

Supporting Information

Solar driven CO₂ reduction with a molecularly engineered periodic mesoporous organosilica containing cobalt phthalocyanine

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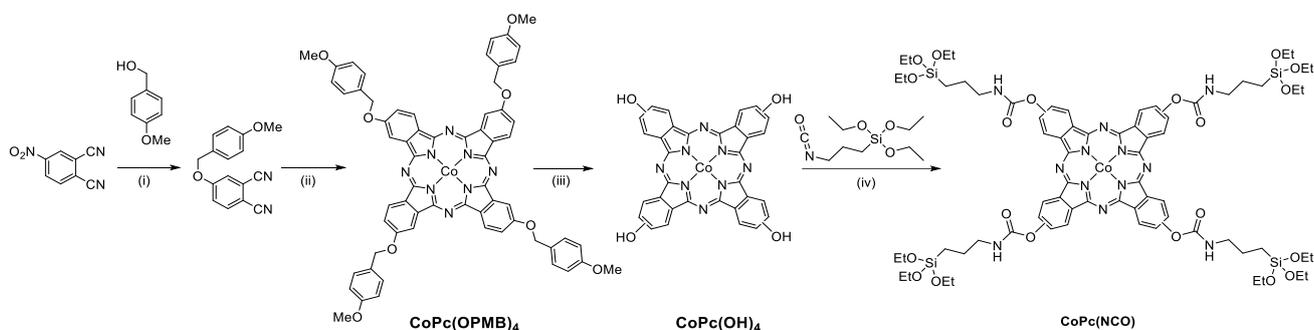
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General Methods and Instrumentation

All chemicals were purchased from commercial suppliers (Fluorochem, Merck and Panreac) and used without further purification. X-ray powder diffraction (XRD) patterns were collected in a Bruker D8 Discover A25 diffractometer using Cu K α radiation (40 kV and 30 mA) from 0.5 to 5.0 (2 θ). Transmission electron microscopy images were obtained using a JEOL JEM 1400 microscope, operating at 300 kV. For TEM measurements, isopropanol solutions of the samples were drop-casted on carbon-coated microgrids (Holey Carbon Film 200) and then dried. N₂ adsorption-desorption isotherms were obtained at -196 °C using Micromeritics ASAP 2020 V4.04J instrument. Prior to measurement, the sample was outgassed overnight at 100 °C. Surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. ATR- and FT-IR measurements were carried out on a Perkin-Elmer 2000 FTIR spectrometer. UV-Vis spectra were recorded on a UV-visible diffuse reflectance spectrophotometer Varian Carey IE UV-vis equipped with a 60 mm integration sphere. X-ray photoelectron spectroscopy (XPS) was performed on a SPECS Phoibos HAS 3500 150 MCD X-ray photoelectron spectrometer with a monochromatic Al anode (1486.7 eV). Accurate binding energies were determined with respect to the position of C 1s peak at 284.4 eV. The charge neutralization function was employed during the measurement to compensate for accumulated charge in solid samples by X-ray irradiation. Inductively coupled plasma mass spectrometry (ICP-MS) for the isotope ⁵⁹Co was performed using a NexION 350X spectrometer. Prior to the measurement, the sample was digested in an UltraWave microwave system. Photocatalysis experiments were performed using a SciSun-LP-150 solar simulator from ScienceTech, equipped with an air mass 1.5 global filter (AM 1.5G) and a UV-filter (>400 nm) unless mentioned otherwise. The quantification of H₂ and CO was conducted using an SRI gas chromatograph (multiple gas analyser #1) equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID) with a built-in methaniser attachment. A silica gel column

(6 ft) column was used to block CO₂ and H₂O, and molecular sieve 13X (6 ft) main column was used to separate H₂ and CO. N₂ was used as the carrier gas at 23 psi pressure. The GC was calibrated regularly using a known standard for H₂, CO and CH₄ (2000 ppm H₂ / 2000 ppm CO / 2000 ppm CH₄ in balance gas N₂). A representative gas chromatogram obtained during photocatalysis is shown in Fig. S11.

Synthetic procedures



Scheme S1. Synthesis of CoPc(NCO) complex : (i) K₂CO₃, DMSO, 50 °C, 16 h; (ii) Co(OAc)₂, DBU, 1-pentanol, 160 °C, 16 h, N₂; (iii) TFA, CH₂Cl₂, r.t., 3h; (iv) acetone, r.t., 3 days, N₂.

