Electronic Supplementary Information

Introducing of proton/electron mediators enhances catalytic ability of iron porphyrin complex for photochemical CO$_2$ reduction

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# Table of contents

1. Experimental details
   - General procedures ................................................................. 3
   - Syntheses .................................................................................. 3
   - Photochemistry .......................................................................... 17
   - $^{13}$CO$_2$ labeling experiment .................................................. 17
   - Electrochemistry .......................................................................... 17

2. UV-vis absorption spectroscopy .................................................... 18

3. Electrochemical measurements ..................................................... 19

4. Photocatalytic activity for CO$_2$ reduction ...................................... 20

5. Quantum chemical calculation ...................................................... 22

6. Emission quenching experiments .................................................. 23

7. Comparison of catalytic ability ...................................................... 24

8. References .................................................................................. 27
1. Experimental details

General procedures

Pyrrole, boron trifluoride diethyl etherate (BF₃·OEt₂) and sodium borohydride were purchased from Sigma-Aldrich Co., LLC. Propanoic acid was purchased from Kishida Chemical Co., LLC. Benzaldehyde, triethylamine (TEA), sodium sulfate (Na₂SO₄), sodium dithionite (Na₂S₂O₄), 2 M hydrochloric acid, sodium chloride, toluene, pyridinium chloride, ethyl acetate (EtOAc), tris(2-phenylpyridinato)iridium(III) (Ir(ppy)₃), potassium hydroxide and iron(II) chloride tetrahydrate (FeCl₂·4H₂O) was purchased from Wako Pure Chemical Industries, Ltd. Sodium hydrogen carbonate (NaHCO₃), iron(III) chloride (FeCl₃), methanol (MeOH), acetone, ethanol (EtOH), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), chloroform (CHCl₃) and acetonitrile (MeCN) were purchased from Kanto Chemical Co., Inc. Acetone-d₆, acetonitrile-d₃ and chloroform-d were purchased from Cambridge Isotopes, Inc. 2,6-lutidine, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), tetra-n-butylammonium perchlorate (TBAP), iodomethane, 2,5-dimethoxybenzaldehyde, 2,6-dimethoxybenzaldehyde, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) and 2,2,2-trifluoroethanol (TFE) were purchased from Tokyo Chemical Industry Co., Ltd. 2-phenylbenzimidazole was purchased from Combi-Blocks, Inc. All solvents and reagents are of the highest quality available and used as received except for TBAP. TBAP was recrystallized from EtOH/H₂O. H₂O was purified using a Millipore MilliQ purifier. ¹H-NMR and ¹³C-NMR spectra were collected at room temperature on a JEOL JNM-ECS400 spectrometer. Elemental analysis was performed on a J-SCIENCE LAB MICRO CORDER JM10 elemental analyzer. MALDI spiral-TOF mass spectra were measured on a JMS-S3000 mass spectrometer. UV-visible absorption spectra were recorded on a UV-Vis Agilent Cary8454 spectrophotometer and a Shimadzu UV-3600 UV-vis-near-IR spectrophotometer. Fluorescence emission spectra were recorded on a SHIMADZU RF-5300PC.

Syntheses

Scheme S1. Synthetic scheme for Fe1.
Synthesis of 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphyrin (1')

1' was synthesized by the modification of a previous report. 2,5-dimethoxybenzaldehyde (1.01 g, 6.08 mmol) was dissolved in CHCl₃ (600 mL), then stirred for 20 min under N₂ atmosphere. After pyrrole (0.45 mL, 6.4 mmol) was added, boron trifluoride diethyl etherate (BF₃·OEt₂) (0.25 mL, 0.95 mmol) was added to the reaction mixture, and the mixture was stirred for 1.5 h at room temperature in the dark. Subsequently, a solution of DDQ (1.05 g, 4.64 mmol) in toluene (20 mL) was added, and the mixture was refluxed. After 1.5 h, the reaction mixture was quenched by TEA (0.5 mL, 3.6 mmol). The resulting mixture was purified by silica gel column chromatography (CHCl₃ as eluent) to afford a dark purple solution. Recrystallization from CHCl₃/MeOH gave a purple solid of 1' (243 mg, yield 19%).

1H-NMR (400 MHz, acetone-d₆) δ 8.80 (d, J = 2.2 Hz, 8H), 7.65 (td, J = 18.9, 2.2 Hz, 4H), 7.41 (m, 8H), 3.94 (t, J = 3.2 Hz, 12H), 3.55 (t, J = 3.7 Hz, 12H), −2.65 (brs, 2H) ppm. 13C-NMR (400 MHz, chloroform-d): δ = 154.20, 154.13, 152.33, 132.13, 132.07, 130.66, 121.35, 121.28, 115.29, 114.77, 112.48, 112.43, 112.22, 56.78, 56.72, 55.92.

