

Supporting Information

Noble metal-free bis-tridentate benzimidazole zinc(II) and iron(II)
complexes for selective CO₂ photoreduction

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1. Experimental Section

1.1 Materials and instruments

All chemical reagents were purchased through commercial channels and used as received. Ligand 2,6-bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridine (abbreviated as Me-bzimpy), 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridine (abbreviated as bzimpy) and photosensitizer 4CzIPN were synthesized according to existing methods.^{1,2} The fourier transform infrared spectrum (FT-IR) spectra were obtained on a Nicolet 670 FT-IR spectrometer. The UV-vis absorption spectra were measured on a G9 spectrophotometer. The CV and SWV tests were performed at room temperature with the electrochemical workstation CHI 660E. The working electrode, reference electrode and counter electrode were respectively glassy carbon electrode, Ag/AgCl electrode and platinum foil. The potential of the Ag/AgCl reference electrode was calibrated by the internal standard oxidation of ferrocene. The gas-phase products of the photocatalytic system were analyzed by Shimadzu GC-2014 (2 m x 3 mm packed column TDX-01, a hydrogen flame ionization detector, and N₂ as carrier gas).

1.2 Synthesis and Characterization of Complexes

Me-bzimpy: Yield: 60%. ¹H NMR (400 MHz, Chloroform-*d*), δ (ppm): 8.43 (d, *J* = 7.9 Hz, 2H), 8.06 (t, *J* = 7.9 Hz, 1H), 7.88 (dd, *J* = 6.8, 1.7 Hz, 2H), 7.48 (dd, *J* = 6.9, 1.7 Hz, 2H), 7.42-7.32 (m, 4H), 4.25 (s, 6H). ¹H NMR results of Me-bzimpy are consistent with previous report.¹

Bzimpy: Yield: 85%. ¹H NMR (400 MHz, Chloroform-*d*), δ (ppm): 8.51 (d, *J* = 8.1 Hz, 2H), 8.09-8.00 (m, 1H), 7.37 (dd, *J* = 5.8, 3.1 Hz, 2H), 7.28 (s, 6H). ¹H NMR results of bzimpy are consistent with previous report.¹

Fe1: Under a N₂ atmosphere, dissolved ligands Me-bzimpy (200 mg, 0.59 mmol) in 30 mL CH₃OH/CH₂Cl₂ (v/v=2/1), and then slowly added FeCl₂·4H₂O (60 mg, 0.3 mmol) in methanol solution. The reaction mixture was stirred at 75°C for 12h. After cooling to room temperature, used a rotary evaporator evaporate and removed CH₂Cl₂ under reduced pressure, then NH₄PF₆ was added to precipitate a solid. The precipitate obtained by filtration was thoroughly washed with water, EtOH and CH₂Cl₂. **Fe1** was obtained (202 mg, yield: 78%). ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 9.16 (s, 1H), 8.97 (d, *J* = 7.8 Hz, 1H), 8.89-8.79 (m, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 8.36 (t, *J* = 7.4 Hz, 1H), 7.94-7.81 (m, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 3.32 (s, 6H). ¹H NMR results of **Fe1** are consistent with previous report.¹ Elemental analysis: found C 49.07, H 3.69, N 13.85 (calcd. C 49.24, H 3.34, N 13.67).

Fe2: The synthesis of **Fe2** was similar to **Fe1**, and finally, a powder (143 mg, yield:

63%) was obtained. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ (ppm): 8.41 (d, $J = 7.8$ Hz, 2H), 8.31-8.23 (m, 1H), 7.82 (dd, $J = 6.0, 3.2$ Hz, 4H), 7.40 (dd, $J = 6.1, 3.1$ Hz, 4H). ^1H NMR results of **Fe2** are consistent with previous report.¹ Elemental analysis: found C 46.97, H 3.07, N 14.63 (calcd. C 47.13, H 2.71, N 14.46).

