

Supporting Information

A Squaraine-Linked Metalloporphyrin Two-Dimensional Polymer Photocatalyst for Hydrogen and Oxygen Evolution

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1. Materials

All reagents and solvents were of commercial reagent grade and were used without further purification unless otherwise noted. Tetrahydrofuran was distilled from sodium with benzophenone prior to use. Pyrrole was passed through basic alumina column till the pure colorless pyrrole was obtained.

5,10,15,20-Tetrakis(3,5-dimethoxyphenyl)porphyrin, 5,10,15,20-Tetrakis(3,5-dihydroxyphenyl)porphyrin^{S1} and CoP-SQ dimer (**2**)^{S2,S3} are prepared and characterized according to the literature report. The synthesis and detailed characterization of **1** and **2DP** is recently reported.²²

2. Methods

Experimental set up for material characterizations.

Infrared spectra were recorded on a PerkinElmer AT-FTIR Spectrometer and the wave numbers of recorded IR-signals are quoted in cm^{-1} . FEI Tecnai F30 S-TWIN HR-TEM, FEI Tecnai G2 F20 XTWIN transmission electron microscopes with accelerating voltage of 200 kV were used for TEM imaging on 200 mesh carbon coated copper grid. Photocatalytic experiments were carried out using a photoreactor (400-W high pressure mercury lamp as visible light source with water circulating pyrex jackets, a NaNO_2 chemical filter) and an Oriel Instruments solar simulator equipped with a 300 W Xenon arc lamp system with an AM 1.5 cut-off filter. Digital lux meter from Kusum Electrical Industries Ltd. (KM-LUX-100K) having lux range of 1,00,000 lux and spectral sensitivity 400-800 nm was used to monitor the lux. The quantification of gas evolution was determined with the Agilent Technologies 7890A gas chromatography (GC) system using 5190-1523 Syringe (500 μL), PTFE, FN, bevel tip Agilent technologies. XPS measurement was made using a custom built ambient pressure XPS system from Prevac and equipped with VG Scienta monochromator (MX650) using Al K α anode (1486.6 eV). The energy of the photoelectrons were analyzed using VG Scienta's R3000HP differentially pumped analyzer.

Experimental Procedure for Photocatalytic Activity Measurements: Photocatalytic HER and OER experiments were carried out under steady state conditions by head space analysis at room temperature (25 °C). Catalyst was dispersed in water by sonication for 15 min and subsequently, nitrogen gas was bubbled for 30 min to remove any dissolved oxygen. During the course of the reaction, the entire suspension is stirred by using a magnetic stirrer. In general, 5 mg of the photocatalyst was suspended in an air tight quartz cell (closed with a silicone rubber septum) of 70 mL capacity containing 10 ml deionized water and 5 ml of sacrificial agent (for HER only) (55 ml dead volume). The progress of the reaction was monitored by illuminating with various visible light sources such as photoreactor, solar simulator and sunlight. Besides, approximately 50,000 lux was confirmed before each photoreactor and sunlight illumination experiments, respectively. The headspace of the reactor was periodically sampled with an offline injection system by a gas phase syringe having injection volume of 500 µl. Gas analysis was carried out by regular sampling every hour and a gas chromatograph (GC) equipped with a TCD detector (Agilent 7890) was employed for quantitative analysis. After saturation regime in the first cycle, the photocatalyst suspension is purged with N₂ for 30 min before starting the next cycle and for repeated experiments, the catalyst is filtered after each photocatalytic cycle, washed with excess methanol and dried under vacuum. The two different photocatalytic conditions followed are given below.

Minimum Additive Condition for Photocatalytic Water Splitting:

HER: 5 mg catalyst, 5 mL MeOH, 10 mL H₂O.

OER: 5 mg catalyst, 10 mL H₂O.

Optimized Condition for Photocatalytic Water Splitting:

HER: 5 mg catalyst, 5 mL TEOA, 10 mL H₂O, (50 µl (1wt %) of Pt cocatalyst).

OER: 5 mg catalyst, 10 mL H₂O, 50 µL AgNO₃ (1 mmol).

Turn over number (TON)

TON = moles of evolved H₂/moles of catalyst used.

TON for **2DP** under direct sunlight condition, where 2.6 µmol of H₂ and 0.95 µmol of O₂ evolution was observed. All the Co metal centers (obtained from MP-AES analysis) are assumed to be active in catalysis for TON calculation.

HER: $2.6 \times 10^{-6} \text{ mol} / 2.4604 \times 10^{-7} \text{ mol} = 10.5673$

OER: $0.95 \times 10^{-6} \text{ mol} / 2.4604 \times 10^{-7} \text{ mol} = 3.8611$

Stability tests for Photocatalysts

At first, the weight loss of the catalyst after each photocatalytic reaction cycle is checked and found negligible mass loss or gain. The decomposition of the catalyst under reaction conditions for longer time also tested and no other gases, except H₂ and O₂, could be detected by GC. The structural stability of the catalyst over time is monitored by FT-IR spectroscopy, TEM and XPS analysis. The consistency in the rate of H₂ and O₂ evolution is closely monitored with repeated cyclic experiments over 300 days.

