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Supplementary Materials for

A flexible cofacial Fe porphyrin dimer as an extremely efficient and selective electrocatalyst for the CO_2 to CO conversion in non-aqueous and aqueous media

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Materials. Chemicals used in this work were used without further purification. Solvents were distilled from appropriate drying agents under nitrogen just prior to use. Mill-Q water (18 M Ω.cm) was used for preparation of aqueous solutions. *O*-Phenylenediamine, pyrrole, pentafluorobenzaldehyde, oxalylchloride, $NaHCO_3$, and *p*-methoxycarbonylbenzaldehyde were purchased from Nacalai. NaOH, tetra-*n*-butylammonium hexafluorophosphate ($TBNPF_6$), and Nafion solution (5%) were purchased from Sigma-Aldrich Co. Ketjen black carbon (KBC; ECP600JD) powder was purchased from Lion Specialty Chemicals Co., Ltd. The rigid cofacial Fe porphyrin dimer, *r*-Fe_2PD was prepared as we previously reported.[1]

Instruments. ^{1}H NMR spectra were recorded on a JEOL JMX-GX 400 (400 MHz) spectrometer. Chemical shifts are reported as parts per million (ppm) with respect to $CHCl_3$. Matrix Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass spectra were measured on a BRUKER Auto flex II LRF20 spectrometer using dithranol as a matrix. UV-vis spectra were recorded using a Shimadzu UV-2500PC spectrophotometer. Diffuse UV-vis reflectance spectra were recorded using a UV-Vis-NIR scanning spectrophotometer, Shimadzu UV-3100PC. Particle morphologies and sizes were observed by scanning electron microscopy, Field Emission Hitachi Model S-4300 scanning electron microscope operated at 15 KV accelerating voltage and 15 mm working distance. XPS spectra were obtained using a Ulvac Phi 5000 VersaProbe CU X-ray Photoelectron Spectrometer with a Multipak data treatment system. The photoelectrons emitted by a monochromated Al Kα (1486.6 eV; 350 W) radiation were collected with path energy of 23.5 eV through a hemispherical analyzer. The pressure in the analyzing chamber was below 1 x 10^{-9} Torr during the measurements. All spectra in XPS were calibrated to C 1s = 284.8 eV. Electrochemical measurements were performed with a Metrohm Autolab Potentiostat/Galvanostat model PGSTAT 302. Gas chromatographic analyses were done with a Shimadzu GC-8A equipped with a capillary column (0.53 mm ID x 15 m) with a Molecular Sieve 5A layer at 40 ^{o}C using Ar as a carrier gas.

Preparation of the flexible cofacial Fe porphyrin dimer (*f*-Fe_2PD). The *f*-Fe_2PD was prepared by stepwise procedures outlined in scheme (Scheme 1, main text).

(a) **Preparation of 5-[4-(methoxycarbonyl)phenyl]-10,15,20-pentafluorophenyl porphyrin (I).** Following similar reported procedures,[1–3] a 2-L three-neck round-bottomed flask was charged with pentafluorobenzaldehyde (16.3 g, 0.083 mol), freshly distilled pyrrole (7.4 g, 0.110 mol), *p*-methoxycarbonylbenzaldehyde (4.5g, 0.027 mol) and $CHCl_3$ (1000 mL). The colorless solution was purged with nitrogen for about 15 min. Then, boron trifluoride diethyl ether complex (BF_3•Et_2O, 7.5 mL) was added via s syringe. The color changed slowly to dark red. The mixture was stirred at room temperature under nitrogen overnight. Excess DDQ (DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone) solution (7 g/150 ml benzene, 0.030 mol) was added to the reaction mixture, where the color changed to dark green. The mixture was stirred at room temperature for further 4 h. The solvent was removed, the residue was dissolved in a small amount of $CHCl_3$, the solution was loaded into an activated Al_2O_3 column and the reaction mixture was eluted with $CHCl_3$. The first broad reddish violet band was collected. The TLC chromatography of this band showed the presence of light red band on the top followed by green band, strong reddish violet band then green and black bands on the bottom. The reddish violet band was collected, the solvent was removed, and the residue was further purified with silica-gel column eluted with *n*-hexane:CH_2Cl_2 (1:1) to give 2.5 g of the pure compound (**I**) in 10.0 % isolated yield. ^{1}H NMR ($CDCl_3$): δ 8.94 (s, 2H), 8.87 (d, 2H), 8.51 (d, 4H), 8.32 (d, 4H), 4.13 (s, 3H, OCH_3), and −2.83 (s, 2H, por-pyrrole H). MALDI-TOF-MS: *m/z* = 942.2 (found), 942.6 (calcd.).

(b) **Preparation of 5-[4-(carboxy)phenyl]-10,15,20-pentafluorophenyl porphyrin (II).** A 100-mL flask was charged with **I** (0.20 g, 0.21 mmol), isopropanol (20 mL), and coc. HCl (20 ml). The solution was refluxed for 48 h. The product was extracted first with $CHCl_3$/ saturated solution of $NaHCO_3$ two times and then with $CHCl_3$/H_2O two times. The organic layer containing the product was dried over anhydrous Na_2SO_4. The compound was further purified with a silica-gel column using $CHCl_3$/10 % MeOH as an eluent. The reddish orange band was collected to give a reddish violet powder (0.102 g, 52.0 % yield). ^{1}H NMR ($CDCl_3$): δ 10.92 (s, 1H, -COOH), 8.95 (d, 1H), 8.91 (s, 2H), 8.86 (d, 1H), 8.60 (d, 4H), 8.37 (d, 4H), and −2.82 (s, 2H, por-pyrrole H). MALDI-TOF-MS: *m/z* = 928.4 (found), 928.6 (calcd.).

(c) **Preparation of 5-[4-(carbonylchloride)phenyl]-10,15,20-pentafluorophenyl porphyrin (III).** A 25-mL flask was charged with **II** (0.134 g, 0.144 mmol), oxalylchloride (8 ml), and one drop of DMF that served as a catalyst. The solution changed immediately from purple to green and strong fumes evolved. The solution was refluxed under Ar overnight. The solvent was removed *in vacuo*. The MALDI-TOF-MS showed peaks for the desired compound *m/z* = 947.0 (found), 947.05 (calcd.). The as-formed residue was directly used without purification for the next reaction.

