

Electronic Supporting Information file for

Highly efficient light-driven hydrogen evolution utilizing porphyrin-based nanoparticles

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1. Experimental section

1.1 Materials

All reagents were purchased from common commercial sources and used without any further purification, unless otherwise stated.

1.2 Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy: The porphyrin moieties were analyzed with ^1H NMR spectroscopy using Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers. All measurements were carried out at room temperature in a deuterated solvent using residual protons as internal reference.

Ultraviolet–visible (UV-vis) absorption spectroscopy: In all studies, spectrometer Shimadzu UV-1700 was used. The reported experiments were performed using quartz cuvettes of 0.2 cm path-length.

1.3 Chemisorption of porphyrins onto Pt-TiO₂

Prior to the porphyrin adsorption onto the titanium dioxide nanoparticles (TiO₂ NPs), it was necessary to prepare the 0.5 wt% platinumized TiO₂ NPs (Pt-TiO₂ NPs), following the experimental procedure described in recent publications of our research group.¹ In order to investigate the hydrogen production, it was necessary to determine the adsorption percentage of all porphyrins onto the Pt-TiO₂ surface. The Pt-TiO₂ NPs were soaked in porphyrin solutions of 1×10^{-5} , 5×10^{-5} , 1×10^{-4} , 1.5×10^{-4} , 2×10^{-4} and 3×10^{-4} M (in a mixture of dry Toluene/Ethanol in 1:1 ratio, see Table S1). The adsorption percentage for all porphyrins was calculated by comparing the absorption spectrum of the initial porphyrin solution with the supernatant solution.

The initial absorption spectrum was recorded, and consequently in each vial 5 mg of Pt-TiO₂ were added. The samples were sonicated for 5 minutes, stirred for 40 minutes and finally centrifuged for 10 minutes in 10000 revolutions per minute (rpm). The absorption spectrum of the supernatant solution was then recorded, in order to quantify the amount of absorbed porphyrin onto the Pt-TiO₂ NPs. The Pt-TiO₂ NPs were dried under high vacuum to remove any remaining solvent residues.

Overall, the DLs varied from 35%-100%, and these values were used to determine the turn over numbers (TONs) and H₂ production rate ($\text{mmol g}^{-1} \text{h}^{-1}$).

1.4 Photocatalytic measurements

The photocatalytic H₂ evolution studies were performed in glass vials (39 mL) sealed with a rubber septum, at ambient temperature and pressure. Before each experiment, a fresh buffer solution was prepared. More precisely, the buffer solution was a 1M aqueous solution of ascorbic acid (AA) that was adjusted to pH=4 using aqueous solution of NaOH (5M). The dyed Pt-TiO₂ (5mg) were added in the glass vial together with 3mL of the buffer solution. The samples were sonicated for 5 minutes. In order to achieve anaerobic conditions, the suspensions were degassed using nitrogen for 5 min (in an ice/water bath). Finally, the samples were sealed with a silicon septum and were irradiated under continuous stirring with a low power white LED lamp ring of 40 W with color temperature 6400 K and lumen of 3800 LM.

The amount of H₂ production of each sample vial was determined using a Shimadzu GC 2010 plus chromatograph with a TCD detector and a molecular sieve 5 Å column (30 m - 0.53 mm). The analyzation of H₂ production was held every 6 hours and 24 hours of sample irradiation. 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 H₂ production values and the Turn Over Number (TON) are the average of three independent experiments.

1.5 Calculation of Turn Over Numbers (TONs) and H₂ evolution mmol (H₂) g (cat)⁻¹ h⁻¹

The TONs were calculated according to the following equation:

$$\text{TON} = \frac{n(\text{H}_2)}{n(\text{PS})}$$

Where: **n(H₂)** is the total amount of the produced H₂ (in mmol) and **n(PS)** is the total amount of the photosensitizer (in mmol).

In every photocatalytic experiment 0.005 g of PtTiO₂ (0.5% (w/w) of Pt) were used. Thus, the final amount of the catalyst (Pt) in each experiment is 0.000025 g. The H₂ evolution rate was calculated according to the equation:

$$\text{H}_2 \text{ evolution mmol(H}_2\text{) g(cat)}^{-1} \text{ h}^{-1} = \frac{n(\text{H}_2)}{m(\text{Catalyst}) \times t}$$

Where: **n(H₂)** is the total amount of the produced H₂ (in mmol), **m(catalyst)** is the total amount of Pt and Pd (in grams) and **t** is the irradiation time in hours (t = 24 h).

All the experiments were conducted in 3 ml Ascorbic Acid (1M) pH=4 as buffer solution, upon low power white LED lamp ring of 40 W.

2. Synthesis and characterization

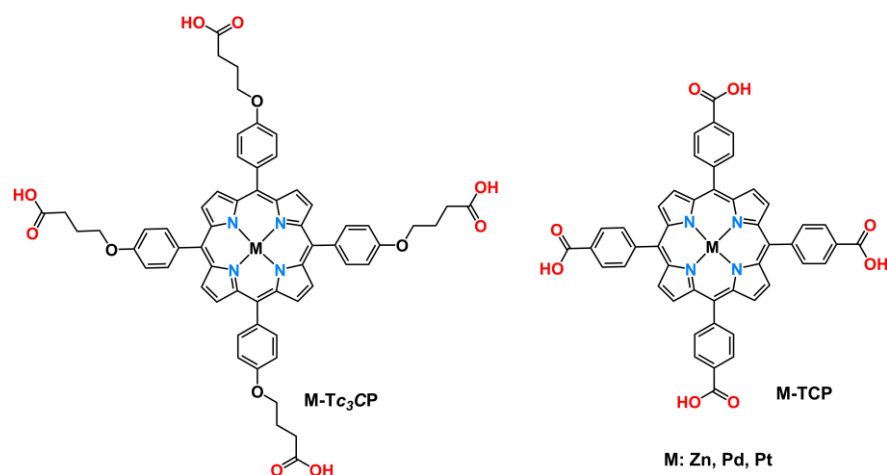
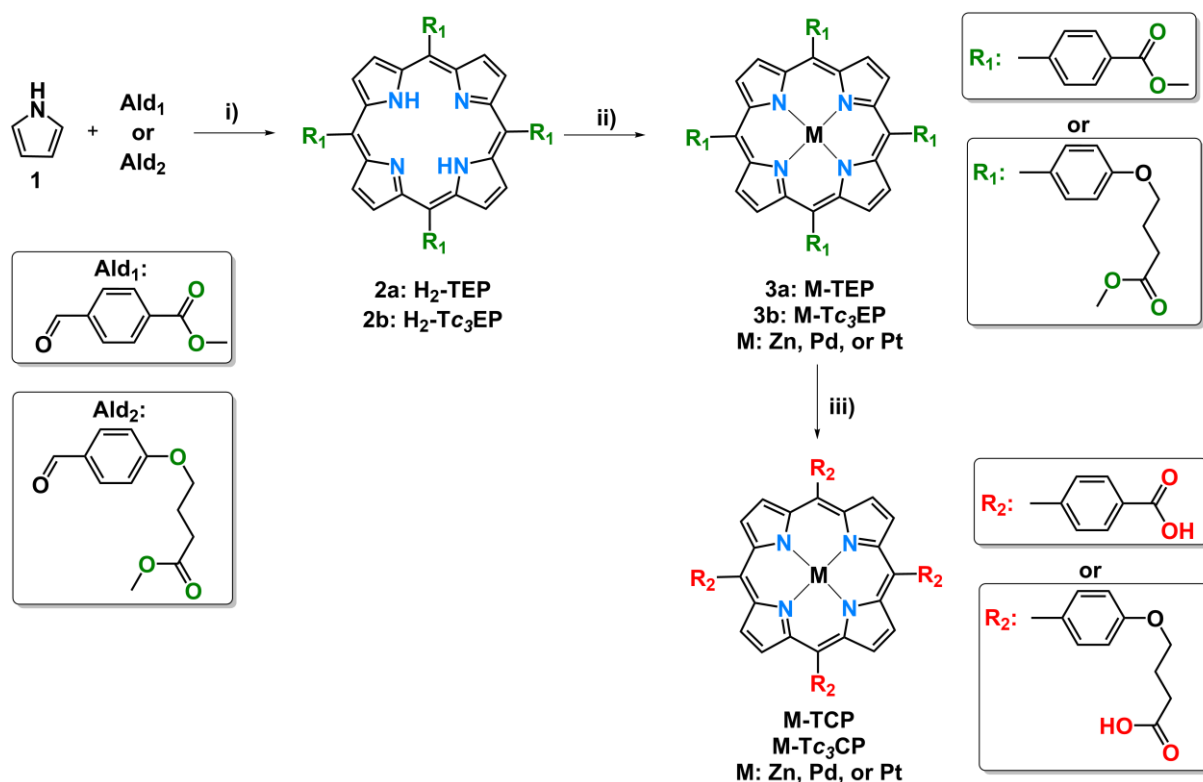