Zn1: Under a N_2 atmosphere, dissolved the ligand Me-bzimpy (200 mg, 0.59 mmol) in 30 mL $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ ($v/v=2/1$), and then slowly added the methanol solution dissolved ZnCl_2 (41 mg, 0.3 mmol). The reaction mixture was stirred at 75°C for 12h. After cooling to room temperature, used a rotary evaporator evaporate and removed CH_2Cl_2 under reduced pressure, then NH_4PF_6 was added to precipitate a solid. The precipitate obtained by filtration was thoroughly washed with water, EtOH and CH_2Cl_2 . **Zn1** was obtained (200 mg, yield: 83%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ (ppm): 8.43 (d, $J = 7.9$ Hz, 2H), 8.06 (t, $J = 7.9$ Hz, 1H), 7.88 (dd, $J = 6.8, 1.7$ Hz, 2H), 7.48 (dd, $J = 6.9, 1.7$ Hz, 2H), 7.42-7.32 (m, 4H), 4.25 (s, 6H). HR-ESI-MS (m/z): found 371.1111 for $[\text{Zn}(\text{Me-bzimpy})_2]^{2+}$ (calcd. 371.1124 $\text{C}_{42}\text{H}_{34}\text{N}_{10}\text{Zn}^{2+}$); found 340.1547 for $[\text{M-H}]^+$ (calcd 340.1562 $\text{C}_{21}\text{H}_{17}\text{N}_5^+$, $\text{M} = \text{Me-bzimpy}$); found 362.1368 for $[\text{M-Na}]^+$ (calcd 362.1382 $\text{C}_{21}\text{H}_{17}\text{N}_5\text{Na}^+$, $\text{M} = \text{Me-bzimpy}$). Elemental analysis: found C 48.63, H 3.65, N 13.71 (calcd. C 48.78, H 3.31, N 13.54).

1.3 Photocatalytic CO_2 reduction

General procedure: Add 5 mL DMF or DMF/ H_2O solution containing **Fe1/Fe2**, 4CzIPN and TEA into a glass tube sealed with a rubber stopper, at room temperature, degassed the solution with CO_2/N_2 for 15 minutes. After the solution was fully degassed, it was irradiated with the white LED lighting equipment (SMPC-LVWT, 420-650 nm, 3 W LEDs) provided by the Institute of Physical Chemistry & Chinese Academy of Sciences. The gaseous products (CO and H_2) generated by the system were sucked from the headspace of the glass tube with a gas-tight syringe in 200 μL aliquots and injected into the GC-2014 instrument equipped with TCD and FID detectors for analysis. The standard curve was obtained by injecting pure H_2 and CO .