HRMS (MALDI): m/z Calcd. for C₅₂H₄₆N₄O₈ [M⁺] 854.33102. Found 854.32859. Elemental analysis Calcd. for C₅₂H₄₇.75N₄O₈.75 (1'・0.75 H₂O): C, 71.92%; H, 5.51%; N, 6.45%. Found: C, 71.82%; H, 5.38%; N, 6.44%. Note that multiple peaks in 13C NMR spectrum of 1' are due to the presence of atropisomers.

Synthesis of 5,10,15,20-tetrakis(2,5-dihydroxyphenyl)porphyrin (1)

1 was synthesized by the modification of a previous report. To a microwave vessel, 1' (101 mg, 0.118 mmol) and pyridinium chloride (2.07 g, 17.9 mmol) were added. The reaction mixture was heated at 220 °C by a microwave reactor. After 1 h, the resulting mixture was dissolved in water and NaHCO₃ was added until pH was neutral. The resulting mixture was extracted with EtOAc. Then, the extract was washed with brine, and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography (CHCl₃/MeOH = 1/0 to 3/1) to afford 1 as a purple solid (57.5 mg, yield 65%). 1H-NMR (400 MHz, acetonitrile-d₃) δ 8.87 (s, 8H), 7.43 (m, 4H), 7.12-7.18 (m, 8H), 6.87 (brs, 4H), 6.32-6.40 (m, 4H), −2.85 (brs, 2H) ppm. 13C-NMR (400 MHz, methanol-d₄): δ = 151.75, 150.34, 130.84, 123.46, 117.70, 117.28, 117.19. HRMS (MALDI): m/z Calcd. for C₄₄H₃₆N₄O₈ [M + H⁺]⁺
$743.21364$ Found $743.21052$.

**Insertion of an iron ion into 1**

Insertion of an iron ion into 1 was carried out following the modification of a previous report.\textsuperscript{51} A solution of 1 (46.1 mg, 0.0621 mmol), FeCl$_2$·4H$_2$O (122 mg, 0.611 mmol) and 2,6-lutidine (17.7 µL, 0.152 mmol) was heated at 50 °C and stirred for 3 h under Ar atmosphere in MeOH (15 mL). After MeOH was removed, the resulting solid was dissolved in EtOAc, washed with water and brine. The solution was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Then, the resulting solid was washed with CHCl$_3$ and the brown solid was obtained (38.7 mg, without further purification).

**Reduction to 5,10,15,20-tetrakis(2,5-dihydroxyphenyl)porphyrinato iron(III) chloride (FeI)**

![Scheme](image)

To reduce oxidized hydroquinone moieties, a solution of the resulting solid (21.0 mg) and Na$_2$S$_2$O$_4$ (53.3 mg, 0.306 mmol) in EtOAc (10 mL) and water (10 mL) was bubbled by Ar gas for 30 minutes. After 30 minutes, the organic layer was washed with saturated aqueous NaHCO$_3$ solution. To the solution, 1 M HCl was added, then bubbled by Ar gas for 5 minutes. After 5 minutes, the organic layer was washed with brine, and hexane was added to the solution. Precipitate was collected by filtration. The brown solid of FeI was obtained (15.3 mg). HRMS (MALDI): $m/z$ Calcd. for C$_{44}$H$_{36}$ClFeN$_4$O$_{12}$ [M - Cl]$^-$ 796.12511. Found 796.12817. Elemental analysis Calcd. for C$_{44}$H$_{36}$ClFeN$_4$O$_{12}$ (FeI·4.00 H$_2$O): C, 58.45%; H, 4.01%; N, 6.20%. Found: C, 58.49%; H, 4.03%; N, 6.10%.
Synthesis of 5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin (H$_2$TDMPP)

