Supporting Information

A Platinum Porphyrin Modified TiO_2 Electrode for Photoelectrochemical Hydrogen Production from Neutral Water Driven by the Conduction Band Edge Potential of TiO_2

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Materials and general measurements

5-(4-Pyridyl)-10,15,20-triphenylporphyrin (**H_2P-py**),[S1] and platinum 5-(4-pyridyl)-10,15,20-triphenylporphyrin (**PtP-py**)[S2] were prepared as described. PVP-Pt (PVP-protected colloidal Pt) was purchased from Tanaka Kikinzoku Kogyou Co., Ltd (PVP = polyvinylpyrrolidone). All other reagents were purchased from Tokyo Chemical Industry Co., Ltd, and were used without further purification.

^{1}H NMR spectra were acquired on a JEOL JNM-ESA 600 spectrometer. ESI-TOF mass spectra were recorded on a JEOL JMS-T100CS spectrometer. ATR-IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR Spectrometer, equipped with a diamond ATR crystal. UV-vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Cyclic voltammograms (CVs) was recorded on a BAS ALS Model 602DKM electrochemical analyzer, using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^+ reference electrode (-0.10 V vs. Fc/Fc^+). The electrolyte solution used was a dichloromethane containing 0.1 M TBAP (tetra(*n*-butyl)ammonium perchlorate) as a supporting electrolyte. Scan rate was 50 mV/s.

Characterization of PtP-py

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.02 (d, *J* = 5.5 Hz, 2H), 8.80 (d, *J* = 4.7 Hz, 2H), 8.77 (S, 4H), 8.69 (d, *J* = 5.5 Hz, 2H), 8.14 (d, *J* = 6.2 Hz, 6H), 8.12 (d, *J* = 6.2 Hz, 2H), 7.78-7.72 (m, 9H). ESI-TOF MS (positive ion, CH_3OH and $CHCl_3$) 809.01 *m/z* (H[**M**]$^+$). Anal. Calcd. for $C_{43}H_{27}N_5Pt\cdot 2.5H_2O$ ([**M**]·$2.5H_2O$): C, 60.49; H, 3.78; N, 8.20. Found: C, 60.33; H, 3.57; N, 8.25.

Preparation of porphyrin-adsorbed TiO_2 electrodes

Mesoporous TiO_2 thin films on a FTO glass substrate (FTO/TiO_2 electrode) were fabricated by screen-printing method followed by sintering process.[S3] The film thickness of the mesoporous TiO_2 films was ca. 12 μm. The active area of the TiO_2 film was 0.25 or 1.0 cm^2. Modification of a pristine FTO/TiO_2 electrode was carried out by submerging it into an immersion bath for 24 h at 20 °C. The amount of porphyrin adsorbed over the TiO_2 surfaces was spectrophotometrically determined by observing the absorbance change in the immersion bath. After the FTO/TiO_2 electrode was removed from the immersion bath, it was rinsed, and dried at room temperature.

Electrochemical measurements for porphyrin-adsorbed TiO_2 electrodes

Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were recorded on a BAS ALS Model 602DKM electrochemical analyzer in a three-electrode electrochemical cell with a porphyrin-adsorbed TiO_2 electrode as a working electrode, a platinum coil counter electrode, and an Ag/AgCl reference electrode (-0.01 V vs. SCE). Scan rate was 50 mV/s. The electrolyte solution used was an aqueous phosphate buffer (0.1 M, pH 7.0) containing 0.1 M Na_2SO_4 as a supporting electrolyte. The whole electrochemical cell was degassed with Ar at least 30 min prior to each measurement. Controlled potential electrolysis (CPE) was performed in the same three-electrode electrochemical cell under various applied potentials. The amount of H_2 evolved was measured by a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector and a Molecular Sieve 5A column (3 mm × 2.5 m; Ar as a carrier). The gas phase of the electrochemical cell was evacuated every 2 h of electrolysis.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) were measured on a PHI 5800 ESCA system at ultrahigh-vacuum pressure less than 1×10^{-8} Torr in the analysis chamber. A standard Al Kα excitation source (1486.6 eV) was used in the measurements. All the samples were placed on a carbon tape, and the binding energies were calibrated with the peak position of carbon 1s (284.4 eV), which is mainly derived from the carbon tape. Deconvolution was carried out using CasaXPS in which a Shirley type background was employed.

DFT calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 package of programs[S4] to estimate the reduction potential of **PtP-py** in aqueous media, which is not observable due to the overlap of catalytic current for H_2 production. The structures were fully optimized using the M06 hybrid functional (either M06 & or UM06), developed by Truhlar *et al*.[S5-7] both in gas phase and in solvated conditions, where the effect of solvation in each solvent was taken into consideration using the polarizable continuum model (PCM) method.[S8-10] The SDD basis set was adopted for the Pt ion, while the 6-31G** basis set was applied to the rest of atoms. The results were not affected when 6-31+G** was adopted instead of 6-31G** (data not shown). All stationary points were characterized by their harmonic vibrational frequencies as minima. The unscaled frequencies were used to compute the zero-point vibrational energy corrections to the energies.

