Noncovalent Immobilization of a Molecular Iron Based Electrocatalyst on Carbon Electrodes for Selective, Efficient CO_2-to-CO Conversion in Water

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Supplementary Materials

1. Chemicals

All starting materials were obtained from Sigma-Aldrich, Fluka, or Alfa Aesar, and used without further purification. 1-pyrenebutanal was synthesized according to a literature procedure.[S1] $CHCl_3$ and CH_2Cl_2 were distilled from calcium hydride and stored under an argon atmosphere. N,N'-dimethylformamide was obtained from Acros (>99.8%, over molecular sieves). NBu_4BF_4 was obtained from Fluka (puriss.) and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance III 400-MHz spectrometer and were referenced to the resonances of the solvent used.

Synthesis of 1-pyrenebutanal

Pyridinium dichromate (411 mg, 1.1 mmol, 1.5 eq.) is suspended in freshly distilled CH_2Cl_2. 1-pyrenebutanol (200 mg, 0.73 mmol, 1 eq.), dissolved in freshly distilled CH_2Cl_2, is rapidly added to the suspension and the mixture is stirred overnight, under Ar, at room temperature. The reaction mixture is diluted with Et_2O (50 mL), and washed with water (2x20 mL) and brine (2x20 mL). The organic phase is then dried over $MgSO_4$, filtered and brought to dryness under reduced pressure. The crude product is further loaded on a silica plug and eluted with CH_2Cl_2. The pure product is isolated as a white powder (192 mg, 97%). ^{1}H NMR is consistent with the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, 1H, C*H*O) 8.29 (d, 1H, ArH_{pyrene}) 8.16 (m, 4H, ArH_{pyrene}) 8.04 (s, 2H, ArH_{pyrene}) 8.00 (t, 1H, ArH_{pyrene}) 7.85 (d, 1H, ArH_{pyrene}) 3.40 (t, 2H, RCH_2CH$_2$CH$_2$CHO) 2.58 (t, 2H, RCH$_2$CH$_2$CH_2CHO) 2.19 (q, 2H, RCH$_2$CH_2CH$_2$CHO) ; **^{13}C NMR** (100 MHz, $CDCl_3$) 202.28 (*C*HO) 135.64 (C_q pyrene) 131.57 (C_q pyrene) 131.04 (C_q pyrene) 130.20 (C_q pyrene) 128.90 (CH pyrene) 127.64 (CH pyrene) 127.62 (CH pyrene) 127.46 (CH pyrene) 126.94 (CH pyrene) 126.04 (CH pyrene) 125.28 (C_q pyrene) 125.14 (CH pyrene) 124.97 (CH pyrene) 123.36 (CH pyrene) 43.58 (RCH$_2$CH$_2$*C*H$_2$CHO) 32.74 (R*C*H$_2$CH$_2$CH$_2$CHO) 24.13 (RCH$_2$*C*H$_2$CH$_2$CHO).

Synthesis of 5,10,15-tris(2,6-dimethoxyphenyl)-20-(3-(pyren-1-yl)propyl)porphyrin (1)

2,6-dimethoxybenzaldehyde (460 mg, 2.8x10^{-3} mol, 3 eq.) and 1-pyrenebutanal (250 mg, 9x10^{-4} mol, 1 eq.) are dissolved in $CHCl_3$ (60mL). The solution is degassed with Ar for 15 min. Pyrrole (255 µL, 3.7x10^{-3} mol, 4 eq.) is added and the reaction mixture is protected from light. $BF_3.Et_2O$ (130 µL, 1.0x10^{-3} mol, 1.1 eq.) is then added and the reaction mixture is stirred at room temperature, under Ar, for 1 hour. 2,3-dichloro-5,6-dicyanobenzoquinone (830 mg, 3.7x10^{-3} mol, 3.7 eq.) is added to the dark purple solution. The reaction mixture is further stirred at room temperature overnight. Triethylamine (150 µl, 1.0x10^{-3} mol, 1.1 eq.) is added and the reaction mixture is stirred for an additional 30 min. The mixture is filtered over a pad of silica, and eluted with CH_2Cl_2. The solvents are removed under reduced pressure and the crude mixture of porphyrins is finally purified by column chromatography on silica ($CHCl_3$/EtOAc, 9:1). A purple solid is isolated (38 mg, 4 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, 2H, $H_{pyrrole}$), 8.66 (d, 2H, $H_{pyrrole}$), 8.56 (4H, q, $H_{pyrrole}$), 8.19-7.89 (9H, m, ArH_{pyrene}), 7.60 (3H, t, ArH_{para}), 6.92-6.88 (6H, 2d, ArH_{meta}), 5.06 (2H, t, CH_2), 3.73 (2H, t, CH_2), 3.42-3.41 (18H, 2s, OCH_3), 3.10 (2H, m, CH_2), -2.56 (2H, bs, N*H*) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 130.4, 130.2, 130.0, 127.4, 127.2, 125.0, 104.4, 56.1, 39.9, 35.1, 33.9 ; **UV-vis** (DCM) λ (ε) 266 (41575) 278 (57632) 329 (33267) 345 (39900) 419 (276722) 514 (13545) 548 (6459) 592 (5478) 648 (2654)