H$_2$TDMPP was synthesized by the modification of a previous report.$^{51}$ 2,6-dimethoxybenzaldehyde (1.04 g, 6.26 mmol) was dissolved in CHCl$_3$ (600 mL), then stirred for 20 min under N$_2$ atmosphere. After pyrrole (0.45 mL, 6.4 mmol) was added, boron trifluoride diethyl etherate (BF$_3$·OEt$_2$) (0.22 mL, 0.84 mmol) was added to the reaction mixture, and the mixture was stirred for 1.5 h at room temperature in the dark. Subsequently, a solution of DDQ (1.03 g, 4.51 mmol) in toluene (20 mL) was added, and the mixture was refluxed. After 1.5 h, the reaction mixture was quenched by TEA (0.50 mL, 3.6 mmol). The resulting mixture was purified by silica gel column chromatography (CHCl$_3$ as eluent) to afford a dark purple solution. Recrystallization from CHCl$_3$/MeOH gave a purple solid of H$_2$TDMPP (297 mg, yield 22%). $^1$H-NMR (400 MHz, chloroform-d) $\delta$ 8.67 (s, 8H), 7.68 (t, $J$ = 8.5 Hz, 4H), 6.97 (d, $J$ = 8.3 Hz, 8H), 3.50 (s, 24H), −2.50 (brs, 2H) ppm. $^{13}$C-NMR (400 MHz, chloroform-d): $\delta$ = 160.67, 129.78, 120.53, 110.70, 104.31, 56.12. HRMS (MALDI): m/z Calcd. for C$_{52}$H$_{46}$N$_4$O$_8$ [M]+ 854.33102. Found 854.32874.

Synthesis of 5,10,15,20-tetrakis(2,6-dihydroxyphenyl)porphyrin (H$_2$TDHPP)

H$_2$TDHPP was synthesized by the modification of a previous report.$^{52}$ To a microwave vessel, H$_2$TDMPP (100 mg, 0.117 mmol) and pyridinium chloride (2.24 g, 19.4 mmol) were added. The reaction mixture was heated at 220 °C by a microwave reactor. After 3 h, the resulting mixture was dissolved in water and NaHCO$_3$ was added until pH was neutral. The resulting mixture was extracted with EtOAc, then the extract was washed with brine, and dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography (CHCl$_3$/MeOH = 10/1 to 5/1) to afford H$_2$TDHPP as a purple solid (25.7 mg, yield 30%). $^1$H-NMR (400 MHz, acetonitrile-d$_3$) $\delta$ 8.83 (s, 8H), 7.54 (t, $J$ = 8.3 Hz, 4H), 6.87 (d, $J$ = 8.2 Hz, 8H), 6.76 (s, 8H), −2.74 (brs, 2H) ppm. $^{13}$C-NMR (400 MHz, methanol-d$_4$): $\delta$ = 159.68, 131.28, 118.22, 112.57, 108.10. HRMS (MALDI): m/z Calcd. for C$_{44}$H$_{30}$N$_4$O$_8$ [M]+ 742.20582. Found 742.20520.
Synthesis of 5,10,15,20-tetrakis(2,6-dihydroxyphenyl)porphyrinato iron(III) chloride (CAT)

CAT was synthesized by the modification of a previous report. A solution of $\text{H}_2\text{TDHPP}$ (22.0 mg, 0.0296 mmol), $\text{FeCl}_2\cdot4\text{H}_2\text{O}$ (53.8 mg, 0.271 mmol) and 2,6-lutidine (7.9 µL, 0.068 mmol) was heated at 50 °C and stirred for 3 h under Ar atmosphere in MeOH (10 mL). After MeOH was removed, the resulting solid was dissolved in EtOAc, and 1 M HCl was added. After 30 min stirring, the organic layer was washed with brine. After removing the solvent, the black solid of CAT was obtained (3.4 mg, yield 14%). HRMS (MALDI): $m/z$ Calcd. for $\text{C}_{44}\text{H}_{41}\text{ClFeN}_4\text{O}_{14.5}$ (CAT·6.50 H$_2$O): C, 55.68%; H, 4.35%; N, 5.90%. Found: C, 55.76%; H, 4.20%; N, 5.71%.

Synthesis of tetraphenylporphyrin ($\text{H}_2\text{TPP}$)

$\text{H}_2\text{TPP}$ was prepared as previously described. Pyrrole (1.7 mL, 25 mmol) and benzaldehyde (2.6 mL, 25 mmol) were dissolved in propanoic acid (50 mL), then refluxed for 45 minutes and cooled to room temperature. The resulting mixture was filtered and washed with methanol. Recrystallization from CHCl$_3$/methanol gave a purple solid (785 mg, yield 20%). $^1\text{H}$-NMR (400 MHz, chloroform-$d$): $\delta = 8.82$ (s, 8H), 8.19-8.21 (m, 8H), 7.71-7.78 (m, 12H), –2.80 (s, 2H) ppm. $^{13}\text{C}$ NMR (400 MHz, chloroform-$d$): $\delta = 142.15, 134.56, 127.70, 126.69, 120.13$. HRMS (MALDI): $m/z$ Calcd. for $\text{C}_{40}\text{H}_{30}\text{N}_4\text{O}_0.25$ ($\text{H}_2\text{TPP}$·0.25 H$_2$O): C, 85.34%; H, 4.96%; N, 9.05%. Found: C, 85.24%; H, 4.68%; N, 9.08%.
Synthesis of 5,10,15,20-tetrakis(phenyl)porphyrinato iron(III) chloride (FeTPP-Cl)