Synthesis of cobalt phthalocyanine bridged alkoxy silane precursor (CoPc (NCO)). The synthesis of CoPc(NCO) is shown in Scheme S1. 4-((4-Methoxybenzyl)oxy)phthalonitrile was synthesised from 4-nitrophthalonitrile following published procedure.¹

CoPc(OPMB)₄: 4-((4-Methoxybenzyl)oxy)phthalonitrile (1.30 g, 5 mmol) was suspended in 1-pentanol (30 mL) in a three-necked round bottom flask, purged with N₂ for 30 min and stirred for 10 min. Co(OAc)₂·4H₂O (2 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2 mmol) was added to the reaction flask under N₂ and the reaction mixture was heated at 160 °C for 16 h. After cooling to room temperature, CH₃OH (20 mL) was added to the reaction mixture and the precipitated solid was collected by filtration. The solid was extracted with CH₂Cl₂ and concentrated under reduced pressure to give a dark blue solid. The solid was dissolved in 15-20 mL CH₂Cl₂ and poured over ~ 50 mL ether. The dark solid was collected by filtration and washed sequentially with water, 0.1 M HCl, water, methanol, and acetone/methanol mixture (1:1) to give CoPc(OPMB)₄ as a dark blue solid. Yield: 0.6 g (43%). ESI-MS (+): m/z calculated for C₆₄H₄₈CoN₈O₈⁺ 1115.2327, found 1115.2930. UV-vis, λ_{max} (nm) (ε, M⁻¹ cm⁻¹) (DMF): 330 (5.5×10⁴), 672 (7.8×10⁴). ATR-IR (cm⁻¹): 1609, 1530, 1458, 1407, 1376, 1340, 1237, 1173, 1096, 1029 (br), 811, 750.

CoPc(OH)₄: CoPc(OPMB)₄ (550 mg, 0.5 mmol) was dissolved in CH₂Cl₂ (20 mL) followed by addition of trifluoroacetic acid (TFA, 6 mL) under stirring. After 3 h, the solvent was removed under reduced pressure and the residue was washed thoroughly with water and ether till washings were colourless. The crude solid was dissolved in CH₃OH (50 mL), filtered, and concentrated under reduced pressure to 5 - 10 mL. The dark blue solution was poured over ether to yield a dark blue solid. The product **CoPc(OH)₄** was collected by filtration and washed with ether. Yield: 0.15 g (47%). ESI-MS (+): m/z calculated for C₃₂H₁₆CoN₈O₄⁺ 635.0626, found 635.0655. UV-vis, λ_{max} (nm) (ε, M⁻¹ cm⁻¹) (DMF): 680 (6.7×10⁴). ATR-IR (cm⁻¹): 3177 (br), 1590, 1480, 1394, 1299, 1250, 1186, 1068 (br), 870 (w), 830, 751.

CoPc(NCO): CoPc(OH)₄ (100 mg, 0.157 mmol) was dissolved in 20 mL of anhydrous acetone under N₂ atmosphere. The green dark solution was stirred at room temperature during 30 min.

Afterwards, 3-(triethoxysilyl)propyl isocyanate (0.165 mL, 0.628 mmol) was slowly added dropwise to the solution under N₂ atmosphere, and it was kept under stirring at room temperature for 3 days. The reaction was monitored through the disappearance of the isocyanate vibration band ($\nu_{\text{N=C=O}}$ 2265 cm⁻¹) together with the appearance of the urethane band ($\nu_{\text{C=O urethane}}$ 1710 cm⁻¹) by ATR-FTIR spectroscopy (Fig. S2).

BIH Synthesis.² To a solution of 2-phenylbenzimidazole (4 g, 20 mmol) and NaOH (1 g, 25 mmol) in absolute MeOH (120 mL), methyl iodide (17.6 mL, 282.7 mmol) was added slowly. The mixture was heated overnight (16 h) at 110 °C in a pressure tube. After cooling the reaction mixture, the solvent was removed under reduced pressure and the crude product was washed with a small amount of acetone. Recrystallisation from absolute ethanol yielded pale yellow crystals of 1,3-dimethyl-2-phenylbenzo[d]imidazolium iodide (3.5 g). ¹H NMR (methanol-d₄): δ = 8.01 (m, 2H), 7.77-7.87 (m, 7H), 3.97 (s, 6H).

The methylated phenylbenzimidazol salt (2.1 g, 6 mmol) was dissolved in 60 mL dry MeOH and NaBH₄ (1.2 g) was added slowly in small portions over 15 min. The reaction mixture was stirred for 1 h under N₂ to form a white suspension. After removal of the solvent, the residue was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over anhydrous MgSO₄ and concentrated under vacuum to give a white solid. The crude product was recrystallized from absolute ethanol to give white crystal (0.75 g). ¹H NMR (CDCl₃): δ 2.58 (s, 6H), 4.98 (s, 1H), 6.52 (m, 2H), 6.77 (m, 2H), 7.44 (m, 3H), 7.60 (m, 2H).