Samples for Transmission Electron Microscope (TEM) analysis

The samples for TEM were prepared by drop casting the 2D polymer dispersions in MeOH on carbon coated Cu grid and allowed to dry overnight in desiccators.

3. Figures

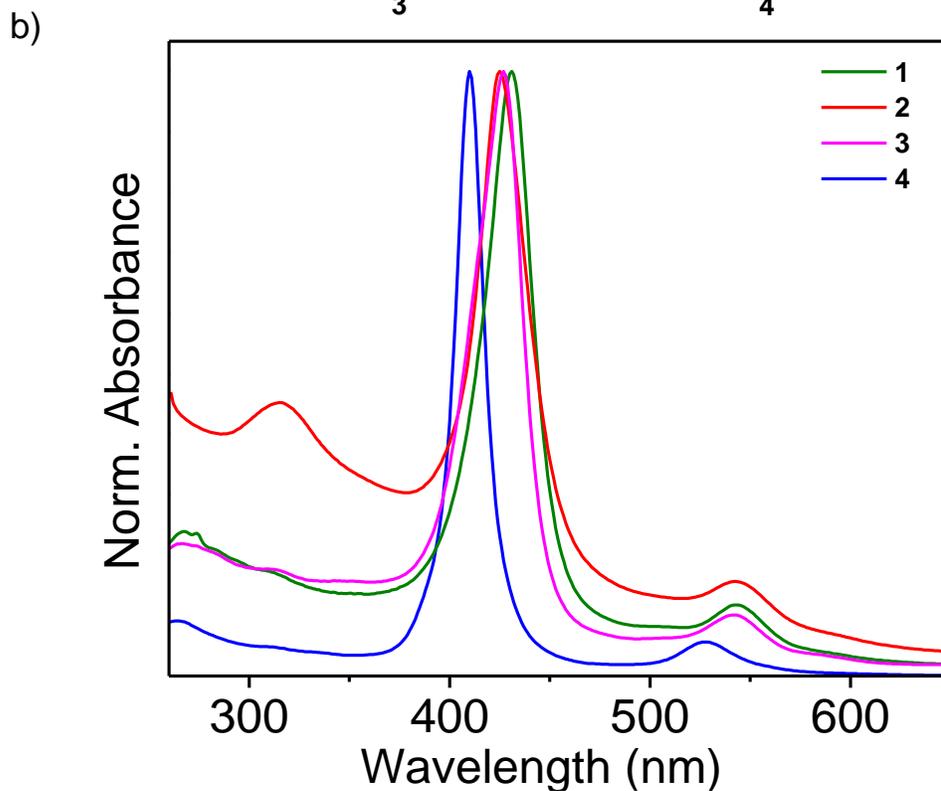
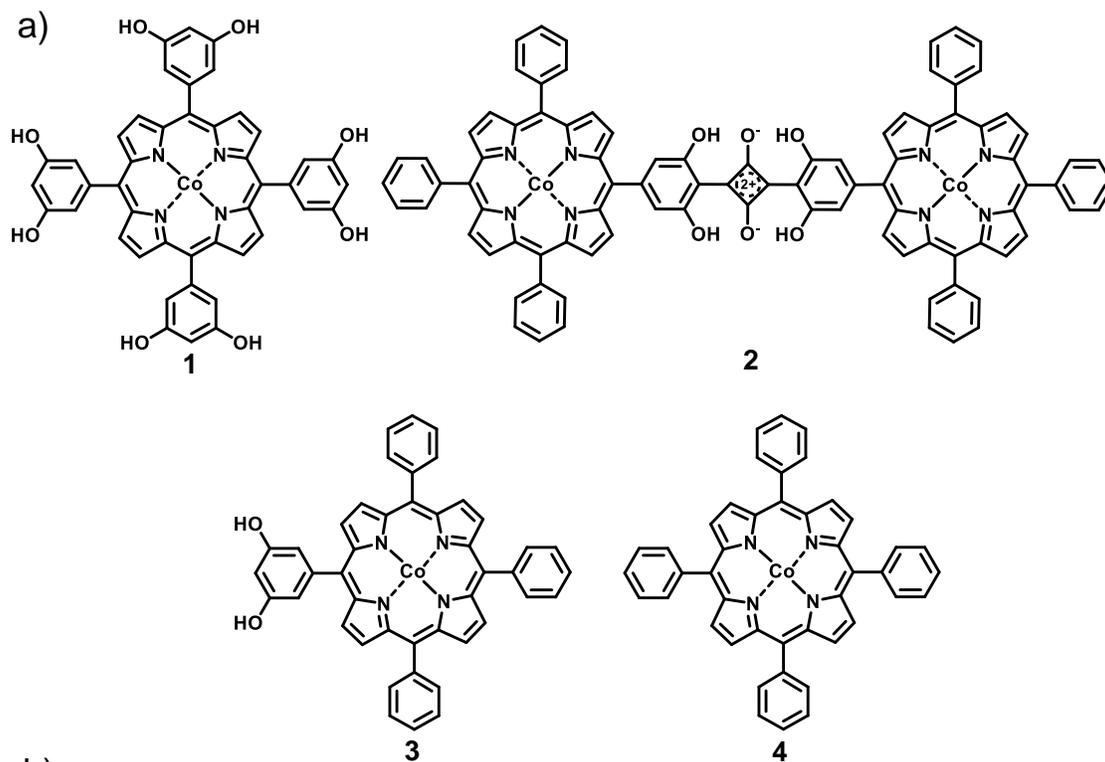


Figure S1. a) Chemical structure and b) normalized solution state absorption spectrum of the supporting catalysts **1-4** (**1** and **3** in MeOH, **2** in THF, **4** in DCM).