FeTPP-Cl was prepared by the modification of a previous report. To a solution of H₂TPP (200 mg, 0.325 mmol) in DMF (10 mL), a DMF 10 mL solution of FeCl₃ (519 mg, 3.20 mmol) was added at room temperature. The mixture was heated at 200 °C for 1 h by a microwave reactor. Diluted HCl (1 M, 50 mL) was added to the resulting solution. Precipitate was collected by filtration and washed with 1 M HCl. Recrystallization from CHCl₃/hexane gave a purple solid (191 mg, yield 85%). HRMS (MALDI): m/z Calcd. for C₄₄H₂₈ClFeN₄ [M - Cl]⁺ 668.16579. Found 668.16517. Elemental analysis Calcd. for C₄₄H₂₈ClFeN₄ (FeTPP-Cl): C, 75.06%; H, 4.01%; N, 7.96%. Found: C, 74.98%; H, 4.08%; N, 8.01%.

Synthesis of 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH)

BIH was synthesized as previously reported. ¹H-NMR (400 MHz, acetonitrile-d₃): δ 7.58–7.55 (m, 2H), 7.46–7.44 (m, 3H), 6.66 (dd, J = 3.2, 5.5 Hz, 2H), 6.45 (dd, J = 3.2, 5.5 Hz, 2H), 4.85 (s, 1H), 2.51 (s, 6H) ppm. ¹³C-NMR (400 MHz, chloroform-d): δ = 142.04, 139.00, 129.30, 128.82, 128.43, 119.27, 105.70, 93.97, 33.14. HRMS (MALDI): m/z Calcd. for C₁₅H₁₅N₂ [M - H]⁺ 223.12297. Found 233.12406.

Fig. S1 ¹H NMR spectrum of 1' in acetone-d₆.
Fig. S2 $^1$H NMR spectrum of 1 in acetonitrile-$d_3$.

Fig. S3 $^1$H NMR spectrum of $\text{H}_2\text{TDMP}$ in chloroform-$d$.

Fig. S4 $^1$H NMR spectrum of $\text{H}_2\text{TDHP}$ in methanol-$d_4$. 
Fig. S5 $^1$H NMR spectrum of $\text{H}_2\text{TPP}$ in chloroform-$d$.

Fig. S6 $^1$H NMR spectrum of BIH in acetonitrile-$d_3$.

Fig. S7 $^{13}$C NMR spectrum of 1’ in chloroform-$d$. 

S10
Fig. S8 $^{13}$C NMR spectrum of 1 in methanol-$d_4$.

Fig. S9 $^{13}$C NMR spectrum of $\text{H}_2\text{TDMPP}$ in chloroform-$d$.

Fig. S10 $^{13}$C NMR spectrum of $\text{H}_2\text{TDHPP}$ in methanol-$d_4$. 
Fig. S11 $^{13}$C NMR spectrum of H$_2$TPP in chloroform-$d$.

Fig. S12 $^{13}$C NMR spectrum of BIH in chloroform-$d$.

Fig. S13 MALDI spiral-TOF mass spectrum of 1$^+$. 
Fig. S14 MALDI spiral-TOF mass spectrum of 1.

Fig. S15 MALDI spiral-TOF mass spectrum of FeI.

Fig. S16 MALDI spiral-TOF mass spectrum of H₂TDMPP.
Fig. S17 MALDI spiral-TOF mass spectrum of H$_2$TDHP.

Fig. S18 MALDI spiral-TOF mass spectrum of CAT.

Fig. S19 MALDI spiral-TOF mass spectrum of H$_2$TPP.
Fig. S20 MALDI spiral-TOF mass spectrum of FeTPP-Cl.

Fig. S21 MALDI spiral-TOF mass spectrum of BIH.
Fig. S22 $^{13}$C NMR spectra of (a) 1' in chloroform-$d_4$ and (b) 1 in methanol-$d_4$ at 20 °C. In $^{13}$C NMR spectrum of 1', many peaks were observed as multiplets, which indicates the existence of several atropisomers. On the other hand, in the spectrum of 1, all the peaks are obtained as singlet peaks, indicating that the hydroquinone moieties freely rotate at 20 °C. Therefore, hydroquinone moieties of Fe1 are indicated to freely rotate during photochemical reaction, and there are no distinguishable atropisomers.
**Photochemistry**

For typical run, a solution of MeCN (2.0 mL) containing 2.0 µM Fe₁, 20 µM Ir(ppy)₃, 0.10 M BIH and 0.10 M TFE was purged with CO₂ for 15 minutes unless otherwise stated. The solution was then irradiated with a 150 W Xe lamp equipped with 400 nm long pass filter (Edmund Industrial Optics) to produce the light in the range of 400 ≤ λ ≤ 750 nm at 20 ºC in a custom made aluminium box with cooling system. The amount of CO and H₂ produced at the headspace of the cell was quantified by a Shimadzu GC-8A with a TCD detector equipped with a packed column with Molecular Sieve 13X-S 60/80. Calibration curves were obtained by sampling known amounts of H₂ and CO.