Synthesis of 5,10,15-tris(2,6-hydroxyphenyl)-20-(3-(pyren-1-yl)propyl)porphyrin (2)

Compound **1** (30 mg, 3.1x10^{-5} mol, 1 eq.) is dissolved in freshly distilled DCM (10 mL) and the solution is cooled to -20°C, and degassed under Ar. A 1 M solution of BBr_3 (630 µL, 6.3x10^{-4} mol, 20 eq.) is slowly added to the reaction mixture, and stirred at -20°C for 1h. The reaction mixture is stirred overnight at room temperature. The solution is then diluted with ethyl acetate (100 mL). The organic

phase is washed with saturated $NaHCO_3$ (2x50 mL), water (2x50 mL) and brine (2x50 mL). The organic phase is further dried with $MgSO_4$, and brought to dryness under reduced pressure. A purple solid is isolated (27 mg, 100 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.46 (d, 2H, $H_{pyrrole}$), 8.92 (m, 6H, $H_{pyrrole}$), 8.46-7.98 (m, 9H, ArH_{pyrene}), 7.61 (t, 3H, ArH_{para}), 6.95 (d, 6H, ArH_{meta}), 5.18 (bm, 2H, C$\underline{H_2}$), 4.88 (bs, 6H, O*H*) 3.90 (bm, 2H, C$\underline{H_2}$), 3.17 (bm, 2H, C$\underline{H_2}$), -2.70 (bs, 2H, N$\underline{H}$)

UV-vis (MeOH) λ (ε) 242 (73685) 277 (49898) 340 (38971) 351 (37981) 416 (272411) 514 (12850) 548 (4643) 590 (3668) 643 (919)

Synthesis of Iron(III) Chloride 5,10,15-tris(2,6-hydroxyphenyl)-20-(3-(pyren-1-yl)propyl)porphyrin ($\underline{CAT_{Pyr}}$)

Compound **$\underline{2}$** (20 mg, $2.3x10^{-5}$ mol, 1 eq.) is dissolved in freshly distilled MeOH (10 mL), and the solution is degassed under Ar. $FeBr_2$ (89 mg, $4.1x10^{-4}$ mol, 18 eq.) and 2,6-lutidine (7 µL, $5.7x10^{-5}$ mol, 2.5 eq.) are added to the solution. The reaction mixture is stirred overnight at 60°C. The solution is diluted with ethyl acetate (100 mL), and 1 M HCl is added. The organic phase is washed with 1 M HCl (2x50 mL), water (2x50 mL) and brine (2x50 mL). The organic phase is dried with $MgSO_4$, and brought to dryness under reduced pressure. A dark purple solid is isolated (20 mg, 91 %).

UV-vis (MeOH) λ (ε) 245 (23211) 280 (17142) 342 (17534) 416 (29814) 494 (4139)
555 (2267) 619 (1827) 658 (1702)

HRMS Calculated for $C_{57}H_{38}FeN_4O_6$ [M]+ m/z = 930.21 Found [M]+ m/z = 930.17

2. Methods and Instrumentation.

Cyclic Voltammetry. Cyclic voltammetry experiments were performed using an AUTOLAB PGSTAT128N potentiostat (Metrohm). The three-electrodes setup consisted of a glassy carbon working electrode (custom made, 0.071 cm^2) polished with diamond paste of various diameter size (successively 15, 6, 3, and 1 µm, 60 seconds each), a Pt wire counter electrode, and a SCE reference electrode (-0.241 V vs NHE). All experiments were performed under Argon or CO_2 atmosphere at 25°C, the double-wall jacketed cell being thermostated by circulation of water. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument.

Preparative Scale Electrolysis. Controlled potential electrolyses were performed using a PARSTAT 4000 potentiostat (Princeton Applied Research). The experiments were carried out in a cell using a glassy carbon plate (S = 2.5 cm^2) as working electrode, and a SCE reference electrode. The Pt grid counter electrode was separated from the cathodic compartment with a glass frit.