Quantum yield determination.

The quantum yield for the photocatalytic CO₂ reduction was determined using the following equation:

$$\phi(\%) = \frac{\text{CO evolution rate (mol s}^{-1}\text{)}}{\text{photon flux rate (Einstein s}^{-1}\text{)}} \times 100\%$$

CO evolution rate was determined using gas chromatograph and the incident photon flux was measured using potassium ferrioxalate as a standard chemical actinometer.

For actinometry, 4 mL (V₁) of an aqueous solution containing the iron actinometer (6.5 mM) in H₂SO₄ (0.15 M) was irradiated with blue LED (LEDXON blue LED 467 nm). During photoreduction, aliquots of 0.25 ml (V₂) were collected at 30 s intervals (0-150 s) and 2 mL of a buffered solution of phenanthroline (2 mg ml⁻¹ in 1 M NaOAc buffer) was added. The mixture was diluted to 25 mL (V₃) with deionised water H₂O. The absorbance of the solutions at 510 nm were recorded. The rate of Fe²⁺ production ($\Delta n(\text{Fe}^{2+})/\Delta t$) from photoreaction was determined from the slope of absorbance (510 nm) versus time (s), using the following equation:

$$\frac{\Delta n(\text{Fe}^{2+})}{\Delta t} = \frac{V_1 \times V_3}{1000 \times V_2 \times \epsilon_{510 \text{ nm}}} \times \frac{\Delta A}{\Delta t}$$

where ($\Delta A/\Delta t$) represent the slope of A_{510nm} vs. t plot (Fig. S5) and $\epsilon_{510 \text{ nm}}$ the extinction coefficient for Fe²⁺-phenanthroline complex at 510 nm (11100 M⁻¹ cm⁻¹).

The incident photon flux per second is calculated using the following equation:

$$I_{467 \text{ nm}} = \frac{\Delta n(\text{Fe}^{2+})}{\phi_{467 \text{ nm}} \times \Delta t}$$

where, $\phi_{467 \text{ nm}}$ is the reported quantum yield of ferrioxalate actinometer at 467 nm (0.93).

Using this method, the final value for the rate of photon flux of the incident light from the blue LED (I_{467 nm}) was determined to be (1.27 × 10⁻⁷) Einstein s⁻¹.

To determine the quantum yield, a colloidal suspension of MeCN/TEOA (4:1 v/v) (4.0 mL) containing CoPc-PMO (2 mg, $2.7 \mu\text{mol Co mg}^{-1}$), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (0.50 mM) and BIH (10 mM) was irradiated with LEDXON blue LED ($\lambda = 467 \text{ nm}$) under identical condition. The CO evolution was monitored using a gas chromatograph from SRI GC and the time course for CO formation over 1.5 h is shown in Fig. S6.

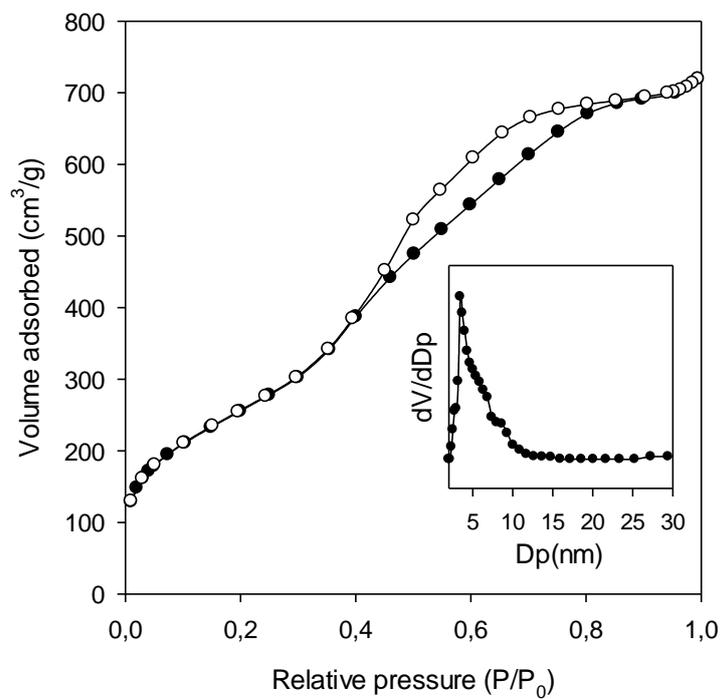


Fig. S1 N₂ adsorption-desorption isotherm and pore size distribution (inset) of CoPc-PMO.