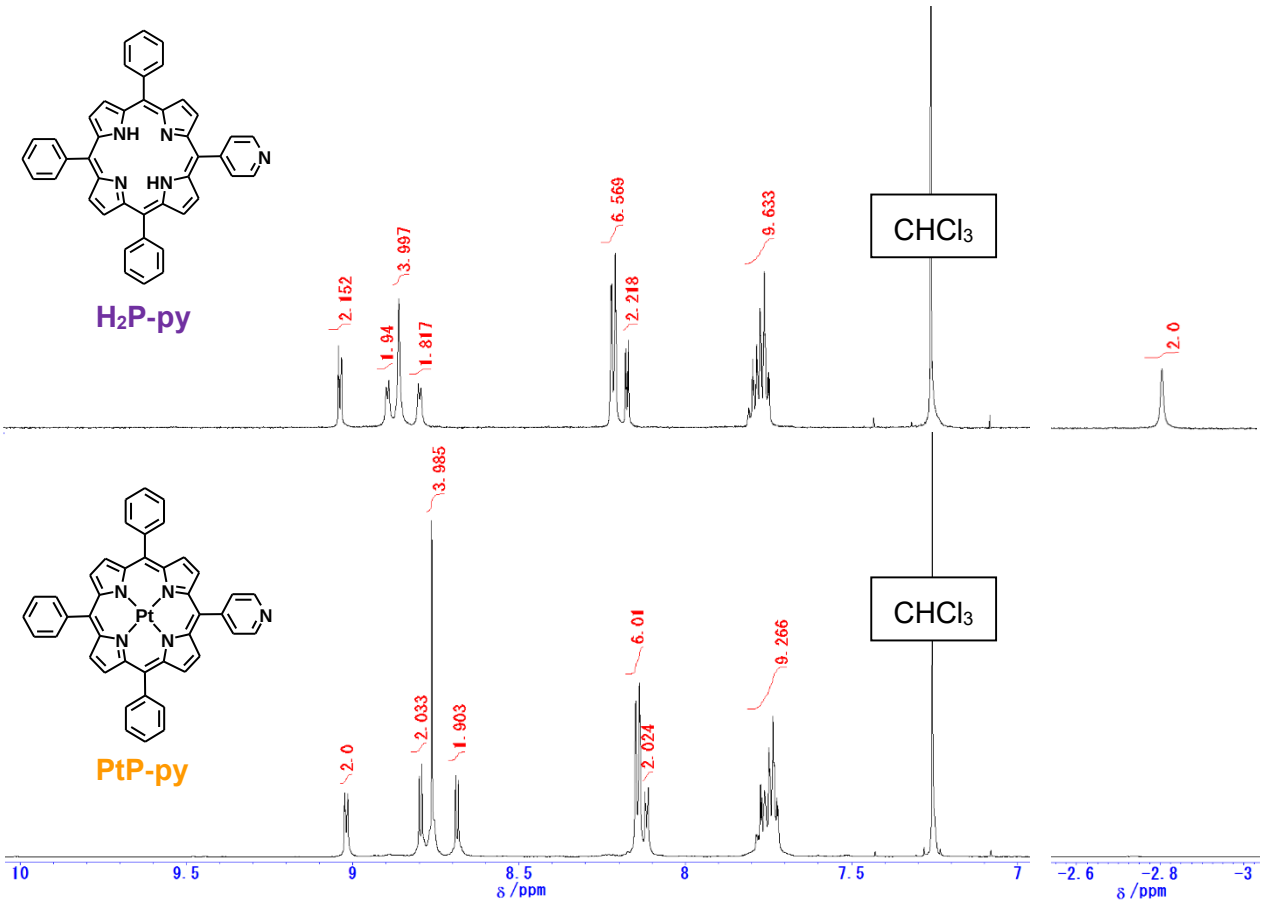

Figure S1. ^{1}H NMR spectra of **H_2P-py** and **PtP-py** in $CDCl_3$.

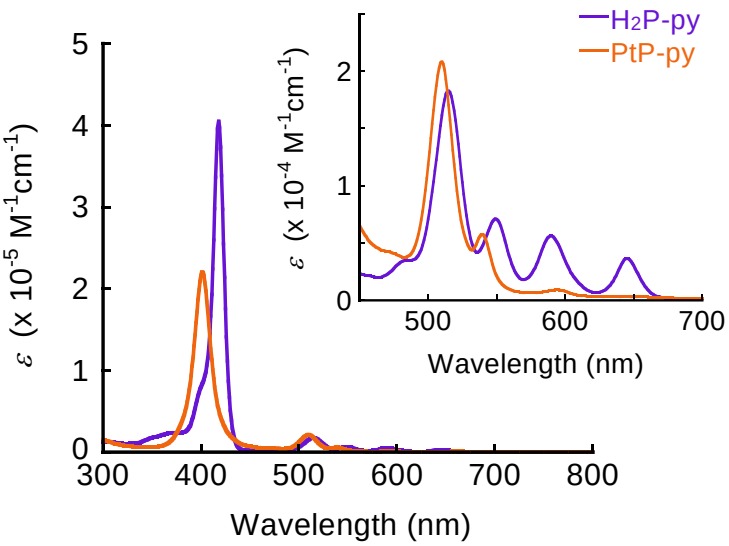

Figure S2. Absorption spectra of **H_2P-py** and **PtP-py** in chloroform.

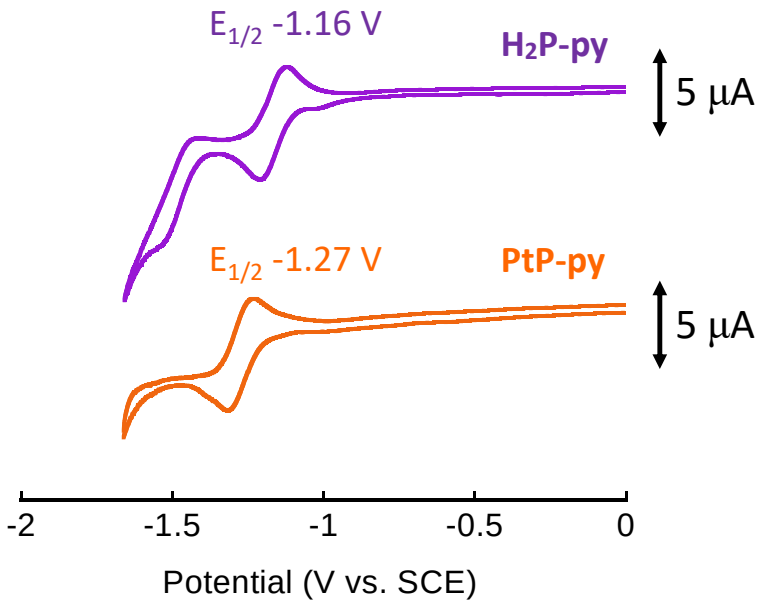

Figure S3. Cyclic voltamograms of **H_2P-py** and **PtP-py** in dichloromethane containing 0.1 M TBAP under Ar, recorded at a scan rate of 50 mV/s.

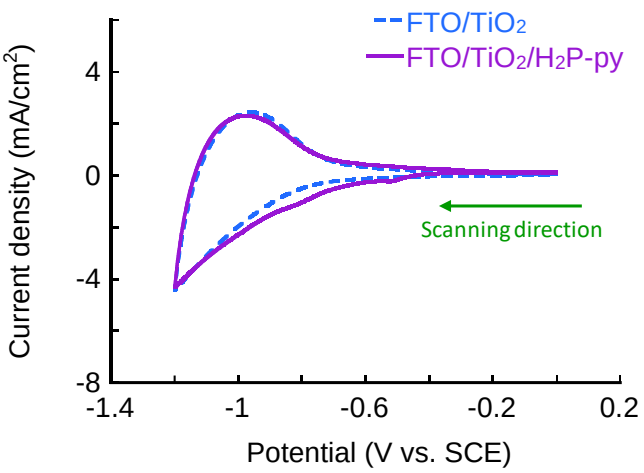

Figure S4. CVs of the FTO/TiO_2 and FTO/TiO_2/**H_2P-py** electrodes in an aqueous phosphate buffer (0.1 M, pH 7.0) containing 0.1 M Na_2SO_4. Scan rate was 50 mV/s. Film thickness of the mesoporous TiO_2 thin film of each electrode was ca. 12 μm, and the amount of **H_2P-py** adsorbed was estimated to be 1.0×10^{-7} mol/cm^2. Active area of the TiO_2 film was 0.25 cm^2.

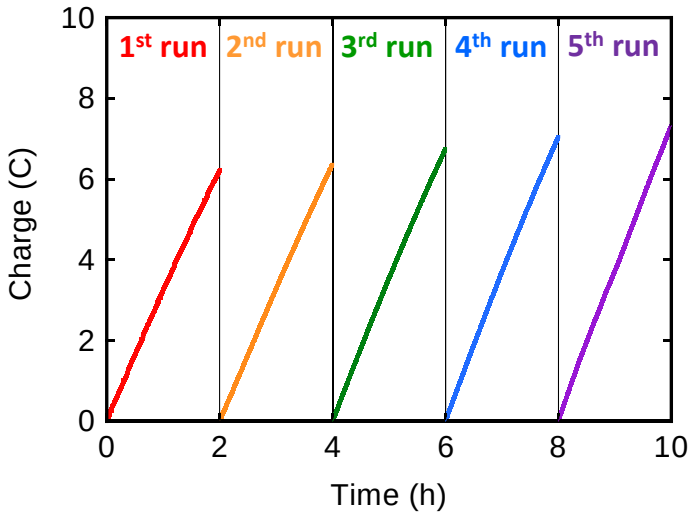

Figure S5. Charge buildup over time during CPE of the FTO/TiO_2/**PtP-py** electrode at the electrode potential held at -0.8 V vs. SCE. Active area of the TiO_2 film was 1.0 cm^2. Measurements were carried out under the same condition depicted in Figure S5. The gas phase of the electrochemical cell was evacuated every 2 h electrolysis.