Preparation of the electrodes

For cyclic voltammetry experiments, a glassy carbon electrode (0.071 cm^2) was polished with diamond paste (successively 15, 6, 3, and 1 µm, 60 seconds each), thoroughly rinsed and sonicated in ethanol, and dried. Multiwalled carbon nanotubes (MWCNTs) were dispersed in 2-propanol (iPrOH, 1 mg mL^{-1}) by sonication (15 minutes), 10 µL of the suspension were dropped on the surface of the electrode, and allowed to dry under ambient conditions. Catalyst immobilization was achieved either by dropping 10 µL of a 1 mM solution of CAT_{Pyr} in iPrOH on the MWCNTs electrode, or by dipping the electrode in a similar solution for 15 minutes. The electrodes were rinsed with iPrOH and allowed to dry under ambient conditions before the experiments.

For controlled potential electrolyses, a glassy carbon plate (2.5 cm^2) was polished with diamond paste (successively 15, 6, 3, and 1 µm, 60 seconds each), thoroughly rinsed and sonicated in ethanol, and

dried. Multiwalled carbon nanotubes (MWCNTs) were dispersed in 2-propanol (iPrOH, 2 mg mL^{-1}) by sonication (15 minutes) and 12 µL Nafion were added. 150 µL of the suspension were dropped on each face of the electrode, and allowed to dry under ambient conditions. Catalyst immobilization was achieved either by dropping 150 µL of a 1 mM solution of CAT_{Pyr} in iPrOH on each face of the MWCNTs electrode, or by dipping the electrode in a similar solution for 15 minutes. The electrodes were rinsed with iPrOH and allowed to dry under ambient conditions before the experiments.

Gas Detection. Gas chromatography analyses of gas evolved in the headspace during the electrolysis were performed with an Agilent Technologies 7820A GC system equipped with a thermal conductivity detector. CO and H_2 production was quantitatively detected using a CP-CarboPlot P7 capillary column (27.46 m in length and 25 µm internal diameter). Temperature was held at 150 °C for the detector and 34 °C for the oven. The carrier gas was argon flowing at 9.5 mL/min at constant pressure of 0.5 bars. Injection was performed via a 250-µL gas-tight (Hamilton) syringe previously degassed with CO_2. Conditions allowed detection of H_2, O_2, N_2, CO, and CO_2. Calibration curves for H_2 and CO were determined separately by injecting known quantities of pure gas.

SEM analysis. Scanning electron microscopy using a field emission gun (SEM-FEG) was performed using a Zeiss Supra 40.

XPS analysis. An X-Ray Photoelectron Spectrometer THERMO-VG ESCALAB 250 (RX source K AI (1486.6 eV)) was used.

3. Additional figures

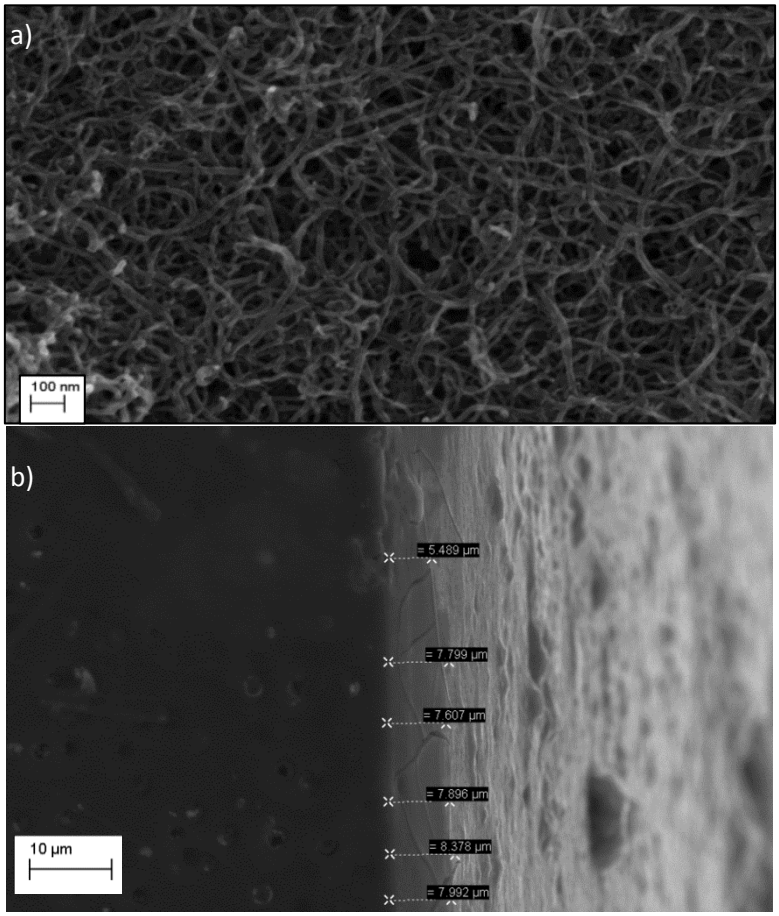

Figure S1. Scanning Electron Microscopy micrograph of a glassy carbon electrode modified with MWCNTs and immobilized CAT_{Pyr} ; a) top view, b) cross section.