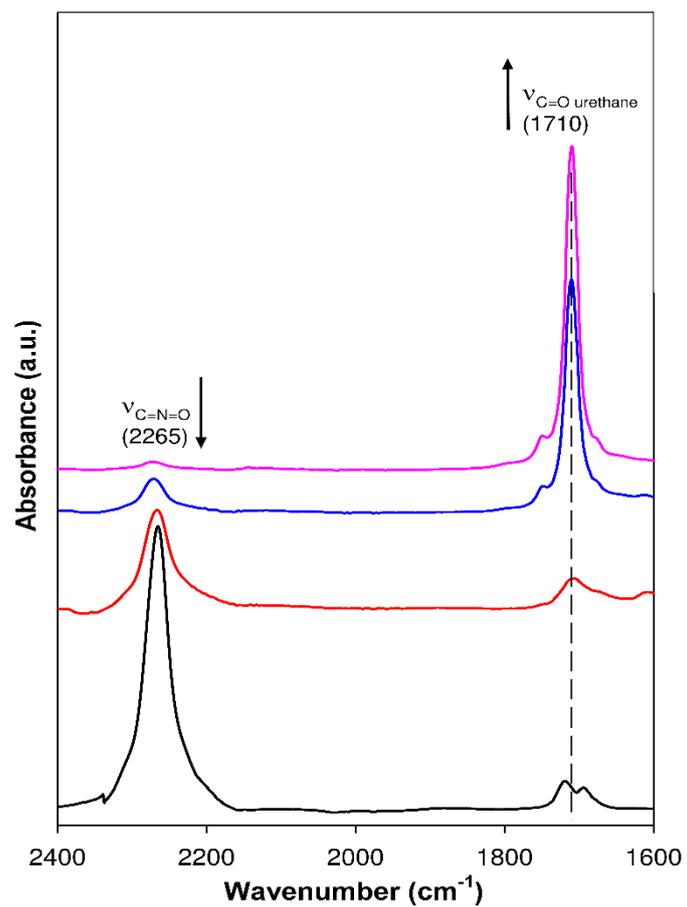


Fig. S2 ATR-FTIR spectrum of 3-(triethoxysilyl)propyl isocyanate (black line) and ATR-FTIR monitoring of the reaction of 3-(triethoxysilyl)propyl isocyanate and CoPc(OH)₄ after 12 h (red line), 24 h (blue line) and 72 h (pink line).