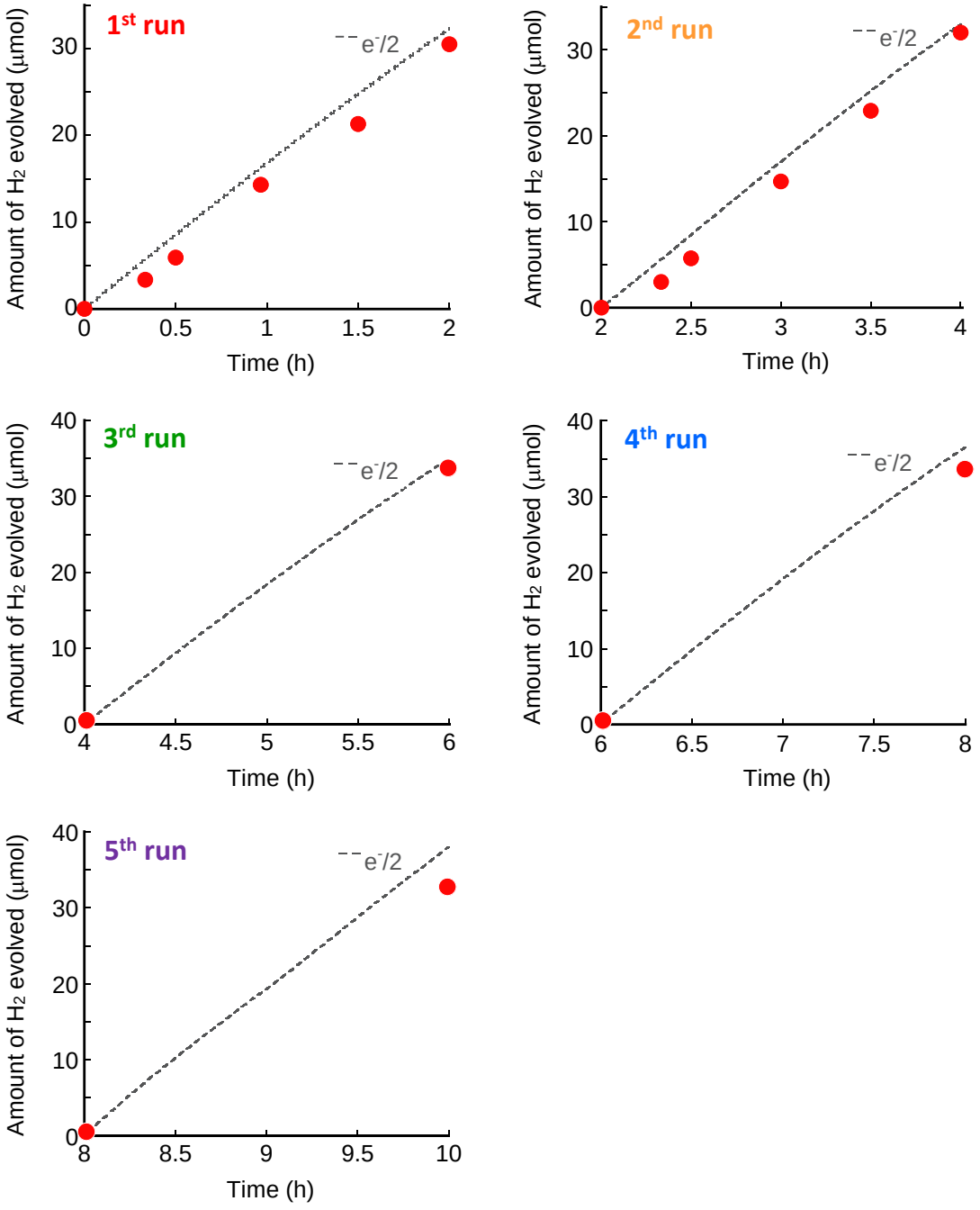

Figure S6. The amount of H_2 evolved over time during 10 h of CPE of the FTO/TiO_2/**PtP-py** electrode at the electrode potential held at -0.8 V vs. SCE. The dashed line corresponds to the amount of H_2 production with 100% Faradaic efficiency. Measurements were carried out under the conditions same to those for Figure S5. The gas phase of the electrochemical cell was evacuated every 2 h electrolysis.

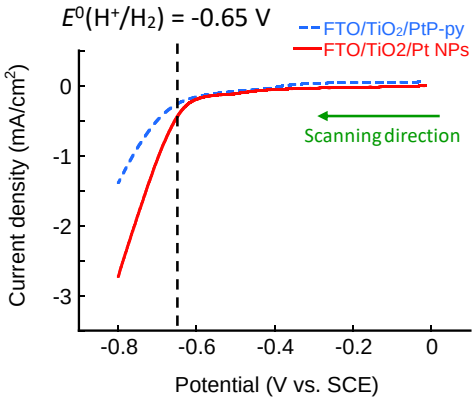

Figure S7. LSVs of the FTO/TiO_2/**PtP-py** and the FTO/TiO_2/**PtNP** electrodes in an aqueous phosphate buffer (0.1 M, pH 7.0) containing 0.1 M Na_2SO_4. Scan rate was 50 mV/s. Film thickness of the mesoporous TiO_2 thin film of each electrode was ca. 12 μm. Active area of each TiO_2 film was 1.0 cm^2. The amount of **PtP-py** adsorbed was estimated to be 1.6×10^{-7} mol/cm^2. The amount of **PtNP** formed over the TiO_2 surfaces was ca. 20 μg, which is almost the same weight to that of **PtP-py** adsorbed. The FTO/TiO_2/**PtNP** electrode was prepared by dropwise casting of an acetone solution of Pt-PVP (PVP-protected colloidal Pt, PVP = polyvinylpyrrolidone) on the FTO/TiO_2 electrode, and followed by calcination at 520 °C for 2 h.

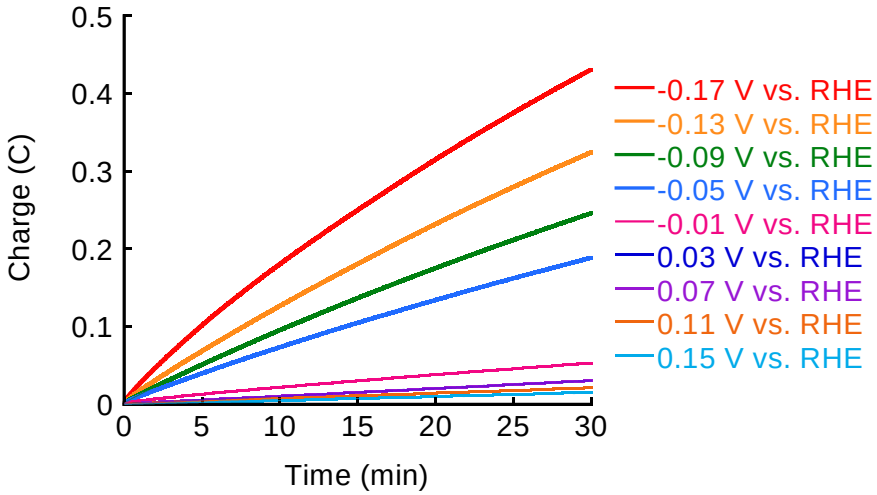

Figure S8. Charge buildup over time during CPE of the FTO/TiO_2/**PtP-py** electrode under various applied potentials. Active area of the TiO_2 film was 0.25 cm^2. All measurements were carried out in a three-electrode electrochemical cell with a Pt coil counter electrode and an Ag/AgCl reference electrode in an aqueous phosphate buffer (0.1 M, pH 7.0) containing 0.1 M Na_2SO_4. The raw data for Figure 3b.

