

Supporting information

Effects of the cross-linked structures of polymer gels containing iron porphyrins on photoreduction of carbon dioxide

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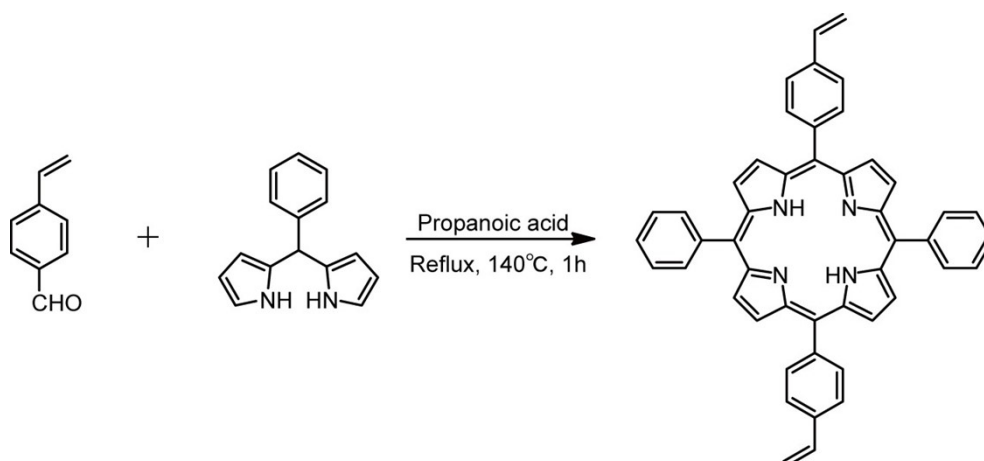
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1. Materials and Methods

The following chemical agents were purchased from commercial sources, and were used as received unless otherwise indicated: benzaldehyde (98%), pyrrole (99%), styrene (St, 99%), divinylbenzene (DVB, > 50%), iodomethane (99.5%), iron tetrphenylporphyrin (FeTPP, 95%), sodium borohydride (NaBH_4 , 95%) and (2,2'-bipyridine)bis(2-phenylpyridinato)iridium (III) hexafluorophosphate ($[\text{Ir}(\text{bpy})_2(\text{ppy})]^{3+}$, 90%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Dichloromethane (DCM, 99.5%), propanoic acid (98%), 4-bromostyrene (95%), magnesium (Mg, 98%), trifluoroacetic acid (TFA, 99%), 2-phenylbenzimidazole (97%), potassium hydroxide (KOH, 85%), triethylamine (TEA, 99%), sodium hydrogen carbonate (NaHCO_3 , 99%), 2,2'-azobis(isobutyronitrile) (AIBN, 98%) and dimethyl sulfoxide (DMSO, 99%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Ammonium chloride (NH_4Cl , 99.5%), dry *N,N*-dimethylformamide (dry DMF, 99.5%), dry tetrahydrofuran (dry THF, 99.5%), sodium hydroxide (NaOH , 95%) were purchased from KANTO CHEMICAL CO., INC. (Tokyo Japan). CO_2 gas of 99.5% purity was used in the reduction experiments. 4-Vinylbenzaldehyde,¹ 5-phenyldipyrromethane (DPM),² and 3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH)³ were synthesized following the same procedure in the previous reports.

Proton nuclear resonance (^1H NMR) spectrum was recorded on a JEOL-ECP400 spectrometer (JEOL, Tokyo, Japan) using chloroform-*d* as a solvent. Ultraviolet-visible (UV-Vis) spectra were recorded on an Agilent 8453 spectroscopy (Agilent technologies Inc., Santa Clara, CA USA). The sample for field emission scanning electron microscopy (FE-SEM) analysis was coated with platinum (approx. 4 nm thickness) using an JEOL JFC-1600 auto fine coater (JEOL Ltd., Tokyo, Japan). FE-SEM analysis was performed on a Hitachi SU8000 microscopy (Hitachi High-Technologies Corporation, Tokyo, Japan). The diffuse reflectance UV-vis spectra were measured by a (JASCO V-770) spectrophotometer equipped with a Φ 60 integrating sphere at room temperature. For measurements of **TPP-M** and **FeTPP-M**, the diluted samples were prepared by mixing 5 mg of the monomers and 95 mg of MgSO_4 . Analysis of Fe content in polymers were recorded on an Energy Dispersive X-ray spectroscopy (EDX-7000, SHIMADZU, Kyoto, Japan) with polymers crushed in a mortar. Gas Chromatograph (GC) analysis was performed on a GC-2014AT (SHIMADZU, Kyoto, Japan) equipped with a GC Stainless Column 2.0 m \times 3.0 mm I.D. Shincarbon-ST 50/80 (SHIMADZU, Kyoto, Japan). The visible-light irradiation was provided by MAX-302 Xenon Light Source 300W (ASAHI SPECTRA, Tokyo, Japan) equipped with a UV-cut filter ($\lambda > 400$ nm). Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR4700 (JASCO, Japan) using KBr. Compressive stress-strain measurements were performed on a MinebeaMitsumi LTS-50NS100 tester (MinebeaMitsumi Inc., Nagano, Japan).