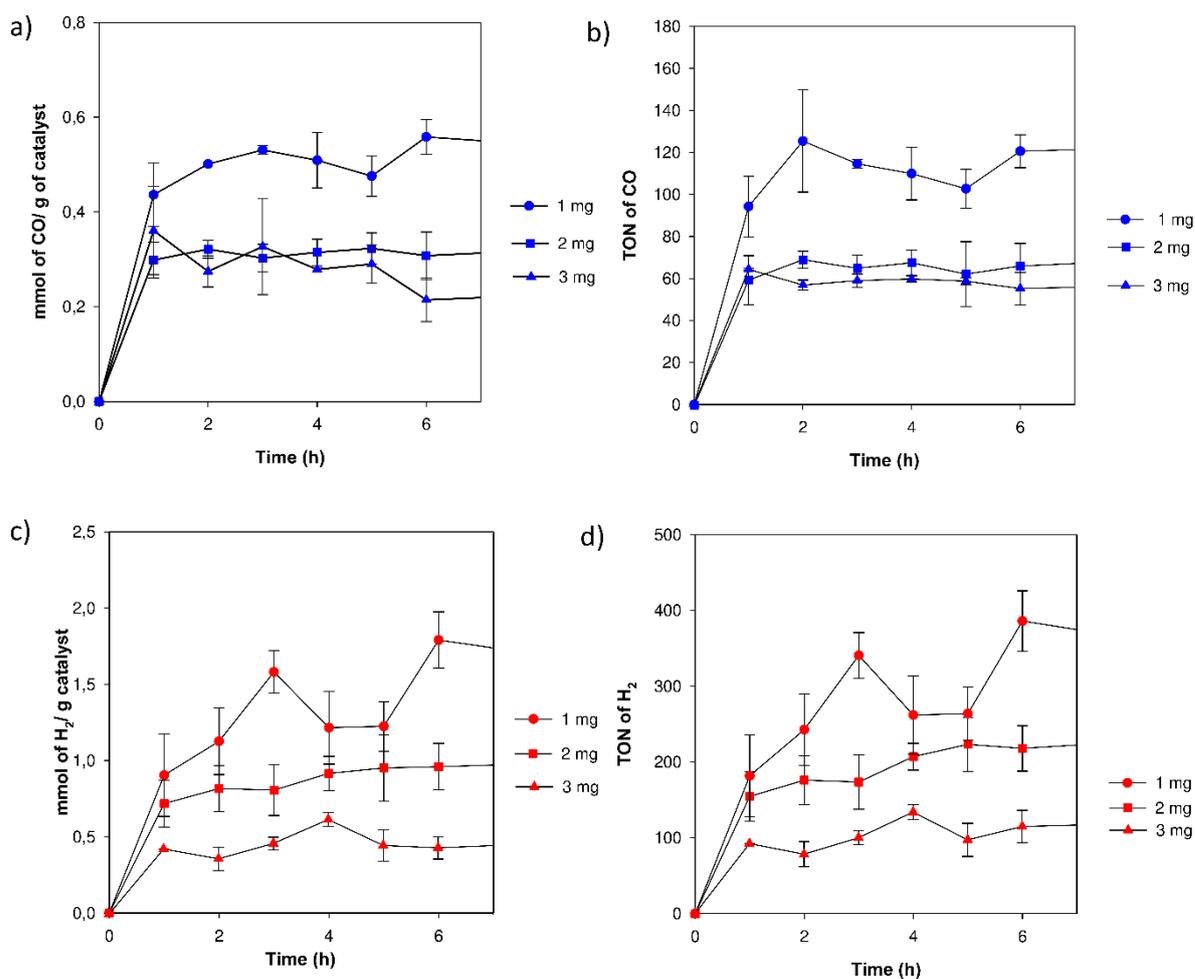


Fig. S3 Photocatalytic CO₂ reduction with different amount of CoPc-PMO catalyst (1-3 mg) under unfiltered UV-visible irradiation: (a-b) CO evolution trace and corresponding TONs, and (c-d) H₂ evolution trace and corresponding TONs. Condition: 1-3 mg CoPc-PMO, 4 ml MeCN/TEOA (4:1), Ru(bpy)₃²⁺ (0.5 mM), UV-visible light irradiation (100 mW cm⁻², AM 1.5G, λ > 300 nm), and CO₂ saturated condition.

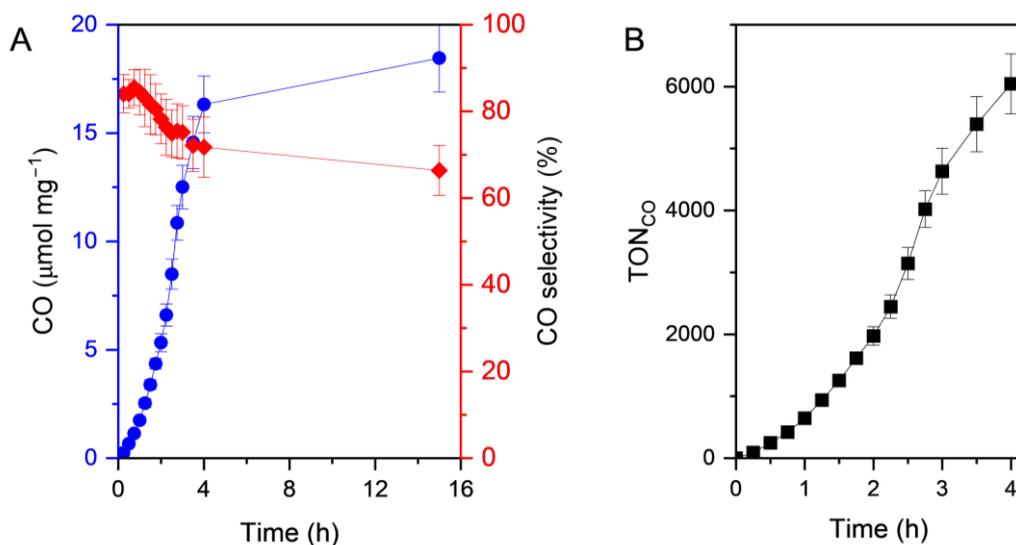


Fig. S4. Photocatalytic CO_2 reduction using CoPc-PMO with $2.7 \mu\text{mol Co}$ loading per gram. (A) Time course for CO evolution and CO selectivity during 16 h reaction, and (B) corresponding Co-based turnover number for CO evolution (TON_{CO}) during the first four hours of irradiation. Condition: 1 mg CoPc-PMO, 4 mL 4:1 MeCN/TEOA (v/v), $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.50 mM), BIH (10 mM), visible light irradiation (100 mW cm^{-2} , AM 1.5G, $\lambda > 400 \text{ nm}$), and CO_2 saturated condition.