2. Supplementary Figures

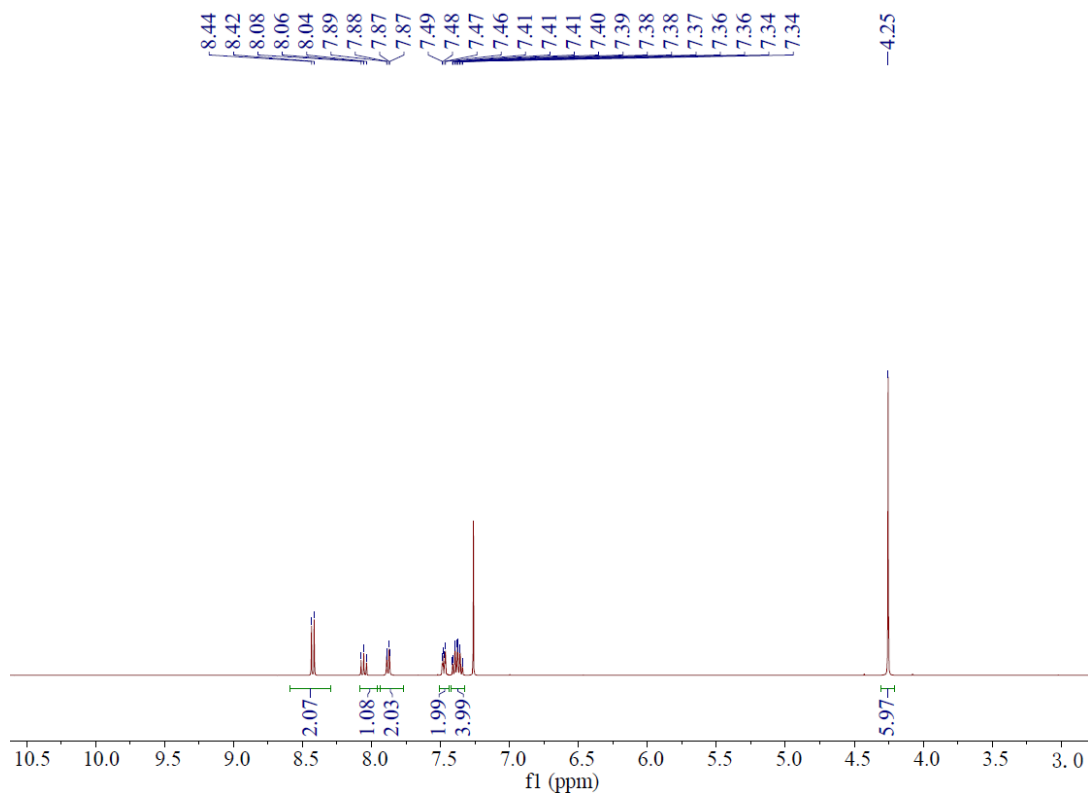


Fig. S1 ^1H NMR spectrum of Me-bzimpy in Chloroform-*d*.

