Electronic Supplementary Material (ESI) for Chemical Science.

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

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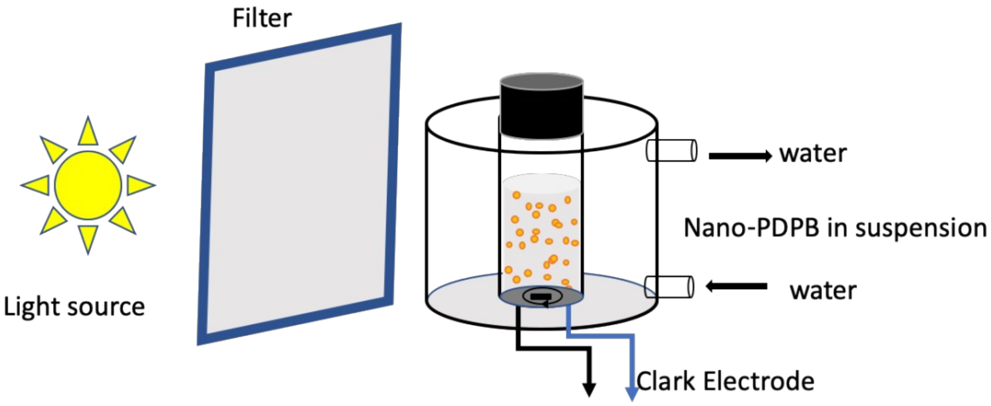
Experimental Procedures

I. General Materials and Methods

All the chemicals used in this work were of reagent-grade. 2,5-dichloro-1,4-benzoquinone DCBQ (98%), $Na_2S_2O_8$ and Silver nitrate $AgNO_3$ (98%) were purchased from Sigma-Aldrich. Ultrapure water (Millipore system, 18.2 MΩ cm) and ethanol (≥ 99% Sigma-Aldrich HPLC) were used as solvents. The Polymer (PDPB) was synthesized by radiolysis under γ-irradiation according to the previously published procedure[1]. This synthesis does not require any initiator for polymerization.

II. Measurements of oxygen evolution

The photocatalytic reactions were carried out using a Hansatech Instruments Liquid-phase Oxygen Electrode System with a Clark-type polarographic sensor with a central platinum cathode and a concentric silver anode, cylindrical optical path containing 2 mL of distilled water and 2 mg of PDPB. The suspension was stirred and thermostated at 20°C. The cell was sealed by a septum and the solution degassed by bubbling with N_2 until the O_2 level was minimal and stabilized. Then the degassed solutions were irradiated with a Flexilux 600 Longlife 150 W 21 V halogen lamp through an ultraviolet cutoff filter ($\lambda \geq 435$ nm) until O_2 production reached a plateau. Incident light intensity reaching the Clark electrode cell was 1 W/cm^2. To test the photocatalytic activity of PDPB in presence of a sacrificial electron acceptor ($Na_2S_2O_8$), In some experiments buffer solutions (50 mM phosphate buffer, pH 6.67 or acetate buffer, pH 4.4) were used instead of distilled water. Head space concentration of O_2 was measured with a NeoFox optical sensor (Ocean Optics).



Scheme Clark electrode for detection of dissolved oxygen

III. Recycling

After completion of the production of O_2 by water oxidation photocatalysis, the medium was changed allowing the use of the catalyst in the next cycle under identical conditions.

IV. Optical Spectra

Diffuse reflectance spectra of the solid nano-PDPB were recorded using an Avantes fiber spectrometer with TiO_2 powder as reference. Absorption coefficients were calculated using the Kubelka-Monk relationship $f(R)=(1-R)^2/(2R)$.

V. IR Spectra

The IR spectra were recorded with a FT-IR Spectrometer Spectrum 1000 Perkin Elmer. FTIR spectra were recorded by putting the sample powder between two KBr windows and spectra were averages of 50 scans. Light-induced ATR-FTIR difference spectra (averages of 200 scans) were recorded on a Nicolet 6700 FTIR spectrometer equipped with a Silicon

ATR prism (SensIR DuraSamplIR) and a MCT-A detector. Approximately 10 µL of an acetonitrile solution of nano-PDPB were dried on the prism, the film was covered with H_2O or D_2O, equilibrated and irradiated via fiber optics form a SugarCUBE blue LED illumination system.

VI. NMR Spectroscopy

Both ^1H and ^{13}C NMR spectra were recorded with a JEOL 400 MHz spectrometer.

VII. Scanning electron microscope analysis

For structural study of polymer structure, scanning electron microscopy analyses were performed using SEM feg column Gemini with a EHT of 2.00 kV, width distance of 5 or 6 mm and several magnifications.

VIII. Mass Spectroscopy

MALDI-TOF MS analyses were performed using an UltrafleXtreme mass spectrometer (Bruker Daltonics, Bremen). Acquisitions were performed in reflectron positive ion mode. The laser intensity was set just above the ion generation threshold to obtain peaks with the highest possible signal-to-noise (S/N) ratio without significant peak broadening. All data were processed using the program FlexAnalysis (Bruker Daltonics, Bremen). Materials: trans-2-[3-(4-ter-Butylphenyl)-2-propenylidene] malonitrile (DCTB, used as the matrix for MALDI-TOF MS, was of the highest grade available and used without further purification) and polyethylene glycol (PEG, used as calibrating for MALDI-TOF MS, was of the highest grade available and used without further purification) were purchased from Sigma Aldrich Co.

IX. Titration with $KMnO_4$

To the 2 mL of the aqueous solution after irradiation a drop of HCl and 25 µL of an aqueous solution of $KMnO_4$ 10 mM were added under stirring. The decrease of the UV-Visible absorption band of $KMnO_4$ was followed at 525-530 nm on an Analytic Jena Specord 210 spectrophotometer.

X. Addition of silver nitrate

For the experiment with Ag^+ ions, a solution of $AgNO_3$ (at 10 µM) was added at the end of a photocatalytic cycle carried (in the same irradiation conditions as described before) when the plateau for O_2 evolution was reached and after the light was tuned off. Few drops of the suspension were then deposited on carbon grids for transmission electron microscopy characterization.

XI. Laser flash photolysis

nano-PDPB was dissolved in acetonitrile in a 1 cm quartz cuvette sealed with a septum. Before the measurements samples were purged with Ar to remove oxygen. Time-resolved emission and absorption data were recorded on an Edinburgh Instruments LP920 flash photolysis spectrometer. Laser excitation pulses were generated from a Continuum Surelite OPO laser (5 ns pulses duration, typical energy 10 mJ per flash) for excitation at 460 nm. The probe source is a pulsed 450 W Xenon lamp and the detectors are either a Hamamatsu photomultiplier tube (PMT) or a water – cooled Andor intensified charge coupled device (ICCD) camera.

XII. Estimation of quantum yield

We use for this estimation the results from experiments with persulfate as electron acceptor because in this case O_2 production is fast and equilibration of dissolved oxygen with the headspace can be neglected. The initial rate of O_2 production is 5 µM/s which yields 10 nmol/s produced in the 2 mL reaction volume or $6{\cdot}10^{15}$ molecules of O_2 per second. Considering that reduction of persulfate creates a very oxidizing sulfate radical which will participate in the oxidation reaction 2 photons/O_2 or a total of $1.2{\cdot}10^{16}$ photons are required. The intensity of the incident white light (>435 nm) was measured as 1 W/cm^2 and the surface of the solution volume hit by the light was 2 cm^2 (200 mm^2). The incident photon flux (taking λ as 500 nm) is therefore $5\cdot10^{18}$ photons/s yielding an external quantum yield of 0.24%.

For determination of the internal quantum yield the number of absorbed photons is required. This is difficult due to the inhomogeneous size of the PDPB particles in suspension. Approximating the suspension by an average particle size of (0.5 mm)^3 an absorption cross section of about 4 mm^2 for 2 mg of PDPB can be estimated. Assuming that every particle absorbs all photons incident on its surface gives an absorption of 4 mm^2/200 mm^2 = 2% of the incident photon flux or $1\cdot10^{17}$ photons absorbed per s. Therefore, for the internal quantum yield a rough value of $1.2\cdot10^{16}$ electrons/s / $1\cdot10^{17}$ photons/s = 12% is obtained.