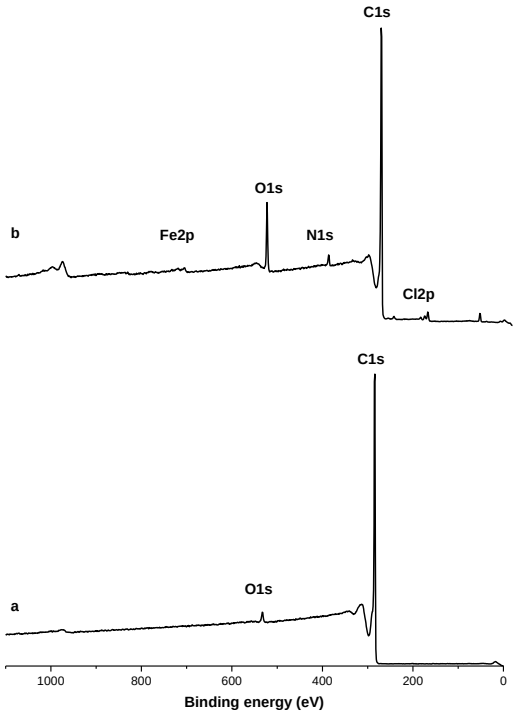

Figure S2. Survey XPS spectra of a) GC/MWCNT electrode, b) GC/MWCNT/CAT_{Pyr} electrode.

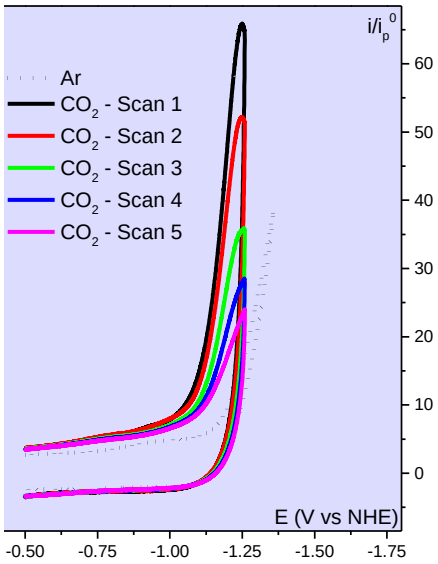

Figure S3. Cyclic voltammetry (v = 0.1 V s^{-1}, successive scans) of CAT_{Pyr} (Γ = 7.7 10^{-10} mol cm^{-2}) immobilized on MWCNTs deposited onto a glassy carbon electrode in water + $KHCO_3$ 0.1 M and $KClO_4$ 0.1 M after saturation with CO_2.

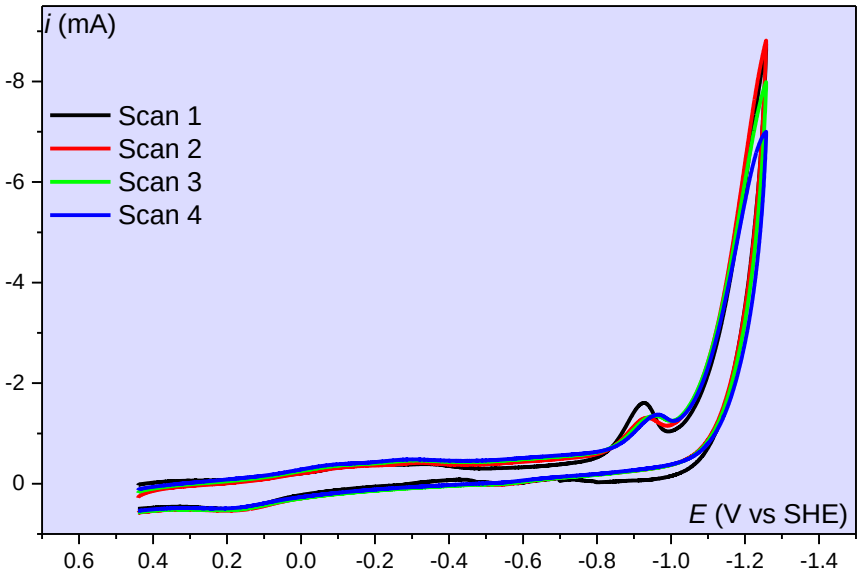

Figure S4. Cyclic voltammetry (v = 0.01 V s^{-1}, successive scans) of CAT_{Pyr} (Γ = 10^{-8} mol cm^{-2}) immobilized on MWCNTs deposited onto a glassy carbon electrode in water + $NaHCO_3$ 0.5 M after saturation with CO_2.