(d) **Preparation of the flexible porphyrin dimer [1,2-bis[5,10,15-tris pentafluorophenyl porphyrinyl]amidobenzene] (IV).** A 25-mL flask was charged with **III** (0.136 g, 0.144 mmol), *o*-phenylenediamine (7.76 mg, 0.072 mmol), dry THF (15 mL), and Et_3N (0.150 ml). The solution was refluxed under Ar overnight. The solvent was removed *in vacuo*. The residue was further purified with a silica-gel column using $CHCl_3$/5 % MeOH as an eluent. The reddish orange band was collected to give a reddish violet powder (0.064 g, 31.2 % yield). ^1H NMR ($CDCl_3$): δ 8.89 (m, 8H), 8.61 (d, 8H), 8.36 (d, 8H), 7.66 (s, 4H), 5.37 (s, 1H), 5.08 (s, 1H), and −2.87 (s, 4H, por-pyrrole H) (Figure S4A). MALDI-TOF-MS: *m/z* = 1929.2 (found), 1929.3 (calcd.) for the whole molecules and peaks for fragments at *m/z* = 884.1 (found), 884.6 (calcd.), 912.2 (found), 912.6 (calcd.), and 118.2 (found), 118.73 (calcd.) (Figure S4B). Anal. Calcd for **IV**, $C_{96}H_{34}F_{30}N_{10}O_2$: C, 59.76; H, 1.78; N, 7.26. Found: C, 59.70; H, 1.75; N, 7.22.

(e) **Preparation of the flexible Fe porphyrin dimer [1,2-bis[5,10,15-tris pentafluorophenyl porphyrinyl]amidobenzene] (*f*-Fe_2PD).** A 50-mL flask was charged with **IV** (41.7 mg, 0.022 mmol), excess $FeBr_2$ (100 mg, 0.46 mmol), and dry DMF (20 mL). The mixture was refluxed overnight. The solvent was then removed, and the desired compound was extracted with $CHCl_3$/HCl (1M in H_2O) three times then with $CHCl_3$/$NaHCO_3$ (saturated) three times and finally with the $CHCl_3$/H_2O three times. The organic layer containing the desired compound was dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the residue was further purified with silica-gel column using $CHCl_3$/5% MeOH as an eluent. The reddish-brown band was collected to give a reddish-brown powder (35 mg, 79.0 % yield) of the desired compound. MALDI-TOF-MS: MALDI-TOF-MS: *m/z* = 2036.5 (found) corresponding to *f*-Fe_2PD (2036.9, calcd.) and 2072.2 corresponding to *f*-[Fe_2PD]Cl (2071.4 calcd.) for the whole molecules and peaks for its fragments (Figure S5A). Anal. Calcd for *f*-Fe_2PD, $C_{96}H_{30}Cl_2F_{30}Fe_2N_{10}O_2$: C, 54.70; H, 1.43; N, 6.64. Found: C, 54.58; H, 1.35; N, 6.60.

Preparation of *f*-Fe_2PD/KBC@GC for heterogeneous electrochemical CO_2-to-CO conversion studies in aqueous solutions. A small caped-tube was charged with ***f*-Fe_2PD** (1.0 mg, 0.49 μmol), KBC (1.0 mg, 83.3 μmole) and MeOH (0.4 ml). The whole solution was sonicated for 10 min. then stirred overnight to allow the adsorption of the dimer on the KBC. The KBC with the adsorbed catalyst was isolated by filtration, washed by MeOH, and allowed to dry in air. The dried KBC containing the catalyst was then mixed with MeOH (0.2 ml) and a 5% Nafion solution (0.02 ml) and sonicated for 15 min. to form a homogeneous *f*-Fe_2PD/KBC ink solution. The *f*-Fe_2PD/KBC ink (40.0 μl) was pipetted onto pre-cleaned GC surface (1.0 cm^2) and allowed to dry at rt for couple of hours before the CV and characterization measurements.

Cyclic voltametric (CV) measurements. Homogeneous CV measurements in non-aqueous solutions were performed using a small three-electrode electrochemical cell. In a typical experiment, a total of 2.0 mL of DMF/10% H_2O solution containing 1.0 M phenol (PhOH), 0.1 M $TBNPF_6$ supporting electrolyte and 0.5 mM of the dimer was used. A glassy carbon (3 mm ø), a Pt wire and a Ag/AgCl (3M NaCl) were used as a working, a counter, and reference electrodes, respectively.

The heterogeneous CV measurements in aqueous solutions were performed using a normal three-electrode electrochemical cell. In a typical experiment, a total of 15.0 mL of 0.5 M $NaHCO_3$ solutions was used. A *f*-Fe_2PD/KBC@GC (1.0 cm^2), a Pt wire and a Ag/AgCl (3M NaCl) were used as a working, a counter, and reference electrodes, respectively. The potentials measured in non-aqueous and aqueous solutions were converted to the potentials versus standard hydrogen electrode (SHE) based on $E^0_{\mathrm{Ag/AgCl}} = 0.198$ V of the standard potential of the Ag/AgCl (3M NaCl) reference electrode, using the following equation:

$$E_{\mathrm{SHE}} = E_{\mathrm{Ag/AgCl}} + E^0_{\mathrm{Ag/AgCl}},$$

where $E_{\mathrm{Ag/AgCl}}$ is the potentials measured versus the Ag/AgCl reference electrode. All measurements were made at room temperature 25°C.

Controlled potential electrolysis for CO_2-to-CO conversion. The homogeneous non-aqueous CO_2-to-CO conversion was carried out under controlled-potential electrolysis in a CO_2-saturated DMF/10%H_2O/PhOH solution containing 0.1 M $TBNPF_6$ as supporting electrolyte. This was performed in a gas tight two-compartment cell separated with a Nafion membrane. A glassy carbon (1 cm^2) working and Ag/AgCl (3 M NaCl) reference electrodes were set close to each other in the cathodic compartment, and a Pt foil (1 cm^2) counter electrode was equipped in the anodic compartment. The cell was filled (15 ml in each compartment) with DMF/10% H_2O/PheOH solution containing 0.1 M $TBNPF_6$ and 0.5 mM of the iron porphyrin dimer. The solution was substituted by Ar for 20 min, then saturated with CO_2 gas by bubbling the gas for 30 min. The evolved gases (CO and H_2) in the working electrode compartment were measured using gas chromatography (GC-8A with a TCD detector and molecular sieve 5A column and Ar carrier gas; Shimadzu Corporation). The Faradaic efficiency was determined from the total amount of charge Q (C) passed through the cell and the total amount of the produced CO or H_2, assuming the two electrons are needed to produce one CO or H_2 molecule. Based on the 6 h bulk electrolysis experiment in DMF/10% H_2O/1.0 M PhOH saturated with CO_2, the catalysis parameters, k_{cat}, and TOF were calculated using equations (S1)~(S3);