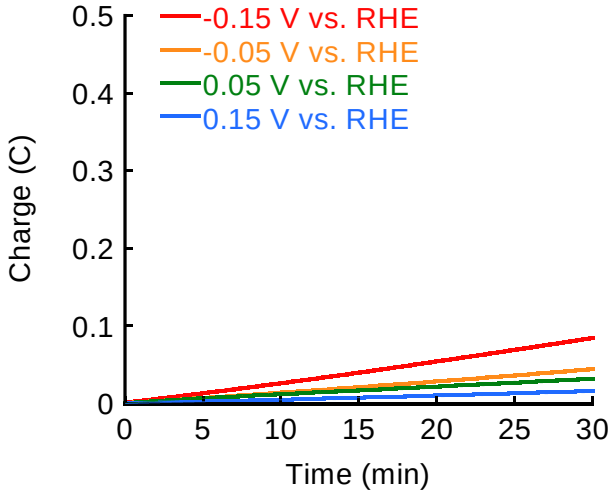

Figure S9. Charge buildup over time during CPE of the FTO/TiO_2 electrode under various applied potentials. Active area of the TiO_2 film was 0.25 cm^2. All measurements were carried out in a three-electrode electrochemical cell with a Pt coil counter electrode and an Ag/AgCl reference electrode in an aqueous phosphate buffer (0.1 M, pH 7.0) containing 0.1 M Na_2SO_4. The raw data for Figure 3b.

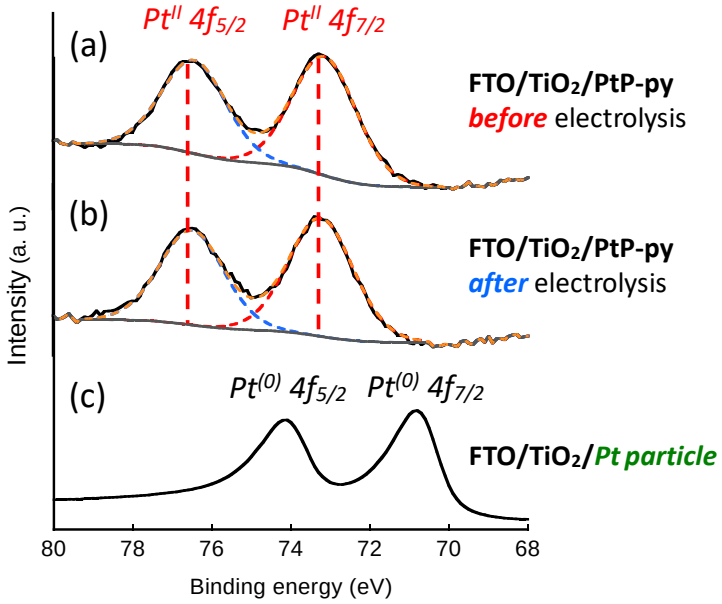

Figure S10. (a) XPS for the FTO/TiO_2/**PtP-py** electrode before CPE. (b) XPS for the FTO/TiO_2/**PtP-py** electrode after 2 h of CPE treatment under the potential held at -0.80 V vs. SCE. (c) XPS for the FTO/TiO_2/Pt nanoparticles electrode. Figures S10a and S10b are same to Figures 4a and 4b in MS, respectively. The FTO/TiO_2/Pt nanoparticles electrode was prepared by dropwise casting of an acetone solution of Pt-PVP (PVP-protected colloidal Pt, PVP = polyvinylpyrrolidone) on the FTO/TiO_2 electrode, and followed by calcination at 520 ^oC for 2 h.

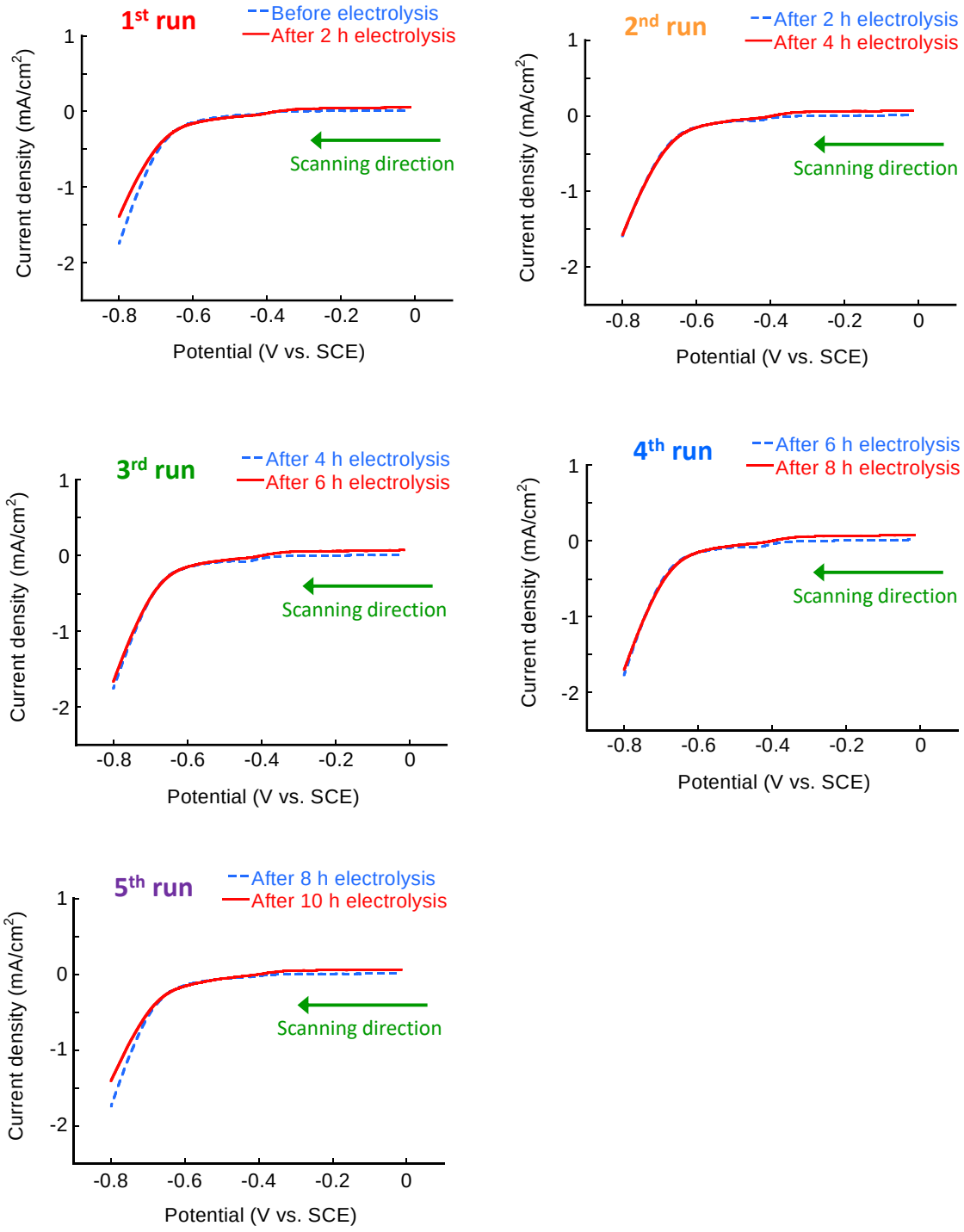

Figure S11. LSVs of the FTO/TiO_2/**Ru-py** electrodes before and after each 2 h of CPE at the electrode potential held at -0.8 V vs. SCE. Measurements were carried out under the conditions same to those for Figure S5.