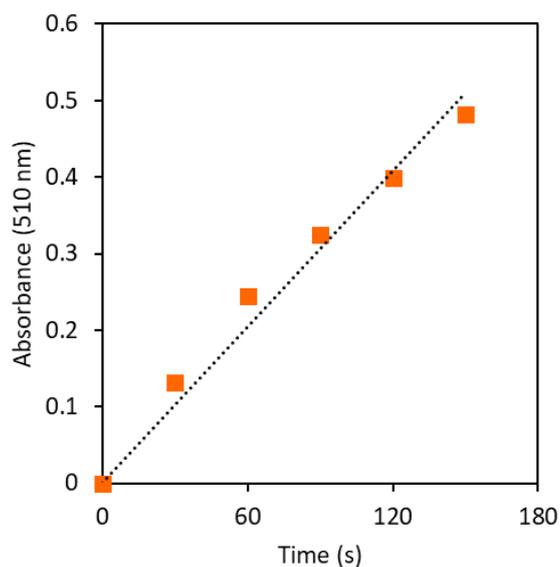


Fig. S5 Time course of absorbance at 510 nm for Fe^{2+} -phenanthroline complex obtained after photoreduction of the chemical actinometer (ferrioxalate) under blue LED irradiation (467 nm). The slope of the linear fit is $3.3 \times 10^{-3} \text{ s}^{-1}$.

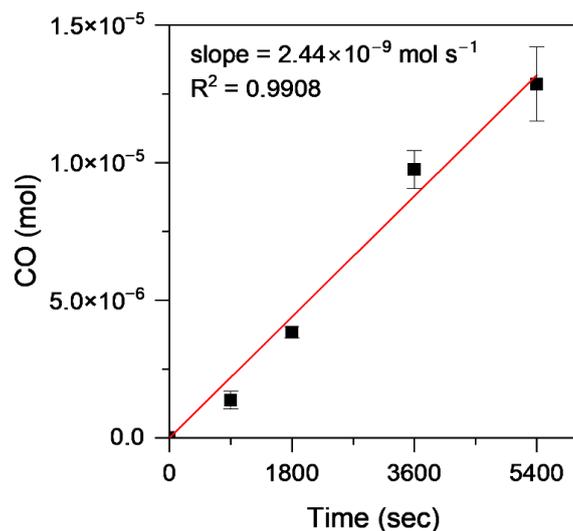


Fig. S6 Time course of CO production for the quantum yield determination in the photocatalytic reaction by irradiation (467 nm) of a MeCN/TEOA (4.0 mL, 4:1 v/v) containing CoPc-PMO (2 mg), [Ru(bpy)₃]²⁺ (0.50 mM) and BIH (10 mM) under CO₂ atmosphere.

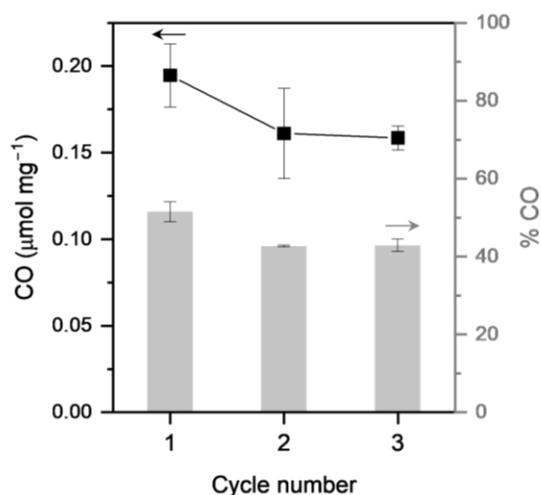


Fig. S7 Recycling experiment with CoPc-PMO in the absence of BIH donor. CO evolved (black trace) and %CO selectivity (grey bar) during three 1-h recycling run is shown. Condition: CO₂-saturated 4:1 MeCN/TEOA, ~ 2 mg PMO-CoPc, 0.5 mM [Ru(bpy)₃]²⁺, and visible light irradiation (100 mW cm⁻², AM 1.5G, λ > 400 nm).