2. Synthesis of TPP-M



To the solution of DPM (836 mg, 3.76mmol) in propionic acid (23 mL), 4-vinylbenzaldehyde (480 μ L, 3.76 mmol) in propanoic acid (7.1 mL) was added dropwise at 140 °C. The solution was refluxed for 1 h. The solution was then divided with saturated NaHCO₃ aq and DCM until the smell of propanoic acid disappeared, after which the organic layer was dehydrated with Na₂SO₄ for 1h. The solution was filtered and concentrated under reduced pressure. The crude product obtained was dried under vacuum and subsequently purified by silica gel chromatography with DCM as eluent ($R_f = 0.9$).

¹H NMR (400 MHz, CDCl₃), δ ppm: 8.86 (m, 8H, β -H), 8.23 (m, 4H, Ar-o-H), 8.18 (m, 4H, Ar-o-H), 7.79 (m, 6H, Ar-m- and p-H), 7.74 (m, 4H Ar-m-H), 7.06 (q, 2H, Vinyl-H), 6.07 (d, 2H, Vinyl-H), 5.49 (d, 2H, Vinyl-H).

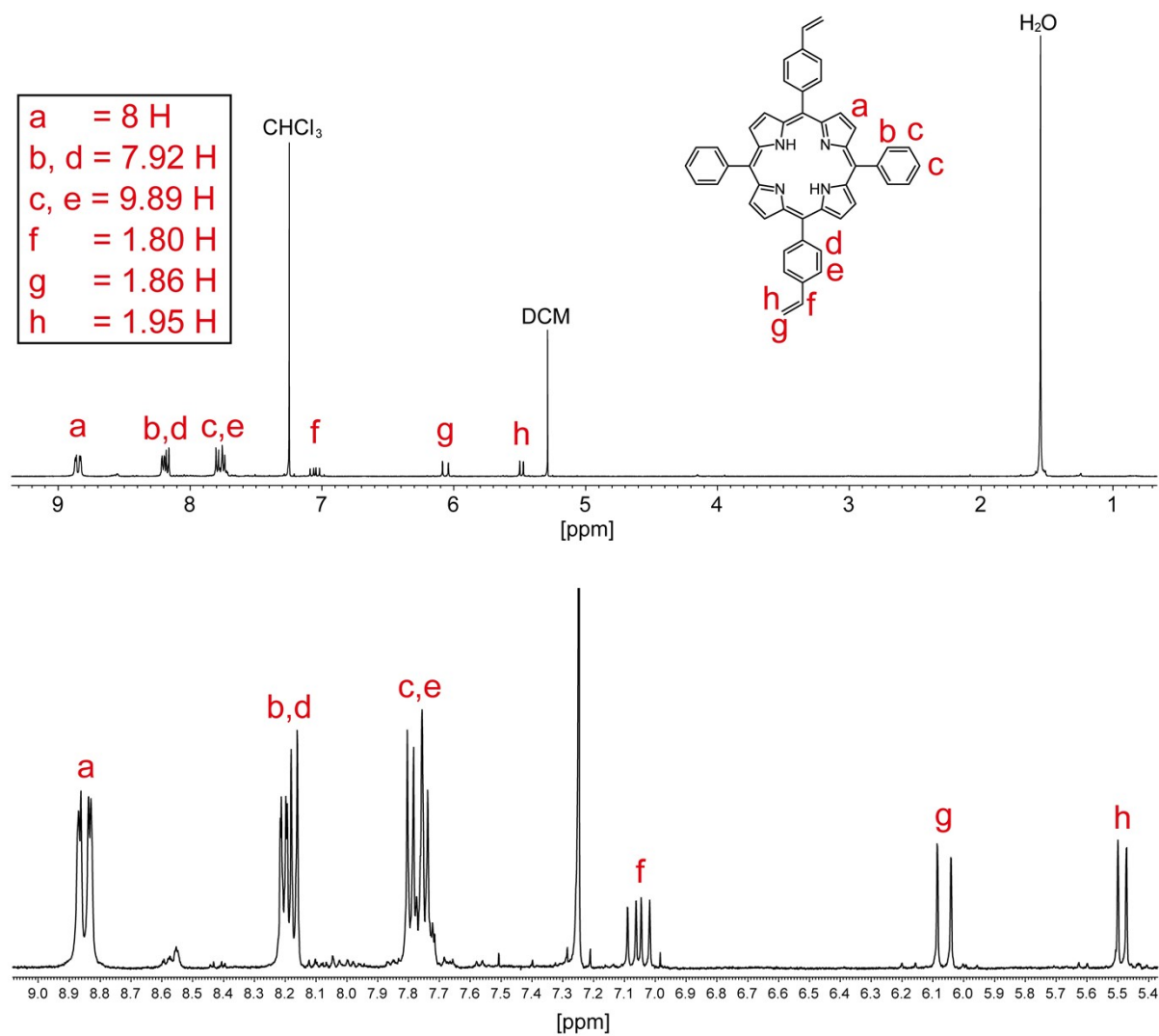
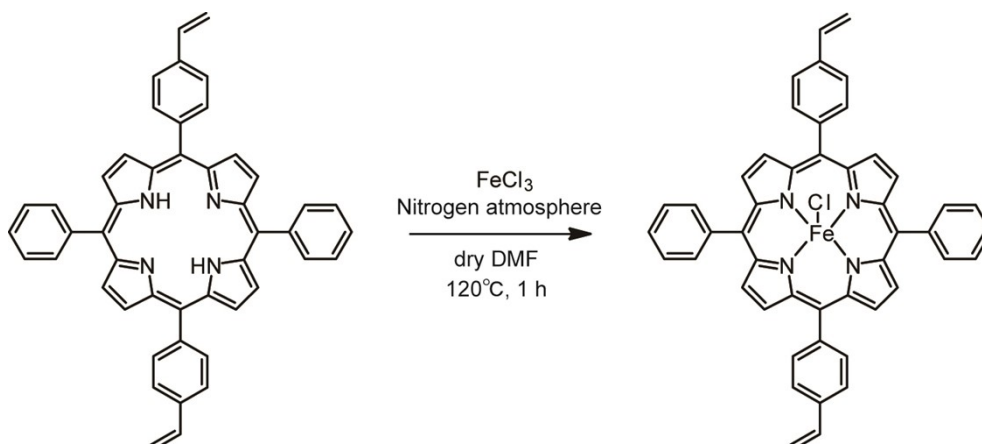


Fig. S1 ¹H NMR spectrum of TPP-M (400 MHz, CDCl₃).

3. Synthesis of FeTPP-M



FeCl₃ (535 mg, 3.3 mmol) and **TPP-M** (220 mg, 0.33 mmol) were dissolved in dry DMF (20 mL). The solution was charged into a three-necked flask equipped with a reflux cooler and magnetic stirring bar and refluxed at 120 °C for 1 h. The solution after the reaction was cooled in an ice bath and Milli-Q water (40 mL) was added. The precipitated solid was filtered and dissolved in DCM (20 mL). The organic solution was washed twice with 1M HCl (10 mL) and dehydrated with Na₂SO₄. The filtered solution was concentrated under reduced pressure and dried *in vacuo*. Fe coordination was confirmed by UV-vis measurement.