XIII. Inductively Coupled Plasma-Optical Emission spectroscopy (ICP-OES)

ICP-OES analyses were performed with a Thermo ICAP 6500 system equipped with a cooled spray chamber, using the radial configuration. The sensitivity of the method was determined by analyzing 0.05, 0.1 and 1 mg.L^{-1} standard solutions of Cu and Pd in EtOH and correlating the signals obtained at three different wavelengths for each element. Although a clear positive signal could be detected at 0.05 mg.L^{-1} for 2 out of the 3 wavelengths picked for each element, a reasonable detection limit was established at 0.1 mg.L^{-1}. Then a 1 g.L^{-1} solution of nano-PDPB in EtOH was analyzed. No Cu or Pd metal traces was detected (Table X). Finally, Cu and Pd standards (final concentration 0.1 mg/L ; *i.e.* 100 ppm) were added to the pdpb sample. In that case, Cu and Pd were unambiguously detected, allowing to discard any attenuation phenomenon due to matrix effects in the first experiment (Fig X). Accordingly, metallic traces are absent from the nano-PDPB sample.

	Sample : 10mg PDPB / 10ml ETOH					
Wavelength (nm)	Cu-224.7	Cu-324.7	Cu-327.3	Pd-324.2	Pd-340.4	Pd-360.9
concentration (mg/L)	**-0.0009**	**0.0007**	**0.0007**	**0.0001**	**0.0013**	**0.0048**
Standard deviation	0.0002	0.0004	0.0002	0.0004	0.0028	0.003
CV%	25.09	59.3	27.85	366.3	219.1	62.08

Table S1. Detected concentrations of Pd and Cu in NS-PDPB (way below the 100 ppm detection limit).

Figures

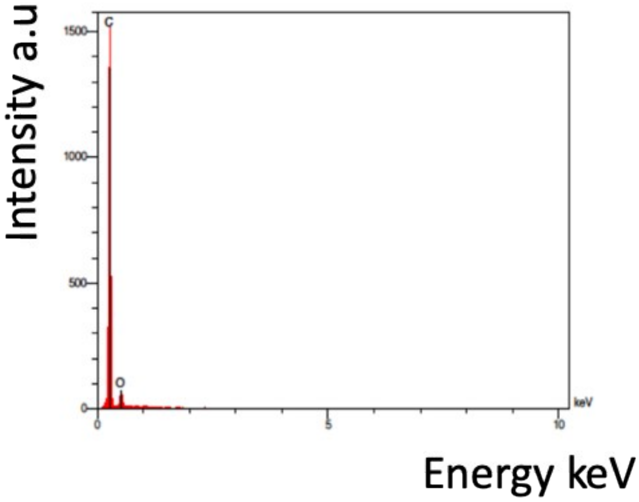


Figure S1. EDS spectra of nano-PDPB indicating only carbon as main constituent, traces of oxygen may come from residual water from purification step.

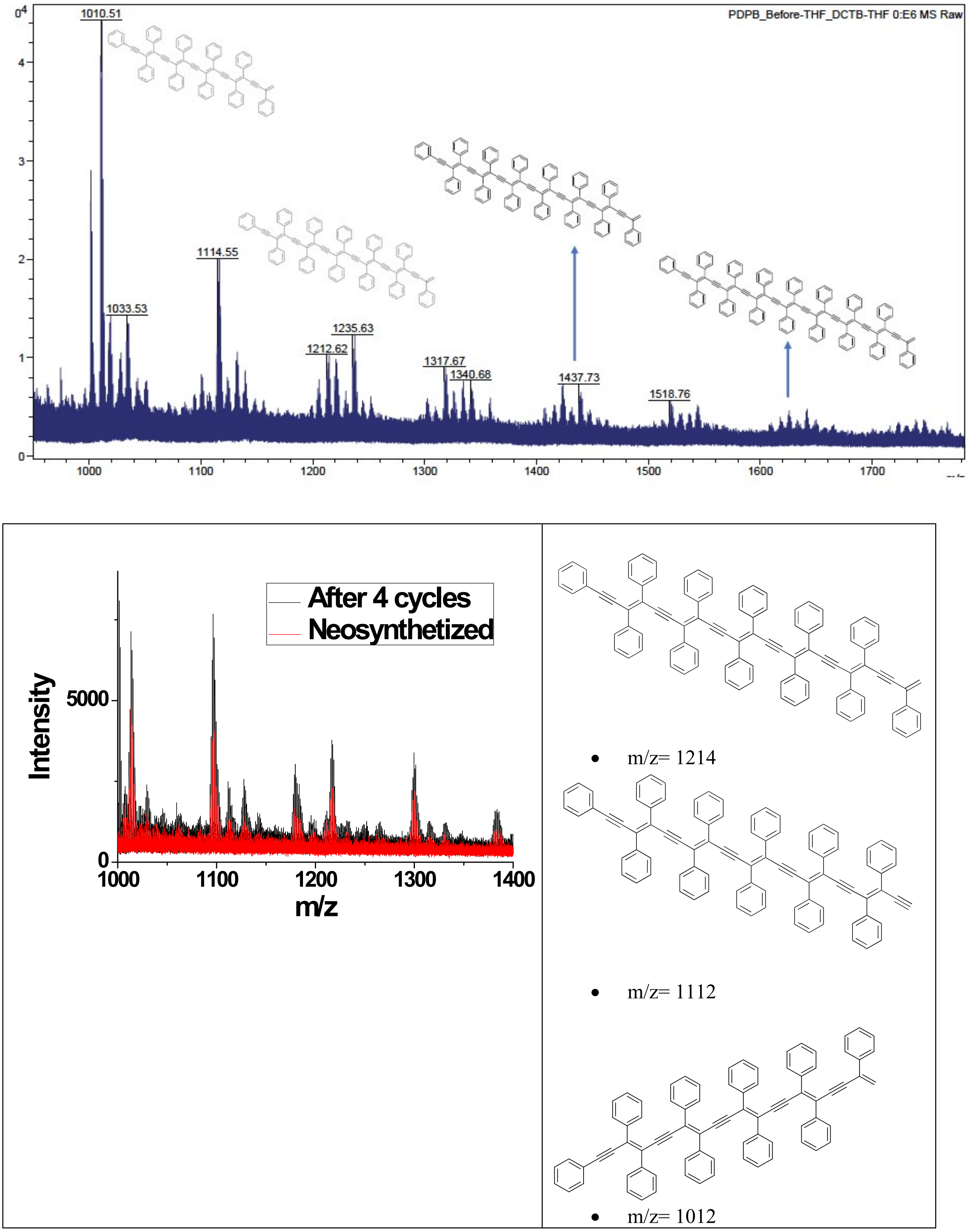


Figure S2. Maldi-Tof of neosynthesized nano-PDPB indicating the repeating units and zooms of nano-PDPB neosynthesized (red) and after 4 cycles of photocatalysis (black); and the main peaks structure proposed. Fragmentation peaks are identical for both samples.

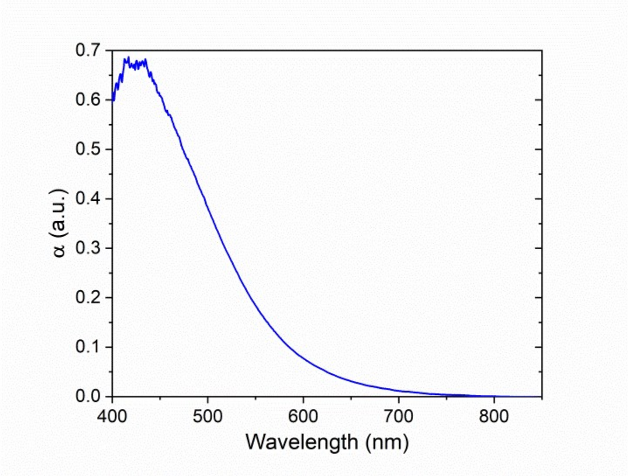


Figure S3. Kubelka-Munk analysis of diffuse reflectance spectrum yielding the absorption coefficient α of solid PDPB.