$$\frac{I}{F}=\frac{(k_{cat}D_{cat})^{1/2}C^{0}_{cat}}{1+\exp(F/RT)(E-E^{0}_{cat})} \qquad \text{(S1)}$$

$$\mathrm{TOF}=\frac{k_{cat}}{1+\exp\left[F/RT\left(E-E^{0}_{cat}\right)\right]} \qquad \text{(S2)}$$

$$\mathrm{TON}=\frac{k_{cat}t}{1+\exp\left[F/RT\left(E-E^{0}_{cat}\right)\right]} \qquad \text{(S3)}$$

where, I = the net current density (the current density obtained from the bulk electrolysis corrected for the Faradic efficiency, D_{cat} is the diffusion coefficient of the catalyst calculated to be 2.5 5 x 10^{-7} cm^2 s^{-1} based on Randles-Sevcik equation,[50] C^0_{cat} is the bulk catalyst concentration, 5 x 10^{-7} mole cm^{-3} (0.5 mM), E is the applied potential, and E^0_{cat} is determined from the 5/5' redox couple in Figure 2A to be −0.98 V vs SHE.

Bulk electrolysis in the heterogeneous system was performed similarly in a CO_2-saturated 0.5 M $NaHCO_3$ aqueous solution 8pH 7.3) using *f*-Fe_2PD/KBC@GC (1 cm^2) as working electrode.

Table S1. Summary of potential-controlled bulk electrolysis in DMF/10 % H_2O/1.0 M PhOH/0.1 M $TBNPF_6$ under CO_2 atmosphere.

Catalyst / mM	Applied potential / V vs SHE (η / V) [a]	E^0_{cat} /V	j / mA cm^{-2}	BE time/ h	Required charge / C	Products / µmol (FE%)[b]	
						H_2	CO
f-Fe_2PD/0.5	−1.0 (0.26)	−0.98	−0.21	6	4.54	0 (0 ± 2)	23.0 (98 ± 2)
f-Fe_2PD/0.50	−1.1 (0.36)	−0.98	−0.48	6	10.37	1.0 (2 ± 2)	52.0 (97 ± 2)
f-Fe_2PD/0.5	−1.2 (0.46)	−0.98	−1.58	6	34.13	7.0 (4 ± 2)	166.0 (94 ± 2)
r-Fe_2PD/0.5	−1.2 (0.46)	−1.25	−0.53	6	11.45	6.0 (10 ± 2)	53.0 (90 ± 2)
FeP/1.0	−1.2 (0.46)	−1.07	−0.17	6	3.67	1.7 (9 ± 2)	17.0 (91 ± 2)
0	−1.2 (0.46)		−0.082	6	1.77	8.5 (93 ± 2)	n.d. [c]

[a] The overpotentials (η) are calculated based on $E^0 = -0.74$ V for the CO_2/CO couple in DMF/10 % H_2O/1.0 M PhOH/0.1 M $TBNPF_6$ solution (ref 57). [b] Faradaic efficiency (FE%) given in parenthesis. [c] n.d. = Not detected.

Table S2: Comparison of *f*-Fe_2PD with the reported state-of-the-art molecule-based homogeneous systems in the bulk electrolysis performance for electrocatalytic CO_2-to-CO conversion.

Catalysts	**Electrolyte**	**[cat] / mM**	***j*** [a] **/ mA cm^{-2}**	**FE_{CO} (%)**	**k_{cat}** [b] **/ s^{-1}**	**log TOF** [b] **/ s^{-1}**	**E_{app} (η / V)**	**References**
f-Fe_2PD	DMF/10% H_2O /1M PhOH	0.5	0.21	98	7.2 x 10^2	2.4	−1.00 (0.26)	This work
f-Fe_2PD	DMF/10% H_2O /1M PhOH	0.5	0.48	98	4.3 x 10^6	4.6	−1.10 (0.36)	This work
f-Fe_2PD	DMF/10% H_2O /1M PhOH	0.5	1.58	94	1.0 x 10^{11}	7.3	−1.20 (0.46)	This work
r-Fe_2PD	DMF/10% H_2O /1M PhOH	0.5	0.53	90	6.7 x 10^2	2.8	−1.20 (0.46)	This work
FeP	DMF/10% H_2O /1M PhOH	1.0	0.17	91	3.4 x 10^5	3.4	−1.20 (0.46)	This work
r-Fe_2PD	DMF/10% H_2O	0.5	1.25	92	1.2 x 10^4	3.8	−1.25 (0.51)	66
Fe-*o*-TMA[c]	DMF/0.1M H_2O /3 M PhOH	0.5	0.08	93	~ 50[d]	1.4[d]	−0.96 (0.22)	65
FeTDHPP[e]	DMF/2.0 M H_2O /3 M PhOH	1.0	0.31	94	3.0 x 10^6	3.5	−1.16 (0.42)	47
[Fe(bpc)Cl(H_2O)][f]	DMF/2% H_2O	1.0	0.25	93	1.9	0.2	−1.15 (0.41)	69
[Co(qpy)[g]$(OH_2)_2$]$^{2+}$	CH_3CN/10% H_2O /1M PhOH	0.5	~0.8	94	NA	NA	−1.27 (0.53)	33

[a] Practical catalytic current density at η V. [b] k_{cat} and log TOF are calculated based on Eq. S1-S3. [c] *o*-TMA = tetra(*o*-N,N,N-trimethylanilinium)porphyrin dianion. [d] These values of k_{cat} and log TOF were reported based on the foot-of-the wave analysis to be 10^{-6} and 6.0 respectively at $\eta = 0.22$ but we recalculated these values based on the bulk electrolysis data using Eq. S1-S3 to be 50 and 1.4 **s^{-1}**, respectively. [e] TDHPP = 5, 10, 15, 20-tetrakis(2',6'-dihydroxyphenyl)-porphyrin dianion. [f] bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboximido)benzene) dianion. [g] qpy = quaterpyridine. NA = not available.

Table S3. Summary of potential-controlled bulk electrolysis of *f*-Fe_2PD/KBC@GC in aqueous 0.5 M $NaHCO_3$ (pH 7.3) under CO_2 atmosphere.

$\boldsymbol{\Gamma}_{\mathbf{cov}}$ [a] / **mol cm^{-2}**	Applied potential / V vs SHE (η / V) [b]	j / mA cm^{-2}	BE time/ h	Required charge / C	Products / µmol (FE%)[c]	
					H_2	CO
1.25 x10^{-8}	−0.79 (0.26)	−3.12	10	112.32	0 (0 ± 2)	559 (96 ± 2)
1.23 x10^{-8}	−0.99 (0.46)	−12.84	10	462.24	95.8 (4 ± 2)	2228 (93 ± 2)
0	−0.99 (0.46)	−0.10	10	3.60	17.7 (95 ± 2)	n.d.