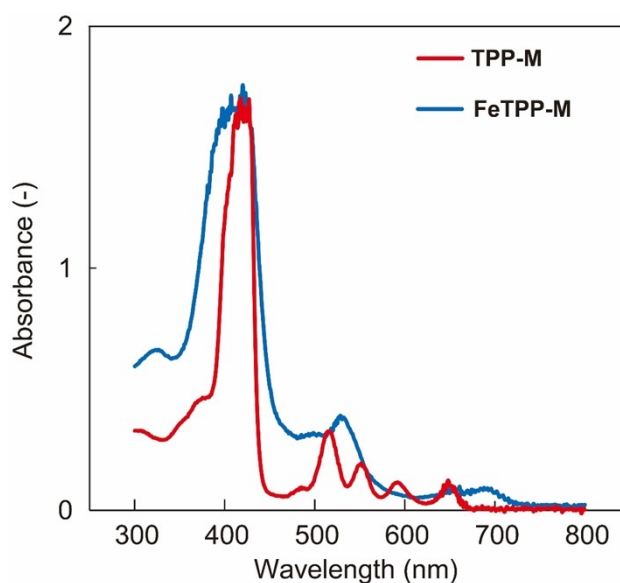
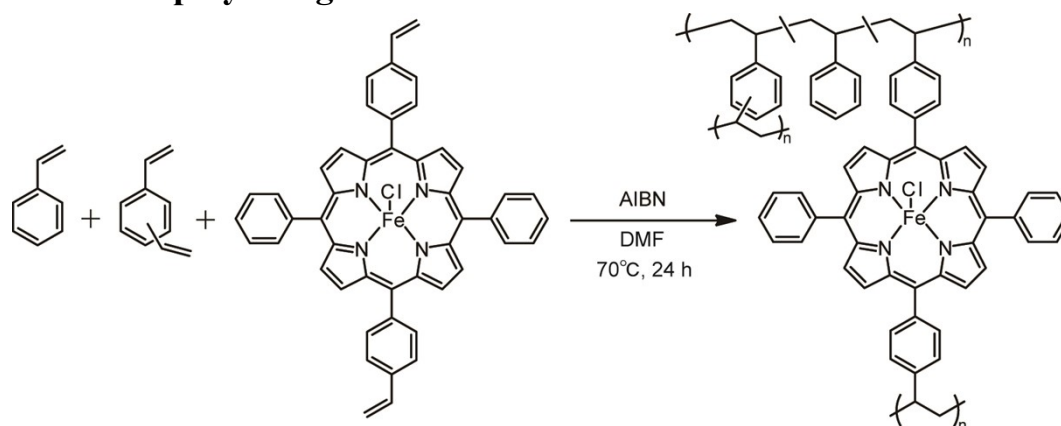


Fig. S2 UV-vis absorbance spectra of **TPP-M** (red line) and **FeTPP-M** (blue line). The sample concentrations were 0.01 and 0.025 g/L in DMSO, respectively. The temperature was 25 °C.

4. Preparation of polymer gels



Styrene, DVB, **FeTPP-M**, and AIBN were dissolved in dry DMF. The volume percentage of the monomers and solvent were 30 and 70 vol%, respectively. The ratios of styrene to DVB are summarized in Table S1. The amounts of **FeTPP-M** and AIBN were 1 wt% with respect to monomers (15 mg each). The prepare solution (totally 5,030 mg) was degassed by freeze-thaw cycles (three times) and placed in an incubator (70 °C) for 24 h. The polymers were taken by crushing the glass tube and washed by immersion in anhydrous THF, anhydrous DMF and MeOH until the washing solution became colorless. The polymers were dried overnight at room temperature *in vacuo*. The polymers were crushed into particles in a mortar. The crushed polymer particles were classified on a sieve and the particle sizes were confirmed by FE-SEM. The absorbance spectra of the polymer particles were obtained by diffuse reflectance (DR)-UV-vis spectroscopy.

Table S1. Detailed conditions for polymerization of cross-linked polystyrene polymers.