Figure S1. The porphyrin derivatives prepared and studied in this work. Left part: **M-TCP** (M = Zn, Pd, Pt), right part: **M-Tc₃CP** (M = Zn, Pd, Pt).

2.1 Synthesis

In **Scheme S1**, the complete synthetic approach for the preparation of **M-Tc₃CP** and **M-TCP** derivatives is described. In brief, the initial step corresponds to the formation of the free base porphyrins **2a** and **2b** via a “Alder and Longo” using pyrrole **1** and the respective benzaldehyde (**Ald₁** or **Ald₂**) in refluxing propionic acid. Subsequently, the formed **H₂-TEP** and **H₂-Tc₃EP** porphyrins were transformed into the corresponding metalated complexes **M-TEP** and **M-Tc₃EP** (M: Zn, Pd, or Pt) in almost quantitative yields using the corresponding metal salts and a refluxing solvent (see caption of Scheme 1 and ESI for details). Finally, upon hydrolysis with potassium hydroxide the final **M-TCP** and **M-Tc₃CP** were formed.

The preparation of **H₂-TEP**², **H₂-Tc₃EP**³, **Pt-Tc₃EP**³, **Pd-Tc₃EP**⁴, **Zn-Tc₃EP**⁵, **Pt-Tc₃CP**³, **Pd-Tc₃CP**⁴, **Zn-Tc₃CP**⁵ has been carried out following literature procedures.²⁻⁵



Scheme S1. Synthetic approach for **M-TCP** and **M-Tc₃CP** derivatives. Experimental details: i) propionic acid, reflux, **Ald₁** (methyl 4-formylbenzoate) or **Ald₂** (ethyl 4(4-formylphenoxy)butanoate),²⁷ pyrrole **1** ii) for **Zn-TEP** and **Zn-Tc₃EP**: Zn(CH₃COO)₂·2H₂O CH₂Cl₂/MeOH, rt; for and **Pd-TEP** and **Pd-Tc₃EP**: PdCl₂, benzonitrile, reflux; for **Pt-TEP** and **Pt-Tc₃EP**: PtCl₂, benzonitrile, reflux; iv) THF, MeOH, KOH, rt.

Zn-TEP: To a CH₂Cl₂ solution (16 mL) of **H₂-TEP** (0.04 gr, 0.047 mmol), a MeOH (2 mL) solution containing 0.104 g of Zn(CH₃COO)₂·2H₂O (0.47 mmol) was added and the reaction mixture was refluxed for 3 h. Upon reaction completion, the volatiles were evaporated, the porphyrin was diluted in CH₂Cl₂ and washed with H₂O (3 x 25 mL). The solvent was consequently removed under reduced pressure and the produced porphyrin then purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 99:1 v/v), yielding the final product **Zn-TEP** (0.038 gr, yield: 88%).

¹H NMR (500 MHz, CDCl₃): δ 8.72 (s, 8H), 8.43 (d, *J* = 8.2 Hz, 8H), 8.23 (d, *J* = 8.2 Hz, 8H), 4.10 (s, 12H) ppm.

Zn-TCP: To a solution of **Zn-TEP** (0.050 gr, 0.055 mmol) in 55 mL of a THF/MeOH mixture (2:1), an aqueous solution of KOH (1.03 gr, 18.4 mmol) was added. The reaction mixture was stirred at room temperature overnight. Subsequently, the organic solvents were evaporated under reduced pressure and distilled H₂O was added to the residue. Acidification of the mixture by using HCl (1 M aq.) resulted in the precipitation of the porphyrin which was filtered, washed with distilled H₂O and finally dried yielding the final **Zn-TCP** (0.045 gr, 96%).

¹H NMR (500 MHz, (CD₃)₂SO): δ 8.80 (s, 8H), 8.37 (d, *J* = 7.9 Hz, 8H), 8.30 (d, *J* = 7.8 Hz, 8H) ppm.

Zn-TCP: HRMS-(MALDI-TOF): *m/z* calc. for [M]⁺ C₄₈H₂₈N₄O₈Zn 852.1199, found 852.1129.

Pt-TEP: PtCl₂ (0.079 gr, 0.030 mmol) was added in 20 mL of benzonitrile and the mixture was refluxed for 1 h. Then, **H₂-TEP** (0.05gr, 0.059 mmol) was added in the solution and the reaction was left under reflux conditions for 2 additional hours. Upon the completion of the reaction, the benzonitrile was removed and the porphyrin was diluted in CH₂Cl₂ and washed with aqueous NaCl (2 x 30 mL) and H₂O (1 x 30 mL). Finally, the solvent was removed under reduced pressure and the produced porphyrin then purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 99:1 v/v) yielding the final **Pt-TEP** (0.047 gr, yield: 77%).

¹H NMR (500 MHz, CDCl₃): δ 8.72 (s, 8H), 8.43 (d, *J* = 8.3 Hz, 8H), 8.23 (d, *J* = 8.2 Hz, 8H), 4.10 (s, 12H) ppm.

Pt-TCP: To a solution of **Pt-TEP** (0.054 gr, 0.052 mmol) in 59 mL of a THF/MeOH mixture (2:1), an aqueous solution of KOH (0.97 gr, 17.3 mmol) was added. The reaction mixture was stirred at room temperature overnight. Subsequently, the organic solvents were evaporated under reduced pressure and distilled H₂O was added to the residue. Acidification of the mixture by using HCl (1 M aq.) resulted in the precipitation of the porphyrin which was filtered, washed with distilled H₂O and finally dried yielding the final **Pt-TCP** (0.05 gr, 98%).

¹H NMR (500 MHz, (CD₃)₂SO): δ 8.76 (s, 8H), 8.37 (d, *J* = 8.1 Hz, 8H), 8.30 (d, *J* = 8.0 Hz, 8H) ppm.

Pt-TCP: HRMS-(MALDI-TOF): *m/z* calc. for [M]⁺ C₄₈H₂₈N₄O₈Pt 983.1555, found 983.1442.

Pd-TEP: PdCl₂ (0.050 gr, 0.059 mmol) was added in 20 mL of benzonitrile and the mixture was refluxed for 1 h. Then, **H₂-TEP** (0.05 gr, 0.059 mmol) was added in the solution and the reaction was left under reflux conditions for 2 additional hours. Upon the completion of the reaction, the benzonitrile was removed and the porphyrin was diluted in CH₂Cl₂ and washed with aqueous NaCl (2 x 30 mL) and H₂O (1 x 30 mL). Finally, the solvent was removed under reduced pressure and the produced porphyrin then purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 99:1 v/v) yielding the final **Pd-TEP** (0.047 gr, yield: 84%).