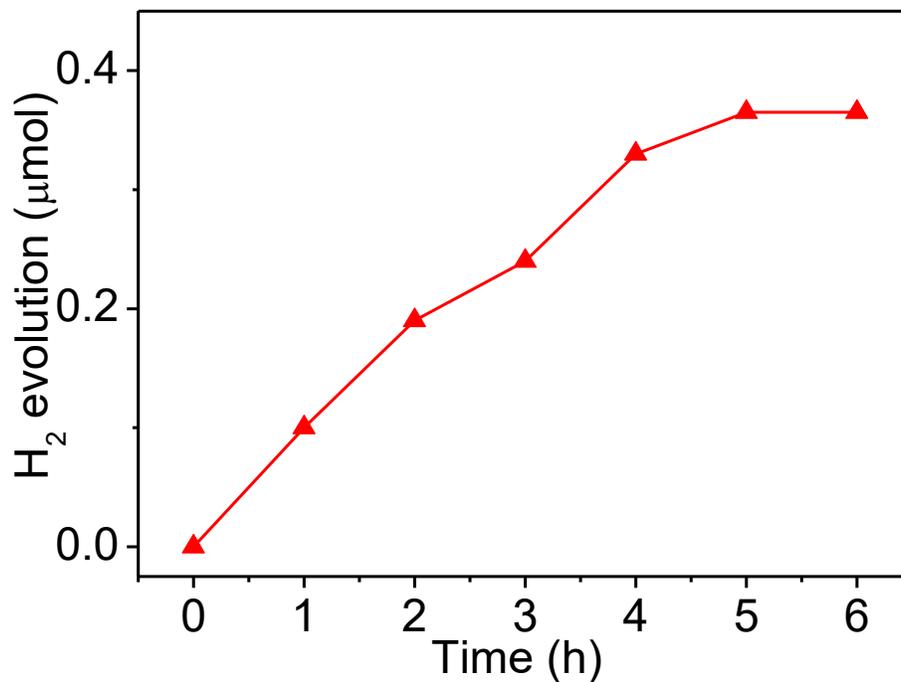


Figure S2. Photocatalytic water splitting performance of **2DP** catalyst showing H₂ evolution (5 mg **2DP**, 5 mL MeOH, 10 mL H₂O) under visible light illumination ($\lambda > 420$ nm) using photoreactor for 6 h.

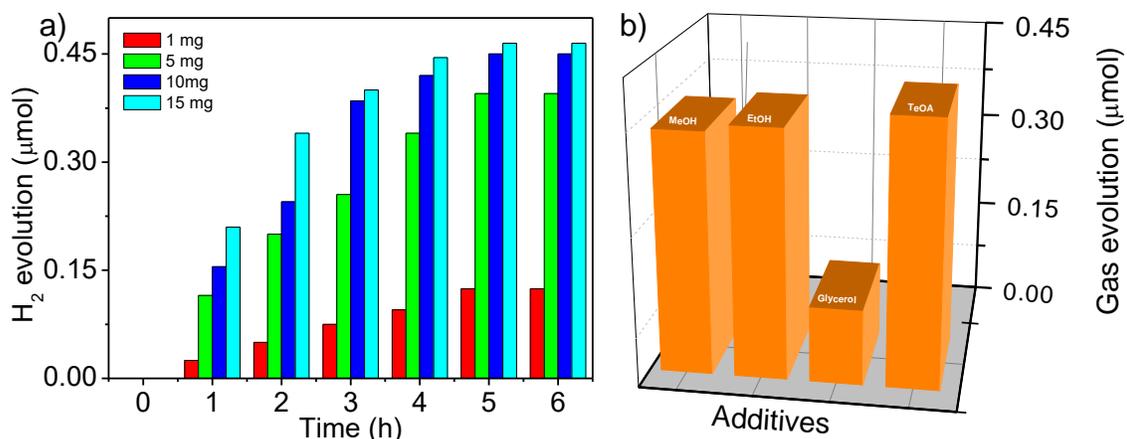


Figure S3. Optimization of H₂ evolution performance of **2DP** from water (10 mL) using a) varying amounts of **2DP** catalyst and b) various additives such as MeOH, EtOH, Glycerol and TEOA (5 mL) under visible light irradiation ($\lambda > 420$ nm) using photoreactor for 6 h.

Variation of the catalyst amount clearly showed a steady increase in HER yield upon increasing the loading of **2DP** catalyst from 1 mg to 5 mg, whereas further increase exhibited only a slight increase in the respective yields. Hence 5 mg of the catalyst is finalized as the optimum catalyst loading.

When HER was repeated with additives such as methanol (0.37 μmol), ethanol (0.38 μmol), glycerol (0.12 μmol) and triethanolamine (TEoA) (0.40 μmol), a significant variation of the amount of H₂ was observed and found that H₂ production was boosted by TEOA as sacrificial electron donor.