[a] surface coverage of *f*-Fe_2PD on KBC. [b] The overpotentials (η) are calculated based on $E^0 = -0.53$ V for the CO_2/CO couple in $NaHCO_3$ (0.5 M, pH 7.3) solution (Ref. 22). [c] Faradaic efficiency (FE%) given in parenthesis.

Table S4: Comparison of *f*-Fe_2PD/KBC@GC with the reported state-of-the-art molecule-based heterogeneous systems in the performance for electrocatalytic CO_2-to-CO conversion in aqueous solutions.

Catalysts	**Electrolyte, pH**	Γ_{cov} / **mol cm^{-2}**	j [a] / **mA cm^{-2}**	**FE$_{CO}$ (%)**	**TOF** [b] / **s^{-1}**	η / **V**	**References**
f-Fe_2PD/KBC@GC	0.5 M $NaHCO_3$, 7.3	1.25×10^{-8}	3.12	91	4.47	0.26	This work
f-Fe_2PD/KBC@GC	0.5 M $NaHCO_3$, 7.3	1.23×10^{-8}	12.84	93	18.1	0.46	This work
Fe(bpc)/N-G@GC	0.5 M $NaHCO_3$, 7.3	1.4×10^{-8}	6.0	90	2.1	0.47	69
$FeCAT_{pyr}$/MWCNTs@GC	0.5 M $KHCO_3$, 7.3	2.4×10^{-8}	0.24	97	0.04	0.48	48
FePB/CNT@GC	0.5 M $KHCO_3$, 7.3	1.13×10^{-9}	0.20	85	0.64	0.51	73
$Fe_2DTPFPP-PO_3H_2/SnO_2$@FTO	0.1 M borate, 7.0	2.6×10^{-10}	1.5	70	20.6	0.42	46
CoPc-PDQ-COF/KBC@CP	0.5 M $KHCO_3$, 7.2	1 mg cm^{-2}	25.0	96	3.17 [c]	0.56	75
CoPPCl@CNT-OH	0.5 M $KHCO_3$, 7.3	9.2×10^{-8}	5.08	90.4	2.13	0.54	35
CoPc-CN/CNTs@CP	0.1 M $KHCO_3$, 6.8	1.8×10^{-8}	15.0	98	4.1	0.52	34
CoPc-CN/CNTs@CP	0.5 M $KHCO_3$, 7.2	1.8×10^{-8}	5.6	88	1.4	0.35	34
CoPc-P4VP@EPG	0.1 M NaH_2PO_4, 4.7	1.3×10^{-9}	2.0	89	4.8	0.65	32
COF-367-CoPor@CP	0.5 M $KHCO_3$, 7.3	1.3×10^{-8}	3.3	91	0.53	0.56	74
CoFPc @C	0.5 M $KHCO_3$, 7.2	1.3×10^{-8}	4.4	93	1.6	0.69	76
$[Co(qpy)]^{2+}$ /MWCNTs @CP	0.5 M $KHCO_3$, 7.3	8.5×10^{-9}	19.9	99	12	0.48	77

[a] Practical catalytic current density at η V. [b] TOF based on the Γ_{cov} value. [c] this value is based on the active Co species not the total coverage. KBC = Ketjen black carbon, GC = glassy carbon, bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboximido)benzene) dianion, CAT_{pyr} = A pyrene-appended iron tetraphenyl porphyrin bearing six pendants OH groups on the phenyl rings in all ortho and ortho′ positions, MWCNTs = multiwalled carbon nanotubes, FePB = supramolecular structure with six Fe tetraphenyl porphyrin monomer building blocks, CNTs = carbon nanotubes, $DTPFPP-PO_3H_2$ = cofacial pentafluoro phenyl porphyrin dimer modified with a phosphonic acid linker, FTO = fluorine

doped tin oxide electrode, Pc-PDQ-COF = 4,5,9,10-pyrenediquinone (PDQ) phenazine-linked phthalocyanine covalent organic frameworks, CP = carbon paper electrode, CoPPCl@CNT-OH = protoporphyrin IX cobalt chloride@ hydroxyl-functionalized carbon nanotube, CoPc-CN = cobalt phthalocyanine modified with cyano groups, CoPc-P4VP = cobalt phthalocyanine immobilized in a poly-4-vinylpridine (P4VP) film, EPG = edge-plane graphite electrodes, COF = covalent organic frameworks, CoFPc = Perfluorinated cobalt phthalocyanine, qpy = quaterpyridine,