¹H NMR (500 MHz, CDCl₃): δ 8.72 (s, 8H), 8.43 (d, *J* = 8.3 Hz, 8H), 8.20 (d, *J* = 8.2 Hz, 8H), 4.10 (s, 12H) ppm.

Pd-TCP: To a solution of **Pd-TEP** (0.047 gr, 0.049 mmol) in 51 mL of a THF/MeOH mixture (2:1), an aqueous solution of KOH (0.92 gr, 16.5 mmol) was added. The reaction mixture was stirred at room temperature overnight. Subsequently, the organic solvents were evaporated under reduced pressure and distilled H₂O was added to the residue. Acidification of the mixture by using HCl (1 M aq.) resulted in the precipitation of the porphyrin which was filtered, washed with distilled H₂O and finally dried yielding the final **Pd-TCP** (0.042 gr, 95%).

¹H NMR (500 MHz, (CD₃)₂SO): δ 8.80 (s, 8H), 8.36 (d, *J* = 8.2 Hz, 8H), 8.29 (d, *J* = 8.0 Hz, 8H) ppm.

Pd-TCP: HRMS-(MALDI-TOF): *m/z* calc. for [M]⁺ C₄₈H₂₈N₄O₈Pd 894.0942, found 894.0912.

2.2 Characterization

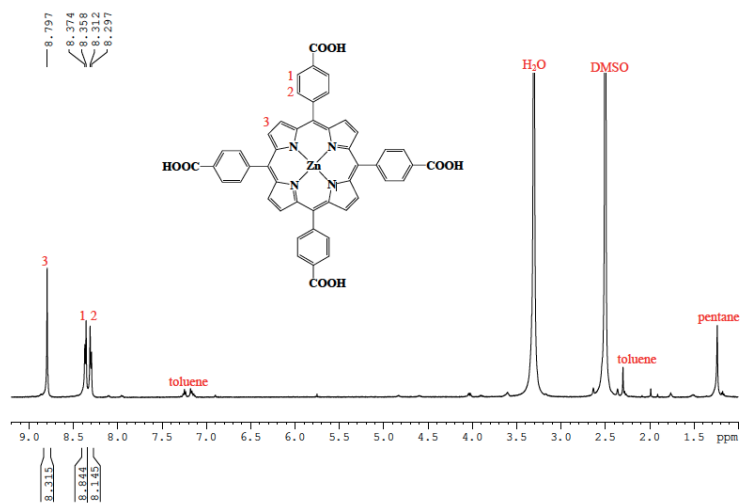


Figure S2. ^1H NMR spectra of Zn-TCP (500 MHz, $(\text{CD}_3)_2\text{SO}$).

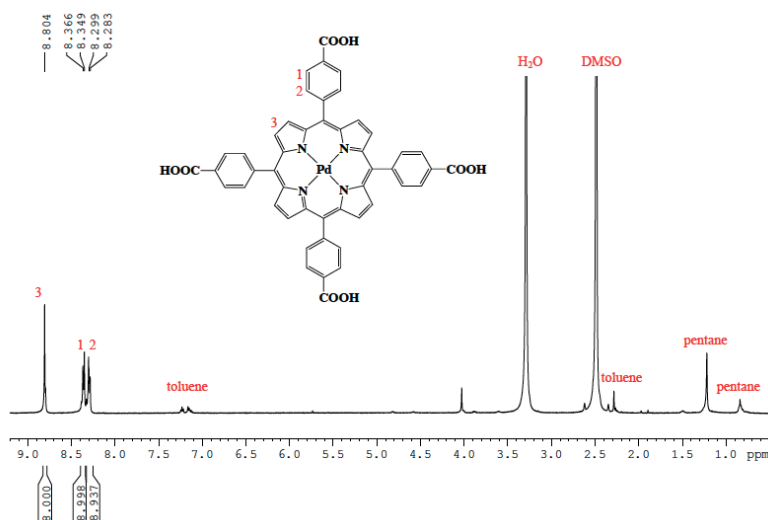


Figure S3. ^1H NMR spectra of Pd-TCP (500 MHz, $(\text{CD}_3)_2\text{SO}$).

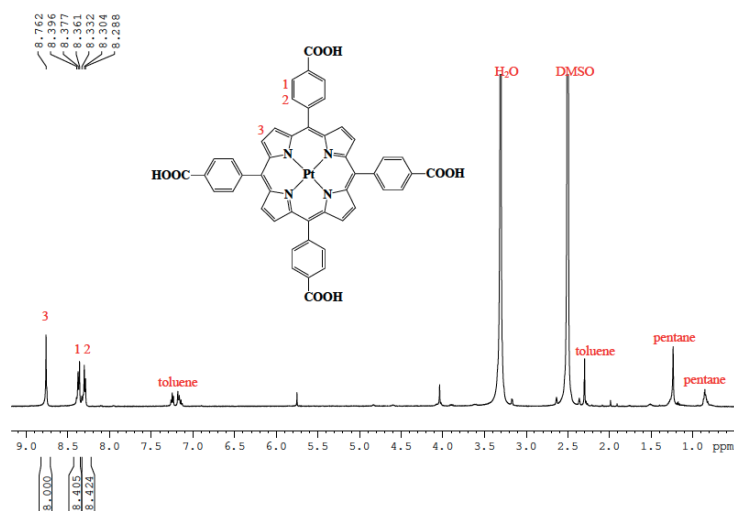


Figure S4. ^1H NMR spectra of Pt-TCP (500 MHz, $(\text{CD}_3)_2\text{SO}$).

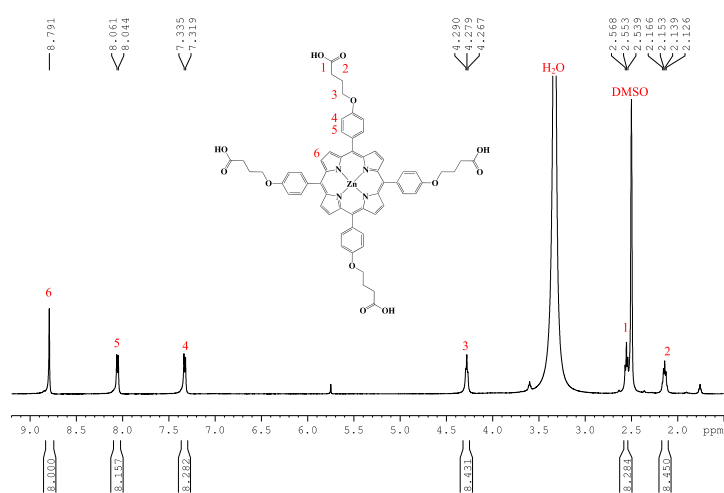


Figure S5. ¹H NMR spectra of Zn-Tc₃P (500 MHz, (CD₃)₂SO)

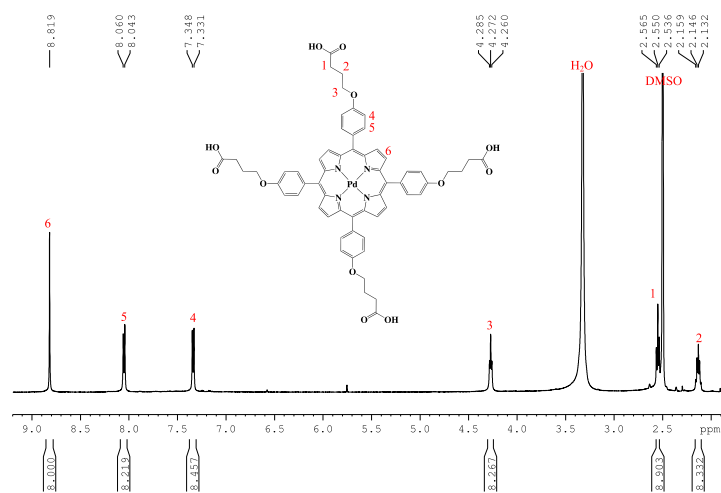


Figure S6. ¹H NMR spectra of Pd-Tc₃P (500 MHz, (CD₃)₂SO)