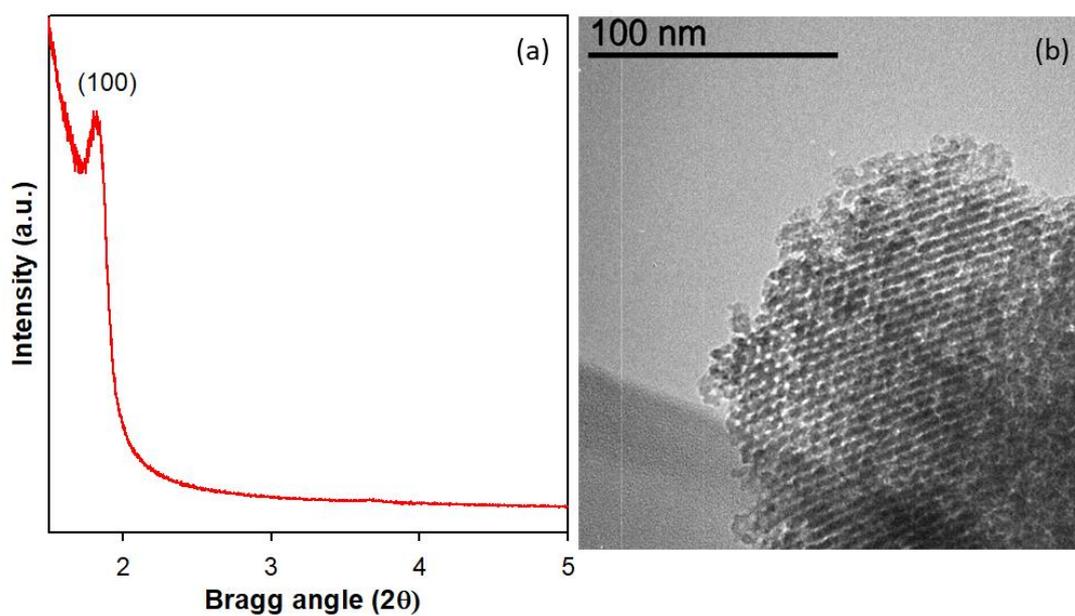


Fig. S8 Powder X-ray diffraction pattern (a) and TEM image (b) of CoPc-PMO catalyst after four catalytic cycles.

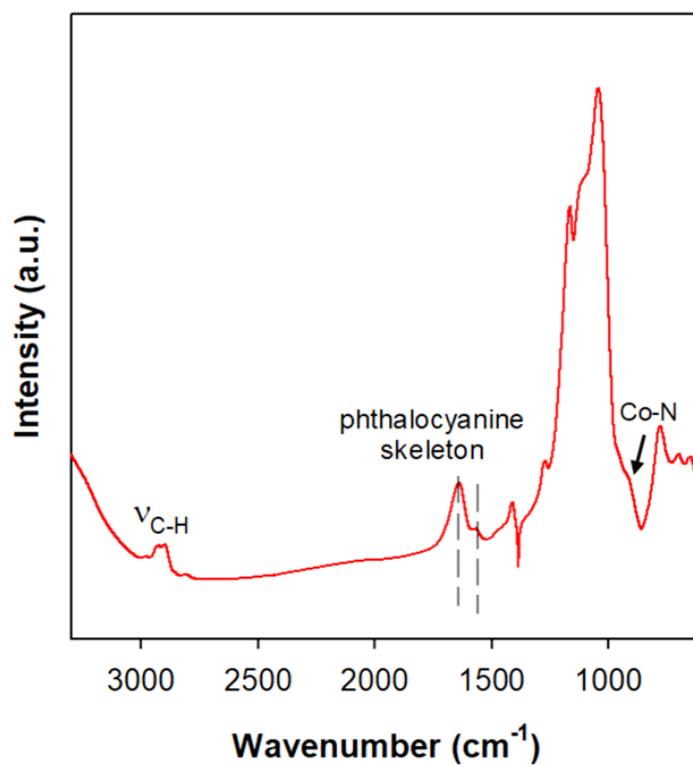


Fig. S9 FT-IR of CoPc-PMO after 4 cycles of reaction.

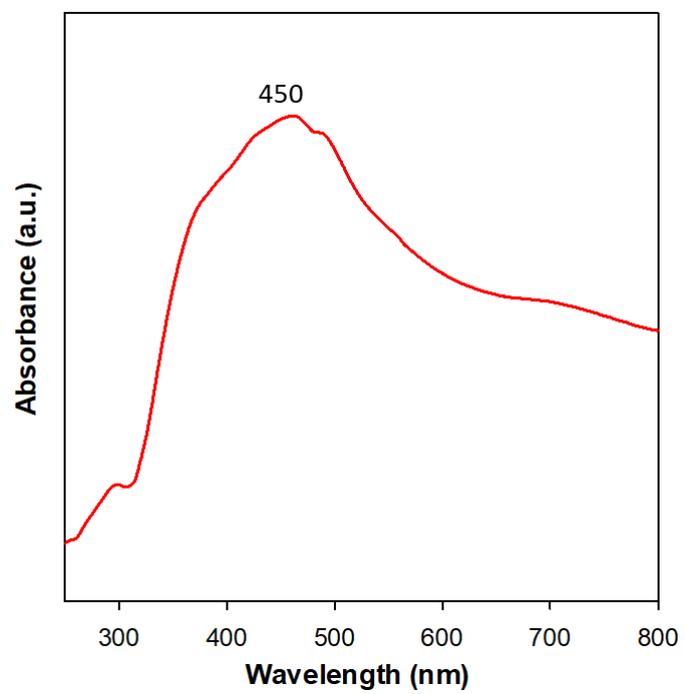


Fig. S10 UV-vis DRS of CoPc-PMO after 4 cycles of reaction.