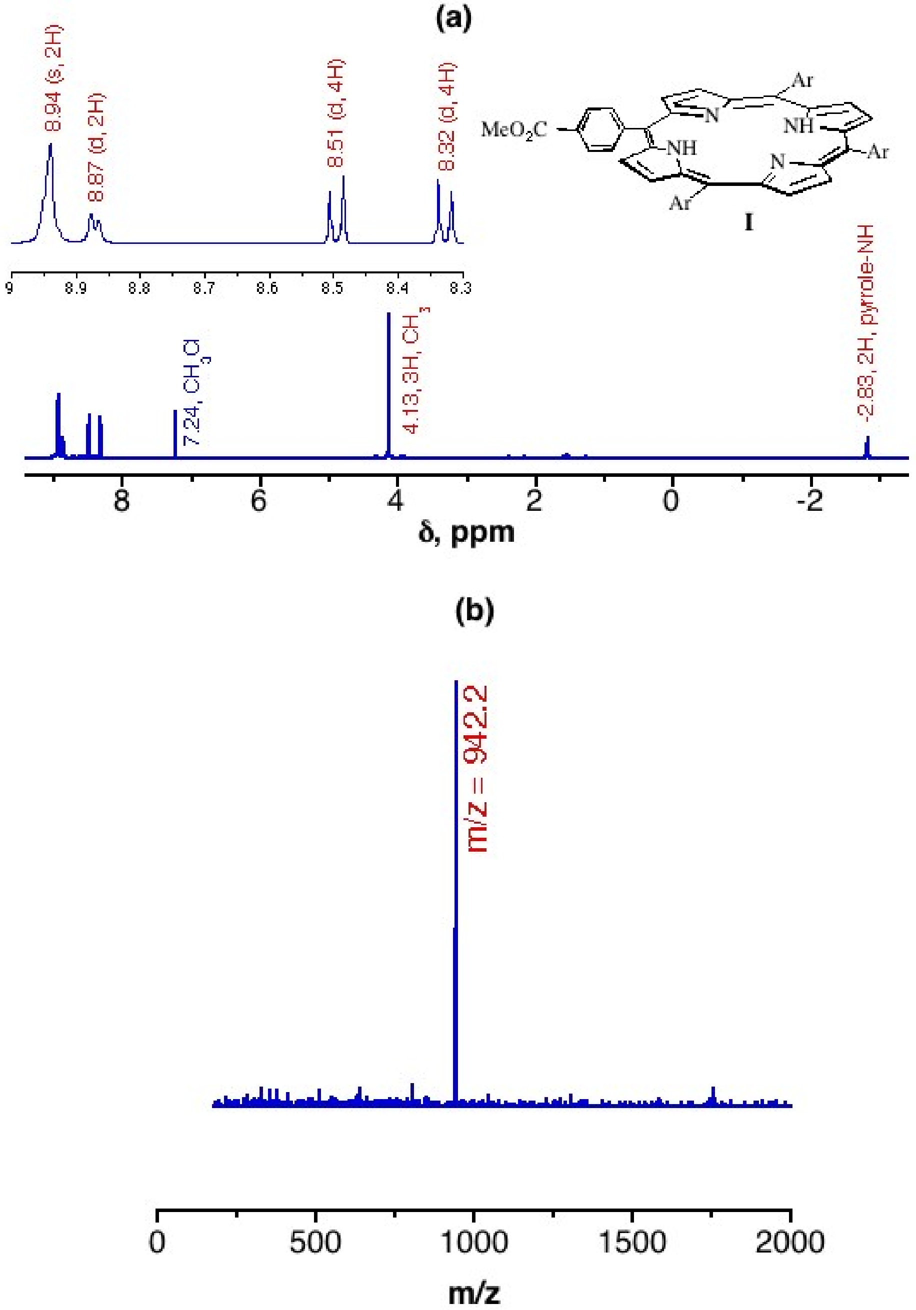

Fig. S1. ^{1}H NMR spectrum (**a**) and MALDI-TOF mass spectra (**b**) of the 5-[4-(methoxycarbonyl)phenyl]-10,15,20-pentafluorophenyl porphyrin (**I**) precursor.

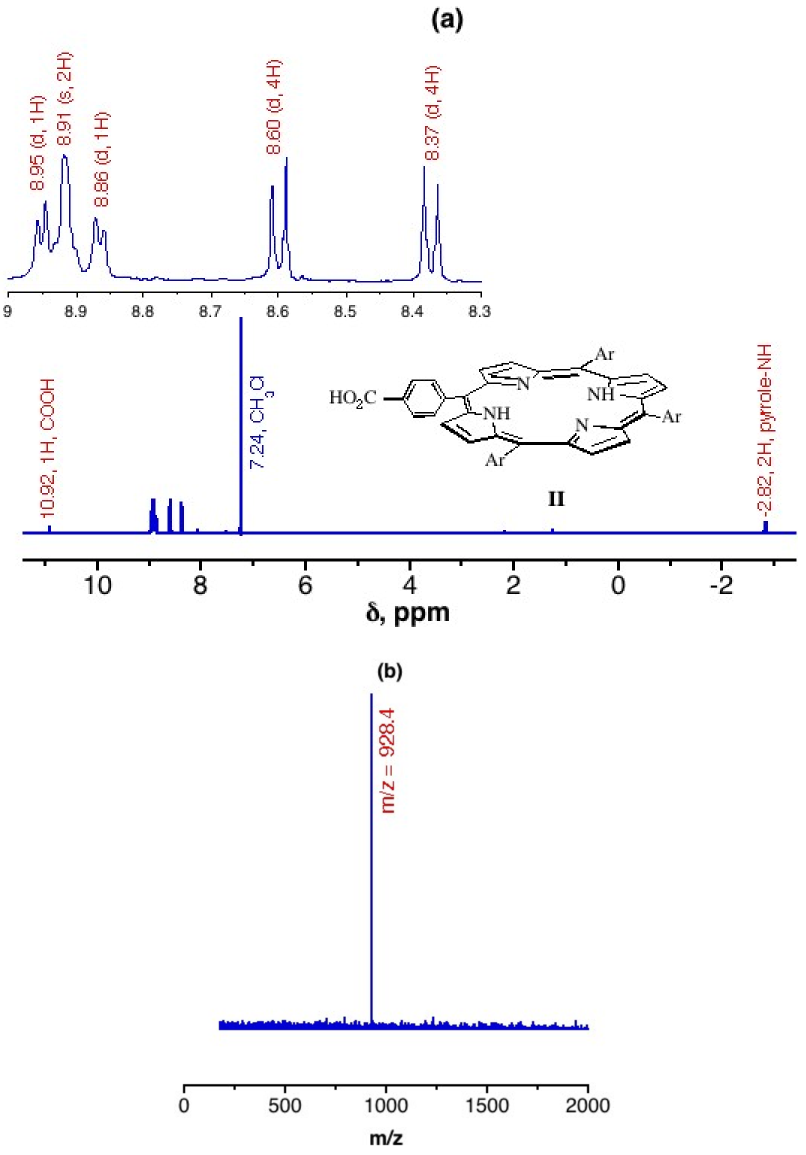

Fig. S2. ^{1}H NMR spectrum (**a**) and MALDI-TOF mass spectra (**b**) of the 5-[4-(carboxy)phenyl]-10,15,20-pentafluorophenyl porphyrin (**II**) precursor.

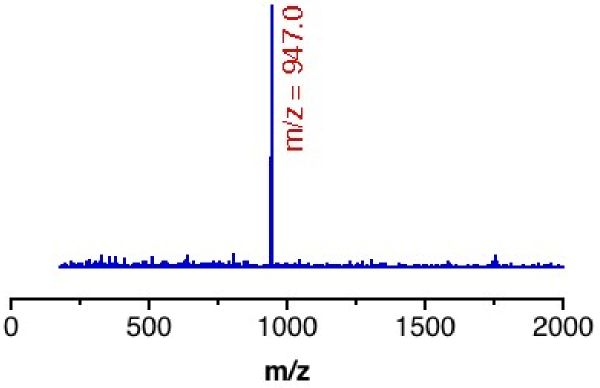

Fig. S3. MALDI-TOF mass spectra of the 5-[4-(carbonyl chloride)phenyl]-10,15,20-pentafluorophenyl porphyrin (**III**) precursor.