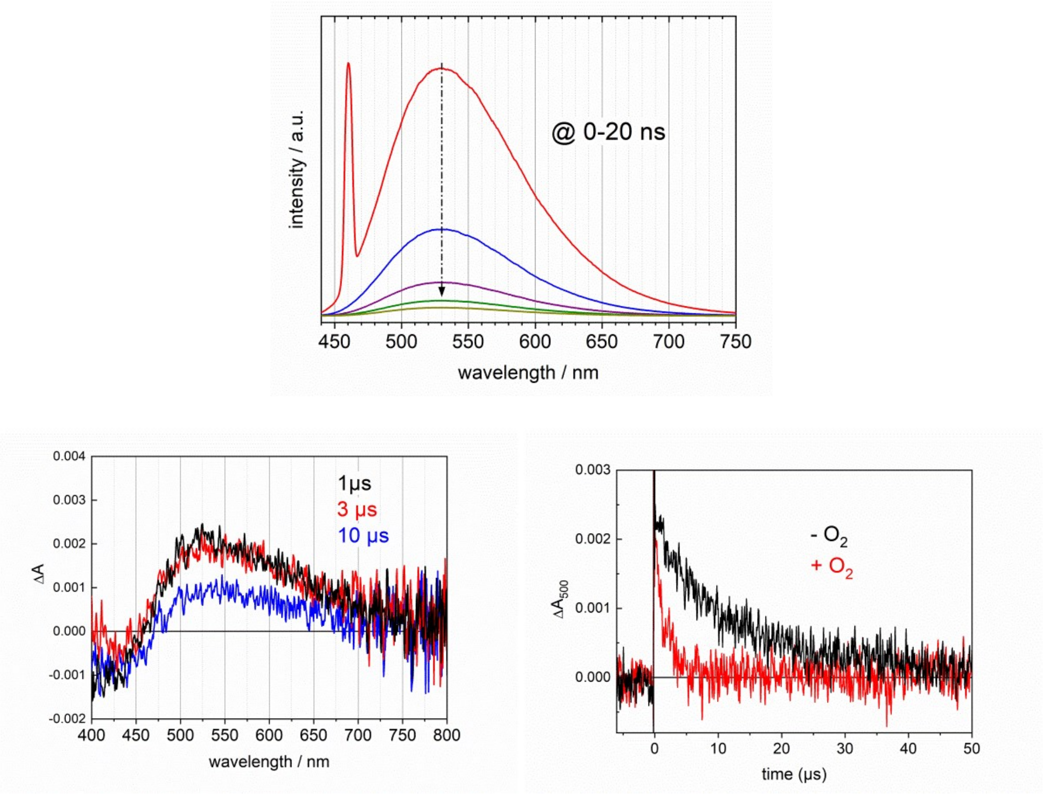


Figure S4. Top: Photoemission band detected upon excitation by a nanosecond laser flash at 460 nm of a solution of nano-PDPB in acetonitrile. From the decay of the emission a life time of the excited singlet state of about 3 ns can be estimated. Bottom: transient absorption data showing formation of a charge separated state which decays with a life time of about 10 µs and which is quenched in the presence of O_2.

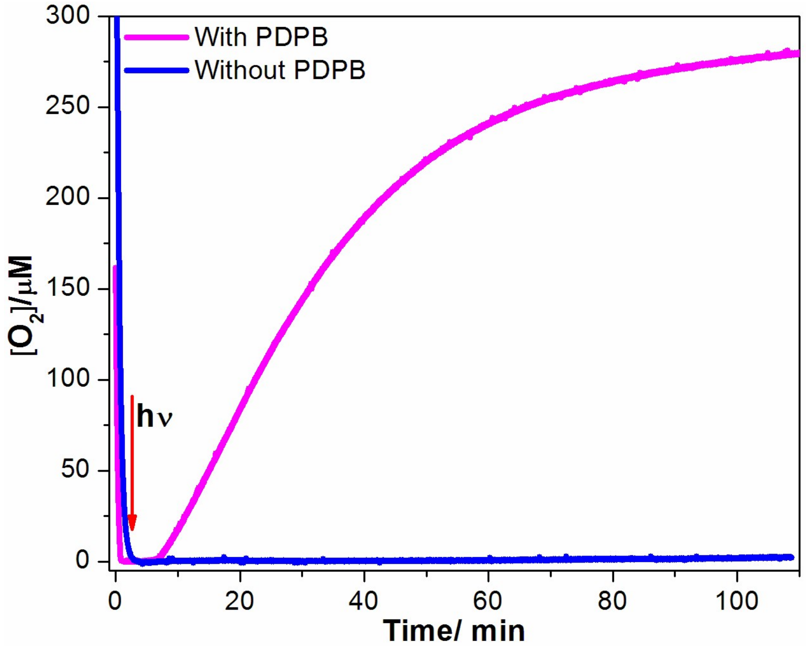


Figure S5. Time courses of oxygen evolution from water measured by a platinum Clark Electrode in the presence (pink curve) and absence (blue curve) of nano-PDPB.

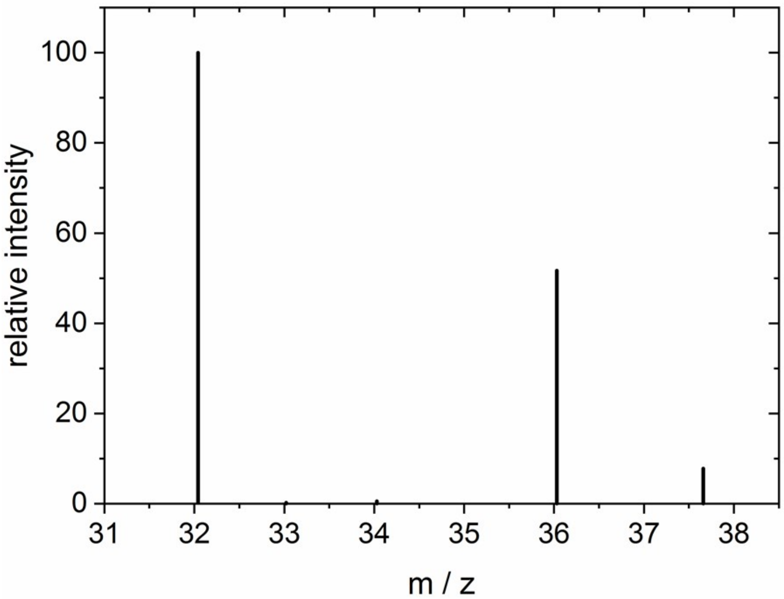


Figure S6. Mass spectra of O_2 observed by head space analysis after photocatalytic cycle in H_2O^{18}. The presence of $^{32}O_2$ is due to introduction of air during sample transfer.

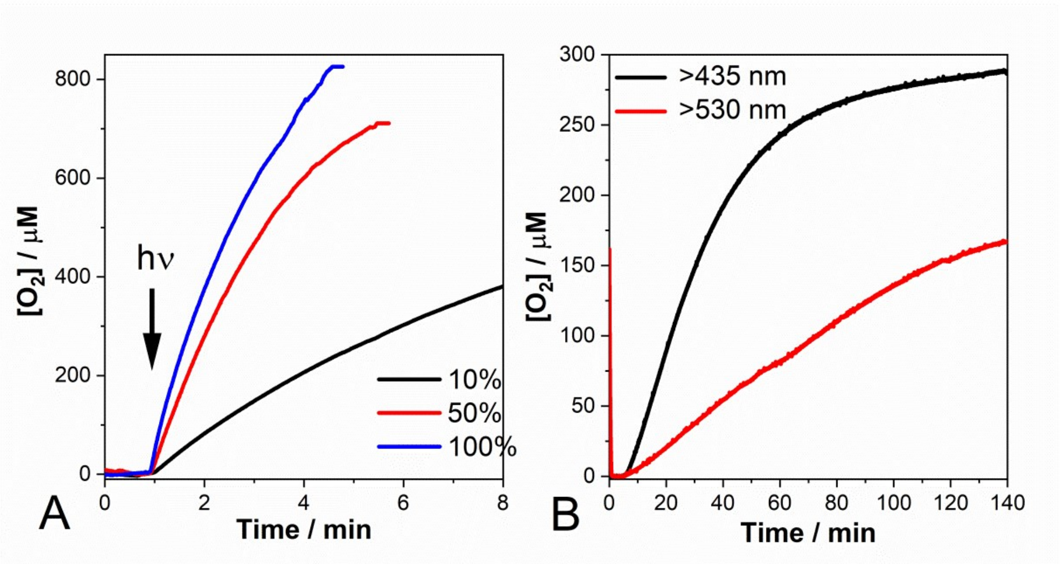


Figure S7. Time courses of oxygen evolution from water measured by a platinum Clark Electrode. A) in the presence of 10 mM $Na_2S_2O_8$ and with the neutral density filters indicated. The rate of O_2 evolution accordingly drops with decreased light intensity. B) in absence of $Na_2S_2O_8$ with the cut-off filters indicated. A decrease in the rate of O_2 evolution is observed due to the lower photon capture in the red part of the absorption spectrum (compare Fig. S3).