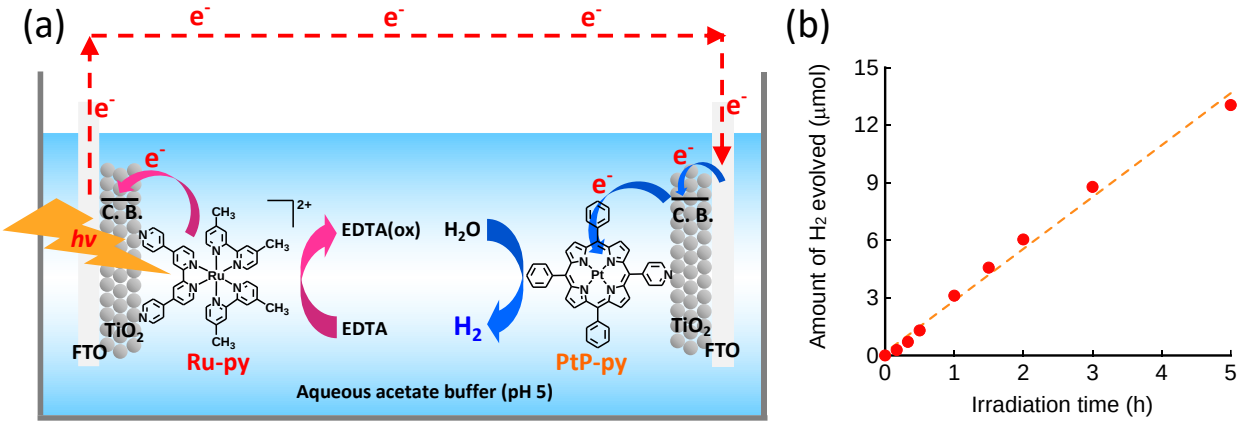

Figure S12. (a) Schematic representation of a half-reaction model cell of the DSPECs. (b) Amount of H_2 evolved over time from a half-reaction model cell of DSPECs used in this study. The FTO/TiO_2/**Ru-py** photoanode[S3a] and the FTO/TiO_2/**PtP-py** cathode are simply connected by a conducting wire (i.e., non-biased condition). Active area of each TiO_2 film was 1.0 cm^2. Electrolyte solution is an aqueous acetate buffer (0.1 M, pH 5.0) containing 30 mM EDTA (EDTA = ethylenediaminetetraacetic acid disodium salt) as a sacrificial electron donor and 0.1 M $NaClO_4$ as a supporting electrolyte. Photoirradiation was carried out by an ILC Technology CERMAX LX-300 Xe lamp (300 W), equipped with a cutoff filter (L-42, HOYA) and a cold filter (SC1201, Asahi Spectra) (ca. 410 < λ < 770 nm). The whole cell system was deaerated with Ar at least 30 min prior to the measurements. The amount of H_2 evolved was measured by a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector and a Molecular Sieves 5A column (3 mm × 2.5 m; Ar as a carrier).

Table S1. DFT-optimized geometry of gaseous Pt Porphyrin (singlet), computed at the M06/SDD(Pt)/6-31G**(HCN) level.[a]

Atom	X	Y	Z
Pt1	0.000000	0.000000	-0.000021
N2	1.806665	0.942552	-0.000071
N3	-1.806665	-0.942552	0.000030
N4	0.942551	-1.806665	-0.000054
N5	-0.942551	1.806665	0.000017
C6	4.059849	1.353242	-0.000098
C7	-0.342790	3.036590	0.000027
C8	3.036591	0.342791	-0.000093
C9	2.017676	2.294493	-0.000046
C10	-2.556738	3.431190	0.000122
C11	-2.017676	-2.294494	0.000057
C12	-3.036591	-0.342791	0.000088
C13	1.025424	3.263825	-0.000007
C14	1.353243	-4.059849	-0.000024
C15	-2.294493	2.017675	0.000083
C16	0.342790	-3.036590	-0.000018
C17	-4.059849	-1.353242	0.000138
C18	3.263825	-1.025424	-0.000095
C19	2.556738	-3.431190	-0.000056
C20	2.294493	-2.017675	-0.000069
C21	3.431190	2.556737	-0.000069
C22	-1.353243	4.059849	0.000088
C23	-3.431190	-2.556737	0.000119
C24	-3.263825	1.025424	0.000109
C25	-1.025424	-3.263825	0.000029
H26	1.352014	4.302137	0.000011
H27	4.302137	-1.352015	-0.000104
H28	-4.302137	1.352014	0.000163
H29	-1.352014	-4.302137	0.000058
H30	5.123643	1.146158	-0.000122

H31	-3.548278	3.868658	0.000171
H32	1.146159	-5.123643	-0.000009
H33	-5.123643	-1.146158	0.000182
H34	3.548278	-3.868658	-0.000069
H35	3.868659	3.548277	-0.000063
H36	-1.146159	5.123643	0.000099
H37	-3.868659	-3.548277	0.000146

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[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -1107.11157458 A.U. after 8 cycles

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Red. masses --	5.5669	5.1679	7.2969

Zero-point correction=	0.275373 (Hartree/Particle)
Thermal correction to Energy=	0.292489
Thermal correction to Enthalpy=	0.293433
Thermal correction to Gibbs Free Energy=	0.231321
Sum of electronic and zero-point Energies=	-1106.836201
Sum of electronic and thermal Energies=	-1106.819086
Sum of electronic and thermal Enthalpies=	-1106.818141
Sum of electronic and thermal Free Energies=	-1106.880254

Item	Value	Threshold	Converged?
Maximum Force	0.000311	0.000450	YES
RMS Force	0.000074	0.000300	YES

Table S2. DFT-optimized geometry of gaseous one-electron-reduced Pt Porphyrin (doublet), computed at the UM06/SDD(Pt)/6-31G**(HCN) level.[a]

Atom	X	Y	Z	Spin Density
Pt1	0.000000	0.000000	0.000475	0.023328
N2	0.992125	-1.781675	0.000425	0.040536
N3	-0.992125	1.781674	0.000522	0.040536
N4	-1.781677	-0.992137	0.000390	0.041355
N5	1.781676	0.992137	0.000461	0.041355
C6	1.463011	-4.024361	-0.000554	0.118045
C7	3.029851	0.424745	-0.000107	0.098829
C8	0.424744	-3.029844	-0.000021	-0.071229
C9	2.351868	-1.956861	-0.000177	0.099272
C10	3.363224	2.650366	-0.000671	0.117369
C11	-2.351866	1.956861	-0.000071	0.099272
C12	-0.424743	3.029844	0.000158	-0.071229
C13	3.294534	-0.937915	-0.000294	-0.084698
C14	-4.024370	-1.463001	-0.000802	-0.043372
C15	1.956866	2.351867	-0.000083	-0.071722
C16	-3.029850	-0.424745	-0.000150	0.098829
C17	-1.463011	4.024361	-0.000319	0.118045
C18	-0.937917	-3.294534	-0.000243	0.308931
C19	-3.363226	-2.650365	-0.000851	0.117369
C20	-1.956866	-2.351867	-0.000237	-0.071722
C21	2.650372	-3.363219	-0.000651	-0.042697
C22	4.024370	1.463003	-0.000689	-0.043372
C23	-2.650372	3.363218	-0.000463	-0.042697
C24	0.937916	3.294534	-0.000038	0.308931
C25	-3.294533	0.937915	-0.000254	-0.084698
H26	4.341013	-1.235754	-0.000841	0.003525
H27	-1.235745	-4.341008	-0.000780	-0.016408
H28	1.235746	4.341007	-0.000510	-0.016408
H29	-4.341012	1.235754	-0.000784	0.003525
H30	1.284406	-5.093183	-0.000802	-0.005939