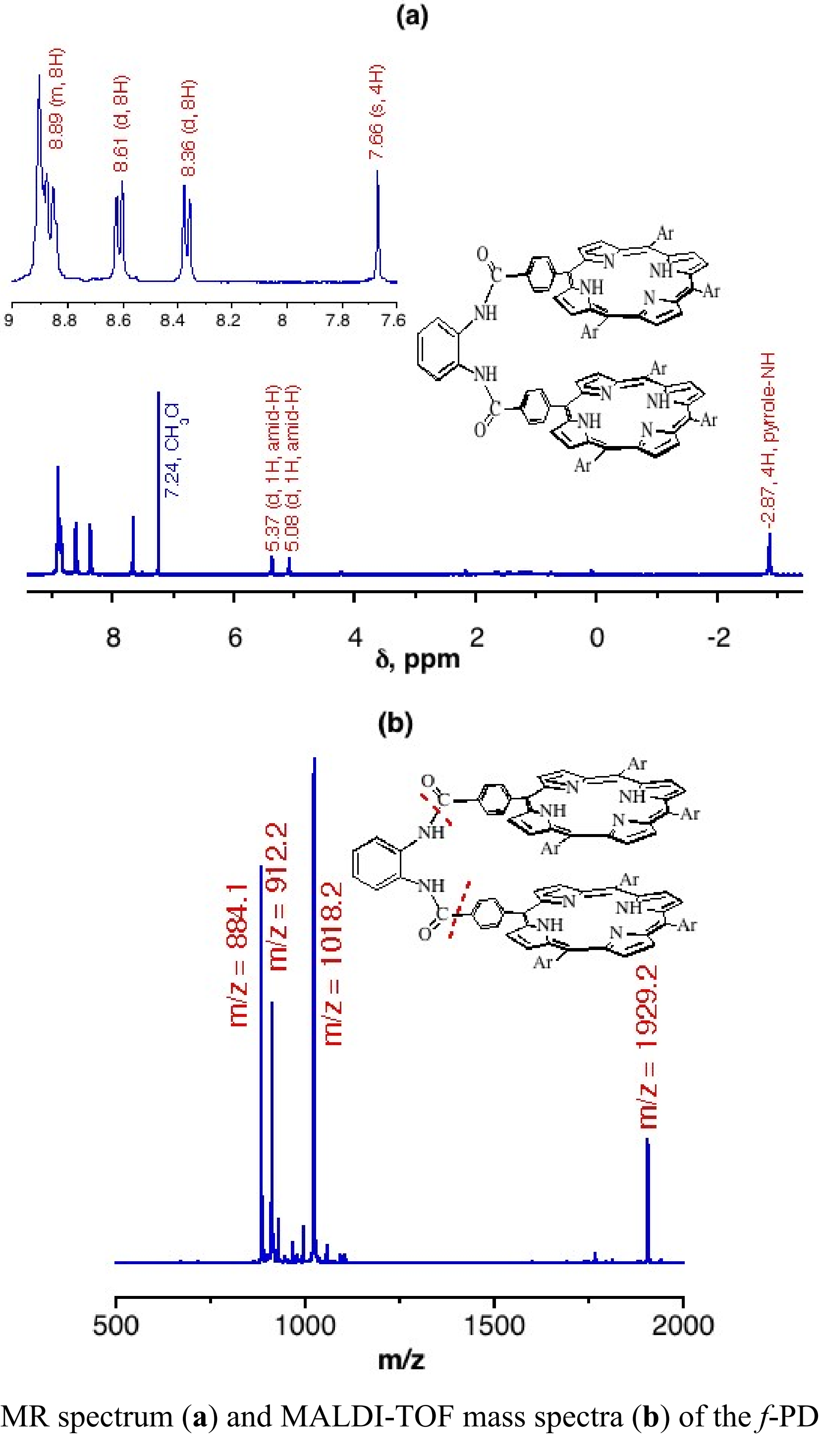

Fig. S4. ^{1}H NMR spectrum (**a**) and MALDI-TOF mass spectra (**b**) of the *f*-PD (IV) precursor.

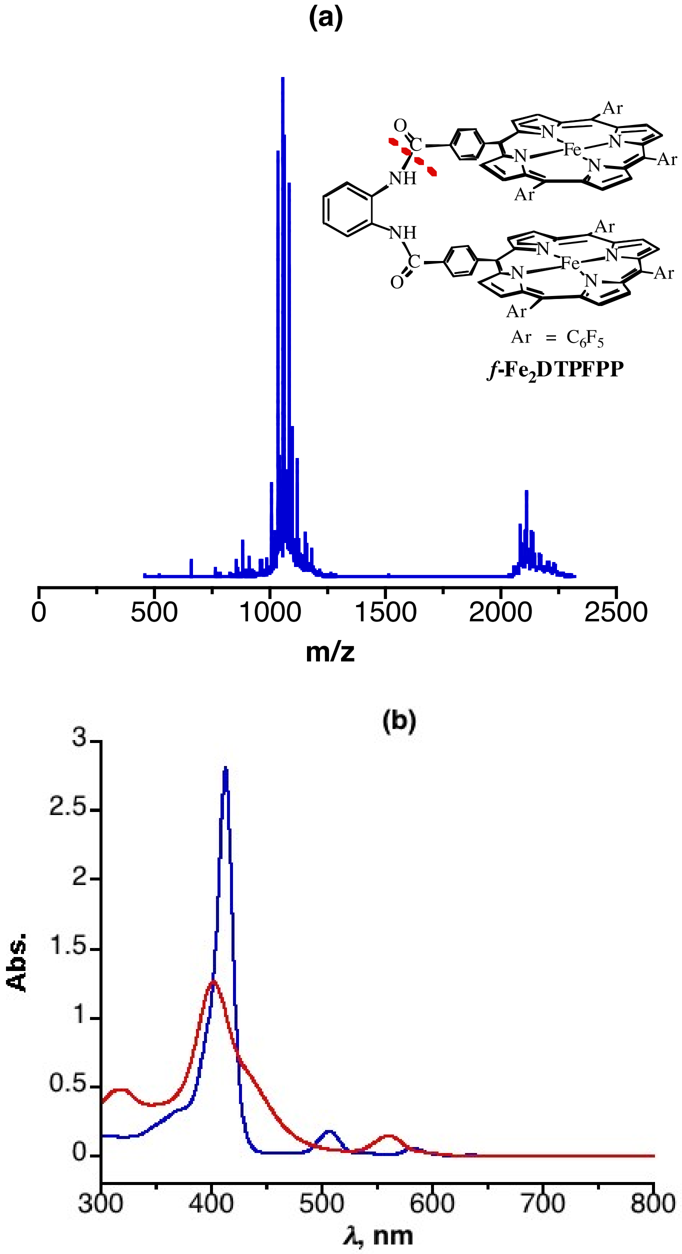

Fig. S5. (**a**) MALDI-TOF mass spectra of *f*-Fe$_2$PD. (**b**) and UV-vis spectra of *f*-PD (3.2 μM, blue) and ***f*-Fe$_2$PD** (3.6 μM, red).