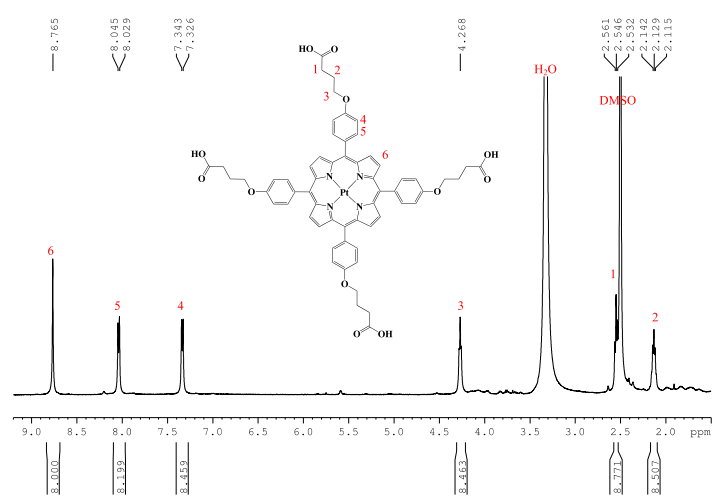


Figure S7. ¹H NMR spectra of Pt-Tc₃P (500 MHz, (CD₃)₂SO)

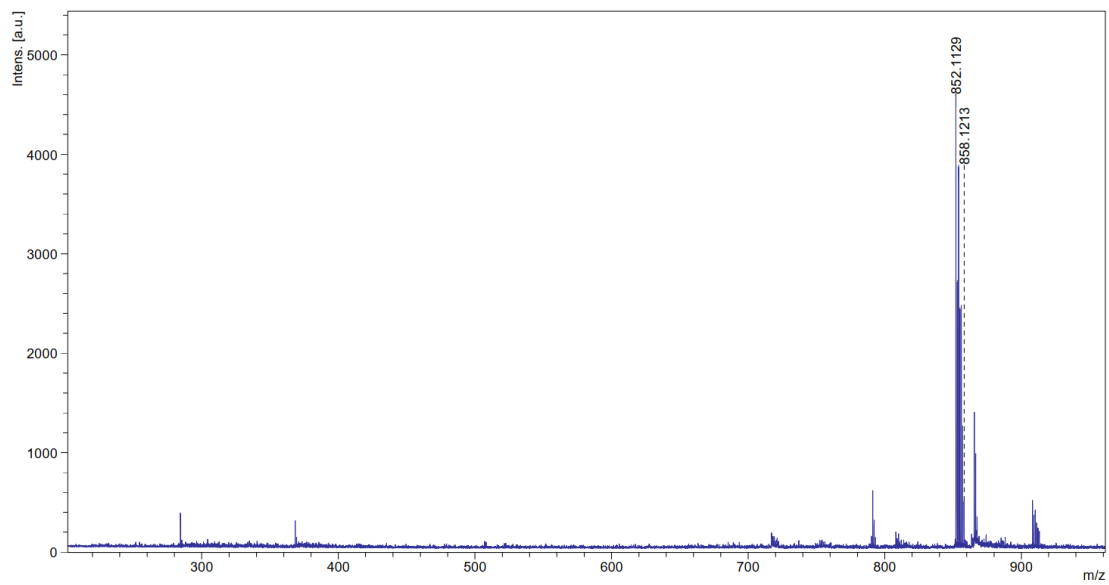


Figure S8. HRMS-(MALDI-TOF) of Zn-TCP.

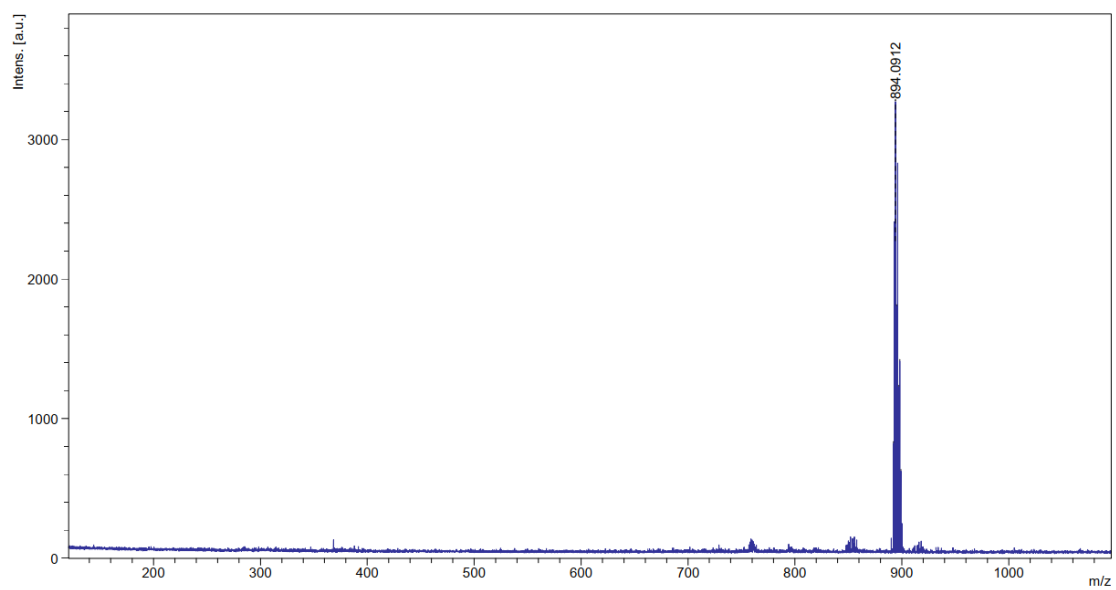


Figure S9. HRMS-(MALDI-TOF) of Pd-TCP.

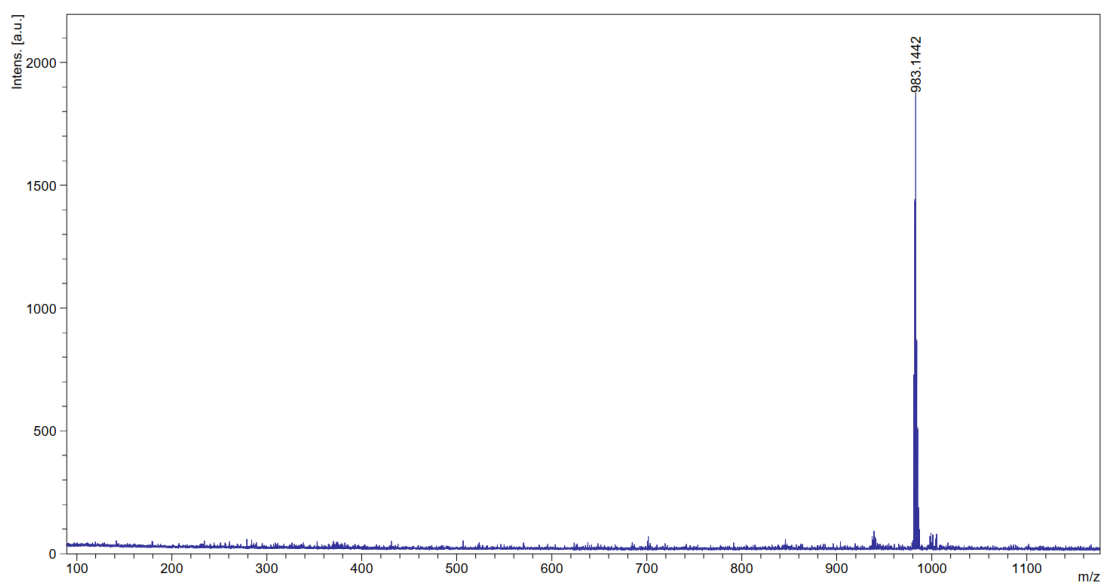


Figure S10. HRMS-(MALDI-TOF) of Pt-TCP.