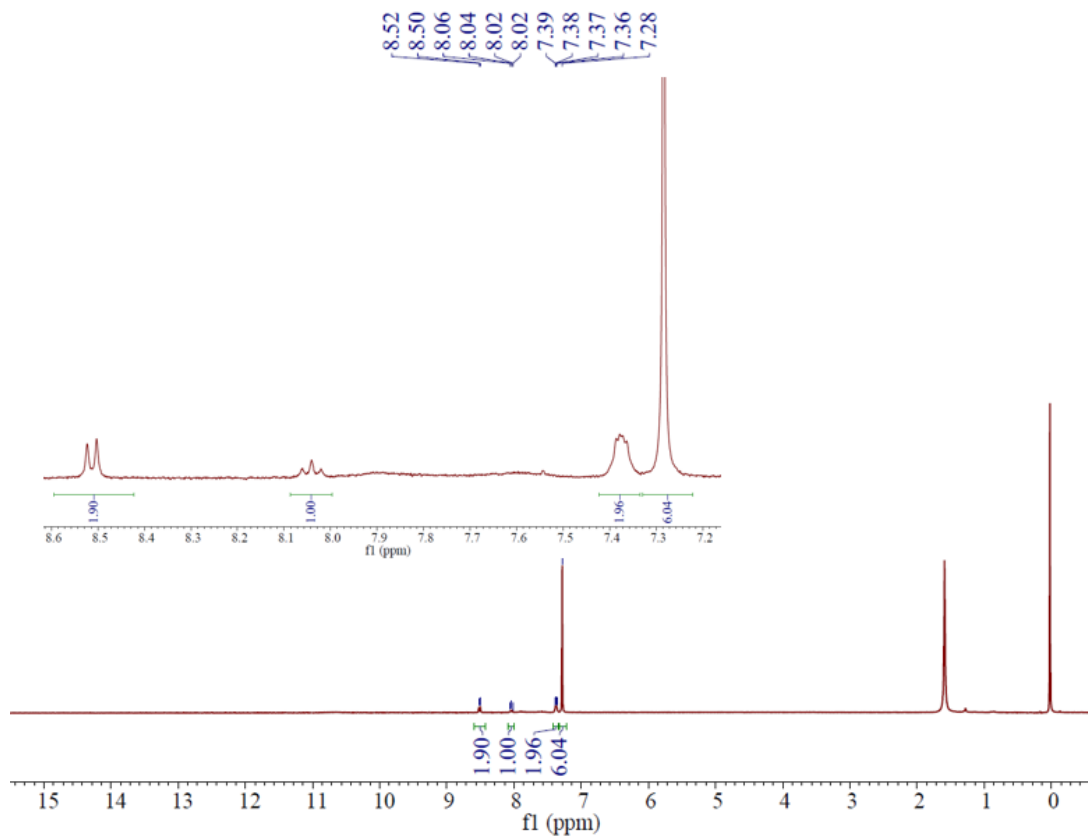


Fig. S2 ^1H NMR spectrum of bzimpy in Chloroform-*d*.

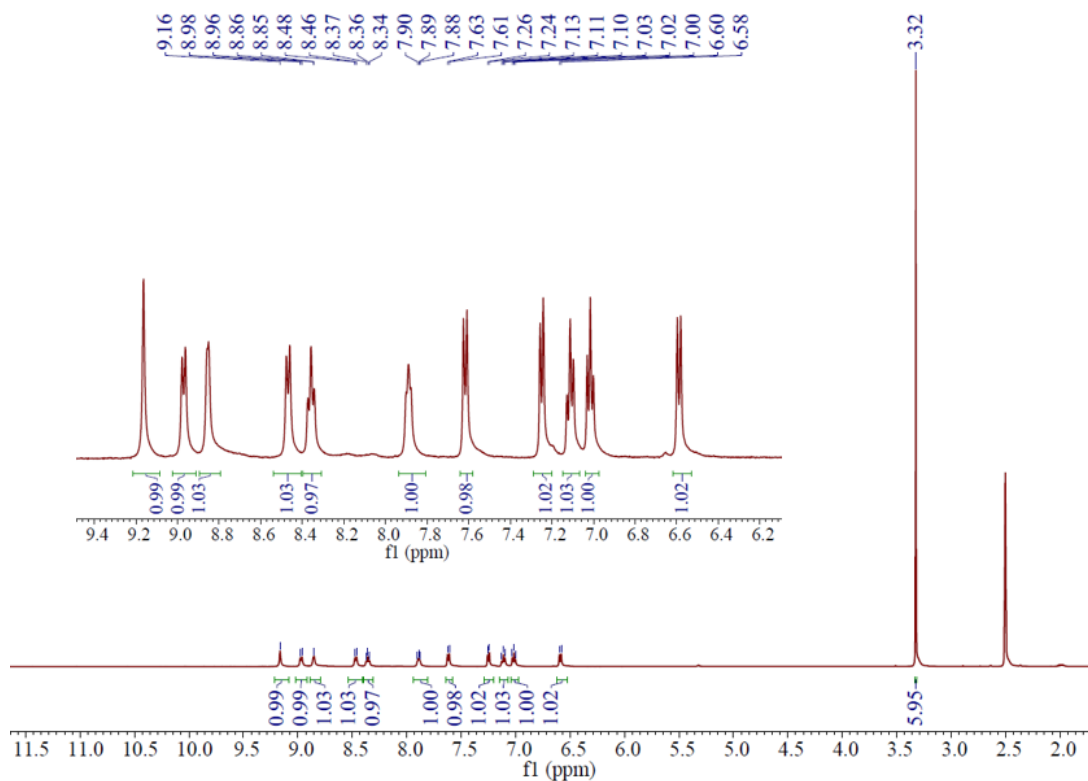


Fig. S3 ^1H NMR spectrum of Fe1 in DMSO- d_6 .