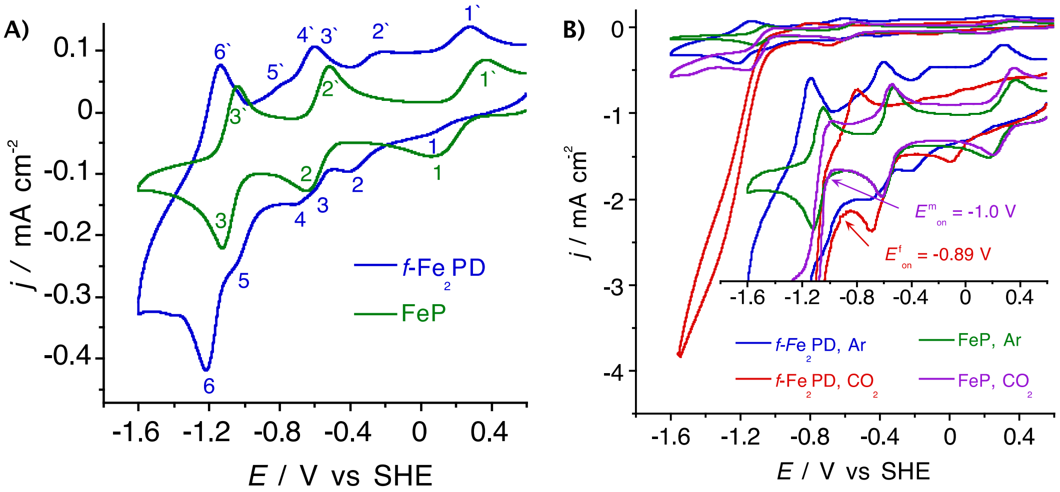

Figure S6. A) CV of (blue) *f*-Fe$_2$PD (0.5 mM) and (green) FeP (1.0 mM) in DMF/0.1 M TBNPF$_6$ at 100 mV s^{-1} scan rate under Ar using a GC electrode. **B)** CVs of *f*-Fe$_2$PD (0.5 mM) and FeP (1.0 mM) in DMF/10 % H$_2$O/1M PhOH/0.1 M TBNPF$_6$ at 100 mV s^{-1} scan rate under Ar (blue and green) and CO$_2$ (red and violet). Inset: magnification of CVs.

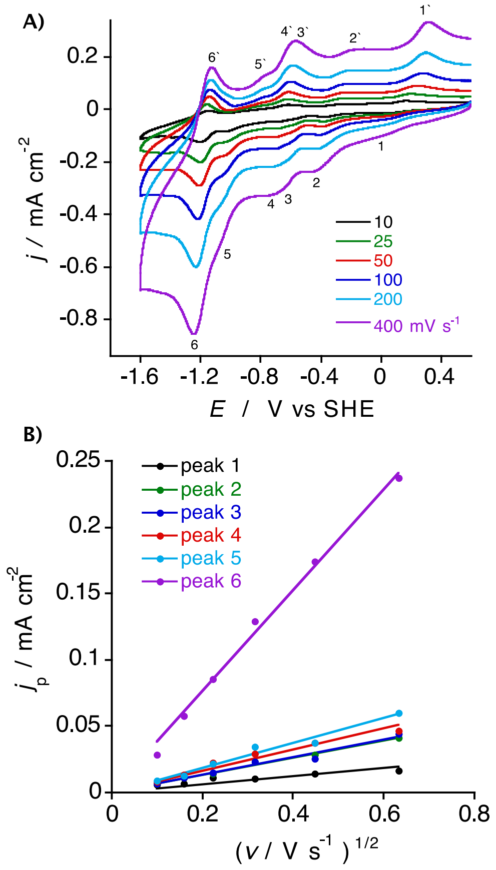

Fig. S7. A) CVs of *f*-FePD (0.5 mM) at different scan rates in a DMF/0.1 M $TBNPF_6$ solution under Ar. B) Reduction peak current densities-square root scan rates (j_p- $v^{1/2}$) relationships for the six redox couples shown in (A**)** indicating diffusion-controlled process.

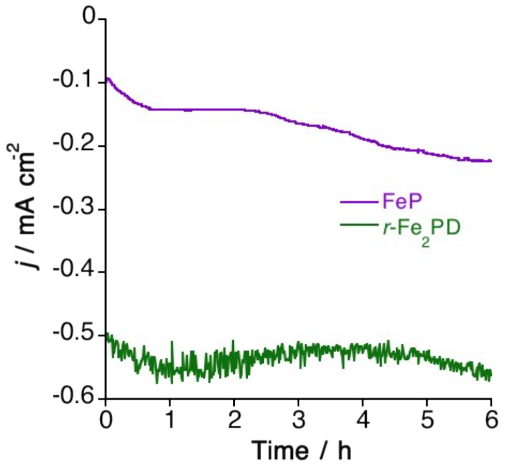

Fig. S8. Current density-time profile in bulk electrolysis (BE) for (green) *r*-Fe_2PD (0.5 mM) and (violet) FeP monomer (1.0 mM) conducted at −1.2 V vs. SHE in DMF/10 % H_2O/ 1M PhOH/0.1 M $TBNPF_6$ under CO_2.

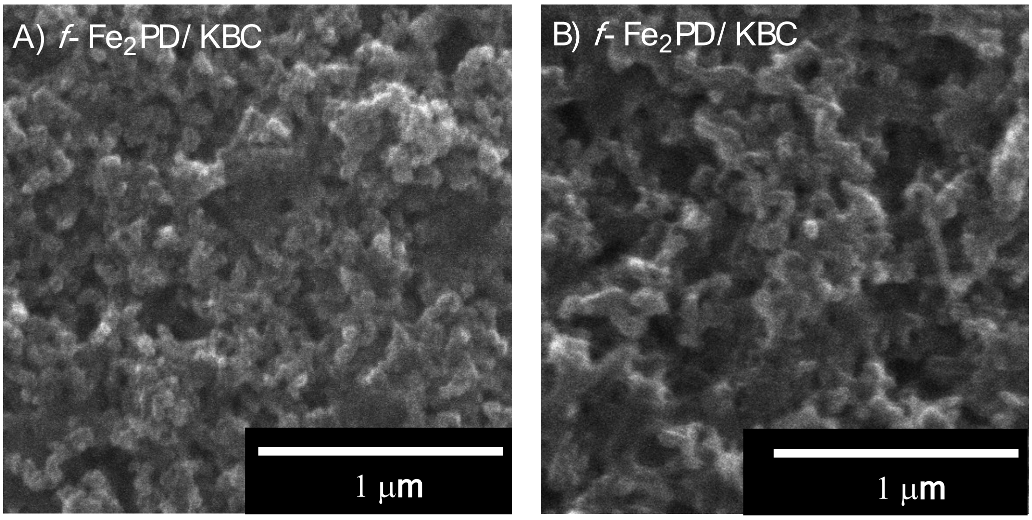

Fig. S9. Top view SEM images of *f*-Fe_2PD/KBC on GC (A) before and (B) after electrolysis.