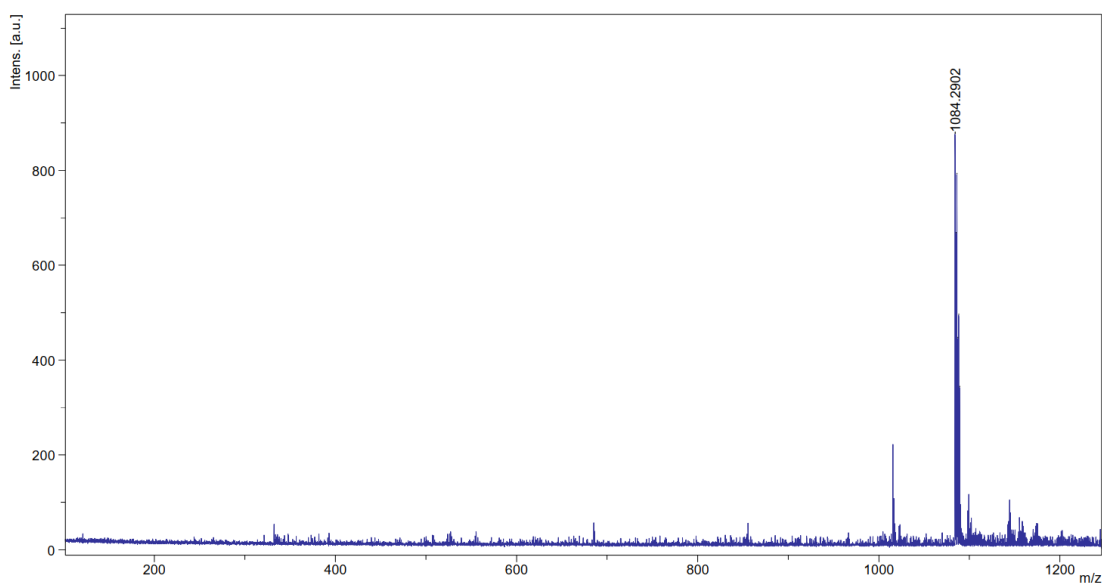


Figure S11. HRMS-(MALDI-TOF) of Zn-Tc₃P.

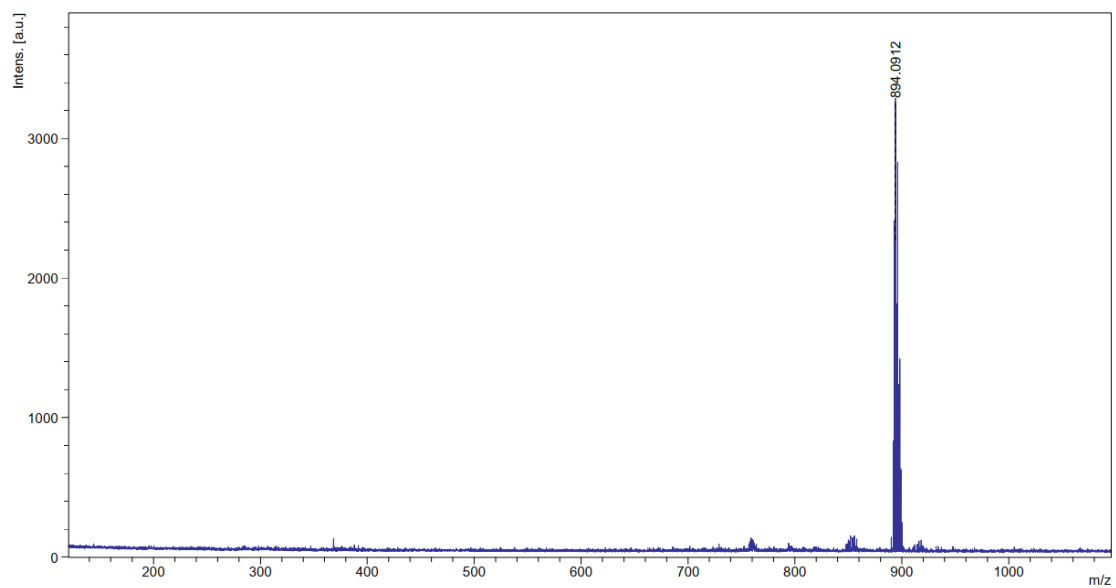


Figure S12. HRMS-(MALDI-TOF) of Pd-Tc₃P.

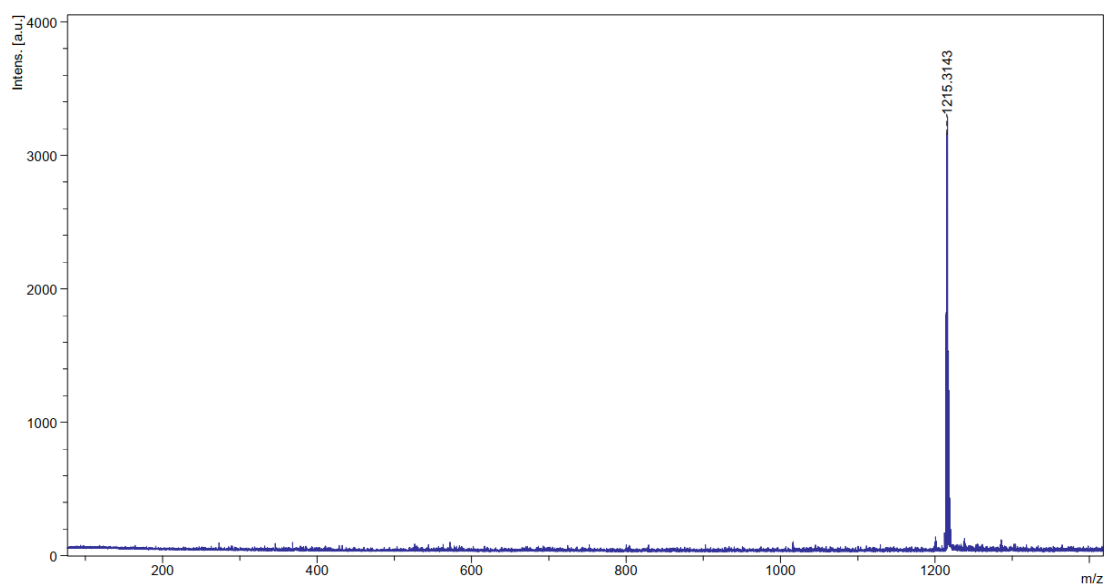


Figure S13. HRMS-(MALDI-TOF) of Pt-Tc₃P.

3. Photophysical investigation

Table S1. Absorption data for **M-TCP** and **M-Tc₃CP** (M: Zn, Pd, or Pt) in Tol/ EtOH 1:1 solvent mixture.

Compound	λ_{max}/nm ($\epsilon / mM^{-1} cm^{-1}$)
Zn-TCP	428 (431.1), 559 (19.8), 600 (8.4)
Zn-Tc ₃ CP	428 (560.9), 560 (160.5), 602 (78.1)
Pd-TCP	409 (255.6), 515 (21.3)
Pd-Tc ₃ CP	421 (238), 526 (15.8)
Pt-TCP	403 (248.5), 510 (23.6)
Pt-Tc ₃ CP	407 (202.3), 512 (21.2)

Table S2. Oxidation and reduction data for **Zn-Tc₃CP**, **Pd-Tc₃CP**, and **Pt-Tc₃CP** reported vs. SCE reference electrode in tetrahydrofuran (THF) at room temperature using tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte.