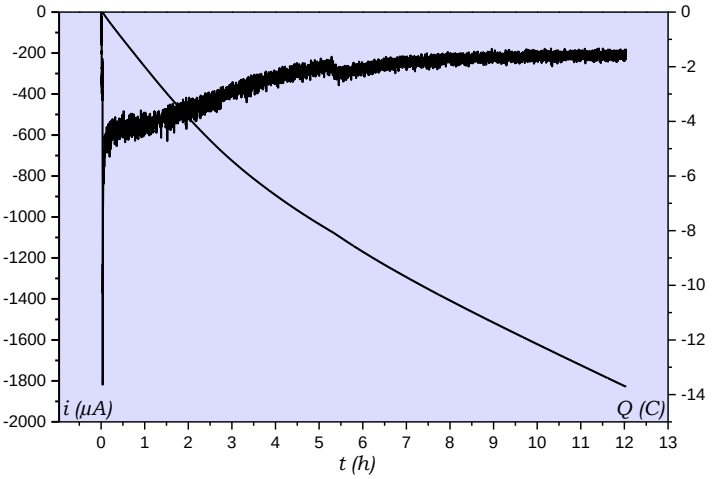

Figure S5. Current (black trace, left) and charge (black thin trace, right) during bulk electrolysis (E = – 1.03 V vs. NHE) with CAT_{Pyr} ($2.4\ 10^{-8}$ mol cm^{-2}) deposited at a carbon surface, in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M.

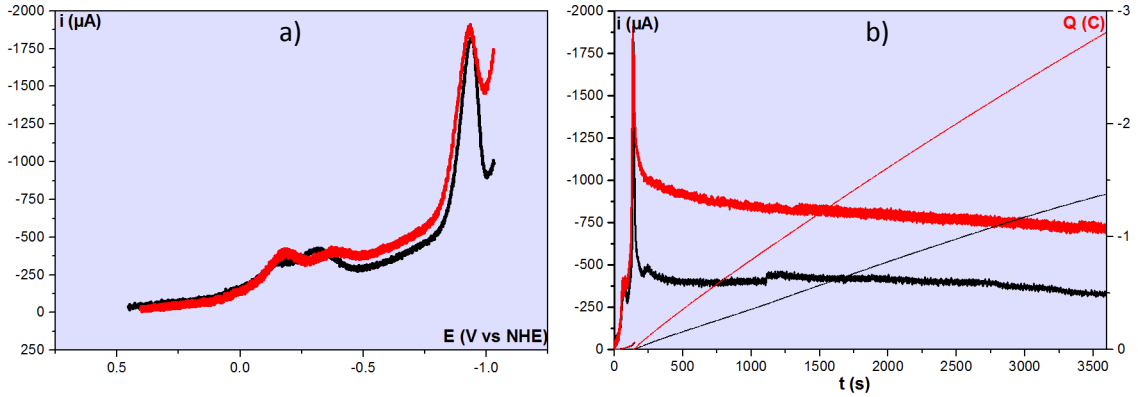

Figure S6. a) Linear scan voltammetry (v = 0.01 V s^{-1}) of CAT (black trace) and CAT_{Pyr} (red trace) immobilized on MWNCTs deposited onto a glassy carbon electrode (Γ = $2\ 10^{-8}$ mol cm^{-2}, obtained from integration of the CV at the Fe^{II}/Fe^{I} wave), in CO_2 saturated water (pH = 7.3) + 0.5 M $NaHCO_3$; b) Current and charge during bulk electrolysis (E = – 1.03 V vs. NHE) with CAT (black traces) and CAT_{Pyr} (red traces) deposited at a carbon surface, in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M.

References

S1. Myung, S.; Yin, P. T.; Kim, C.; Park, J.; Solanki, A.; Reyes, P. I.; Lu, Y.; Kim, K. S.; Lee, K. B. *Adv. Mater.* **2012**, *24*, 6081.