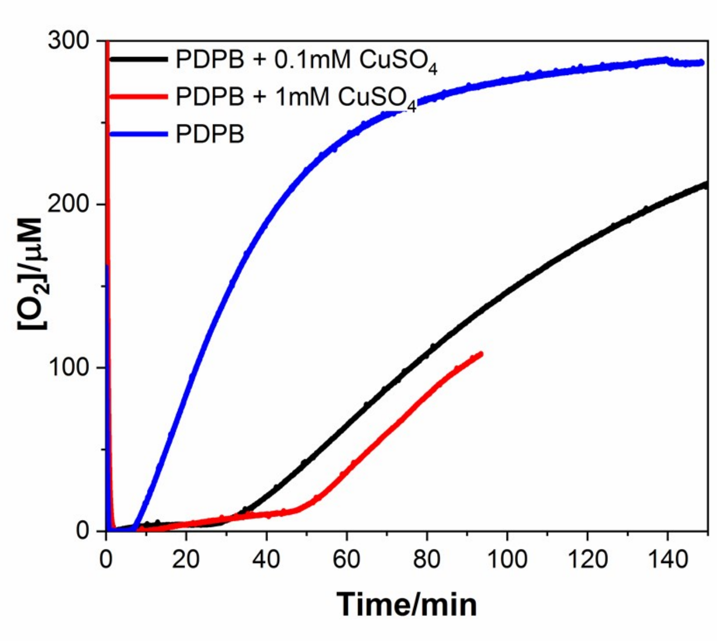


Figure S8. Effect of added $CuSO_4$ on the time course of oxygen evolution from water measured by a platinum Clark electrode.

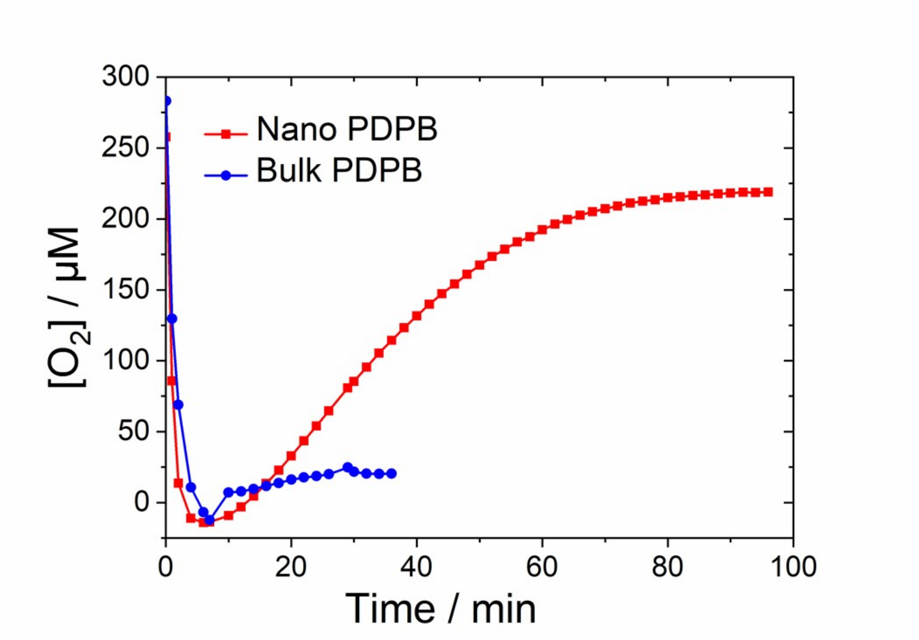


Figure S9. Time courses of oxygen evolution from water measured by a platinum Clark Electrode. Blue curve: with nano-PDPB (synthesized in mesophases), Red curve: with bulk PDPB (obtained without template).

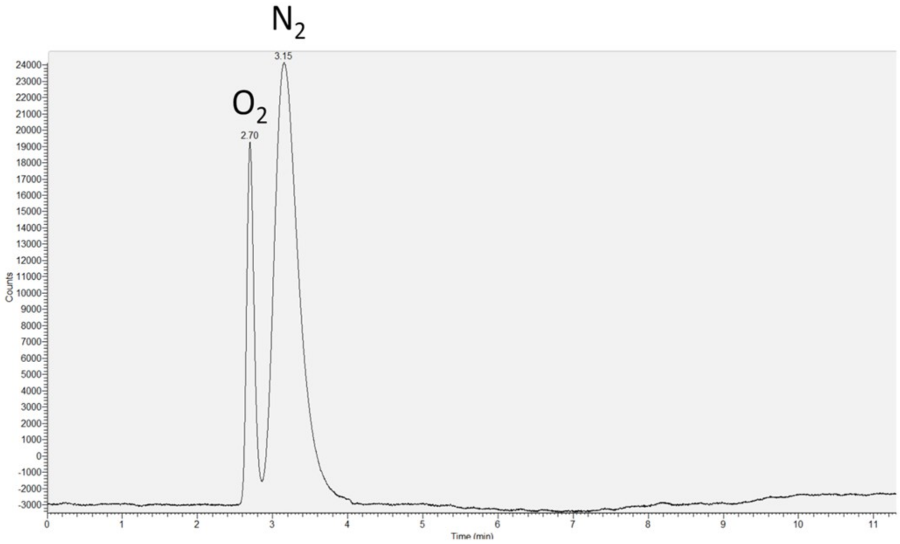


Figure S10. Gas Chromatography monitoring of a typical photocatalytic experiment of O_2 production by nano-PDPB in water. RT(O_2)=2.70 RT(N_2)=3.15. No H_2 detected at retention time (RT) 1.95 neither CO_2 or CO at RT 9.45 to 11min.

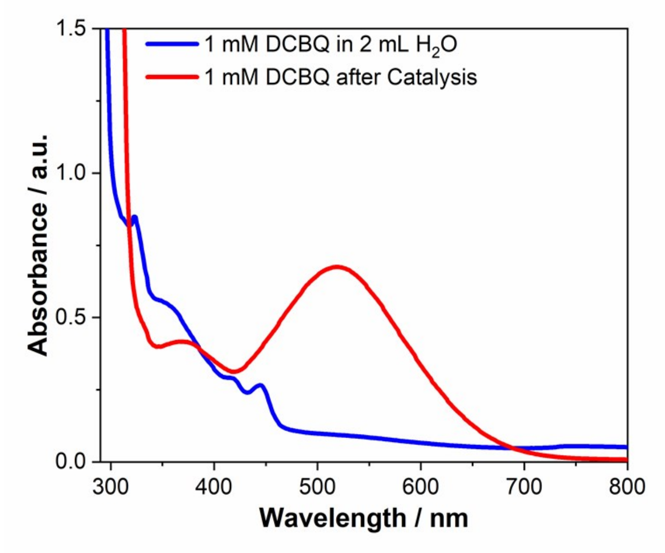


Figure S11. UV-visible spectra of 1 mM DCBQ (blue) in 2 mL of distilled water and in the solution resulting from the photocatalysis by nano-PDPB (Red).

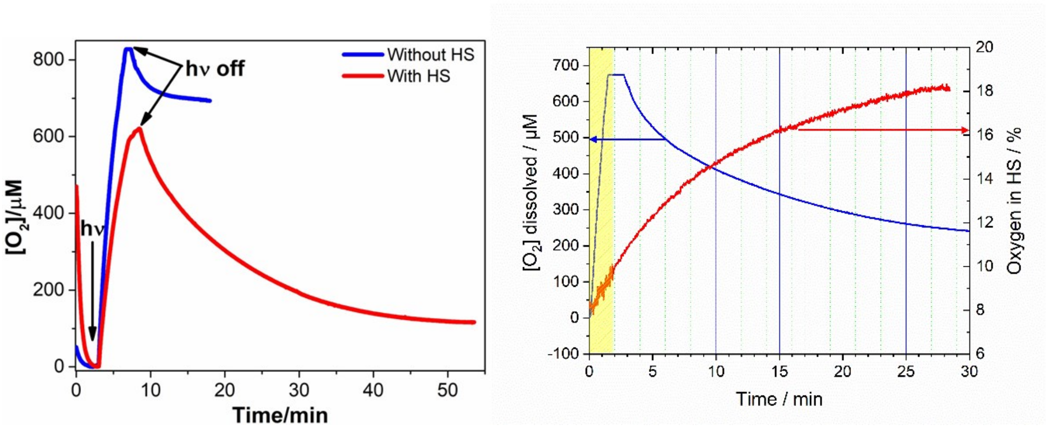


Figure S12. Left: Time courses of oxygen evolution from 2 mL distilled water measured by a Clark Electrode under visible light irradiation (λ>435 nm) in presence of 2 mg of nano-PDPB and 10 mM $Na_2S_2O_8$ with headspace (ca 1.5 mL, red) and with minimal headspace (<0.2 mL, blue). Right: Simultaneous recording of dissolved O_2 (blue trace) and O_2 concentration in the headspace (red trace).