**¹³CO₂ labeling experiment**

A solution of MeCN (2.0 ml) containing 2.0 µM Fe₁, 20 µM Ir(ppy)₃, 0.10 M BIH and 0.10 M TFE was purged with Ar for 15 min, followed by ¹³CO₂ bubbling for 5 min. The ¹³CO₂ gas was produced by adding 2.0 M HCl to solid Ba¹³CO₃ (98 atom % ¹³C, Sigma Aldrich). The evolved CO was detected by a GCMS-QP2020 (Rt®-Msieve 5A (30 m, 0.53 mm ID, 50 µm df) He carrier gas, 40 ºC).

**Electrochemistry**

Electrochemical experiments were performed at room temperature on a BAS ALS Model 650DKMP electrochemical analyzer. Cyclic voltammetry (CV) measurements were performed by using a one-compartment cell with a three-electrode configuration, which consisted of a glassy carbon disk (diameter 3 mm, BAS Inc.), platinum wire, and Ag/Ag⁺ electrode (Ag/0.01 M AgNO₃) as the working, auxiliary, and reference electrodes, respectively. The glassy carbon disc working electrode was polished using 0.05 µm alumina paste (from BAS Inc.) and washed with purified H₂O prior to each measurement. Ferrocene was used as an internal standard and all potentials are referenced to the ferrocenium/ferrocene (Fc/Fc⁺) couple at 0 V.
2. UV-vis absorption spectroscopy

**Fig. S23** UV-vis absorption spectra of (a) FeI, (b) hydroquinone, and (c) I in MeCN. The insets exhibit the enlarged UV-vis absorption spectra at Q-bands region.
3. Electrochemical measurements

Fig. S24 Cyclic voltammogram of FeTPP·Cl (0.20 mM) in DMF with TBAP (0.1 M) under Ar (scan rate: 100 mV s⁻¹).

Table S1. Redox potentials of Fe1, FeTPP·Cl, and CAT.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}(1)$</th>
<th>$E_{1/2}(2)$</th>
<th>$E_{1/2}(3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>-0.72</td>
<td>-1.60</td>
<td>-2.11</td>
</tr>
<tr>
<td>FeTPP·Cl</td>
<td>-0.64</td>
<td>-1.51</td>
<td>-2.13</td>
</tr>
<tr>
<td>CAT⁺</td>
<td>-0.84</td>
<td>-1.67</td>
<td>-2.11</td>
</tr>
</tbody>
</table>

*Reported values.⁹⁴*
4. Photocatalytic activity for CO₂ reduction

All photocatalytic reactions were performed at 20 °C using a custom-made photoreactor with coolant to control the temperature of sample during photoreaction. The schematic illustration and photograph of the experimental setup are shown in Fig. S25.

**Fig. S25** Custom-made photoreactor. Schematic illustration and a photograph are shown. The coolant was set to 20 °C to maintain a constant sample temperature during measurement.

**Fig. S26** Time course of CO production by FeI. A CO₂-saturated MeCN solution containing 2.0 μM FeI, 20 μM Ir(ppy)_3, 0.10 M BIH, and 0.10 M TFE was irradiated using a Xe lamp (400 ≤ λ ≤ 750 nm) at 20 °C.
Table S2. Photochemical CO$_2$ reduction by Fe1 and CAT for 1 h.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Photosensitiser</th>
<th>Electron donor</th>
<th>Gas</th>
<th>Light/µm</th>
<th>Media</th>
<th>TON CO</th>
<th>TON H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>Ir(ppy)$_3$</td>
<td>BIH</td>
<td>CO$_2$</td>
<td>400 ≤ λ ≤ 750</td>
<td>0.10 M TFE/MeCN</td>
<td>1.3 × 10$^4$</td>
<td>0</td>
</tr>
<tr>
<td>CAT</td>
<td>Ir(ppy)$_3$</td>
<td>BIH</td>
<td>CO$_2$</td>
<td>400 ≤ λ ≤ 750</td>
<td>0.10 M TFE/MeCN</td>
<td>1.0 × 10$^3$</td>
<td>1$'$</td>
</tr>
</tbody>
</table>