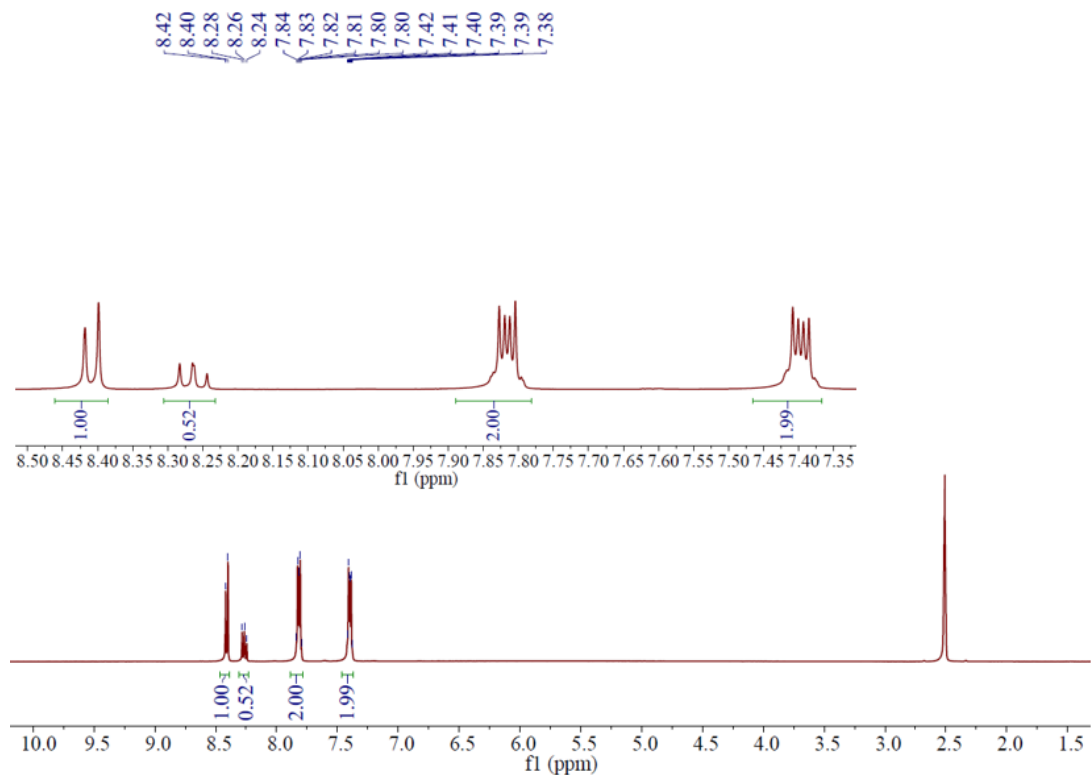


Fig. S4 ^1H NMR spectrum of Fe2 in DMSO- d_6 .

