Electronic Supplementary Information

Controlled Electropolymerisation of a Carbazole-Functionalized

Iron Porphyrin Electrocatalyst for CO₂ Reduction

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Materials and Experimental Procedures

Materials. All chemical reagents were commercially available and used as received unless otherwise stated. HPLC grade solvents from Sigma-Aldrich were used for all experiments. Dichloromethane and acetonitrile for electrochemistry were dried over 4Å molecular sieves prior to use. The supporting electrolytes, tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) and tetraethylammonium tetrafluoroborate (Et₄NBF₄), were prepared using standard procedures. The monomer, chloro iron(III)–tetrakis(carbazol-9-ylphenyl)porphyrin (FeTCPP), was synthesized according to previously reported procedures.^{S1}

Electrodes. Glassy carbon (GC) disk (0.1 cm diameter rod, Sigradur G, HTW) embedded in epoxy resin, GC plates (1 cm × 1 cm × 0.1 cm, Sigradur G, HTW), and indium tin oxide (ITO, 370 nm thick, 8–12 ohms, SOLEMS) deposited on glass plates (2 cm × 1 cm × 0.11 cm), were used as working electrodes. GC disk electrodes were polished using diamond pastes (Struers, grain size: 9, 3, 1, and 0.25 μ m) followed by sonication in acetone for 10 min. GC and ITO plates were cleaned by sonication for 10 min in water, acetone, dichloromethane, and pentane. A platinum wire and a Ag/AgI pseudoreference electrode were used as counter and reference electrode, respectively. The formal redox potential of the Fc⁺/Fc couple was used for calibration of the potentials at the end of each experiment. All potentials were referenced against SCE using a previous determination of E^0 (Fc⁺/Fc) = 0.41, 0.48, and 0.45 V vs SCE in acetonitrile, ^{S2} *N*,*N*-dimethylformamide, ^{S2} and dichloromethane, ^{S3} respectively.

Ellipsometry. Thicknesses of the polymer films on GC plates were measured on a rotating analyzer ellipsometer (Dre, Germany). The angle of incidence was set at 65° with the laser having a spot size of ~2 mm in diameter. The ellipsometric parameters (Δ and ψ) of the bare and the modified GC plates were collected under ambient

condition, where Δ is the phase shift and ψ is the amplitude ratio upon reflection. A three-layer optical model consisting of a substrate, the deposited polymer film, and the surrounding air was used to calculate the overall reflection coefficients for in-plane (R_p) and out-of-plane (R_s) polarized lights. The complex refractive index of the substrate was calculated from the measured Δ and ψ values on the bare GC plate, and the refractive index of the organic polymer film and air was set at 1.55 and 1.0, respectively. The same area of the plates before and after film deposition and three spots on one plate for each film were measured.

Infrared Reflection Absorption Spectroscopy (IRRAS). IRRAS spectra of the polymer films on GC plates were collected on a Thermo Scientific Nicolet 6700 FTIR-spectrometer equipped with a Varian external Experiment Module with a narrow band mercury-cadmium-telluride detector cooled with liquid nitrogen. All spectra were recorded at room temperature in dry air atmosphere. The infrared beam was p-polarized by a gold wire polarizer. The GC plates with film deposited were irradiated at an incident grazing angle of 60°. The spectral resolution and number of scans for each substrate were 4 cm⁻¹ and 200, respectively. The p-polarized reflectivity of the film, $R_p(d)$, was divided by the reflectivity of the bare GC plate, $R_p(0)$, and presented as IRRAS absorbance, $-\log[R_p(d)/R_p(0)]$, after baseline correction using the OMNIC software.

Ultraviolet-visible Spectroscopy (**UV-vis**). Absorption spectra of the polymer films on ITO plates were recorded on a Thermo Scientific GENESYS 10S UV-vis spectrophotometer. A clean blank ITO plate was used as reference for baseline correction. For comparative purposes the absorption maximum of the monomer in dichloromethane was normalized to that of PF-5.

X-Ray Photoelectron Spectroscopy (XPS). XPS analysis was performed on a

Kratos Axis Ultra-DLD instrument operated with a monochromatic Al K α X-Ray source at a power of 150 W. The pressure in the main chamber during the analysis was kept around 10^{-11} bar. Survey spectra were collected by accumulating two sweeps in the 0–1350 eV range at pass energy of 160 eV. High-resolution spectra of the element of interest were acquired at pass energy of 20 eV and fitted using Gaussian-Lorentzian line shapes and a Shirley background. The CasaXPS software was used for fitting and C 1s at 285.0 eV for binding energy calibration. The atomic percentage of the detected elements was determined from survey spectra following Shirley background subtraction using the manufacturer's sensitivity factors and the transmission function correction supplied with the instrument data system.