$^a$2.0 µM of Catalyst $^b$20 µM Ir(ppy); $^c$0.10 M BIH $^d$Xe lamp (150 W) with long pass filter $^e$Measured after 75 min of photoirradiation.
5. Quantum chemical calculation

Quantum chemical calculation was performed to determine the optimized structure of CO\(_2\) adducts of the three electron-reduced species of Fe1. B3LYP\(^{57-58}\) were used as a functional. Here, LANL2DZ (with core potential) basis set was used on iron, and 6-31G(d) basis set was used on the rest of the atoms (C, H, N and O). Solvation effects were included implicitly by the conductor-like polarizable continuum model (CPCM), with a dielectric constant mimicking MeCN.\(^{59}\) All calculations were performed with the Gaussian 16 program package.\(^{810}\)

![Fig. S27 Optimized structure of CO\(_2\) adduct of the three electron-reduced species of Fe1. (a) Side view of Fe1. (b) Top view of Fe1. C = gray, H = white, N = blue and O = red, Fe = orange.](image-url)
6. Emission quenching experiments

Samples for the quenching experiments were prepared in a 4 mL glass cuvette with a septum screw cap. In a typical experiment, the emission spectrum of a 10 µM solution of Ir(ppy)$_3$ in MeCN was collected. Ir(ppy)$_3$ was irradiated at 420 nm. Luminescence spectra were collected on Shimazu RF5300PC spectrofluorophotometer.

![Fig. S28](image)

**Fig. S28** (a) Emission spectra of 10 µM Ir(ppy)$_3$ upon increasing concentration of hydroquinone (H$_2$Q) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in MeCN under Ar after excitation at 420 nm ([H$_2$Q] = [DBU]). (b) Results of Stern-Volmer analysis, where $I_0/I$ is the emission intensity without quencher ($I_0$) divided by the emission intensity with a known concentration of quencher ($I$).

![Fig. S29](image)

**Fig. S29** Emission spectra of 10 µM Ir(ppy)$_3$ in the presence of (a) DBU and (b) H$_2$Q in MeCN under Ar after excitation at 420 nm.
7. Comparison of catalytic ability

Table S3. A comparison of TOFs of iron porphyrin complexes for photochemical CO$_2$ reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Media</th>
<th>Electron donor</th>
<th>Photosensitizer</th>
<th>Light/nm</th>
<th>TOF/h$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1 (2.0 µM)</td>
<td>MeCN/TFE</td>
<td>BIH</td>
<td>Ir(ppy)$_3$</td>
<td>400 ≤ λ ≤ 750</td>
<td>12954</td>
<td>This work</td>
</tr>
<tr>
<td>CAT (0.2 µM)</td>
<td>DMF</td>
<td>BIH</td>
<td>CuPP</td>
<td>λ ≥ 400</td>
<td>7650</td>
<td>S11</td>
</tr>
<tr>
<td>FePor1 (0.2 µM)</td>
<td>DMF/H$_2$O</td>
<td>BIH</td>
<td>Ru(bpy)$_2^{2+}$</td>
<td>λ = 460</td>
<td>3720</td>
<td>S12</td>
</tr>
<tr>
<td>FePor2 (0.005 µM)</td>
<td>MeCN/H$_2$O</td>
<td>TEA</td>
<td>[Ir(ppy)$_2$bpj]PF$_6$</td>
<td>White LED</td>
<td>1375</td>
<td>S13</td>
</tr>
<tr>
<td>FePor3 (2 µM)</td>
<td>MeCN/H$_2$O</td>
<td>TEA</td>
<td>[Ir(ppy)$_2$bpj]PF$_6$</td>
<td>White LED</td>
<td>871</td>
<td>S13</td>
</tr>
<tr>
<td>FePor4 (2 µM)</td>
<td>MeCN/H$_2$O</td>
<td>TEA</td>
<td>[Ir(ppy)$_2$bpj]PF$_6$</td>
<td>White LED</td>
<td>68</td>
<td>S13</td>
</tr>
<tr>
<td>FePor5 (2 µM)</td>
<td>MeCN/H$_2$O</td>
<td>TEA</td>
<td>[Ir(ppy)$_2$bpj]PF$_6$</td>
<td>White LED</td>
<td>57</td>
<td>S13</td>
</tr>
<tr>
<td>FePor6 (34 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>p-terphenyl</td>
<td>λ ≥ 300</td>
<td>71</td>
<td>S14</td>
</tr>
<tr>
<td>FeTPP-Cl (100 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>p-terphenyl</td>
<td>λ ≥ 300</td>
<td>14</td>
<td>S15</td>
</tr>
<tr>
<td>FePor3 (2 µM)</td>
<td>MeCN/TFE</td>
<td>TEA</td>
<td>Ir(ppy)$_3$</td>
<td>λ ≥ 420</td>
<td>5.1</td>
<td>S16</td>
</tr>
<tr>
<td>CAT (2 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>Ir(ppy)$_3$</td>
<td>λ ≥ 420</td>
<td>2.5</td>
<td>S17</td>
</tr>
</tbody>
</table>