Entry	DMF		DVB		Styrene		TPP-M	FeTPP-M	AIBN
	(mg)	(μ L)	(mg)	(μ L)	(mg)	(μ L)			
Pg	3500	3708	150	165	1350	1490	-	-	15
PgTPP	3500	3708	150	165	1350	1490	15	-	15
PgFeTPP-DVB10	3500	3708	150	165	1350	1490	-	15	15
PgFeTPP-DVB50	3500	3708	750	824	750	828	-	15	15
PgFeTPP-DVB100	3500	3708	1500	1648	0	0	-	15	15

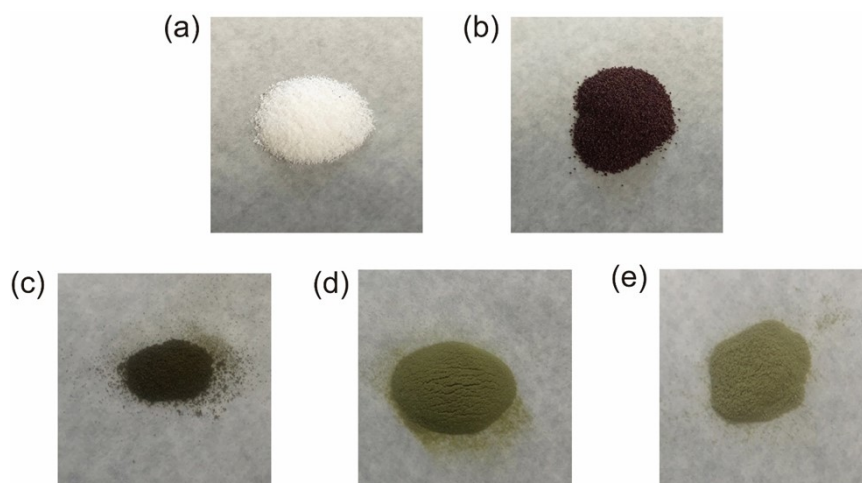


Fig. S3 Photo images of crushed polymer gels. (a) **Pg**, (b) **PgTPP**, (c) **PgFeTPP-DVB10**, (d) **PgFeTPP-DVB50**, and (e) **PgFeTPP-DVB100**.

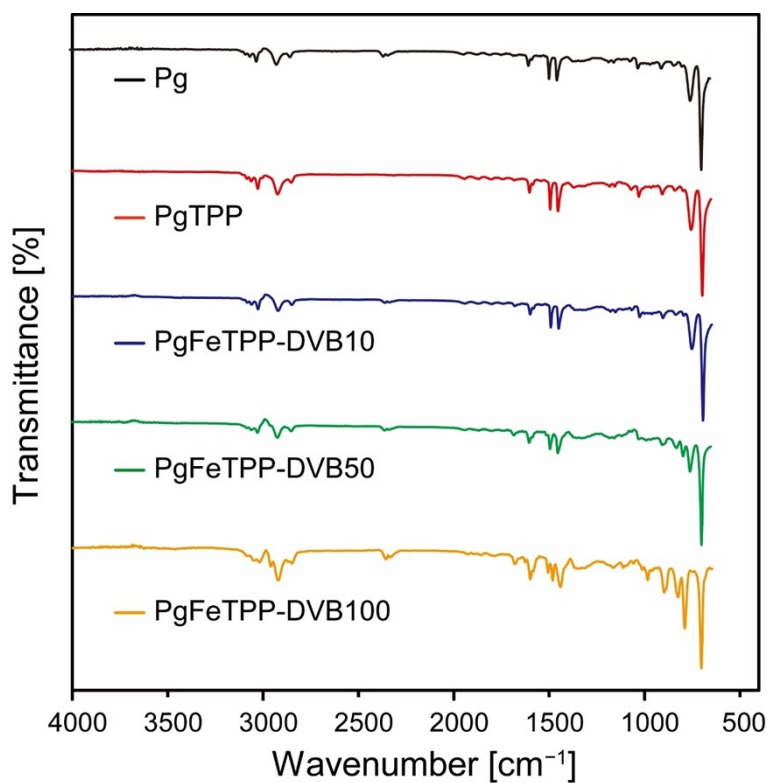


Fig. S4 FT-IR spectra for the polymer gels. **Pg** (black line), **PgTPP** (red line), **PgFeTPP-DVB10** (blue line), **PgFeTPP-DVB50** (green line), and **PgFeTPP-DVB100** (yellow line).