Scanning Electron Microscopy (SEM). SEM images were acquired on a FEI Nova NanoSEM 600 microscope at an accelerating voltage of 5 kV. The polymer film deposited on the GC plates could be observed directly.

Transmission Electron Microscopy (TEM). TEM was performed on a FEI Talos microscope at an accelerating voltage of 200 kV. The polymer film on an ITO plate was peeled off and dispersed in ethanol using extensive sonication. The suspension was drop casted on a copper TEM grid with a lacey carbon film (Ted Pella), which was dried in oven at 60 °C and studied in the TEM.

Film Fabrication via Oxidative Electropolymerisation. A standard three-electrode electrochemical setup (CH Instruments) was used. The polymer films were prepared by performing voltammetric cycles (2, 5, and 10 cycles, respectively) on 0.2 mM FeTCPP using a sweep rate, v, of 0.2 V s⁻¹ in the potential range of 0.4–1.4 V vs SCE in deaerated 0.1 M Bu₄NBF₄/dichloromethane. The resulting films were washed with dichloromethane to remove unreacted monomer and supporting electrolyte and dried by blowing with nitrogen gas.

Electrochemical Characterization and Reduction of CO₂. A standard three-electrode electrochemical setup (CH Instruments) was used. The electrochemical analysis of the blank and modified electrodes was performed in a dry and deaerated 0.1 M Et₄NBF₄/acetonitrile solution at v = 0.1 V s⁻¹. The surface coverage of electroactive catalyst was calculated by integrating the Fe^{1/II} oxidation wave after linear background subtraction. The area of the film deposited on the ITO plates is 1.6 cm × 1 cm. For the electrochemical reduction of CO₂, the solution was saturated with the CO₂ gas under stirring for 15 min prior to measurements.

Results

Controlled Film Growth. Figure S1a and S1b show the linear dependency of the thickness, UV-vis absorbance (at 437 nm), and integrated IR absorbance (1660–1381 cm⁻¹) of the films on the number of voltammetric cycles. This shows that the film growth can be electrochemically controlled. Yet, the surface coverage of electroactive catalyst (Γ) is neither linearly proportional to the number of voltammetric cycles, nor to the the film thickness (magenta squares in Figure S1a). Rather the plot shows that Γ approaches an upper limit of 7×10^{-10} mol cm⁻² for the thickest films.



Figure S1. Plots of (a) thickness (GC plates) and surface coverage (ITO plates) and (b) UV-vis absorbance at 437 nm (A_{437nm} ; ITO plates) and integrated IR absorbance in the aromatic region (1650–1381 cm⁻¹; GC plates) of the PF-2, PF-5, and PF-10 films as a function of the number of voltammetric cycles.

UV-vis Spectra. Figure S2a show the UV-vis spectra of the PF-2, PF-5, and PF-10 films recorded on ITO plates. The three films display the same absorption maximum at 437 nm, corresponding to the Soret band of the iron-porphyrin or porphyrin. The band is red-shifted by 15 nm compared to that of the monomer in a dichloromethane solution as a result of porphyrin aggregation taking place in the surface film.^{S4} For comparative purposes the absorption maximum of the monomer in dichloromethane was normalized to that of PF-5.

After CO₂ reduction, the three films show blue-shifted absorption by \sim 5 nm and a weakened Soret absorption band. The later observation can be ascribed to the desorption of remaining FeTCPP monomers in the film occurring during the first cycles. The blue shift of the absorption spectrum suggests that alteration of the porphyrin structure occurs as a result of the CO₂ reduction.

The extinction coefficient at the Soret band (437 nm) of the monomer in dichloromethane was determined to be $1.18 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Given that the electropolymerisation occurs on the pendant carbazole while the iron-porphyrin core structure remains untouched (based on XPS analysis), we can assume that the extinction coefficient at the Soret peak for the polymer film is the same as that of the monomer. Based on the calculated extinction coefficient and the observed UV-vis absorbance at 437 nm shown in Figure S2, the coverage of the catalyst on ITO may be determined to be 0.46, 1.25, and 2.05×10^{-9} mol cm⁻² for PF-2, PF-5, and PF-10. The corresponding numbers obtained by electrochemistry (*vide infra*) for the coverage of electroactive catalyst were 2.3, 6.3, and 6.9×10^{-10} mol cm⁻², suggesting that ~50% of the porphyrins in PF-2 and PF-5 are electroactive and only ~35% for the thicker PF-10 film.