Porphyrin	$E_{1/2}^{ox1}/V$	$E_{1/2}^{ox2}/V$	$E_{1/2}^{red1}/V$	$E_{1/2}^{red2}/V$	E_{00}	ΔG_{inj}	ΔG_{reg}
Zn-Tc ₃ CP	0.81	1.09	-1.31	-1.73	2.12	-0.67	-0.35
Pd-Tc ₃ CP	1.21	1.47	-1.31	-1.53	1.92	-0.71	-0.75
Pt-Tc ₃ CP	1.27	1.54	-1.27	-1.60	1.95	-0.75	-0.81

^a E_{00} in eV was calculated with the wavelength at the intersection of normalized absorption and emission spectra.

^c ΔG_{inj} in eV was calculated according to $\Delta G_{inj} = E_{ox}(Por^+/Por) - E_{00} - E_{CB}(TiO_2)$ measured at pH = 4 with $E_{CB}(TiO_2) = -0.4 - 0.059 \cdot pH$;⁷

^d ΔG_{reg} in eV was calculated according to $\Delta G_{reg} = E_{ox}(SED^+/SED) - E_{ox}(Por^+/Por)$. $E_{ox}(SED^+/SED) = 0.46$ V vs. SCE⁸

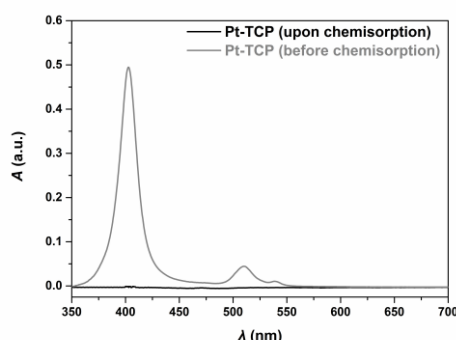


Figure S14. Absorption spectra of **Pt-TCP** (1.0×10^{-5} M) before and after chemisorption onto Pt-TiO₂ NPs.

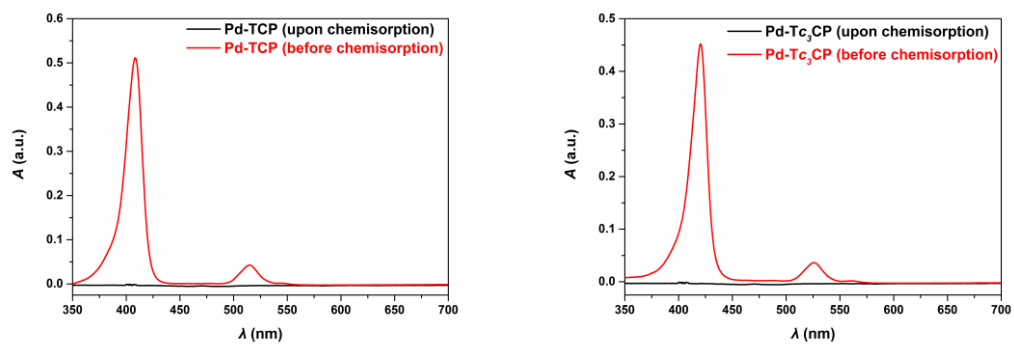


Figure S15. Absorption spectra of a) **Pd-Tc₃CP** and b) **Pd-TCP** (1.0×10^{-5} M) before and after chemisorption onto Pt-TiO₂ NPs.

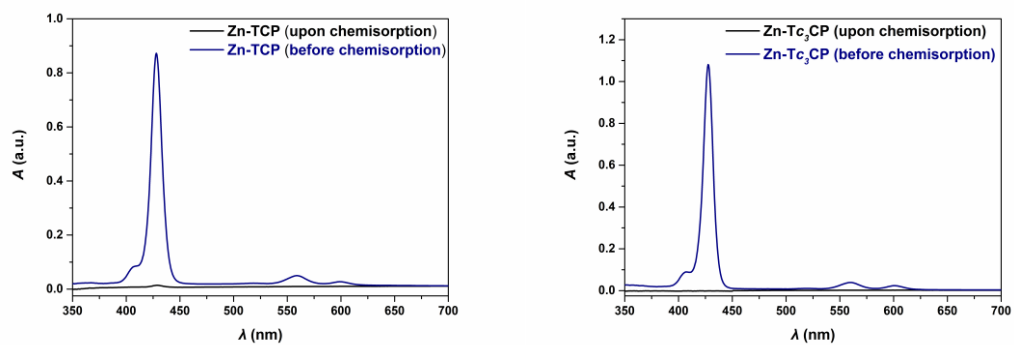


Figure S16. Absorption spectra of a) **Zn-Tc₃CP** and b) **Zn-TCP** (1.0×10^{-5} M) before and after chemisorption onto Pt-TiO₂ NPs.

4. Photocatalysis

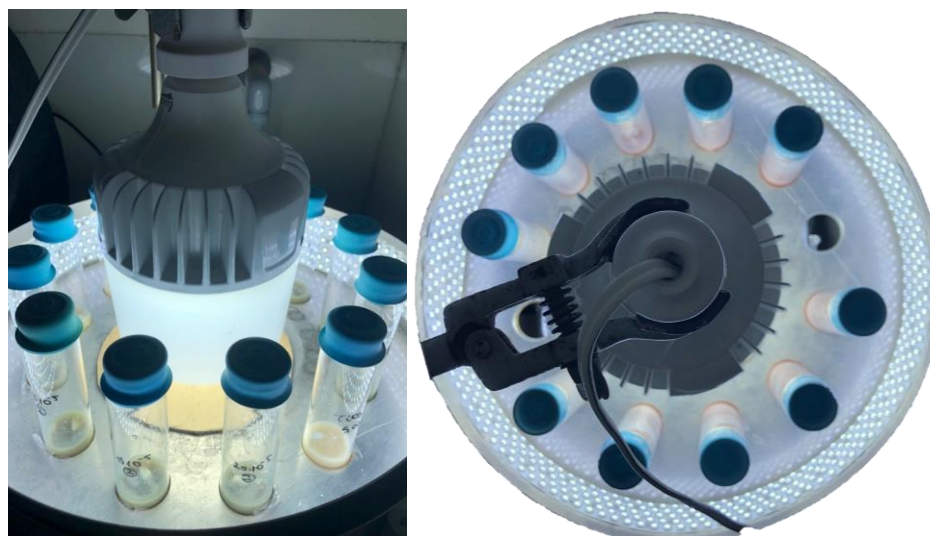


Figure S17. The experimental set up using a LED lamp.

Table S3. Photocatalytic data for **Zn-TCP** in several concentrations.

Sample	Concentration (M) ^[a]	DL (%) ^[b]	PS ^[c]	TONs ^[d]	Activity (mmol g ⁻¹ h ⁻¹) ^[e]
Zn-TCP	1.0 x 10 ⁻⁵	100	3.0 x 10 ⁻⁸	1192	60
Zn-TCP	5.0 x 10 ⁻⁵	100	1.5 x 10 ⁻⁷	1078	270
Zn-TCP	1.0 x 10 ⁻⁴	74	2.2 x 10 ⁻⁷	691	257
Zn-TCP	1.5 x 10 ⁻⁴	60	2.8 x 10 ⁻⁷	796	360
Zn-TCP	2.0 x 10 ⁻⁴	42	2.5 x 10 ⁻⁷	671	280

Table S4. Photocatalytic data for **Zn-Tc₃CP** in several concentrations.