*The turnover frequency was calculated by dividing the turnover number with duration of photoirradiation. *The turnover frequency calculated from the numbers in the articles are listed. *The turnover frequency was calculated by dividing the approximate turnover number with duration of photoirradiation.

Fig. S30 Chemical structures of iron porphyrin complexes in Table S3.
Table S4. A comparison of TONs of iron-complex-based catalysts for photochemical CO₂ reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Media</th>
<th>Electron donor</th>
<th>Photosensitizer</th>
<th>Light/nm</th>
<th>TON</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ppy)Y2Me]³⁺ (0.2 μM)</td>
<td>MeCN</td>
<td>BIH</td>
<td>[Ru(bpy)₂]²⁺</td>
<td>λ = 460 (45 min)</td>
<td>30349</td>
<td>S18</td>
</tr>
<tr>
<td>CAT (0.2 μM)</td>
<td>DMF</td>
<td>BIH</td>
<td>CuPP</td>
<td>λ ≥ 400</td>
<td>16109 (23 h)</td>
<td>S11</td>
</tr>
<tr>
<td>FeLa (4 μM)</td>
<td>DMF/H₂O</td>
<td>TEA</td>
<td>4CzPN</td>
<td>420 ≤ λ ≤ 650</td>
<td>14956 (2 h)</td>
<td>S19</td>
</tr>
<tr>
<td>[Fe(ppy)(OH)₂]³⁺ (5 μM)</td>
<td>MeCN/H₂O</td>
<td>BIH</td>
<td>[Ru(phen)₂]²⁺</td>
<td>λ = 460 (centered at)</td>
<td>14095 (68 h)</td>
<td>S20</td>
</tr>
<tr>
<td>FePor1 (0.2 μM)</td>
<td>DMF/H₂O</td>
<td>BIH</td>
<td>[Ru(bpy)₂]²⁺</td>
<td>λ = 460</td>
<td>13299 (2 h)</td>
<td>S12</td>
</tr>
<tr>
<td><strong>Fe1 (2.0 μM)</strong></td>
<td>MeCN/TFE</td>
<td>BIH</td>
<td>Ir(ppy)₃</td>
<td>400 ≤ λ ≤ 750</td>
<td>12954 (1 h)</td>
<td><strong>This work</strong></td>
</tr>
<tr>
<td>FeQPY (0.2 μM)</td>
<td>MeCN</td>
<td>BIH/TEOA</td>
<td>Al-4</td>
<td>λ = 405</td>
<td>10250 (4 h)</td>
<td>S21</td>
</tr>
<tr>
<td>Fe(Ntpy)Ir(10 μM)</td>
<td>DMP/H₂O</td>
<td>TEA</td>
<td>[Ru(bpy)₂]²⁺</td>
<td>420 ≤ λ ≤ 650</td>
<td>6320 (2 h)</td>
<td>S22</td>
</tr>
<tr>
<td>FePor2 (0.005 μM)</td>
<td>MeCN/H₂O</td>
<td>TEA</td>
<td>[Ir(ppy)₂(bpy)]PF₆</td>
<td>White LED</td>
<td>5500 (4 h)</td>
<td>S13</td>
</tr>
<tr>
<td>[Fe(ppy)(OH)₂]³⁺ (5 μM)</td>
<td>MeCN</td>
<td>BIH</td>
<td>[Ru(phen)₂]²⁺</td>
<td>λ = 460 (centered at)</td>
<td>3844</td>
<td>S23</td>
</tr>
<tr>
<td>FeTotpy (10 μM)</td>
<td>DMF/H₂O</td>
<td>TEA</td>
<td>4CzPN</td>
<td>420 ≤ λ ≤ 650</td>
<td>2250 (3 h)</td>
<td>S24</td>
</tr>
<tr>
<td>FePB-2(P)(2 μM)</td>
<td>MeCN/TFE</td>
<td>BIH</td>
<td>Ir(ppy)₃</td>
<td>λ = 440</td>
<td>1168 (1 h)</td>
<td>S25</td>
</tr>
<tr>
<td>Fe³⁺(dmp)(NCS)₂ (50 μM)</td>
<td>MeCN</td>
<td>TEOA</td>
<td>Cu2Bph</td>
<td>λ = 436</td>
<td>778 (48 h)</td>
<td>S26</td>
</tr>
<tr>
<td>[Fe] (5 μM)</td>
<td>NMP</td>
<td>TEOA</td>
<td>[Ir(dF(CF)₃)ppy] (dcbppy)PF₆</td>
<td>400 ≤ λ ≤ 700</td>