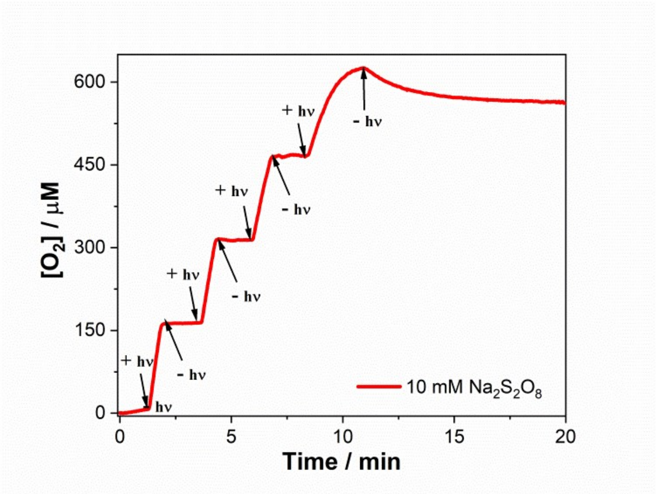


Figure S13. Time courses of oxygen evolution from 2 mL distilled water measured by a Clark Electrode under intermittant visible light irradiation (λ>435 nm) in presence of 2 mg of nano-PDPB and 10 mM $Na_2S_2O_8$ with minimal headspace (<0.2 mL). Alternate cycles of irradiation and dark periods as indicated.

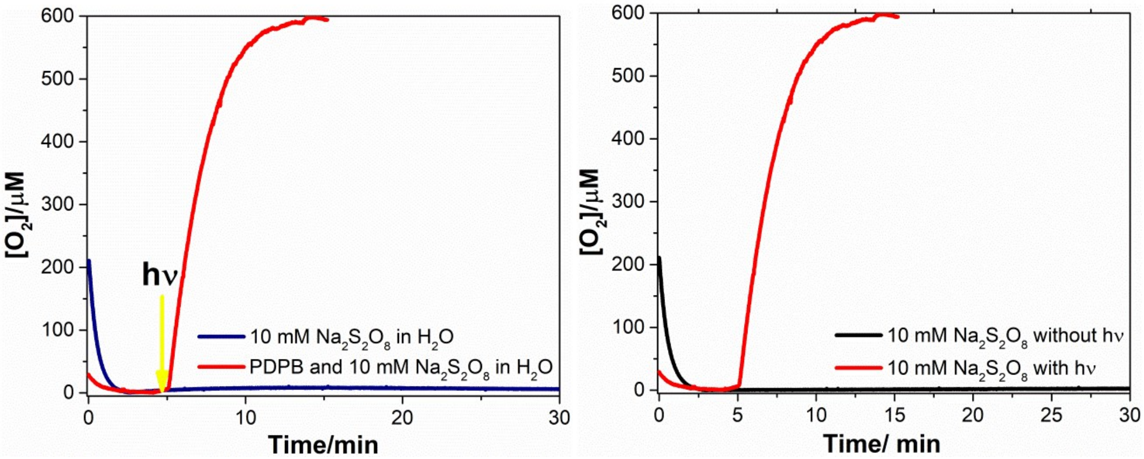


Figure S14. Time courses of oxygen evolution from 2 mL distillated water, . Left: in the absence and presence of 2 mg of nano-PDPB; right: in presence of nano-PDPB without and with illumination (λ>435 nm).

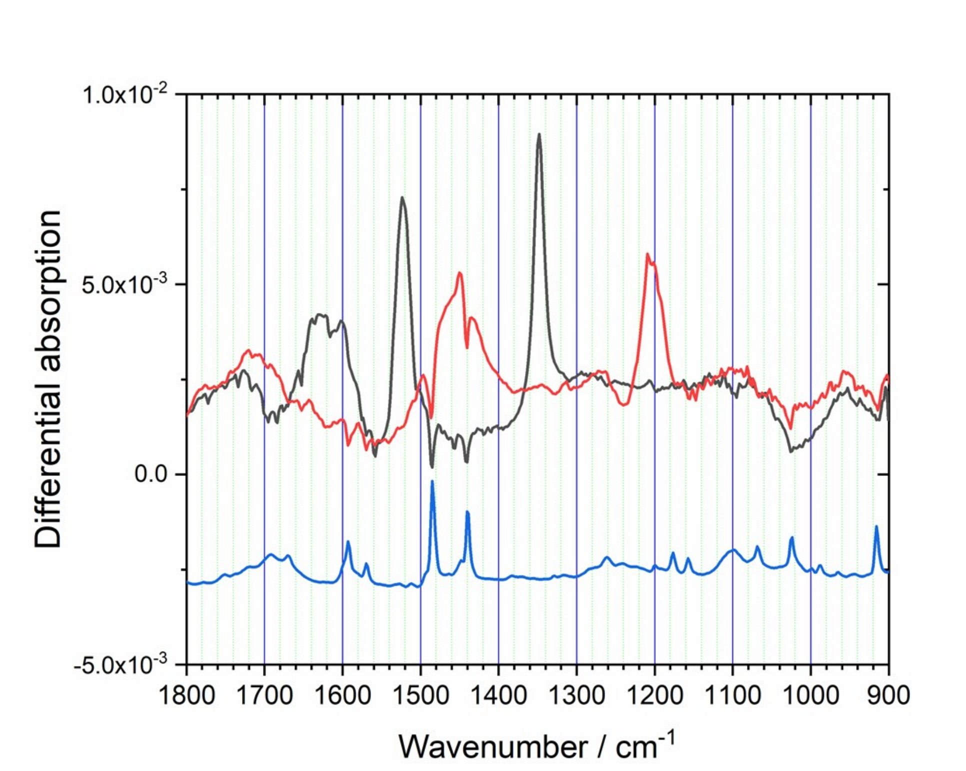


Figure S15. Light-induced ATR-FTIR difference spectra of a nano-PDPB layer in contact with H_2O (black) or D_2O (red). The absolute absorption spectrum of a dry film of nano-PDPB (blue, not at scale) is shown for comparison.

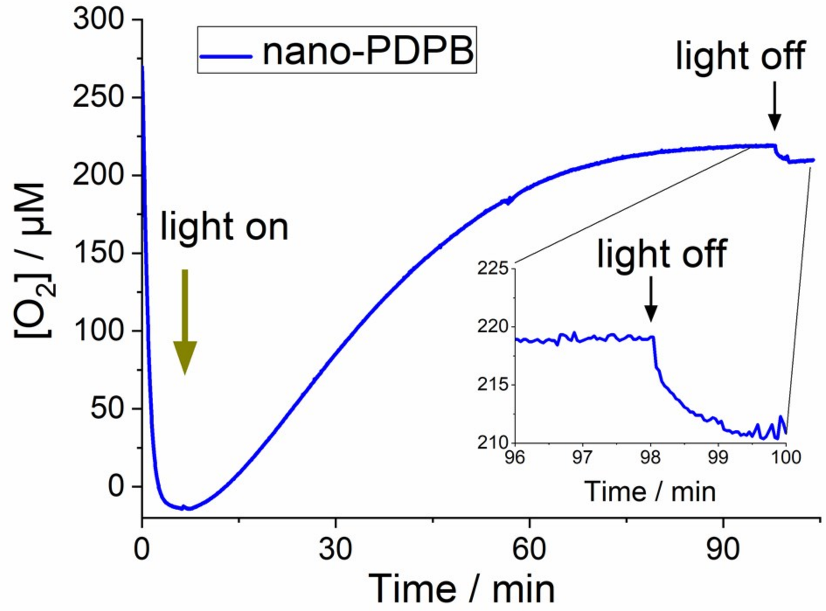


Figure S16. Time course of oxygen evolution from water measured by a Clark Electrode with nano-PDPB under visible-light irradiation. Inset: Zoom on O_2 evolution following switch off of the light.