Sample	Concentration (M) ^[a]	DL (%) ^[b]	PS ^[c]	TONs ^[d]	Activity (mmol g ⁻¹ h ⁻¹) ^[e]
Zn-Tc ₃ CP	1.0 x 10 ⁻⁵	100	3.0 x 10 ⁻⁸	1012	51
Zn-Tc ₃ CP	5.0 x 10 ⁻⁵	100	1.5 x 10 ⁻⁷	868	216
Zn-Tc ₃ CP	1.0 x 10 ⁻⁴	74	2.2 x 10 ⁻⁷	904	331
Zn-Tc ₃ CP	1.5 x 10 ⁻⁴	58	2.6 x 10 ⁻⁷	788	344
Zn-Tc ₃ CP	2.0 x 10 ⁻⁴	41	2.5 x 10 ⁻⁷	1031	421

Table S5. Photocatalytic data for **Pd-TCP** in several concentrations.

Sample	Concentration (M) ^[a]	DL (%) ^[b]	PS ^[c]	TONs ^[d]	Activity (mmol g ⁻¹ h ⁻¹) ^[e]
Pd-TCP	1.0 x 10 ⁻⁵	100	3.0 x 10 ⁻⁸	1096	49
Pd-TCP	5.0 x 10 ⁻⁵	100	1.5 x 10 ⁻⁷	1004	153
Pd-TCP	1.0 x 10 ⁻⁴	80	2.4 x 10 ⁻⁷	902	178
Pd-TCP	1.5 x 10 ⁻⁴	62	2.8 x 10 ⁻⁷	970	206
Pd-TCP	2.0 x 10 ⁻⁴	51	3.0 x 10 ⁻⁷	1131	250
Pd-TCP	3.0 x 10 ⁻⁴	35	3.2 x 10 ⁻⁷	1147	257

Table S6. Photocatalytic data for **Pd-Tc₃CP** in several concentrations.

<i>Sample</i>	<i>Concentration (M) ^[a]</i>	<i>DL (%) ^[b]</i>	<i>PS ^[c]</i>	<i>TONs ^[d]</i>	<i>Activity (mmol g⁻¹ h⁻¹) ^[e]</i>
Pd-Tc ₃ CP	1.0 × 10 ⁻⁵	100	3.0 × 10 ⁻⁸	7722	342
Pd-Tc ₃ CP	5.0 × 10 ⁻⁵	100	1.5 × 10 ⁻⁷	3889	593
Pd-Tc ₃ CP	1.0 × 10 ⁻⁴	98	3.0 × 10 ⁻⁷	2226	485
Pd-Tc ₃ CP	1.5 × 10 ⁻⁴	75	3.4 × 10 ⁻⁷	2114	487
Pd-Tc ₃ CP	2.0 × 10 ⁻⁴	65	3.9 × 10 ⁻⁷	1760	430
Pd-Tc ₃ CP	3.0 × 10 ⁻⁴	48	4.4 × 10 ⁻⁷	1481	376

Table S7. Photocatalytic data for **Pt-TCP** in several concentrations.

<i>Sample</i>	<i>Concentration (M) ^[a]</i>	<i>DL (%) ^[b]</i>	<i>PS ^[c]</i>	<i>TONs ^[d]</i>	<i>Activity (mmol g⁻¹ h⁻¹) ^[e]</i>
Pt-TCP	1.0 × 10 ⁻⁵	100	3.0 × 10 ⁻⁸	2018	82
Pt-TCP	5.0 × 10 ⁻⁵	99	1.5 × 10 ⁻⁷	2078	238
Pt-TCP	1.0 × 10 ⁻⁴	92	2.8 × 10 ⁻⁷	2139	312
Pt-TCP	1.5 × 10 ⁻⁴	66	3.0 × 10 ⁻⁷	2380	355
Pt-TCP	2.0 × 10 ⁻⁴	50	3.0 × 10 ⁻⁷	2525	378
Pt-TCP	30.0 × 10 ⁻⁵	36	3.2 × 10 ⁻⁷	2176	332

Table S8. Photocatalytic data for **Pt-Tc₃CP** in several concentrations.

<i>Sample</i>	<i>Concentration (M) ^[a]</i>	<i>DL (%) ^[b]</i>	<i>PS ^[c]</i>	<i>TONs ^[d]</i>	<i>Activity (mmol g⁻¹ h⁻¹) ^[e]</i>
Pt-Tc ₃ CP	1.0 × 10 ⁻⁶	100	3.0 × 10 ⁻⁹	0	0
Pt-Tc ₃ CP	5.0 × 10 ⁻⁶	100	1.5 × 10 ⁻⁸	11607	500
Pt-Tc ₃ CP	1.0 × 10 ⁻⁵	100	3.0 × 10 ⁻⁸	10819	707
Pt-Tc ₃ CP	5.0 × 10 ⁻⁵	100	1.5 × 10 ⁻⁷	3981	459
Pt-Tc ₃ CP	1.0 × 10 ⁻⁴	93	2.8 × 10 ⁻⁷	2511	367
Pt-Tc ₃ CP	1.5 × 10 ⁻⁴	71	3.2 × 10 ⁻⁷	2771	422
Pt-Tc ₃ CP	2.0 × 10 ⁻⁴	58	3.5 × 10 ⁻⁷	2337	365
Pt-Tc ₃ CP	3.0 × 10 ⁻⁴	43	3.9 × 10 ⁻⁷	1997	320

^[a]The concentration of the initial solutions (3 mL in dry Tol / EtOH 1:1) that were used for the adsorption of the porphyrin, ^[b]Dye-loading percentage (DL), ^[c]The amount of the photosensitizer (PS) in each photocatalytic experiment upon its adsorption (in moles), ^[d]The turnover number (TON) in 24h was calculated as the number the produced mole of H₂ divided by the number of mole of PS attached onto Pt-TiO₂ and ^[e] The activity was defined as the millimole of H₂ evolved per gram of Pt plus the Pt and Pd-porphyrin (whenever is present) per hour in the first 24 hours.

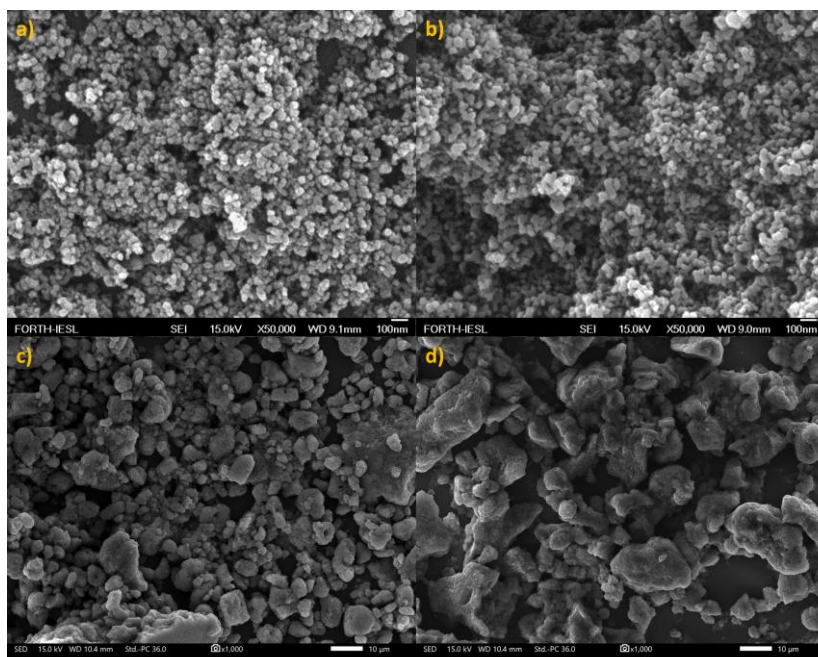


Figure S18. FESEM images of: a) Pt-TiO₂, b) Pt-Tc₃CP@PtTiO₂, c) Zn-TCP@PtTiO₂, and d) Pt-TCP@PtTiO₂

