sub> acting as an escape channel of charge relief at the photocatalytic material.<sup>[19]</sup> In all, these findings open new perspectives in the field of artificial photosynthesis to convert solar energy and store it in a chemical form without the prompt



need to separate the gaseous mixture produced by the water splitting reaction. Preliminary results also point out that nano-PDPB can also oxidize natural water from a river source with the same efficiency (see ESI Fig. S24) and be used on a TiO<sub>2</sub> photoanode (see ESI Fig. S25). These results will be further confirmed in upcoming studies. Many challenges are ahead of us to fully understand the fundamental charge transport dynamics to unravel the photophysical processes and mechanistic aspects of these carbon-based materials.

### Conflicts of interest

There are no conflicts to declare.

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