H31	3.774382	3.652964	-0.001036	-0.005897
H32	-5.093194	-1.284384	-0.001124	0.001239
H33	-1.284406	5.093183	-0.000498	-0.005939
H34	-3.774384	-3.652963	-0.001278	-0.005897
H35	3.652979	-3.774369	-0.001032	0.001197
H36	5.093194	1.284388	-0.001016	0.001239
H37	-3.652978	3.774368	-0.000831	0.001197

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[a]Part of the Gaussian output file:

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Annihilation of the first spin contaminant:
S**2 before annihilation 0.7902, after 0.7511

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Red. masses --	5.2379	5.6158	7.3121

Zero-point correction= 0.268402 (Hartree/Particle)
Thermal correction to Energy= 0.286630
Thermal correction to Enthalpy= 0.287574
Thermal correction to Gibbs Free Energy= 0.222625
Sum of electronic and zero-point Energies= -1106.880909
Sum of electronic and thermal Energies= -1106.862681
Sum of electronic and thermal Enthalpies= -1106.861737
Sum of electronic and thermal Free Energies= -1106.926687

Item	Value	Threshold	Converged?
Maximum Force	0.000039	0.000450	YES
RMS Force	0.000006	0.000300	YES

Table S3. DFT-optimized geometry of Pt Porphyrin (singlet) in water, computed at the M06/SDD(Pt)/6-31G**(HCN) level using PCM.[a]

Atom	X	Y	Z
Pt1	0.000000	0.000000	0.000475
N2	0.992125	-1.781675	0.000425
N3	-0.992125	1.781674	0.000522
N4	-1.781677	-0.992137	0.000390
N5	1.781676	0.992137	0.000461
C6	1.463011	-4.024361	-0.000554
C7	3.029851	0.424745	-0.000107
C8	0.424744	-3.029844	-0.000021
C9	2.351868	-1.956861	-0.000177
C10	3.363224	2.650366	-0.000671
C11	-2.351866	1.956861	-0.000071
C12	-0.424743	3.029844	0.000158
C13	3.294534	-0.937915	-0.000294
C14	-4.024370	-1.463001	-0.000802
C15	1.956866	2.351867	-0.000083
C16	-3.029850	-0.424745	-0.000150
C17	-1.463011	4.024361	-0.000319
C18	-0.937917	-3.294534	-0.000243
C19	-3.363226	-2.650365	-0.000851
C20	-1.956866	-2.351867	-0.000237
C21	2.650372	-3.363219	-0.000651
C22	4.024370	1.463003	-0.000689
C23	-2.650372	3.363218	-0.000463
C24	0.937916	3.294534	-0.000038
C25	-3.294533	0.937915	-0.000254
H26	4.341013	-1.235754	-0.000841
H27	-1.235745	-4.341008	-0.000780
H28	1.235746	4.341007	-0.000510
H29	-4.341012	1.235754	-0.000784

H30	1.284406	-5.093183	-0.000802
H31	3.774382	3.652964	-0.001036
H32	-5.093194	-1.284384	-0.001124
H33	-1.284406	5.093183	-0.000498
H34	-3.774384	-3.652963	-0.001278
H35	3.652979	-3.774369	-0.001032
H36	5.093194	1.284388	-0.001016
H37	-3.652978	3.774368	-0.000831

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[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -1107.12473523 A.U. after 8 cycles

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	A	A	A
Frequencies --	59.5488	72.2810	73.9847
Red. masses --	5.5258	5.1638	7.1327

Zero-point correction= 0.275373 (Hartree/Particle)
Thermal correction to Energy= 0.292489
Thermal correction to Enthalpy= 0.293433
Thermal correction to Gibbs Free Energy= 0.231321
Sum of electronic and zero-point Energies= -1106.836201
Sum of electronic and thermal Energies= -1106.819086
Sum of electronic and thermal Enthalpies= -1106.818141
Sum of electronic and thermal Free Energies= -1106.880254

Item	Value	Threshold	Converged?
Maximum Force	0.000332	0.000450	YES
RMS Force	0.000075	0.000300	YES

Table S4. DFT-optimized geometry of one-electron-reduced Pt Porphyrin in water (doublet), computed at the UM06/SDD(Pt)/6-31G**(HCN) level using PCM.[a]

Atom	X	Y	Z	Spin Density
Pt1	0.000000	0.000000	-0.000003	0.018288
N2	0.004268	-2.053653	-0.000008	-0.019230
C3	1.113279	-2.869943	0.000077	0.048129
C4	0.699807	-4.225188	0.000032	0.080171
C5	-0.681762	-4.228226	-0.000093	0.080422
C6	-1.101146	-2.874696	-0.000105	0.047885
C7	2.448786	-2.416392	0.000157	0.118259
N8	-2.049748	-0.004210	0.000003	0.101217
N9	-0.004268	2.053653	-0.000007	-0.019230
N10	2.049748	0.004210	0.000002	0.101217
C11	-2.438481	-2.426681	-0.000165	0.118747
C12	2.866020	-1.105521	0.000101	-0.024275
C13	-2.861165	-1.117474	-0.000072	-0.024512
C14	-2.866020	1.105521	0.000102	-0.024275
C15	-1.113278	2.869943	0.000077	0.048129
C16	1.101146	2.874696	-0.000105	0.047885
C17	2.861165	1.117475	-0.000073	-0.024512
C18	4.243588	-0.668488	0.000104	-0.007276
C19	-4.240575	-0.686574	-0.000014	-0.007074
C20	-4.243588	0.668488	0.000105	-0.007277
C21	-2.448786	2.416392	0.000157	0.118259
C22	-0.699807	4.225189	0.000032	0.080171
C23	0.681762	4.228226	-0.000093	0.080422
C24	2.438481	2.426681	-0.000165	0.118747
C25	4.240575	0.686575	-0.000014	-0.007074
H26	3.223054	-3.182225	0.000188	-0.006426
H27	-3.209611	-3.195649	-0.000206	-0.006448
H28	-3.223053	3.182224	0.000187	-0.006426
H29	3.209611	3.195649	-0.000205	-0.006448

H30	1.375224	-5.073903	0.000063	-0.004744
H31	-1.353395	-5.079926	-0.000164	-0.004754
H32	5.094370	-1.341147	0.000186	0.000387
H33	-5.088302	-1.363095	-0.000042	0.000379
H34	-5.094370	1.341147	0.000187	0.000387
H35	-1.375224	5.073903	0.000063	-0.004744
H36	1.353395	5.079926	-0.000165	-0.004754
H37	5.088302	1.363095	-0.000043	0.000379

---

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1107.22573134 A.U. after 18 cycles

Annihilation of the first spin contaminant:
S**2 before annihilation 0.7645, after 0.7501

	1	2	3
	A	A	A
Frequencies --	59.3404	59.5357	70.9098
Red. masses --	5.2171	5.6329	7.4798

Zero-point correction= 0.270472 (Hartree/Particle)
Thermal correction to Energy= 0.288339
Thermal correction to Enthalpy= 0.289283
Thermal correction to Gibbs Free Energy= 0.224979
Sum of electronic and zero-point Energies= -1106.955260
Sum of electronic and thermal Energies= -1106.937392
Sum of electronic and thermal Enthalpies= -1106.936448
Sum of electronic and thermal Free Energies= -1107.000752

Item	Value	Threshold	Converged?
Maximum Force	0.000090	0.000450	YES
RMS Force	0.000016	0.000300	YES

Table S5. DFT-optimized geometry of Pt Porphyrin (singlet) in dichloromethane, computed at the M06/SDD(Pt)/6-31G**(HCN) level using PCM.[a]