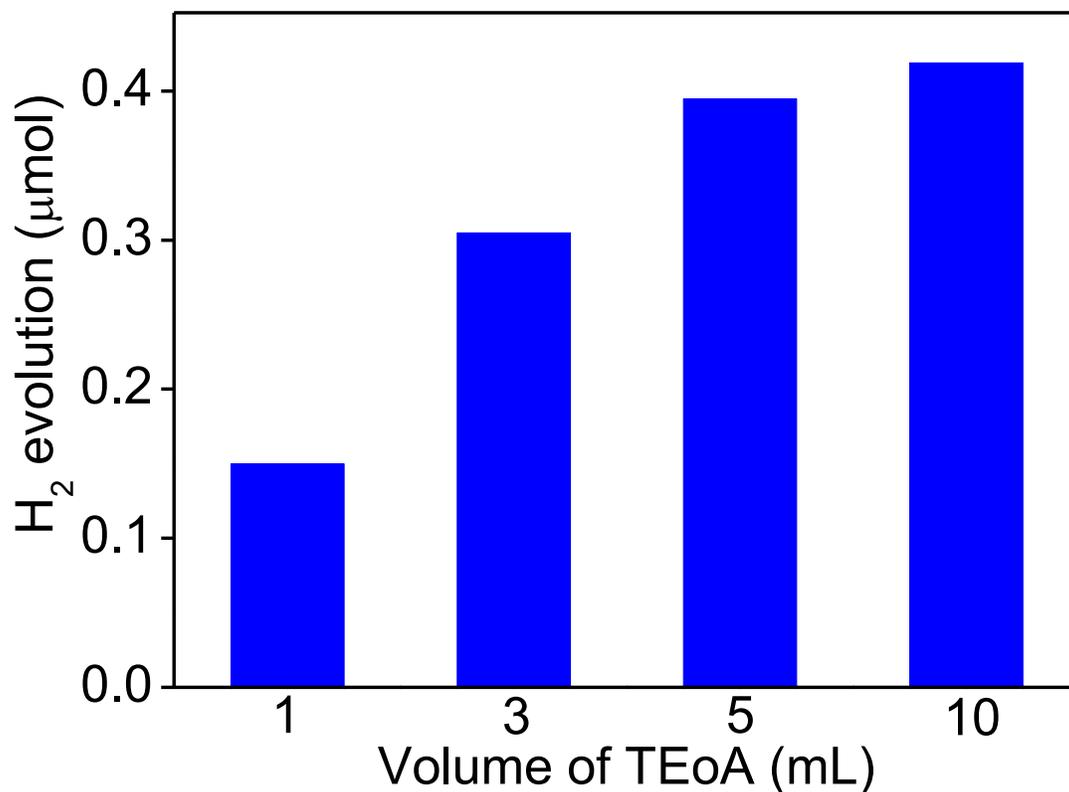


Figure S4. Optimization for volume of TEOA in H₂ evolution from water using **2DP** catalyst (5 mg **2DP**, 10 mL H₂O) under visible light illumination ($\lambda > 420$ nm) by photoreactor for 6 h.

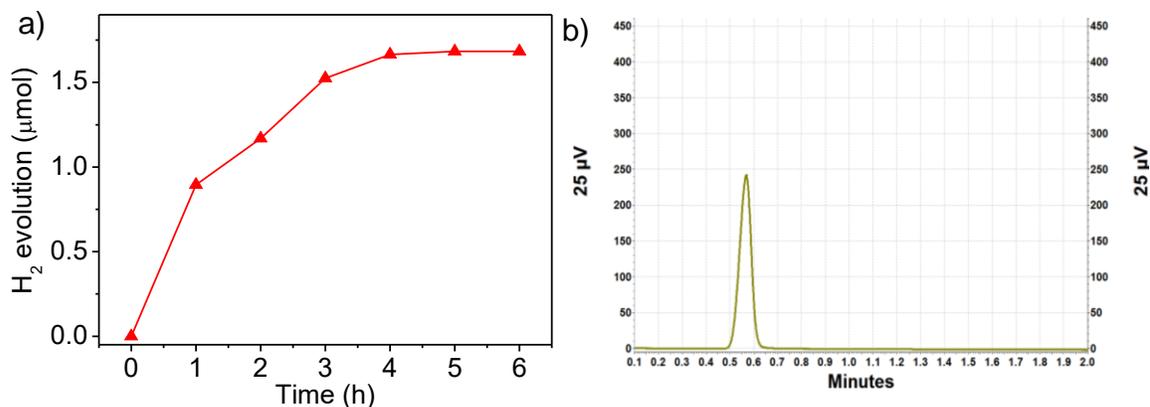


Figure S5. a) Photocatalytic HER performance of **2DP** (5 mg **2DP**, 5 mL TEOA, 10 mL H₂O) in the presence of Pt cocatalyst (1wt%, 50 μ l) under visible light irradiation ($\lambda > 420$ nm) using photoreactor for 6 h and b) corresponding chromatogram.