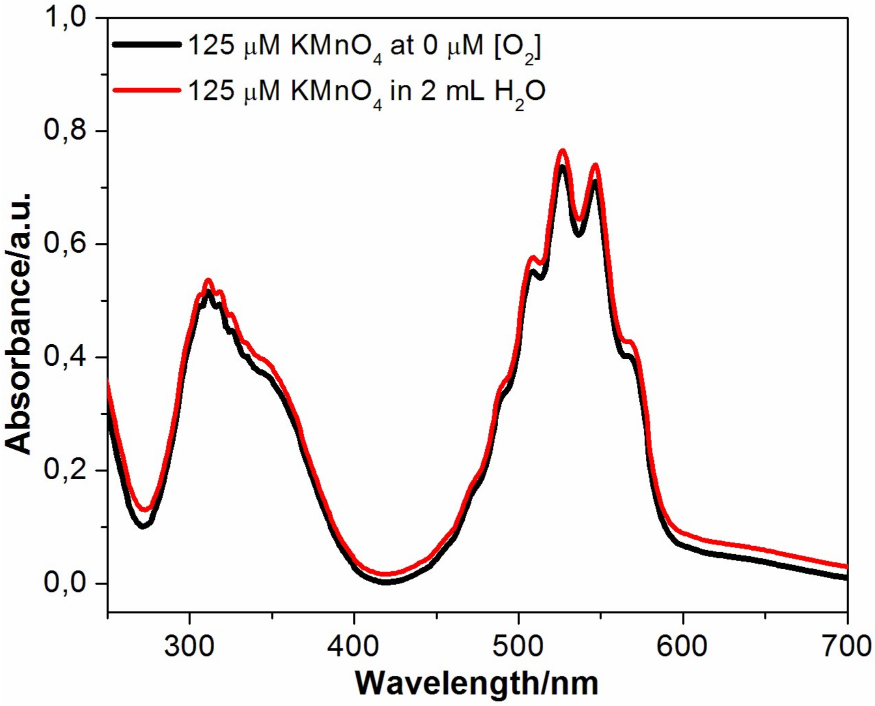


Figure S17: Titration of H_2O_2 by addition of 125 µM $KMnO_4$ to the photocatalytic solution at the beginning of the production of oxygen by the nano-PDPB (Black) and to 2 mL of distilled water (red).

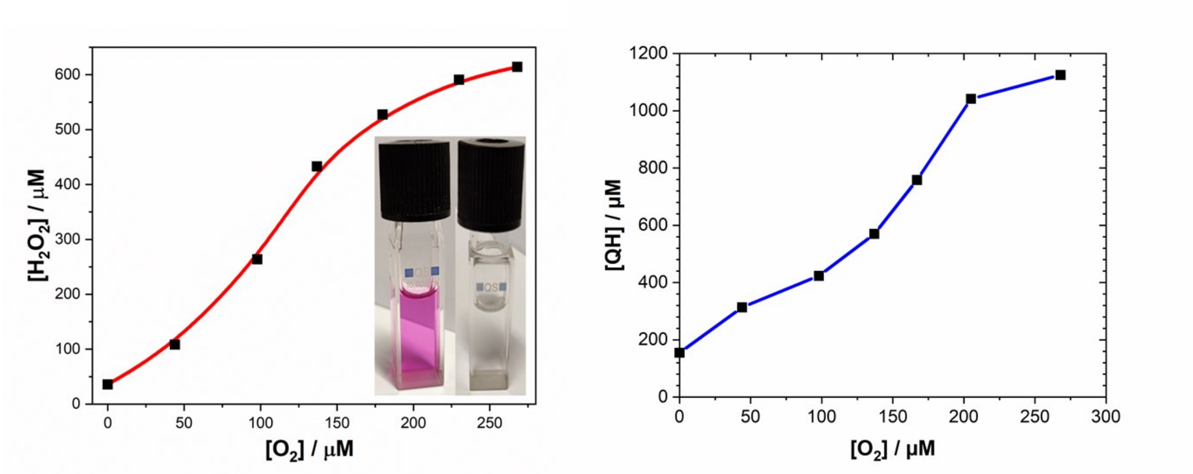


Figure S18: Left: Detection of [H_2O_2] in a photocatalytic solution at the different concentrations of evolved oxygen. [H_2O_2] concentrations were calculated based on the equation $2\ MnO_4^- + 6\ H^+ + 5\ H_2O_2 \rightarrow 2\ Mn^{2+} + 8\ H_2O + 5\ O_2$. Inset: Photocatalytic solution with 125 μM $KMnO_4$ at the beginning (left) and at the plateau (right) of oxygen production. **Right**: Detection of quinhydrone complex [QH] in a photocatalytic solution at the different concentrations of evolved oxygen. [QH] concentrations were calculated based on a molar extinction coefficient of 300 $M^{-1}cm^{-1}$.

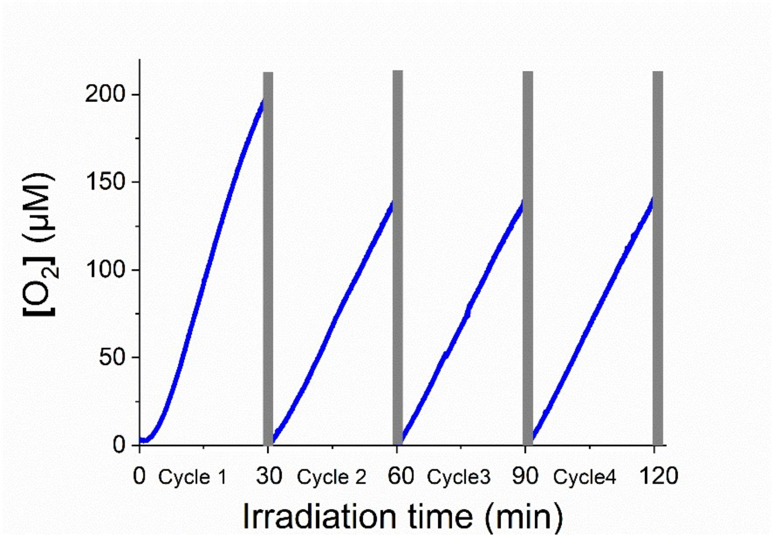


Figure S19: a) Time course of oxygen evolution from nano-PDPB in presence of 10 mM persulfate as electron acceptor. Alternate cycles of irradiation and dark periods as indicated. b) Consecutive 30 mins cycles of oxygen evolution with nano-PDPB in H_2O in absence of electron acceptor under visible light irradiation. The cycles were performed by filtering the solid, airdried and running the photocatalysis in new water sample.

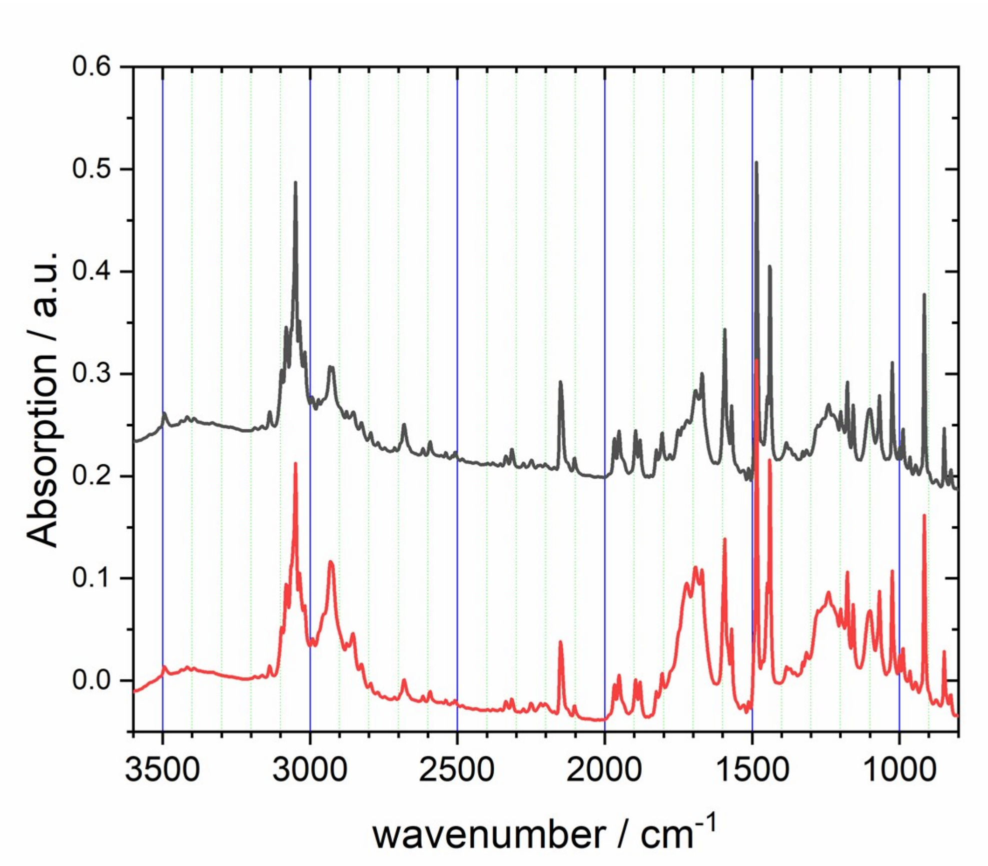
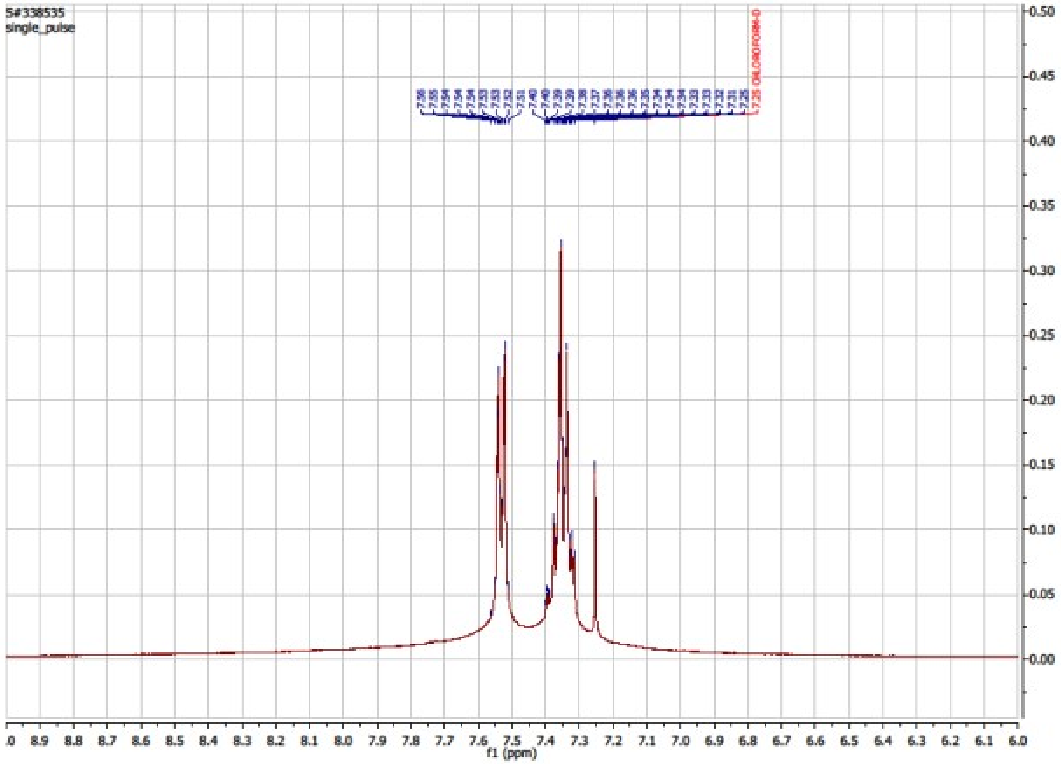