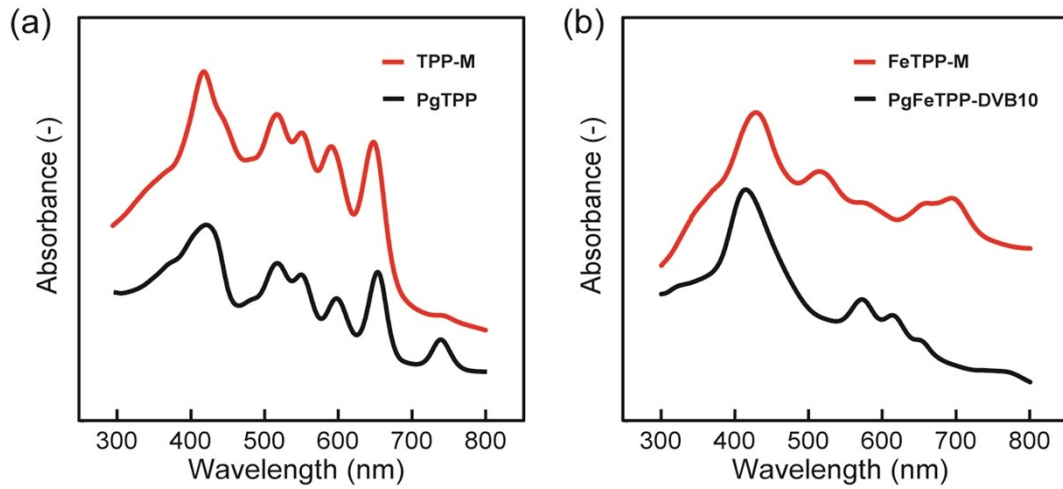


Fig. S5 Diffuse reflectance UV-vis spectra for samples. (a) **TPP-M** (red line) and **PgTPP** (black line). (b) **FeTPP-M** (red line) and **PgFeTPP-DVB10** (black line).

5. Compression Tests of PgFeTPP

The compression tests were performed on DMF-swollen **PgFeTPP** using a tensile compressive tester. The cylindrical **PgFeTPP** with diameter of 16 mm and thickness of 3 mm was set on a lower plate and compressed by an upper plate, which was connected to a loadcell, at a strain rate of 10 mm min⁻¹. Stress and strain were defined as follows:

$$\text{Stress} = \text{Uniaxially exerted force} / \text{Cross-sectional area of the } \mathbf{PgFeTPP}$$

$$\text{Strain} = \Delta(\text{Thickness}) / \text{Free-standing thickness}$$

The compressive stress-strain curves were obtained for **PgFeTPP-DVB10**, **-DVB50**, and **-DVB100** (Figure 3 in the main text).

6. Photoreduction of CO₂

Photoreduction experiments were conducted in a closed headspace vial with rubber plug and magnetic stirring. The headspace of the vial was 20.6 mL. A reaction solution was prepared by adding DMF (9.4 mL), PhOH (600 μ L), IrBPY (0.1 mM), BIH (50 mM), and **PgFeTPP** (10 mg) to the vial. The concentration of the porphyrin catalyst was calculated as 13 μ M based on the feed amount of **FeTPP-M** in the polymerization. After sealing the vial with a rubber cap, the reaction solution was bubbled with CO₂ for 30 min. Irradiation of a white Xenon Light setup ($\lambda > 400$ nm, MAX-302 Xenon Light Source 300W ASAHI SPECTRA) started the reaction. The gaseous products were analyzed by Shimadzu GC-2014 gas chromatography equipped with GC Stainless Column 2.0 m \times 3.0 mm i.d.. Shincarbon-ST 50/80 A thermal conductivity detector (TCD) was used to detect H₂ and CO. Argon was used as the carrier gas.

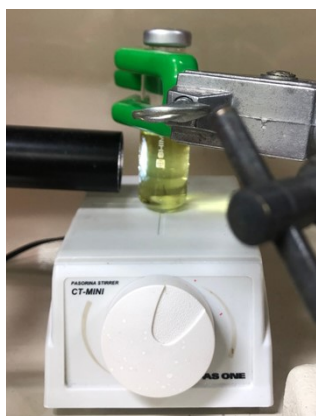


Fig. S6 A photograph of setup of photoreduction experiments.

Table S2. Results of CO₂ photoreduction after 1 hours of visible light irradiation.