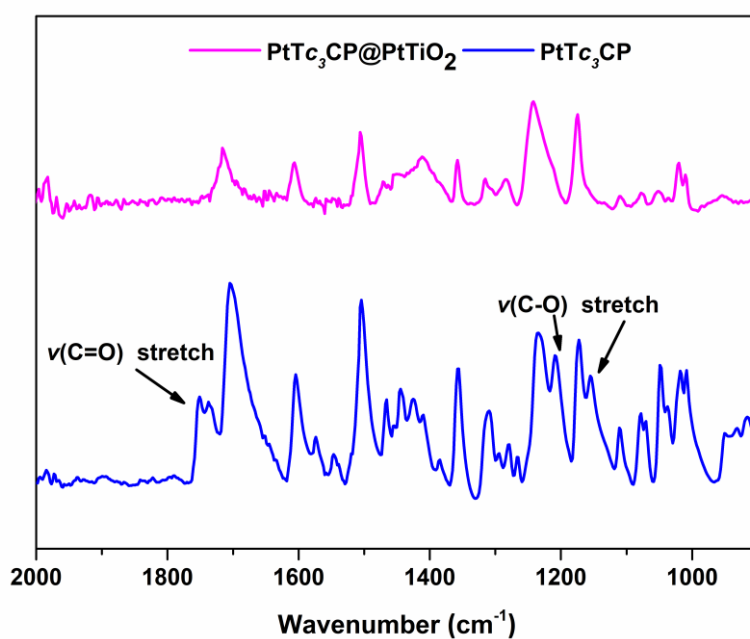


Figure S19. FT-IR-ATR spectra of Pt-Tc₃CP solid and adsorbed on Pt-TiO₂ NPs.

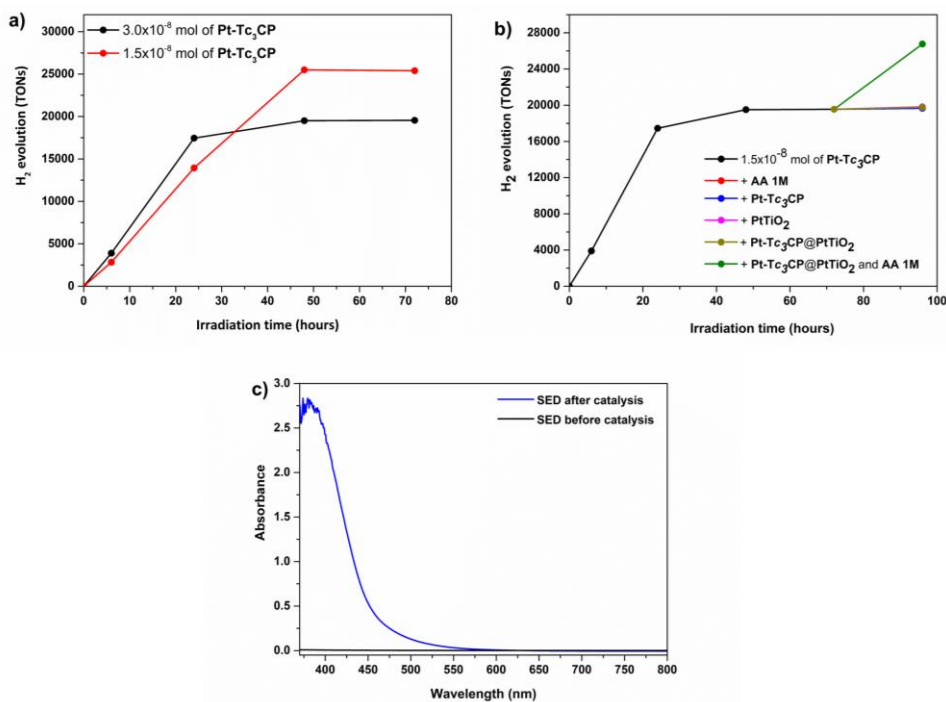


Figure S20. a) Photocatalytic H₂ evolution plots of Pt-Tc₃CP-PtTiO₂ in different concentrations: 3.0x10⁻⁸ mol (mol (black line) and 1.5x10⁻⁸ mol (red line). The photo-catalytic experiments were conducted in an aqueous buffer 1M ascorbic acid at pH=4, b) regeneration experiments after adding additional amount of either i) Pt-Tc₃CP or ii) AA 1M or iii) Pt-TiO₂. Only when all three necessary components we added, H₂ was produced. c) UV-Vis spectrum of the SED medium before and after catalysis.

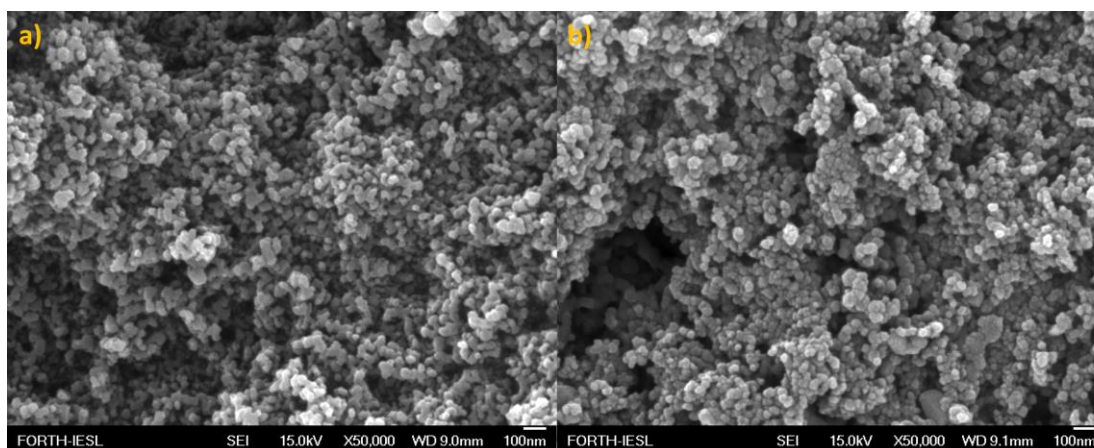


Figure S21. FESEM images of Pt-Tc₃CP@PtTiO₂ before (a) and after catalysis (b, 48h).

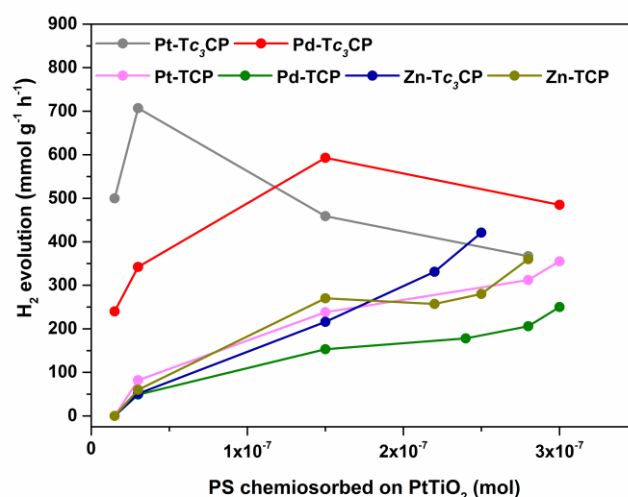


Figure S22. Plot of the H₂ evolution activity (in mmol g⁻¹ h⁻¹) vs. the amount of the porphyrin onto PtTiO₂.

5. References

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