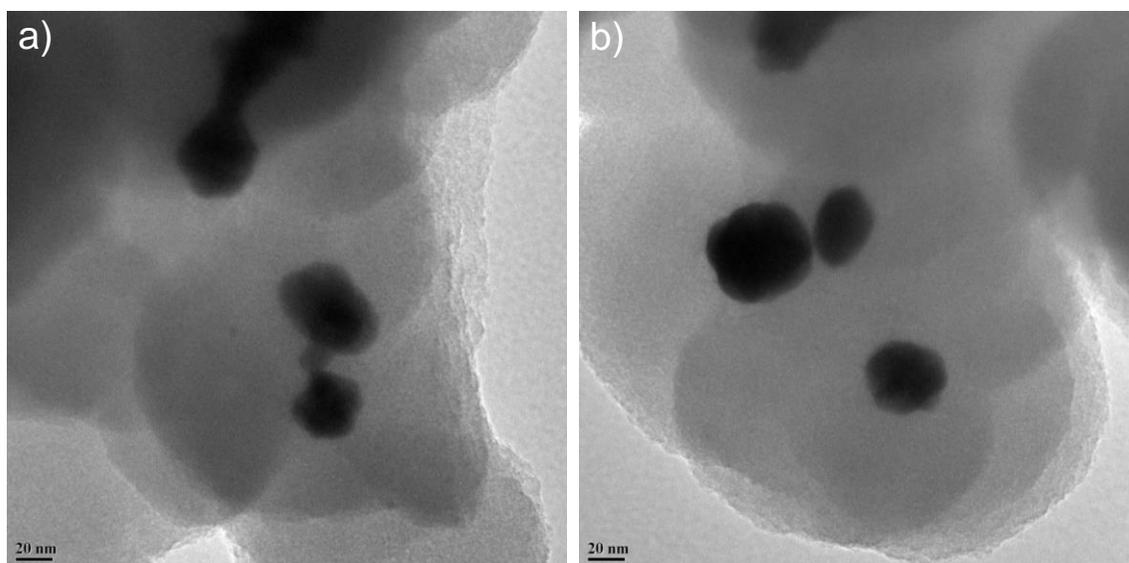


Figure S6. a), b) TEM image of the *in situ* formed Pt cocatalyst nanoparticles on the surface of **2DP** sheets drop casted on carbon coated Cu grid after photocatalytic experiments.

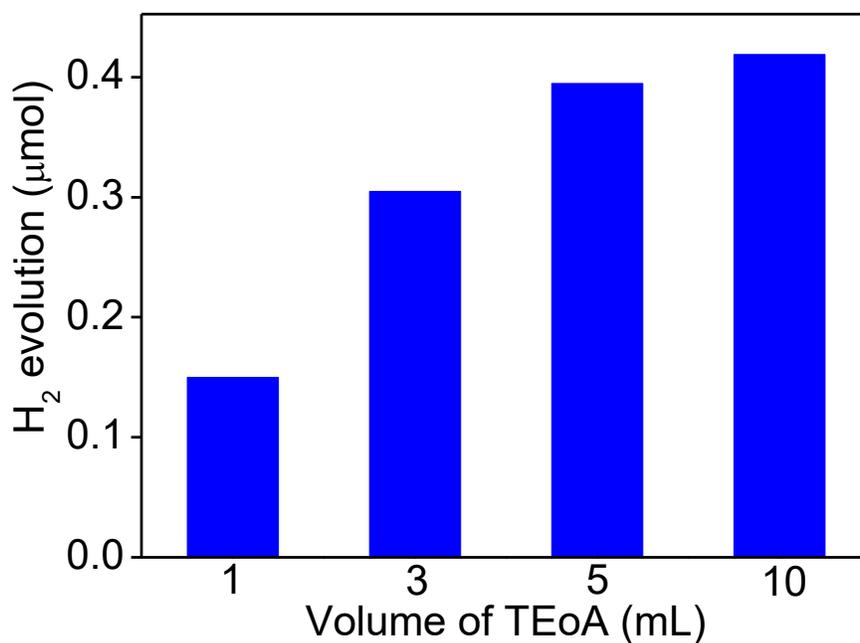


Figure S7. Photocatalytic water splitting performance of **2DP** catalyst showing O₂ (5 mg **2DP**, 10 mL H₂O) evolution under visible light illumination ($\lambda > 420$ nm) using photoreactor for 6 h.