Figure S20. ATR-FTIR spectra of nano-PDPB neosynthetized (black) and after 1 cycle of water oxidation photocatalysis (red). No marked changes can be noticed in the whole frequency window from 3500 to 800 cm^{-1}.



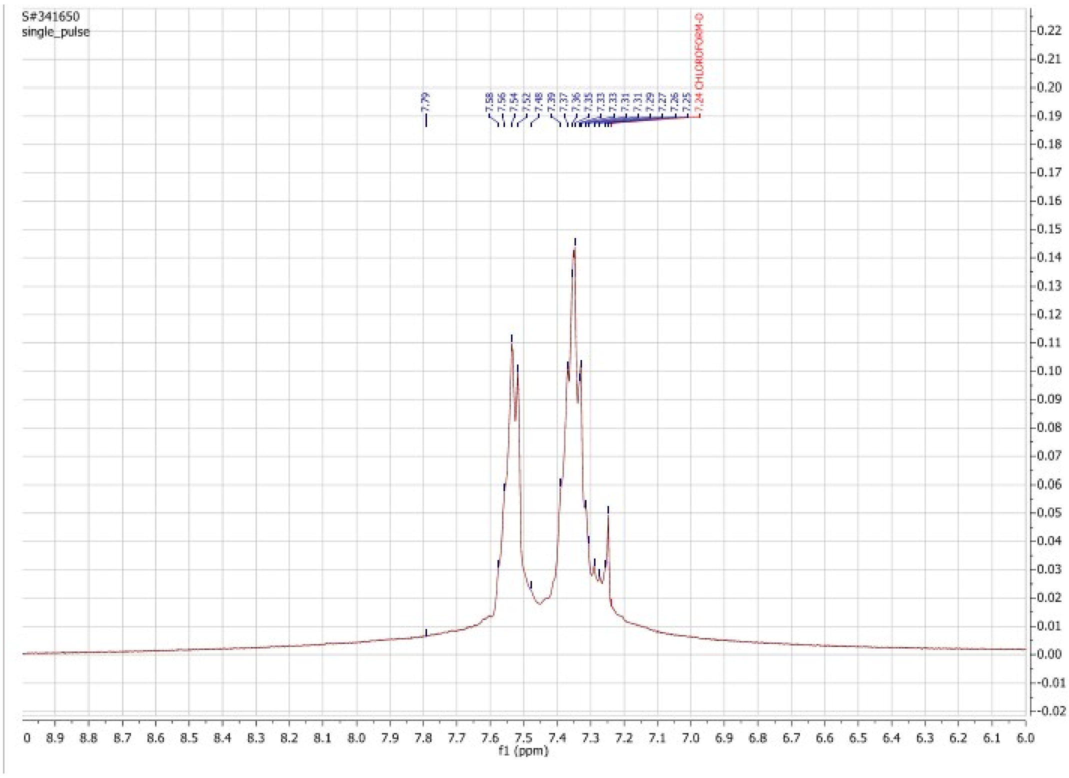
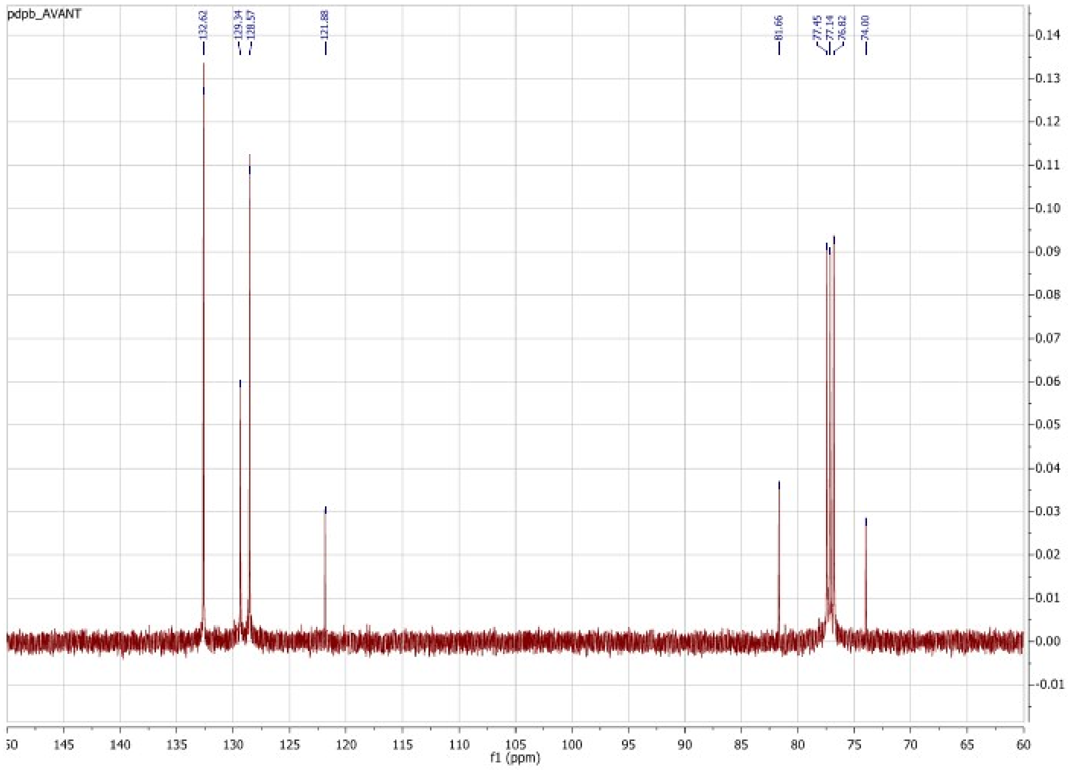


Figure S21. ^{1}H NMR spectra of nano-PDPB neosynthetized (top) and after a photocatalytic run (bottom).