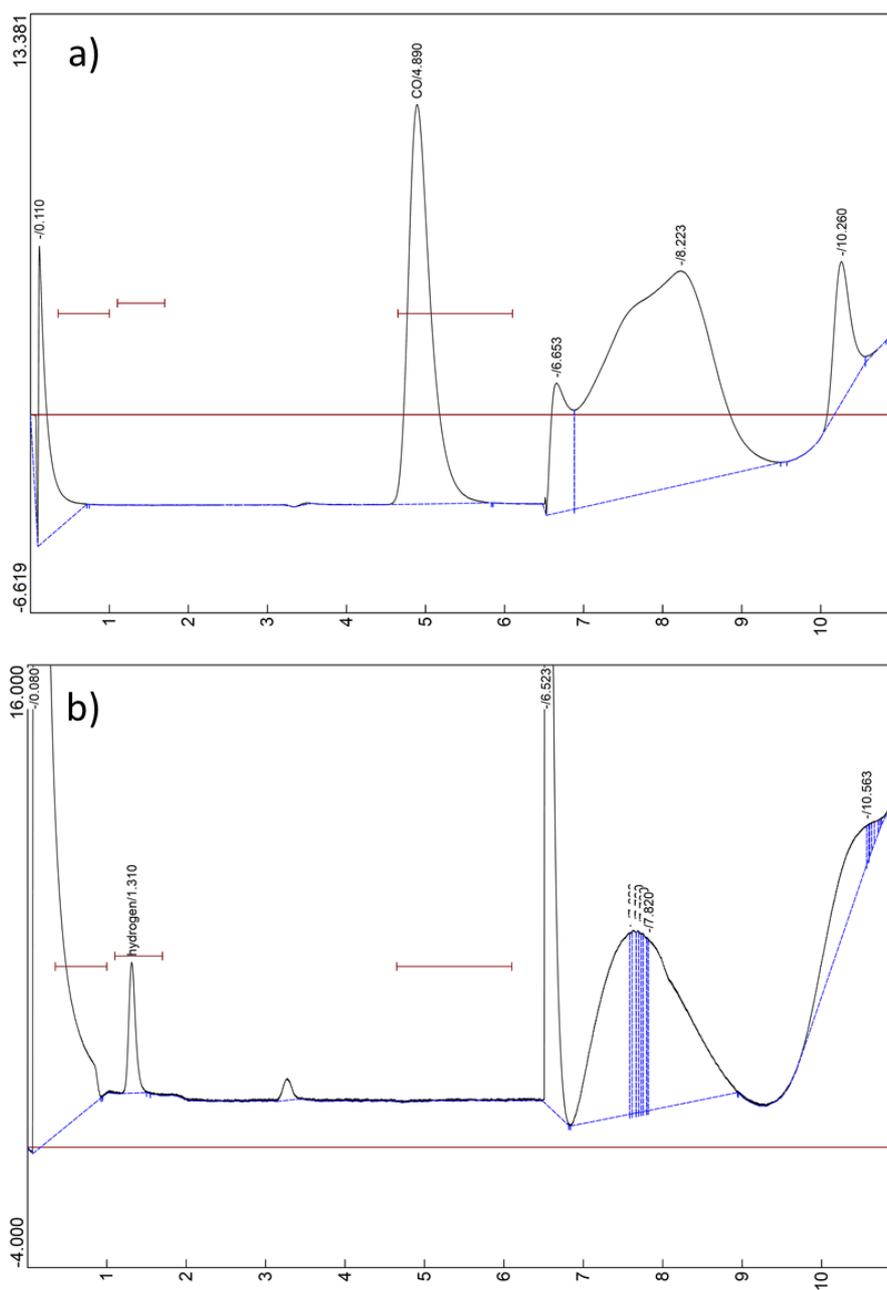


Fig. S11 Representative gas chromatogram of the headspace gas during photocatalysis with CoPc-PMO in the presence of $\text{Ru}(\text{bpy})_3^{2+}$ (0.5 mM) and BIH (10 mM) in MeCN/TEOA. The chromatograms from FID detector (a) and TCD detector (b) are shown. GC program with 11.1 min runtime: (1) column oven temperature held at 40 °C for 6.5 min, (2) column oven heated at a ramping rate of 50 °C min^{-1} till 220 °C (3.6 min), and (3) column oven held at 220 °C for 1 min.

References

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