Supporting Information for

Enhanced photocatalytic hydrogen production of porphyrin nanostructures: spheres vs fibrils, a case study.

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Experimental

Materials and techniques.

Reagents and solvents were purchased as reagent grade from usual commercial sources and were used without further purification, unless otherwise stated. **Fmoc-FF-Por** was synthesized according to previously published procedures.¹ The ¹H and ¹³C NMR spectra were recorded on Bruker DPX-300 MHz spectrometer using CDCl₃ as deuterated solvent with the solvent peak as the internal standard. The high resolution mass spectrum of **Fmoc-FF-(Zn)Por** was recorded on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile as the matrix.

Photophysical Measurements.

UV-Vis absorption spectra in solution were obtained (in quartz cuvettes of 1 cm path-length) using a Shimadzu UV-1700 spectrophotometer, while the spectra in the solid state were obtained (on quartz slides 2 × 2 cm) using a UV/Vis/NIR Lambda 19, PerkinElmer spectrophotometer. Emission spectra were recorded on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range: 200–850 nm). In all the samples the absorbance (A) was 0.1 at the excitation wavelength (550 nm). Emission lifetimes were determined by the time-correlated single-photon counting (TCSPC) technique using an Edinburgh Instruments mini-tau lifetime spectrophotometer equipped with an EPL 405 pulsed diode laser at 406.0 nm and a high-speed red-sensitive photomultiplier tube (H5773-04) as detector. During these measurements the absorbance (A) of all the samples was 0.1 at 550 nm.

Scanning electron microscopy measurements.

For SEM observations the samples were covered with 10 nm Au/Pd sputtering and were observed directly. SEM experiments were performed by using a JEOL JSM-6390LV microscope operating at 15 and 20 kV.

Preparation of self-assembled nanostructures.

For the formation of the nanostructures, the "good-bad" solvent methodology was applied. Initially **Fmoc-FF-(Zn)Por** was dissolved in a chaotropic "good" solvent such as dichloromethane (DCM) or tetrahydrofuran (THF). Then a "bad" solvent like heptane (HEPT) or methanol (MeOH) was introduced in the solution, to induce the self-assembly process. Two different systems were chosen for this purpose; a DCM/HEPT (1:4) mixture and a THF/MeOH (1:1) mixture. In both cases the final concentration of the porphyrin hybrid was 1 mM. After 24 hours of incubation the solvents were removed and the desired spherical or fibrilar nanostructures were obtained.

Preparation of the amorphous solid sample.

For the preparation of the solid sample **Fmoc-FF-(Zn)Por** was dissolved in DCM with a final concentration of 1 mM. The clear solution was incubated for 24 hours and after the evaporation of the solvent the solid sample was obtained. SEM studies of this sample verified that no nanostructures were formed under these conditions.

Photocatalytic measurements.

The photocatalytic H₂ evolution studies were performed in a glass vial (10 mL) sealed with a rubber septum, at ambient temperature and pressure. Before each experiment, a fresh buffer solution was prepared. In detail, the buffer solution was a 1 M aqueous solution of ascorbic acid (AA) that was adjusted to pH=4 using aqueous solution of NaOH. Initially, 4 mg of each prepared nanostructure or the corresponding solid sample were dispersed in the aqueous AA buffer solution. Then 5% (w/w) Na₂PtCl₆·6H₂O (0.2 mg) was added in the dispersions in order to form Pt nanoparticles as co-catalyst by the in situ photoreduction deposition method. The suspensions were sonicated for 5 min and degassed with nitrogen for 15 min (in an ice/water bath), to ensure anaerobic conditions. Finally, the vials were sealed with a silicon septum and placed in the experimental setup were their photo-excitation took place under continuous stirring. The samples were irradiated using a low power white LED lamp ring of 40 W, with color temperature of 6400 K and lumen of 3800 LM. The H₂ evolution was determined using gas chromatography (GC) using a Shimadzu GC 2010 plus chromatograph with a TCD detector and a molecular sieve 5 Å column (30 m - 0.53 mm). For every measurement, 100 µL were taken from the headspace of the vial and were instantly injected in the GC. In all cases, both the reported H_2 production values and the Turn Over Number (TON) are the average of three independent experiments. Control experiments were performed under the same experimental conditions by removing the nanostructures or the SED from the H_2 generating systems; however, we did not detect any H₂ production.

Calculation of TONs and H₂ evolution rates (mmol g⁻¹ h⁻¹)

The Turnover Numbers (TONs) were calculated according to the following equation:

$$\frac{n(H_2)}{\text{TON} = n(Catalyst)}$$

<u>*Where:*</u> $n(H_2)$ is the total amount of the produced H_2 (in mmol) within 430 h of irradiation and n(Catalyst) is the total amount of Pt nanoparticles (in mmol).

As mentioned above, in every photocatalytic experiment 0.2 mg (0.000356 mmol) of $Na_2PtCl_6GH_2O$ were used as platinum, source. Thus, the total amount of Pt nanoparticles is 0.000356 mmol or 0.0694 mg.

The H₂ evolution rate was calculated according to the equation:

H₂ evolution rate (mmol g⁻¹ h⁻¹) =
$$\frac{n(H_2)}{m(Catalyst) x t}$$

Where: $n(H_2)$ is the total amount of the produced H_2 (in mmol) within 24 h of irradiation, m(Catalyst) is the total amount of Pt nanoparticles (in grams) and t is the irradiation time in hours (t = 24 h).