From a theoretical point of view these numbers do not seem unreasonable, considering that the surface coverage of a close-packed monolayer of FeTCPP

catalyst may be calculated to be 3.8×10^{-11} mol cm⁻², assuming that the foot print of the monomer molecule FeTCPP is ~4.4 nm² (effectively ~6 nm² with an atomic packing factor of 0.74). This area was estimated based on the diameter (= 2.38 nm) of a FeTCPP molecule provided by the Chem3D program (CambridgeSoft Corporation), which also provides the height (0.65 nm), assuming that the pendant carbazole is perpendicular to the porphyrin plane (Figure S2b). Clearly, this may not always be the case, meaning that this thickness of the individual layers should be considered as a maximum value. Given the coverage of electroactive catalyst determined by electrochemistry (2.3, 6.3, and 6.9×10^{-10} mol cm⁻² for PF-2, PF-5, and PF-10) and the thickness of the dry film determined by ellipsometry (6.0, 18.6, and 38.4 nm for PF-2, PF-5, and PF-10), we can predict that at most ~90%, ~80%, ~42% of the porphyrins in PF-2, PF-5, and PF-10 are electroactive. The tendency in these roughly estimated numbers is in agreement with that determined from the UV-vis spectra (*vide supra*).



Figure S2. (a) UV-vis spectra of the FeTCPP monomer in dichloromethane and of the PF-2, PF-5, and PF-10 films on ITO plates before (solid curve) and after (dashed curve) electrocatalytic reduction of CO₂. (b) Estimation of the diameter and height of the porphyrin molecule using the Chem3D program (CambridgeSoft Corporation).

XPS analysis. Table S1 presents the composition of the PF-2, PF-5, and PF-10 films prepared on GC plates. While PF-5 and PF-10 have a similar composition as the monomer, PF-2 shows a significantly higher C/N ratio. This is due to the fact that the thickness of the PF-2 film (= 6 nm) is smaller than the photoelectron escape depth (= 10 nm) in XPS, meaning that surface atoms of the GC plate will contribute to the C/N ratio. After CO₂ reduction, small amounts of Na (2.16 at%) and F (2.26 at%) appear, where the latter is suggested to originate from BF_4 (i.e., the anion of the supporting electrolyte). The Na element most likely originates from contaminations with Na⁺ serving as counterion of the carboxylate introduced during the CO₂ reduction (vide infra).

Concerning assignment of the signals in Figure 2b (main text), the Fe LMM Auger peak is observed at 840 eV, while O KLL Auger peaks appear at 980 and 1000 eV. The O KLL Auger peaks are quite prominent because of a high oxygen content of the films as evidenced by the strong peak at 533 eV. The origin of the two signals around 1023 and 1046 eV is unknown.

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Film/ monomer	Voltam. cycles	C (at%)	N (at%)	O (at%)	Fe (at%)	Cl (at%)	C/N	N/Fe	Fe/Cl
FeTCPP ^a	_	92	8	0	1	1	11.5	8	1
PF-2	2	90.74	5.17	2.42	0.54	0.57	17.55	9.57	0.95
PF-5	5	89.85	7.2	1.61	0.65	0.69	12.48	11.02	0.95
PF-10	10	90.16	7.02	1.47	0.67	0.68	12.84	10.48	0.99
$PF-10^{b,c}$	10	82.36	5.51	7.16	0.44	0.10	14.95	12.52	4.40

Table S1. Composition of the PF-2, PF-5, and PF-10 Films on GC Plates Obtained by

^a Theoretical composition of the monomer. ^b Analysed after electrocatalytic reduction of CO₂. ^c Small amounts of Na (2.16 at%) and F (2.26 at%) are also present.

7.16

10

82.36

5.51

Table S1 shows for the three films, i.e. PF-2, PF-5, and PF-10, that the at% of Fe (and Cl) relative to that of N is only 70–80% of the theoretically expected value. We mainly attribute this to adventitious amounts of nitrogen present along with, possibly, non-coordinated porphyrin ligands in the film. Since the ligands are electroinactive at the Fe redox potentials this could partly explain the discrepancy seen between the Γ values calculated from UV-vis, which comprises all porphyrin moieties, and those from electrochemistry that considers iron porphyrins only.