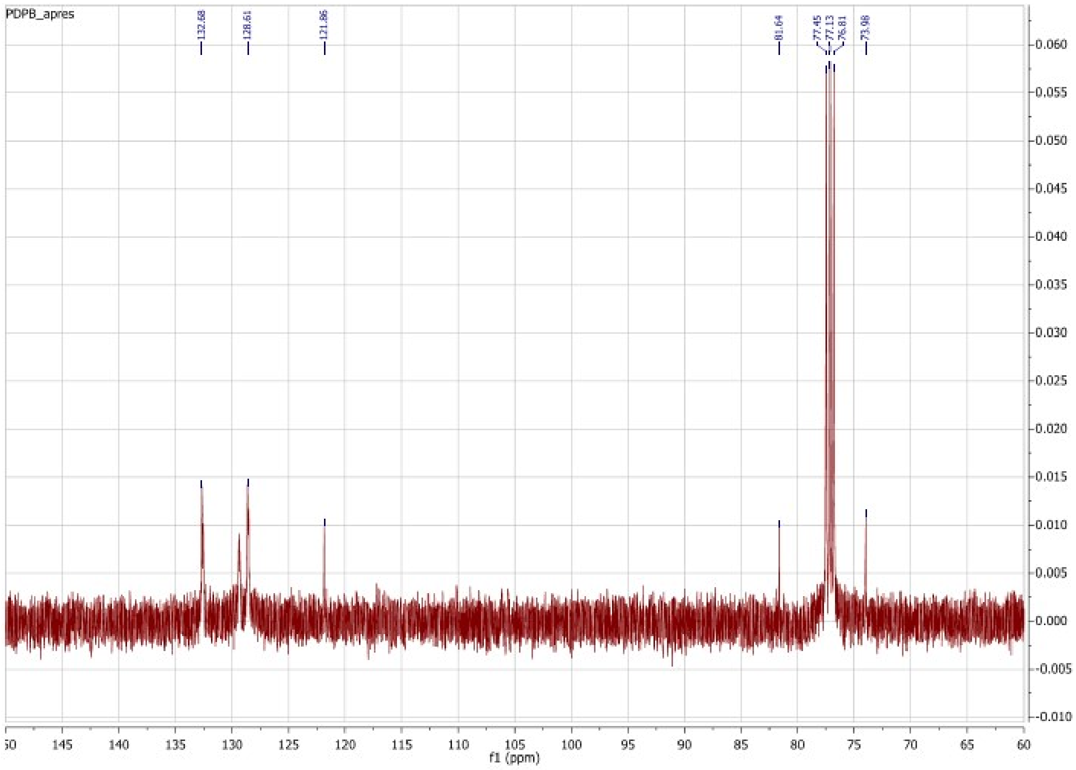


Figure S22. ^{13}C NMR spectra of nano-PDPB neosynthetized (top) and after a photocatalytic run (bottom).

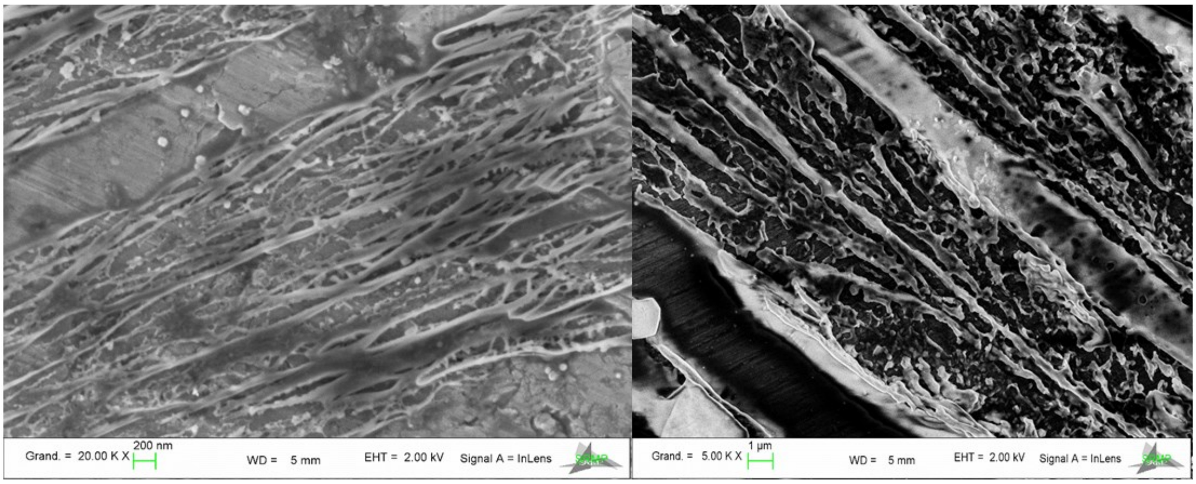


Figure S23. SEM of nano-PDPB neosynthesized (left) and after 6 cycles of photocatalysis (right).

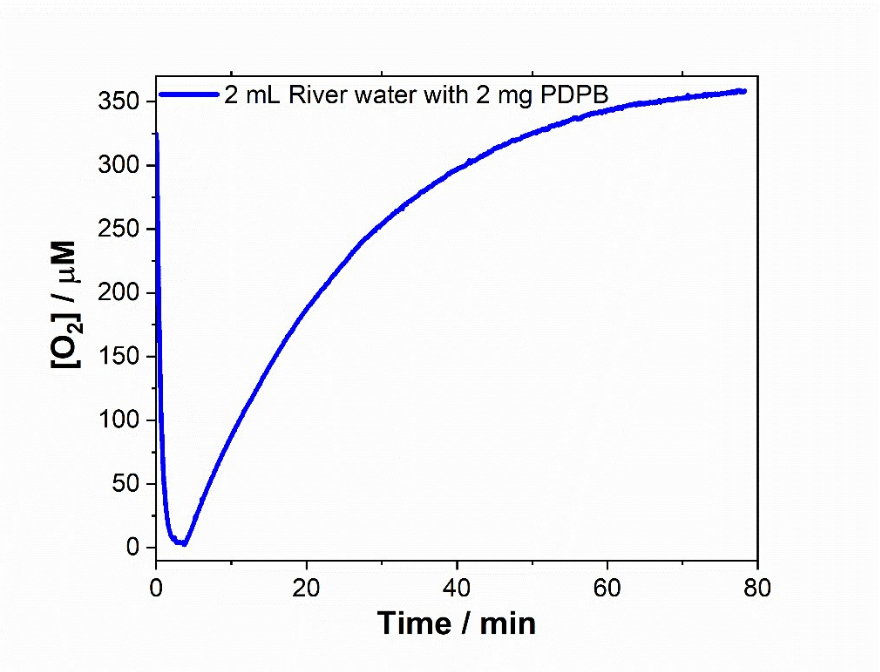


Figure S24. Time course of oxygen evolution from river water measured by a Clark Electrode with nano-PDPB under visible-light irradiation.

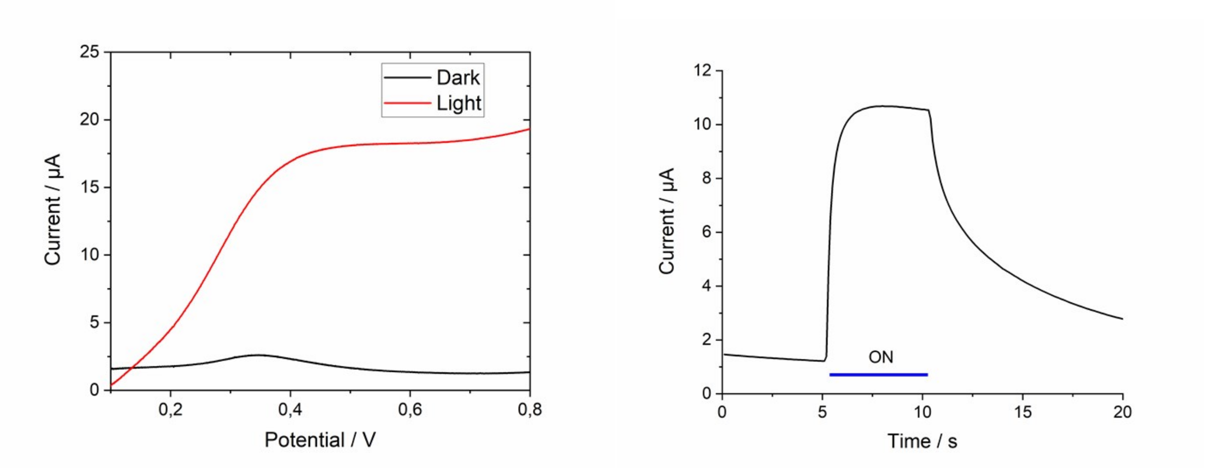


Figure S25. Left: Current as a function of potential applied on a FTO/TiO_2 electrode covered with a nano-PDPB layer in water in the dark and under irradiation with visible-light. Right: photocurrent transient upon a 5 sec light pulse at an applied potential of 0.4 V. Supporting electrolyte was 100 mM sodium sulfate. A Pt wire was used as counter electrode and Ag/AgCl as reference electrode.

References

[1] S. Ghosh, N. A. Kouame, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P. H. Aubert and H. Remita, *Nat Mater*, 2015, **14**, 505-511.