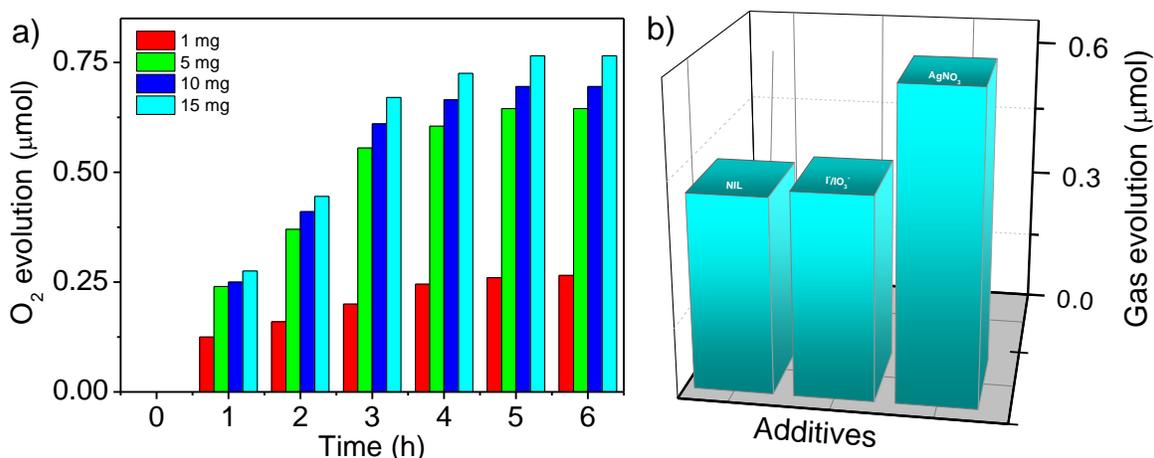


Figure S8. Optimization of O₂ evolution performance of **2DP** catalyst a) by varying amounts of **2DP** catalyst and b) using various additives such as I⁻/IO₃⁻ (5 mL), AgNO₃ (50 μL, 1 mmol) for OER under visible light illumination ($\lambda > 420$ nm) using photoreactor for 6 h.

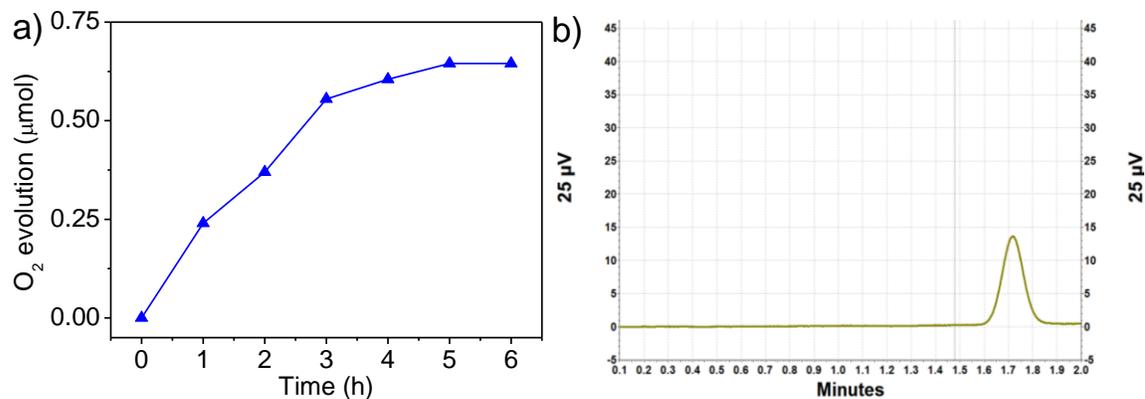


Figure S9. a) Photocatalytic performance of **2DP** showing O₂ evolution (5 mg **2DP**, 5 mL TEOA, 10 mL H₂O) in the presence of AgNO₃ (1 mmol, 50 μL) under visible light irradiation ($\lambda > 420$ nm) using photoreactor for 6 h and b) corresponding chromatogram.

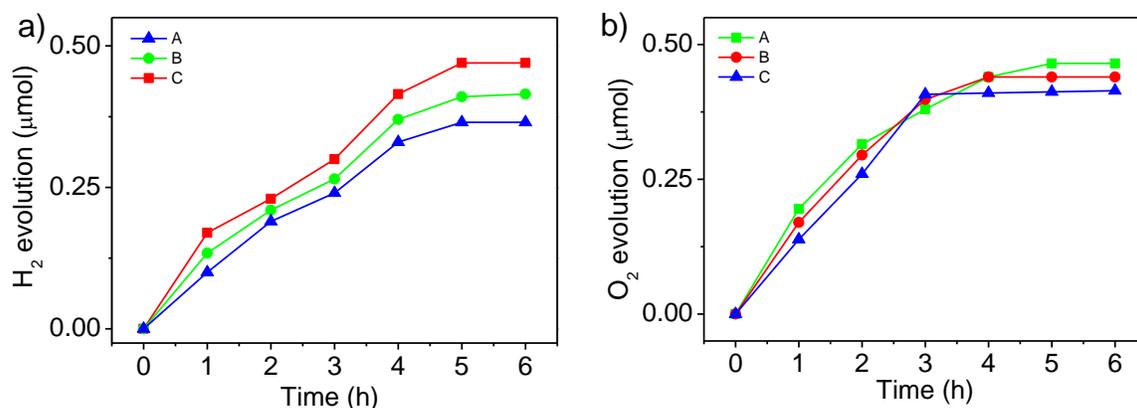


Figure S10. Time dependent a) HER (5 mg **2DP**, 5 mL MeOH, 10 mL H₂O) and b) OER (5 mg **2DP**, 10 mL H₂O) yield for **2DP** in the minimum additive condition under various visible light sources, A. photoreactor, B. solar simulator, C. sunlight.