Atom	X	Y	Z
Pt1	0.000000	0.000000	0.000000
N2	-2.032243	-0.165168	-0.000047
N3	2.032243	0.165168	0.000050
N4	-0.165168	2.032243	-0.000035
N5	0.165169	-2.032243	0.000032
C6	-4.268565	0.334361	-0.000108
C7	-0.867817	-2.933112	0.000016
C8	-2.933112	0.867817	-0.000084
C9	-2.753966	-1.329560	-0.000049
C10	1.019882	-4.158013	0.000083
C11	2.753966	1.329560	0.000054
C12	2.933112	-0.867817	0.000094
C13	-2.217330	-2.609645	-0.000022
C14	0.334361	4.268565	-0.000065
C15	1.329560	-2.753966	0.000074
C16	0.867817	2.933112	-0.000026
C17	4.268565	-0.334361	0.000127
C18	-2.609645	2.217329	-0.000099
C19	-1.019882	4.158013	-0.000098
C20	-1.329560	2.753966	-0.000078
C21	-4.158013	-1.019882	-0.000087
C22	-0.334361	-4.268565	0.000047
C23	4.158013	1.019882	0.000101
C24	2.609645	-2.217329	0.000105
C25	2.217330	2.609645	0.000016
H26	-2.922225	-3.438636	-0.000028
H27	-3.438636	2.922225	-0.000132
H28	3.438636	-2.922225	0.000140
H29	2.922225	3.438636	0.000021

H30	-5.167797	0.939052	-0.000137
H31	1.762915	-4.946827	0.000113
H32	0.939052	5.167797	-0.000069
H33	5.167797	-0.939052	0.000166
H34	-1.762915	4.946827	-0.000133
H35	-4.946827	-1.762915	-0.000095
H36	-0.939052	-5.167797	0.000040
H37	4.946827	1.762915	0.000115

---

[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -1107.12148143 A.U. after 9 cycles

	1	2	3
	A	A	A
Frequencies --	55.7521	68.6244	70.2703
Red. masses --	5.5941	5.1392	7.4225

Zero-point correction=	0.275167 (Hartree/Particle)
Thermal correction to Energy=	0.292355
Thermal correction to Enthalpy=	0.293299
Thermal correction to Gibbs Free Energy=	0.230934
Sum of electronic and zero-point Energies=	-1106.846314
Sum of electronic and thermal Energies=	-1106.829127
Sum of electronic and thermal Enthalpies=	-1106.828182
Sum of electronic and thermal Free Energies=	-1106.890548

Item	Value	Threshold	Converged?
Maximum Force	0.000273	0.000450	YES
RMS Force	0.000061	0.000300	YES

Table S6. DFT-optimized geometry of one-electron-reduced Pt Porphyrin in dichloromethane (doublet), computed at the UM06/SDD(Pt)/6-31G**(HCN) level using PCM.[a]

Atom	X	Y	Z	Spin Density
Pt1	0.000000	0.000000	0.000000	0.019801
N2	-0.003345	-2.053778	-0.000001	-0.019229
C3	1.101869	-2.873529	0.000002	0.047180
C4	0.683804	-4.227686	0.000001	0.081783
C5	-0.697592	-4.225451	-0.000003	0.081494
C6	-1.111253	-2.869962	-0.000004	0.047477
C7	2.438668	-2.424935	0.000004	0.118897
N8	-2.049626	0.003339	0.000000	0.101955
N9	0.003345	2.053778	-0.000001	-0.019229
N10	2.049626	-0.003339	0.000000	0.101955
C11	-2.446554	-2.416993	-0.000006	0.118236
C12	2.860616	-1.115495	0.000004	-0.025273
C13	-2.864243	-1.106224	-0.000001	-0.024968
C14	-2.860616	1.115495	0.000004	-0.025273
C15	-1.101869	2.873529	0.000002	0.047180
C16	1.111253	2.869962	-0.000004	0.047477
C17	2.864243	1.106224	-0.000002	-0.024968
C18	4.240037	-0.684406	0.000004	-0.007604
C19	-4.242234	-0.670654	0.000001	-0.007878
C20	-4.240037	0.684406	0.000005	-0.007604
C21	-2.438668	2.424935	0.000005	0.118897
C22	-0.683804	4.227686	0.000001	0.081783
C23	0.697592	4.225451	-0.000003	0.081494
C24	2.446554	2.416993	-0.000006	0.118236
C25	4.242234	0.670654	0.000001	-0.007878
H26	3.210337	-3.193570	0.000005	-0.006541
H27	-3.220726	-3.183113	-0.000006	-0.006509
H28	-3.210337	3.193570	0.000006	-0.006541
H29	3.220726	3.183113	-0.000006	-0.006509

H30	1.356311	-5.078840	0.000003	-0.004884
H31	-1.372856	-5.074419	-0.000004	-0.004872
H32	5.088013	-1.360815	0.000006	0.000412
H33	-5.092410	-1.344300	0.000000	0.000424
H34	-5.088013	1.360815	0.000006	0.000412
H35	-1.356311	5.078840	0.000003	-0.004884
H36	1.372856	5.074419	-0.000004	-0.004872
H37	5.092410	1.344300	-0.000001	0.000424

---

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1107.21540752 A.U. after 17 cycles

Annihilation of the first spin contaminant:
S**2 before annihilation 0.7648, after 0.7502

	1	2	3
	A	A	A
Frequencies --	56.6448	61.2464	70.8076
Red. masses --	5.2077	5.6629	7.3979

Zero-point correction= 0.270092 (Hartree/Particle)
Thermal correction to Energy= 0.288058
Thermal correction to Enthalpy= 0.289002
Thermal correction to Gibbs Free Energy= 0.224483
Sum of electronic and zero-point Energies= -1106.945316
Sum of electronic and thermal Energies= -1106.927349
Sum of electronic and thermal Enthalpies= -1106.926405
Sum of electronic and thermal Free Energies= -1106.990924

Item	Value	Threshold	Converged?
Maximum Force	0.000050	0.000450	YES
RMS Force	0.000010	0.000300	YES

Table S7. DFT-optimized geometry of Pt Porphyrin (singlet) in N,N-dimethylformamide, computed at the M06/SDD(Pt)/6-31G**(HCN) level using PCM.[a]

Atom	X	Y	Z
Pt1	0.000000	0.000000	-0.000001
N2	-1.544417	-1.331346	0.000006
N3	1.544417	1.331345	0.000112
N4	-1.331347	1.544416	-0.000115
N5	1.331347	-1.544415	-0.000031
C6	-3.645525	-2.246342	0.000090
C7	1.028212	-2.881165	0.000192
C8	-2.881167	-1.028211	-0.000243
C9	-1.441062	-2.698433	0.000475
C10	3.275442	-2.757755	-0.000600
C11	1.441062	2.698433	0.000594
C12	2.881167	1.028211	-0.000055
C13	-0.252601	-3.415662	0.000568
C14	-2.246341	3.645524	-0.000244
C15	2.698435	-1.441061	-0.000474
C16	-1.028211	2.881164	0.000146
C17	3.645525	2.246342	0.000327
C18	-3.415665	0.252602	-0.000700
C19	-3.275442	2.757757	-0.000781
C20	-2.698435	1.441062	-0.000637
C21	-2.757757	-3.275442	0.000580
C22	2.246342	-3.645524	-0.000109
C23	2.757756	3.275442	0.000769
C24	3.415666	-0.252601	-0.000487
C25	0.252602	3.415662	0.000621
H26	-0.332843	-4.500840	0.000836
H27	-4.500843	0.332837	-0.000983
H28	4.500844	-0.332844	-0.000721
H29	0.332839	4.500843	0.000917