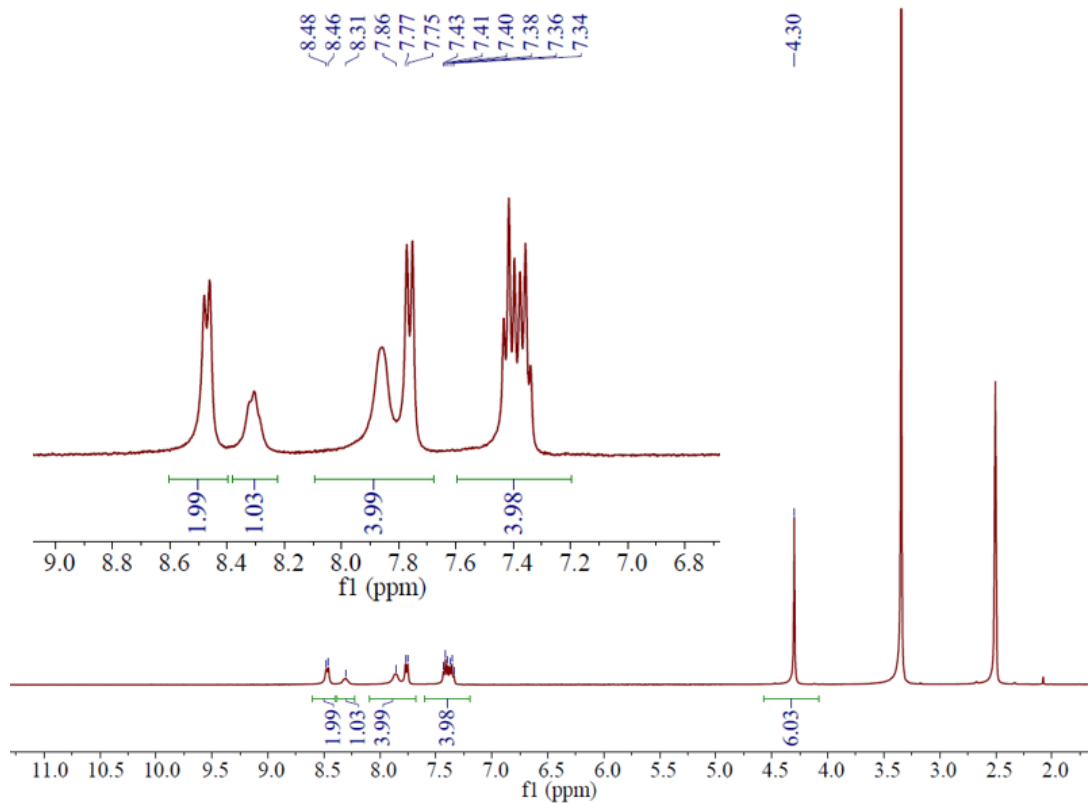


Fig. S5 ^1H NMR spectrum of **Zn1** in $\text{DMSO-}d_6$.

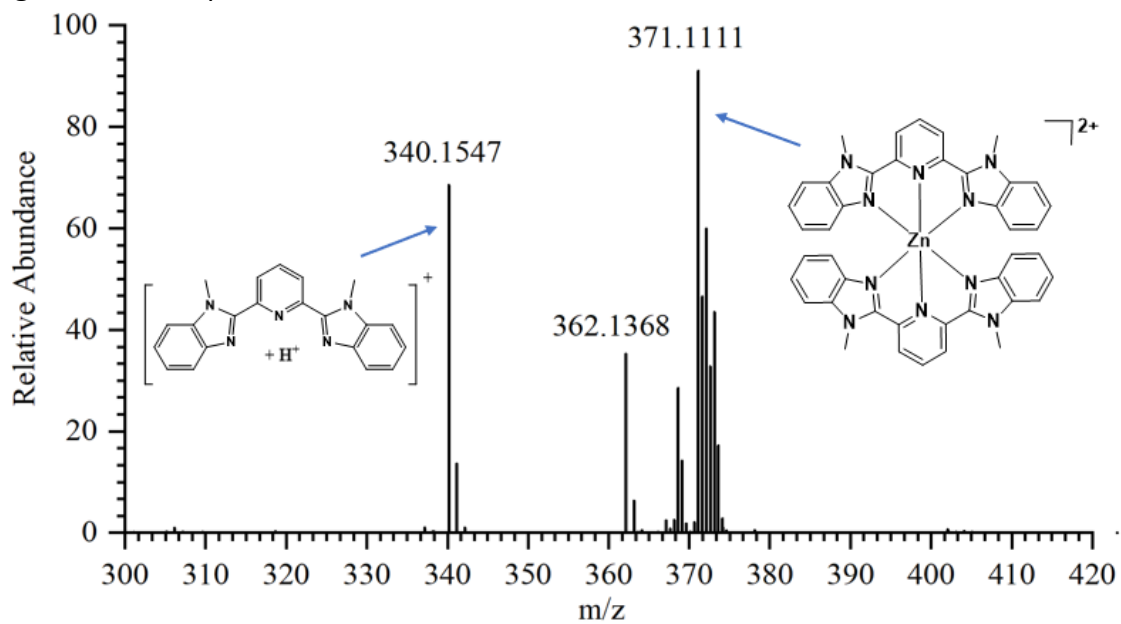


Fig. S6 HR-ESI-MS spectrum of **Zn1**.