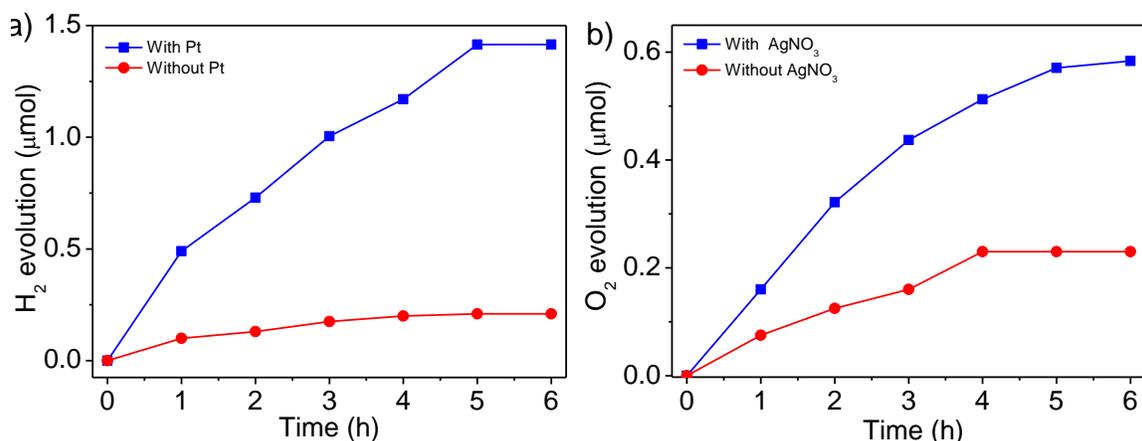


Figure S11. Comparison of the time dependent photocatalytic a) HER and b) OER yield for photocatalyst **1** in the presence and absence of Pt cocatalyst and AgNO₃, respectively, under visible light irradiation ($\lambda > 420$ nm) using photoreactor for 6 h.

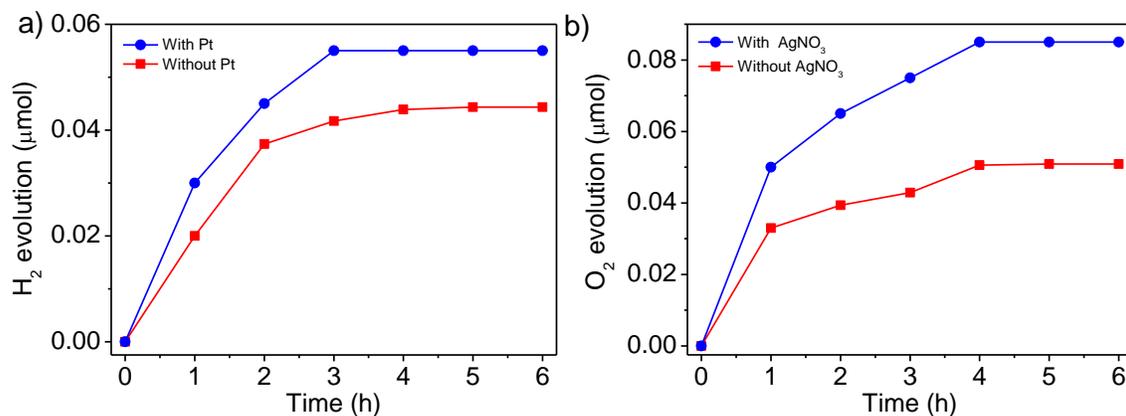


Figure S12. Comparison of the time dependent photocatalytic a) HER and b) OER yield for photocatalyst **2** in the presence and absence of Pt cocatalyst and AgNO₃, respectively, under visible light irradiation ($\lambda > 420$ nm) using photoreactor for 6 h.

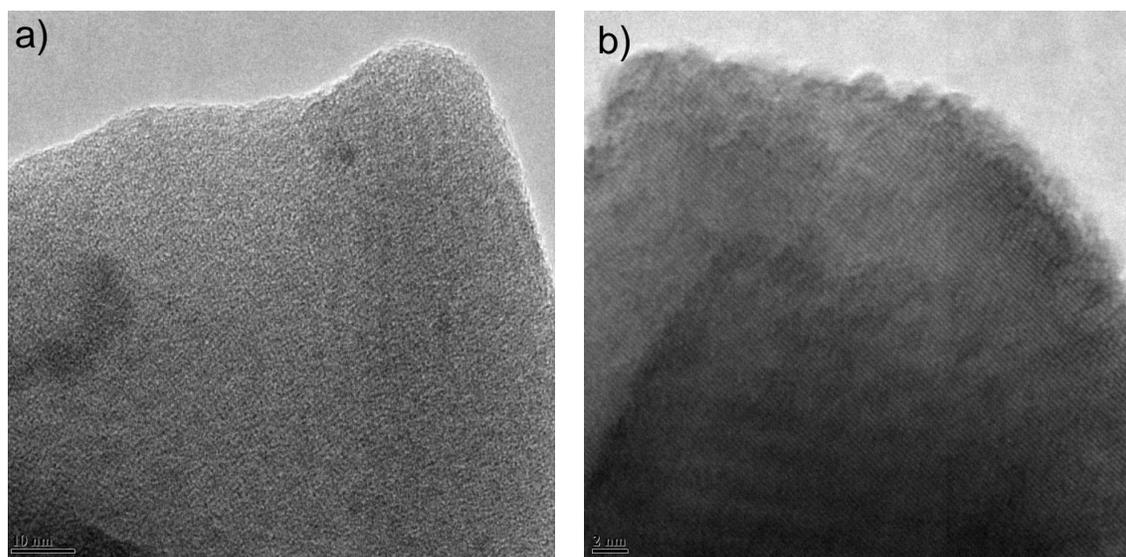


Figure S13. a), b) TEM image of the **2DP** after photocatalytic experiments upon drop casting onto carbon coated copper grid.