Figure S3 presents the deconvolution of C 1s, N 1s, Fe 2p, and Cl 2p XPS core-level spectra of PF-10 before and after CO₂ reduction. The PF-10 before CO₂ reduction shows two primary peaks centered at 284.8 and 285.4 eV, corresponding to the aromatic carbon and N-bonded carbon species, respectively (Figure S3a). A small peak pertaining to an oxygen-bonded carbon at 287.7 eV is detected and is consistent with the small amount of oxygen found as well (Table S1). After CO₂ reduction, the two primary peaks remained unchanged, but the oxygen-bonded carbon at 287.7 eV increases significantly, in agreement with the increasing percentage of oxygen. This peak is ascribed to the carbon species in O=C-O,^{S5} suggesting that carboxylation occurs on the ligand during CO₂ reduction. At the same time this explains the detection of Na⁺ which is needed to balance the charge.

The PF-10 before CO_2 reduction exhibits two types of N in a ratio that is close to 1:1 (Figure S3b). These correspond to the tertiary N species from the carbazole (400.5 eV) and the porphyrin coordinated to Fe (399.1 eV). After CO_2 reduction the percentage of N coordinated to Fe decreases, which, together with the increasing N/Fe ratio, indicates a partial leaching of Fe.

Deconvolution of the Fe 2p spectra reveals similar peaks before and after CO₂ reduction (Figure S3c), which indicates that the remaining Fe is still in its +3 oxidation state. The binding energies at 712.3 and 725.7 eV correspond to Fe $2p_{3/2}$ and $2p_{1/2}$. In addition, two satellite peaks are located left to these two.

Deconvolution of the Cl 2p spectra (Figure S3d) reveals that the Cl weakly bonded to Fe is completely gone after CO₂ reduction since the peaks centered at 198.7 ($2p_{3/2}$) and 200.1 eV ($2p_{1/2}$) disappear. The film before and after CO₂ reduction contains some organically bound Cl (200.7 eV, $2p_{3/2}$; 202.2 eV, $2p_{1/2}$), which may arise from chlorination of the ligand during the oxidative electropolymerisation in dichloromethane.^{S6}



Figure S3. XPS spectra pertaining to (a) C 1s, (b) N 1s, (c) Fe 2p, and (d) Cl 2p core-level of PF-10 on GC plates before and after reduction of CO₂.



Figure S4. (a) SEM (on GC plate) and (b) TEM images (peeled off from ITO plate) of PF-10.



Figure S5. Cyclic voltammograms recorded at a GC disk electrode (geometrical area = 7.85×10^{-3} cm²) on 0.12 mM FeTCPP using v = 0.1 V s⁻¹ in 0.1 M Bu₄NBF₄/DMF in the absence (dark curve) and presence (blue curve) of CO₂.

Charge Transfer Kinetics. For cyclic voltammograms recorded on a PF-5 film immobilised on GC disk electrode at v < 0.05 V s⁻¹, almost symmetrical and bell-shaped Fe^{I/0} redox waves with a small peak separation of 20 mV are observed (Figure S6). This is in line with the charge transfer process being relatively fast, although the peak separation increases upon increasing the sweep rate, e.g. at v = 0.2 V s⁻¹ it becomes 80 mV.

A plot of ln i_p vs ln v is linear with a slope close to unity in the range of v's between 0.02 and 0.2 V s⁻¹, in agreement with a surface confined redox couple (Figure S6 inset). At even higher values of v deviations may occur because of the aforementioned effect from the charge transfer kinetics. Hence, the electrode surface coverage can be calculated from the relationship $\frac{\partial i_p}{\partial v} = \frac{n^2 F^2}{4RT} A\Gamma$ for an assumed reversible electrode process using the slope from a plot of i_p vs v (not shown).^{S7} In this manner we find $\Gamma = 2.5 \times 10^{-10}$ mol cm⁻², which is comparable to the value of 3.4×10^{-10} mol cm⁻² obtained from an integration of the Fe^{I/II} oxidation peak at a GC disk electrode (*vide infra*). Note that the latter procedure is the most reliable one, since it is less affected by the effect from charge transfer kinetics.



Figure S6. Cyclic voltammograms recorded at a PF-5 film (immobilised on GC disk electrode; geometrical area = 7.85×10^{-3} cm²) using different sweep rates in 0.1 M Et₄NBF₄/acetonitrile. Inset depicts a plot of the natural logarithm of the reduction peak current, ln *i*_p, against ln *v* for the Fe^{1/0} wave. The voltammograms shown are recorded after 15 voltammetric cycles under an argon atmosphere.