H30	-4.728398	-2.287403	-0.000065
H31	4.340778	-2.956594	-0.000986
H32	-2.287400	4.728397	-0.000106
H33	4.728397	2.287404	0.000264
H34	-4.340778	2.956594	-0.001211
H35	-2.956592	-4.340778	0.000994
H36	2.287406	-4.728396	-0.000004
H37	2.956593	4.340777	0.001136

---

[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -1107.12423791 A.U. after 9 cycles

	1	2	3
	A	A	A
Frequencies --	60.0566	67.3180	72.7437
Red. masses --	5.5718	5.1255	7.2760

Zero-point correction= 0.275442 (Hartree/Particle)
Thermal correction to Energy= 0.292537
Thermal correction to Enthalpy= 0.293481
Thermal correction to Gibbs Free Energy= 0.231385
Sum of electronic and zero-point Energies= -1106.848796
Sum of electronic and thermal Energies= -1106.831701
Sum of electronic and thermal Enthalpies= -1106.830757
Sum of electronic and thermal Free Energies= -1106.892853

Item	Value	Threshold	Converged?
Maximum Force	0.000423	0.000450	YES
RMS Force	0.000074	0.000300	YES

Table S8. DFT-optimized geometry of one-electron-reduced Pt Porphyrin in N,N-dimethylformamide (doublet), computed at the UM06/SDD(Pt)/6-31G**(HCN) level using PCM.[a]

Atom	X	Y	Z	Spin Density
Pt1	0.000000	0.000000	-0.000019	0.018523
N2	-0.014530	-2.053703	-0.000035	-0.019227
C3	-1.127762	-2.864027	0.000710	0.048692
C4	-0.721573	-4.221351	0.000502	0.079727
C5	0.659945	-4.231820	-0.000517	0.081305
C6	1.086364	-2.880252	-0.000731	0.047096
C7	-2.460913	-2.403794	0.001189	0.116812
N8	2.049765	-0.014486	0.000002	0.101322
N9	0.014530	2.053703	-0.000035	-0.019227
N10	-2.049765	0.014486	-0.000001	0.101322
C11	2.425884	-2.438936	-0.001247	0.120239
C12	-2.871688	-1.090937	0.000707	-0.023702
C13	2.855029	-1.131736	-0.000664	-0.025328
C14	2.871688	1.090937	0.000708	-0.023702
C15	1.127762	2.864028	0.000710	0.048692
C16	-1.086364	2.880252	-0.000731	0.047096
C17	-2.855029	1.131736	-0.000665	-0.025328
C18	-4.247041	-0.646703	0.000572	-0.007974
C19	4.236683	-0.708309	-0.000382	-0.006558
C20	4.247041	0.646703	0.000572	-0.007974
C21	2.460913	2.403793	0.001189	0.116812
C22	0.721573	4.221351	0.000501	0.079727
C23	-0.659945	4.231820	-0.000518	0.081305
C24	-2.425884	2.438936	-0.001246	0.120239
C25	-4.236683	0.708309	-0.000382	-0.006558
H26	-3.238889	-3.165810	0.001622	-0.006371
H27	3.193285	-3.211649	-0.001688	-0.006532
H28	3.238893	3.165814	0.001619	-0.006371
H29	-3.193285	3.211649	-0.001684	-0.006532

H30	-1.401633	-5.066448	0.000899	-0.004738
H31	1.327041	-5.087149	-0.000927	-0.004802
H32	-5.101536	-1.314747	0.001031	0.000418
H33	5.080719	-1.389534	-0.000784	0.000359
H34	5.101536	1.314748	0.001030	0.000418
H35	1.401633	5.066448	0.000899	-0.004738
H36	-1.327042	5.087149	-0.000927	-0.004802
H37	-5.080719	1.389534	-0.000783	0.000359

---

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1107.22416975 A.U. after 16 cycles

Annihilation of the first spin contaminant:
S**2 before annihilation 0.7646, after 0.7502

	1	2	3
	A	A	A
Frequencies --	58.7752	59.7789	70.8543
Red. masses --	5.2194	5.6359	7.4682

Zero-point correction= 0.270410 (Hartree/Particle)
Thermal correction to Energy= 0.288294
Thermal correction to Enthalpy= 0.289238
Thermal correction to Gibbs Free Energy= 0.224897
Sum of electronic and zero-point Energies= -1106.953760
Sum of electronic and thermal Energies= -1106.935876
Sum of electronic and thermal Enthalpies= -1106.934932
Sum of electronic and thermal Free Energies= -1106.999273

Item	Value	Threshold	Converged?
Maximum Force	0.000062	0.000450	YES
RMS Force	0.000015	0.000300	YES

Estimation of Reduction Potential by DFT calculation[S11,12]

The standard reduction potential, E^o, is determined from the calculated free energy of reduction, $\Delta G_{solv}^{o,red}$, using the relation

$$E^o = -\frac{\Delta G_{solv}^{o,red}}{nF} \quad \text{---------- (1)}$$

The free energy of reduction is defined as the free energy change associated with the following reaction

$$Ox_{solv} + e^- \rightarrow Red_{solv} \quad \text{---------- (2)}$$

The calculating $\Delta G_{solv}^{o,red}$ by quantum chemistry methods can be obtained with structures optimized in the gas phase through a Born-Haber thermodynamic cycle, shown in Scheme S1, or with structures optimized in solution.

$$\begin{array}{ccccc} \boldsymbol{PtP-py}_{gas} & + & e^- & \xrightarrow{\Delta G_{gas}^{o,red}} & \boldsymbol{PtP-py^-}_{gas} \\ \Big\downarrow \Delta G_s^o(\boldsymbol{PtP-py}) & & \Big\downarrow & & \Big\downarrow \Delta G_s^o(\boldsymbol{PtP-py^-}) \\ \boldsymbol{PtP-py}_{solv} & + & e^- & \xrightarrow[\Delta G_{solv}^{o,red}]{} & \boldsymbol{PtP-py^-}_{solv} \end{array}$$

Scheme S1. Born-Haber thermodynamic cycle for calculating the free energy of reduction

$$\Delta G_{solv}^{o,red} = \Delta G_{gas}^{o,red} + \Delta G_s^o(\boldsymbol{PtP-py^-}) - \Delta G_s^o(\boldsymbol{PtP-py}) \quad \text{---------- (3)}$$

Table S9. Thermal free energies and estimated reduction potentials

Solvent	$G^0(\boldsymbol{PtP\text{-}py})$ $(G^0(\boldsymbol{PtP\text{-}py^-}))$ / $hartree$	$\Delta G_s^o(\boldsymbol{PtP\text{-}py})$ $(\Delta G_s^o(\boldsymbol{PtP\text{-}py^-}))$ / $\frac{kcal}{mol}$	$\Delta G_{solv}^{o,red}$ / $\frac{kcal}{mol}$	E^o / V	E_{obs} / V vs. SCE	E_{calc} [a] / V vs. SCE
vacuo	-1106.880 (-1106.927)					
water	-1106.893 (-1107.001)	-8.013 (-46.48)	-67.60	2.894	NA	-1.08
CH_2Cl_2	-1106.891 (-1106.991)	-6.460 (-40.31)	-62.12	2.694	-1.27	-1.29
DMF	-1106.893 (-1106.999)	-7.916 (-45.55)	-65.91	2.858	-1.13	-1.11

[a] The E_{calc} values are calculated using both the reduction potentials (E_{obs}) in CH_2Cl_2 and DMF as benchmarks.

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