Synthesis of Fmoc-FF-(Zn)Por.



Scheme S1: Synthesis of Fmoc-FF-(Zn)Por.

<u>Fmoc-FF-(Zn)Por:</u> Fmoc-FF-Por¹ (40 mg, 0.034 mmol) and zinc acetate dihydrate (100 mg, 0.46 mmol) were dissolved in a mixture of DCM (7 mL) and MeOH (2 mL) and the solution was stirred at room temperature overnight. After the completion of the reaction, the solvent was removed using a rotary evaporator and the crude compound was purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 100:3 v/v) as a purple solid (38 mg, 90%).

 $\frac{1}{14}$ NMR (CDCl₃, 300 MHz): δ 8.94 (m, 8H), 8.22 (d, J = 6.4 Hz, 6H), 8.09 (d, J = 8.2 Hz, 2H), 7.73 (m, 12H), 7.61 (m, 2H), 7.43 (m, 2H), 7.34 (m, 2H), 7.20 (m, 8H), 6.97 (d, J = 6.7 Hz, 2H), 6.87 (br s, 2H), 6.21 (br s, 1H), 4.61 (br s, 1H), 4.22 (m, 2H), 4.07 (m 2H), 3.85 (d, J = 6.0 Hz, 1H), 2.86 (d, J = 6.7 Hz, 2H), 2.47 (d, J = 6.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ 170.6, 168.4, 156.2, 150.3, 143.7, 143.5, 143.0, 141.4, 139.2, 136.8, 136.1, 135.6, 135.1, 134.6, 132.2, 129.3, 129.2, 129.0, 128.9, 127.9, 127.6, 127.4, 127.3, 126.7, 125.0, 121.2, 120.6, 120.2, 118.3, 67.3, 56.0, 54.7, 47.1, 37.4.

<u>HR-MS (MALDI-TOF)</u>: m/z calculated for C₇₇H₅₇N₇O₄Zn: 1207.3763 [M]⁺; found: 1207.3766. UV-Vis (THF) = 424 nm, 556 nm, 595 nm. Emission (THF, λ_{ex} 555 nm) = 606 nm, 655 nm.

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Fig. S2 ¹³C NMR spectrum of Fmoc-FF-(Zn)Por in CDCl₃



Fig. S3 Aromatic region of the ¹³C NMR spectrum of Fmoc-FF-(Zn)Por in CDCl₃.



Fig. S4 Self-assembly of a) **Fmoc-FF-(Zn)Por** in DCM/HEPT 1:1, b) **Fmoc-FF-(Zn)Por** in DCM/HEPT 3:7, c) **Fmoc-FF-Por** in DCM/HEPT 1:1 and d) **Fmoc-FF-Por** in DCM/HEPT 3:7. The scale bars in the figures are: $1 \mu m$ in a and b, $2 \mu m$ in c and $5 \mu m$ in d.



Figure S5. Emission lifetime decay curves of solid (red line), fibrils (blue line), spheres (black line) and in solution (green line) concerning **Fmoc-FF-(Zn)Por**.



Figure S6. Photo-catalytic hydrogen evolution plots of Fmoc-FF-(Zn)Por.



Figure S7. UV-Vis absorption spectra of **Fmoc-FF-(Zn)Por** in THF solution before (red line) and after (black line) photocatalysis.



Figure S8. Emission spectra of **Fmoc-FF-(Zn)Por** in THF solution before (red line) and after (black line) photocatalysis. The two solutions were isoabsorbing (A = 0.1), at the excitation wavelength (550 nm).



Figure S9. MALDI-TOF spectra of Fmoc-FF-(Zn)Por before (blue line) and after (red line) photocatalysis.



Figure S10. Isotopic pattern of Fmoc-FF-(Zn)Por before (blue line) and after (red line) photocatalysis.



Figure S11. SEM image of solid Fmoc-FF-(Zn)Por.

Table S1. Comparison between this work and literature reports regarding self-assembled systems and photocatalytic H₂ production.

Self-assembled compound	Catalyst	TONs	H_2 evolution	Reference
Polyethylenimine	Co(TPA)Cl2	131	5.54 μmol g ⁻¹ h ⁻¹	J. Mater. Chem. A, 2020 , <i>8</i> , 21690
Perylene Bisimide	Pt	-	6.5 μmol g ⁻¹ h ⁻¹	Adv. Energy Mater., 2020, <i>10</i> , 2002469
Carbon Dots	[FeFe] hydrogenase	-	11 µmol	ACS Catal., 2020 , <i>10</i> , 9943
Graphitic carbon nitride	Pt	-	5.8 mmol g ⁻¹ h ⁻¹	Appl. Surf. Science, 2020 , <i>499</i> , 143942
Porphyrin	Pt	62.5	5.4 mmol g ⁻¹ h ⁻¹	ACS Appl. Nano Mater., 2020 , <i>3</i> , 7040
Porphyrin	Pt	1265	0.9 mmol g ⁻¹ h ⁻¹	Chem. Commun., 2018 , <i>54</i> , 11614
Perylene monoimide	[Ni(P ₂ ^{ph} N ₂ ^{ph}) ₂](BF ₄) ₂ (NiP ₂ N ₂)	340	118 μL	Nat. Chem. 2014 , <i>6</i> , 964
Porphyrin	Pt	155	1.96 mmol g ⁻¹ h ⁻¹	this work

References.

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