Catalyst	Particle size (μ m)	CO (μ mol)	H ₂ (μ mol)	Selectivity (CO%)
PgFeTPP-DVB10	~53	0.40 \pm 0.02	0.06 \pm 0.01	87
PgFeTPP-DVB10	53~100	0.40 \pm 0.06	0.04 \pm 0.01	91
PgFeTPP-DVB10	100~150	0.44 \pm 0.06	0.07 \pm 0.03	86
PgFeTPP-DVB10	150~200	0.43 \pm 0.03	0.05 \pm 0.002	91
PgFeTPP-DVB50	53~100	0.16 \pm 0.05	0.03 \pm 0.01	84
PgFeTPP-DVB100	53~100	0.05 \pm 0.04	0.04 \pm 0.004	56

Table S3. Results of CO₂ photoreduction after 2 hours of visible light irradiation.

Catalyst	Particle size (μm)	CO (μmol)	H ₂ (μmol)	Selectivity (CO%)
PgFeTPP-DVB10	~53	1.50 ± 0.13	0.19 ± 0.03	89
PgFeTPP-DVB10	53~100	1.34 ± 0.07	0.08 ± 0.02	94
PgFeTPP-DVB10	100~150	1.50 ± 0.10	0.18 ± 0.04	89
PgFeTPP-DVB10	150~200	1.65 ± 0.20	0.11 ± 0.02	94
PgFeTPP-DVB50	53~100	0.39 ± 0.08	0.07 ± 0.03	85
PgFeTPP-DVB100	53~100	0.28 ± 0.03	0.11 ± 0.02	72

Table S4. Results of CO₂ photoreduction after 3 hours of visible light irradiation.

Catalyst	Particle size (μm)	CO (μmol)	H ₂ (μmol)	Selectivity (CO%)
PgFeTPP-DVB10	~53	2.42 ± 0.06	0.31 ± 0.03	89
PgFeTPP-DVB10	53~100	2.37 ± 0.08	0.12 ± 0.03	95
PgFeTPP-DVB10	100~150	2.54 ± 0.06	0.29 ± 0.06	90
PgFeTPP-DVB10	150~200	2.69 ± 0.35	0.16 ± 0.03	94
PgFeTPP-DVB50	53~100	0.62 ± 0.04	0.12 ± 0.04	84
PgFeTPP-DVB100	53~100	0.48 ± 0.09	0.14 ± 0.02	77

Table S5. Results of CO₂ photoreduction after 4 hours of visible light irradiation.

Catalyst	Particle size (μm)	CO (μmol)	H ₂ (μmol)	Selectivity (CO%)
PgFeTPP-DVB10	~53	3.31 ± 0.11	0.43 ± 0.05	89
PgFeTPP-DVB10	53~100	3.24 ± 0.04	0.16 ± 0.04	95
PgFeTPP-DVB10	100~150	3.59 ± 0.11	0.40 ± 0.09	90
PgFeTPP-DVB10	150~200	3.72 ± 0.40	0.22 ± 0.05	94
PgFeTPP-DVB50	53~100	0.84 ± 0.06	0.18 ± 0.07	82
PgFeTPP-DVB100	53~100	0.59 ± 0.06	0.15 ± 0.03	80

Table S6. Results of CO₂ photoreduction after 5 hours of visible light irradiation.

Catalyst	Particle size (μm)	CO (μmol)	H ₂ (μmol)	Selectivity (CO%)
PgFeTPP-DVB10	~53	4.15 ± 0.17	0.55 ± 0.07	88
PgFeTPP-DVB10	53~100	4.13 ± 0.06	0.19 ± 0.05	96
PgFeTPP-DVB10	100~150	4.49 ± 0.18	0.50 ± 0.12	90
PgFeTPP-DVB10	150~200	4.62 ± 0.50	0.27 ± 0.06	94
PgFeTPP-DVB50	53~100	1.09 ± 0.08	0.24 ± 0.11	82
PgFeTPP-DVB100	53~100	0.75 ± 0.03	0.18 ± 0.05	81

Reference:

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- (2) X. Zhao, L. Yuan, Z.-Q. Zhang, Y.-S. Wang, Q. Yu, and J. Li, *Inorg. Chem.*, **2016**, *55*, 5287–5296.
- (3) X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, and J.-P. Cheng, *J. Am. Chem. Soc.*, **2008**, *130*, 2501–2516.