<td>596 (5 h)</td>
<td>S27</td>
</tr>
<tr>
<td>Fe(2N4H)(Cl)₂ (25 μM)</td>
<td>DMF</td>
<td>TEOA</td>
<td>[Carbathocuprone] (xantphos)PF₆</td>
<td>λ ≥ 400</td>
<td>565 (8 h)</td>
<td>S28</td>
</tr>
<tr>
<td>Fe(4ctpy)(H₂O)²⁺ (50 μM)</td>
<td>DMF/TFE</td>
<td>BIH</td>
<td>PP</td>
<td>λ = 460 (centered at)</td>
<td>544 (15 h)</td>
<td>S29</td>
</tr>
<tr>
<td>[Fe] (133 μM)</td>
<td>NMP</td>
<td>BIH/TEOA</td>
<td>[Carbathocuprone] (POP-xantphos)PF₆</td>
<td>400 ≤ λ ≤ 700</td>
<td>505 (5 h)</td>
<td>S30</td>
</tr>
<tr>
<td>[Fe] (1 μM)</td>
<td>NMP</td>
<td>TEOA</td>
<td>Cu PS (generated in situ)</td>
<td>400 ≤ λ ≤ 700</td>
<td>487 (5 h)</td>
<td>S31</td>
</tr>
<tr>
<td>FePor3 (2 μM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>Ir(ppy)₃</td>
<td>λ ≥ 420</td>
<td>367 (102 h)</td>
<td>S16</td>
</tr>
<tr>
<td>FePor3 (2 μM)</td>
<td>MeCN/H₂O</td>
<td>TEA</td>
<td>[Ir(ppy)₂(bpy)]PF₆</td>
<td>White LED</td>
<td>282 (4 h)</td>
<td>S13</td>
</tr>
<tr>
<td>Fe³⁺(dmp)(NCS)₂ (50 μM)</td>
<td>MeCN</td>
<td>TEOA</td>
<td>[Ir(ppy)₂(bpy)]PF₆</td>
<td>λ = 436</td>
<td>273 (12 h)</td>
<td>S32</td>
</tr>
<tr>
<td>FePor4 (2 μM)</td>
<td>MeCN/H₂O</td>
<td>TEA</td>
<td>[Ir(ppy)₂(bpy)]PF₆</td>
<td>White LED</td>
<td>272 (4 h)</td>
<td>S13</td>
</tr>
<tr>
<td>FePor5 (2 μM)</td>
<td>MeCN/H₂O</td>
<td>TEA</td>
<td>[Ir(ppy)₂(bpy)]PF₆</td>
<td>White LED</td>
<td>226 (4 h)</td>
<td>S13</td>
</tr>
<tr>
<td>CAT (2 μM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>Ir(ppy)₃</td>
<td>λ ≥ 420</td>
<td>140 (55 h)</td>
<td>S17</td>
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</tbody>
</table>
Table S4. Continued.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Media</th>
<th>Electron donor</th>
<th>Photosensitizer</th>
<th>Light/nm</th>
<th>TON</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePor6 (34 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>p-terphenyl</td>
<td>λ ≥ 300</td>
<td>63 (21 h)</td>
<td>S14</td>
</tr>
<tr>
<td>ClFe(tdcc) (45 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>p-terphenyl</td>
<td>λ ≥ 310</td>
<td>50 (4 h)</td>
<td>S33</td>
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<tr>
<td>ClFe(tpfc) (48 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>p-terphenyl</td>
<td>λ ≥ 310</td>
<td>46 (8.2 h)</td>
<td>S33</td>
</tr>
<tr>
<td>FeTPP-Cl (100 µM)</td>
<td>MeCN</td>
<td>TEA</td>
<td>p-terphenyl</td>
<td>λ ≥ 300</td>
<td>20 (3 h)</td>
<td>S15</td>
</tr>
</tbody>
</table>

[a]Iron, tricarbonyl[(1,3,3a,7a-η)-4,5,6,7-tetrahydro-1,3-bis(trimethylsilyl)-2H-inden-2-one]. [b]The approximate turnover number from the figures in the articles are listed.
8. References