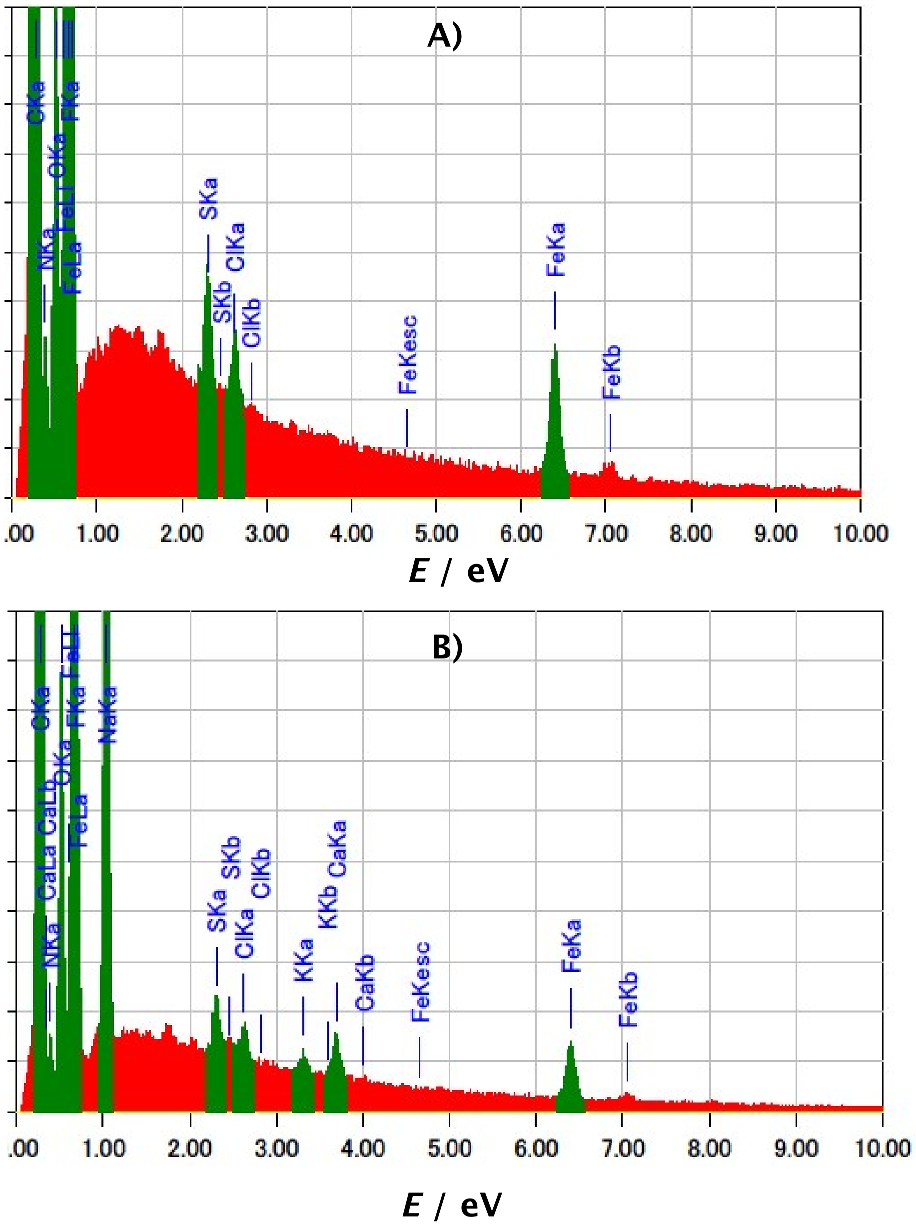

Fig. S10. EDS spectra of *f*-Fe_2PD/KBC@GC (A) before and (B) after electrolysis.

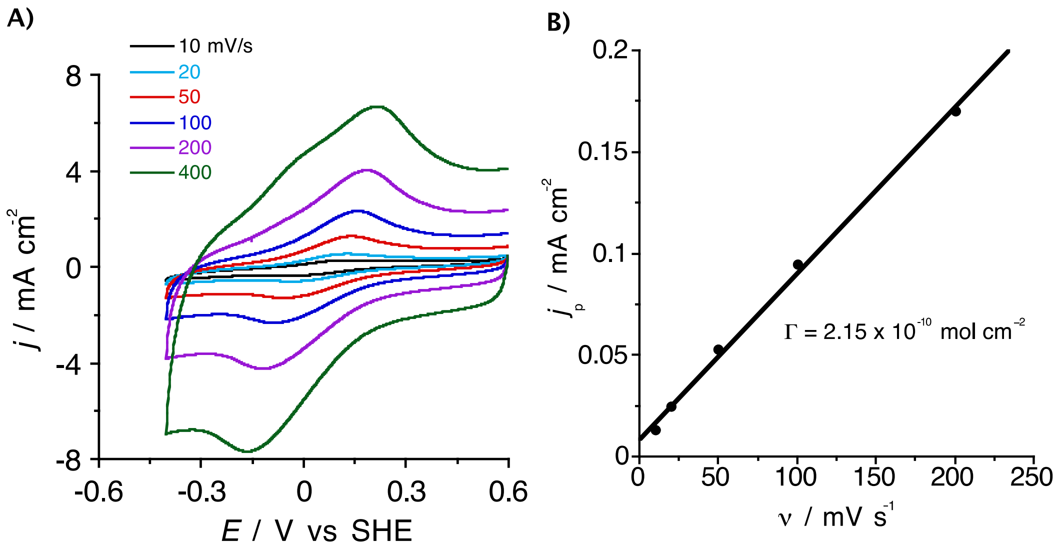

Fig. S11. A) CVs of *f*-Fe_2PD/KBC/GC at different scan rates under Ar. B) Reduction peak current, j_p–scan rate, v relationship derived from Fig. S10A.