Electrochemical Behavior and Stability of PF-5 Films. Figures S7 and S8 show successive cyclic voltammograms of PF-5 recorded on GC and ITO substrates, respectively. The fact that they are not completely alike indicates that the substrate exerts an effect on the overall film structure. Yet, the electrochemical stability of the PF-5 film is found to be comparable on the two kinds of substrate. On ITO 12% of activity is lost after the first voltammetric cycle, accompanied by additional 13% loss after the next four cycles (Figure S8).



Figure S7. First five cyclic voltammograms recorded at a PF-5 film electropolymerised on a GC disk electrode (geometrical area = 7.85×10^{-3} cm²) using v = 0.1 V s⁻¹ in 0.1 M Et₄NBF₄/acetonitrile. The dashed black curve is a cyclic voltammogram recorded at a blank GC electrode.



Figure S8. First five cyclic voltammograms recorded at a PF-5 film on an ITO plate (geometrical area = 1.6 cm^2) using $\nu = 0.1 \text{ V s}^{-1}$ in 0.1 M Et₄NBF₄/acetonitrile. The dashed black curve is a cyclic voltammogram recorded at a blank ITO plate.

Pre-peaks are apparent for all films before the $Fe^{1/0}$ reduction peak at -1.6 V vs SCE, independent of substrate (Figure 3a, S7, and S8). Such pre-peaks, better known as charge-trapping peaks,^{S8-S10} are not unusual for polymerized films, where redox units may become entrapped. These are electronically isolated from the electrode surface, and their charges are released at the potential just before the iron-based reduction.

In our case the pre-peak at -1.4 V vs SCE is particularly prominent on GC (Figure S7), which may very well originate from a catalytic reduction of residual water trapped in the film.^{S10} Noteworthy, the pre-peak shifts negatively and becomes smaller upon multiple cycling due to the water becoming depleted. This also explains why no pre-peaks were seen for the voltammograms shown in Figure S6, where multiple cycling was applied prior to the recordings. Finally, introducing CO₂ to the electrochemical makes the pre-wave disappear due to the fact that the reaction of Fe^{1/0} with CO₂ now takes over (see Figure 3b).

Another interesting feature of the voltammograms in Figure S8 is that the redox peak for $Fe^{III/II}$ is hardly discernible. This indicates that the films do not become redox active, until a certain threshold potential corresponding to, in this case, the redox potential of $Fe^{II/I}$ is reached. At this potential inflow of ions occurs and Fe^{III} may be converted to Fe^{I} in a two-electron process which is the reason that this wave is larger than the subsequent $Fe^{I/0}$ reduction wave. Somewhat surprisingly, the oxidation waves are both found to be of the same size as the $Fe^{I/0}$ wave, suggesting that some of the injected charge on the forward sweep is lost to the surroundings. On GC (Figure 3b and S7) the situation is even more profound, in that the film is, by and large, redox inactive, until the $Fe^{I/0}$ reduction wave is reached. Hence, it may be concluded that the substrate exerts a strong effect on the nature of the film structure with GC seeming to form a more compact and less accessible film.

Calculation of Surface Coverage. To determine the surface coverage of the electroactive catalyst, Γ , the charge associated with the Fe^{I/II} oxidation peak of the second cyclic voltammogram of each film was calculated (Figure S9). This oxidation wave was chosen, since it is unaffected by any catalysis processes occurring on the forward sweep and at the same time the background is well defined and easily accounted for using a simple linear approach.

Figure S9 illustrates the integration procedure for the background-subtracted Fe^{1/II} oxidation wave. In this manner we find on ITO plates (geometrical area = 1.6 cm²) that Γ = 2.3, 6.3, and 6.9 × 10⁻¹⁰ mol cm⁻² for PF-2, PF-5, and PF-10, respectively. On a GC disk electrode (geometrical area = 7.85 × 10⁻³ cm²) PF-5 gives Γ = 3.4 × 10⁻¹⁰ mol cm⁻², which is a factor two lower than that on ITO plate. Once again this indicates that the substrate exerts a pronounced effect on the film structure, presumably, leading to a less accessible film on the GC disk electrode. To estimate how much activity is lost during cycling, the charge associated with the first, second, and fifth cyclic voltammogram on either ITO plates or GC disk electrode was also calculated (see main text).



Figure S9. Cyclic voltammograms used in the determination of the surface coverage (linear background subtraction, dashed red curve) in the case of (a) PF-2, (b) PF-5, and (c) PF-10 on ITO plates (geometrical area = 1.6 cm^2) and (d) PF-5 on a GC disk electrode (geometrical area = $7.85 \times 10^{-3} \text{ cm}^2$).

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