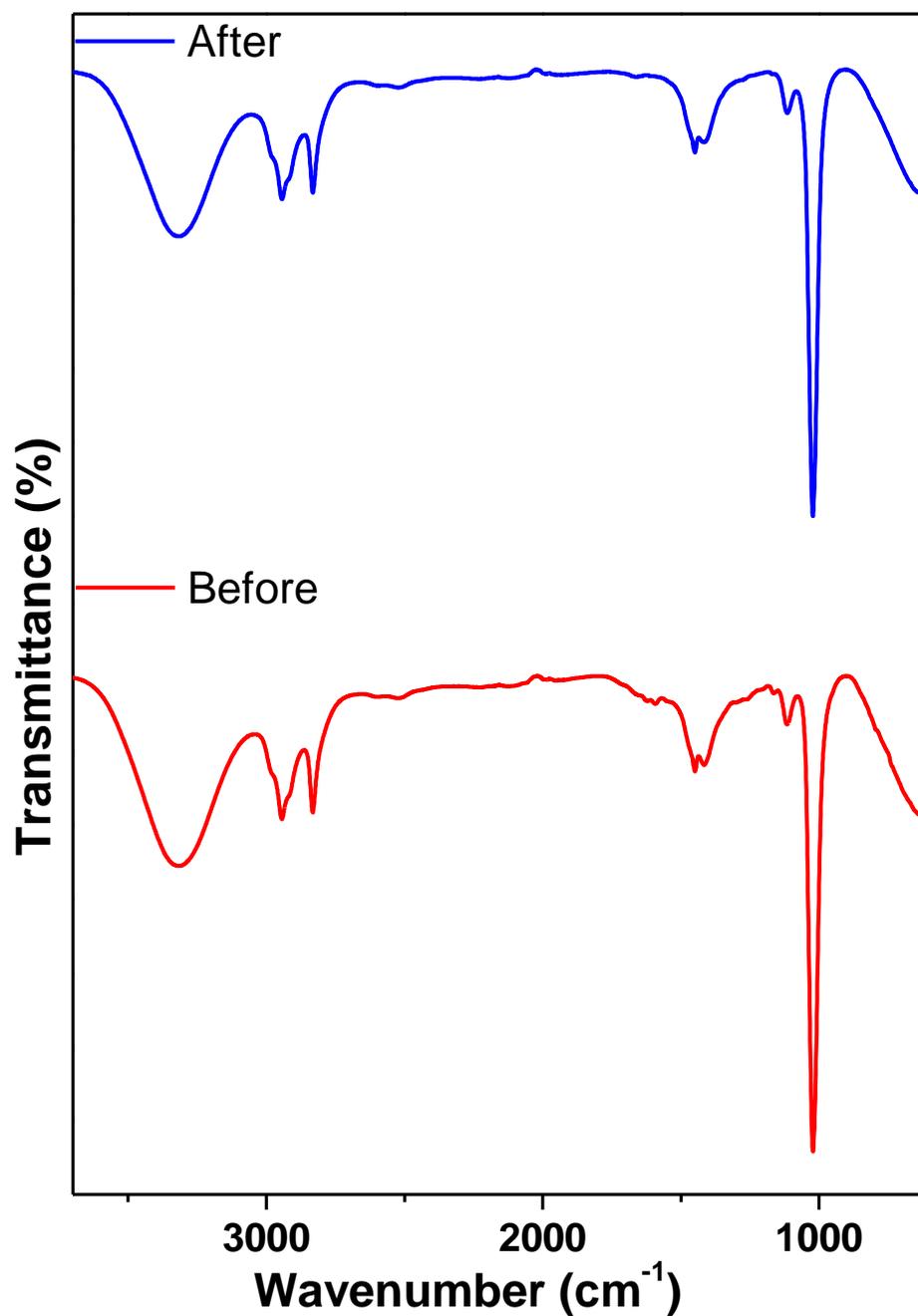


Figure S14. Solid state FT-IR spectrum of **2DP** in KBr before and after photocatalytic experiment.

Table S1. Optical band gap of **1-4** and **2DP**.

Sample	λ_{onset}	Band gap (eV)
1	571	2.17
2	629	1.97
3	575	2.16
4	559	2.22
2DP	683	1.82

4. References

- S1. B. Wu, K. Chen, Y. Deng, J. Chen, C. Liu, R. Cheng and D. Z. Chen, *Chem. Eur. J.* 2015, **21**, 3671-3681.
- S2. (a) A. Treibs and K. Jacob, *Angew. Chem. Int. Ed.* 1965, **4**, 694; (b) H.-E. Sprenger and W. Ziegenbein, *Angew. Chem. Int. Ed.* 1968, **7**, 530-535.
- S3. T. Tanaka, K. Endo and Y. Aoyama, *Bull. Chem. Soc. Jpn.* 2001, **74**, 907-916.