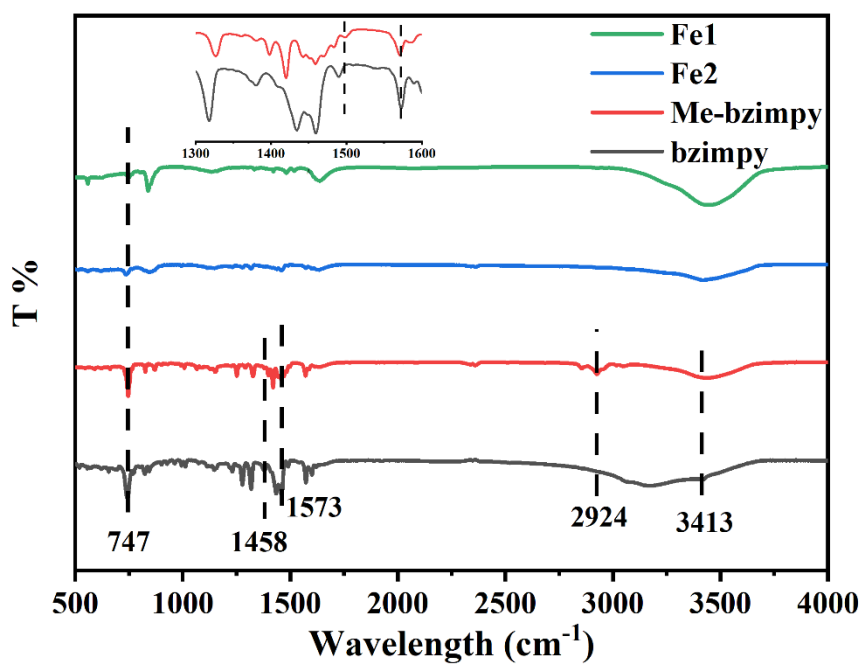


Fig. S7 FT-IR spectra of **Fe1** (green line), **Fe2** (blue line), Me-bzimpy (red line) and bzimpy (black line).

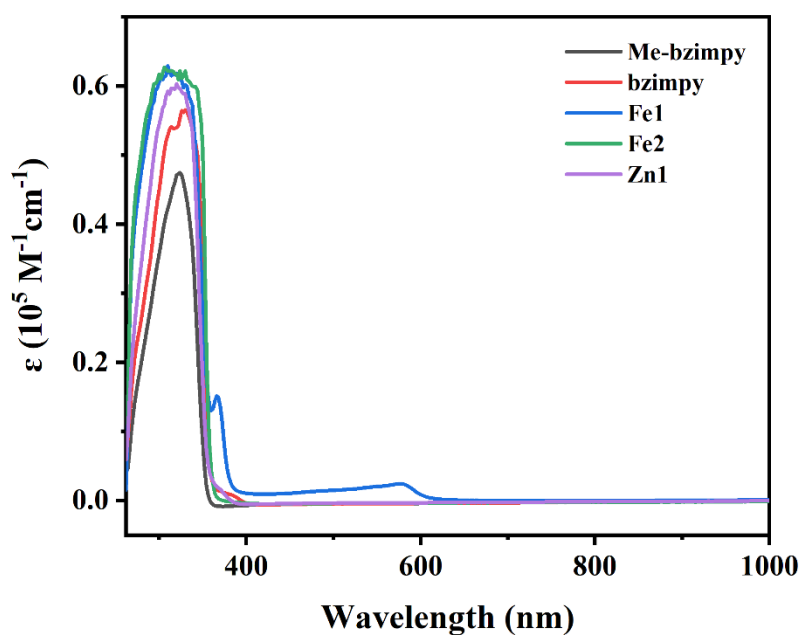


Fig. S8 UV-vis absorption spectra of 40 μM Me-bzimpy (black line), bzimpy (red line), **Fe1** (blue line), **Fe2** (green line) and **Zn1** (purple line) in DMF solution.

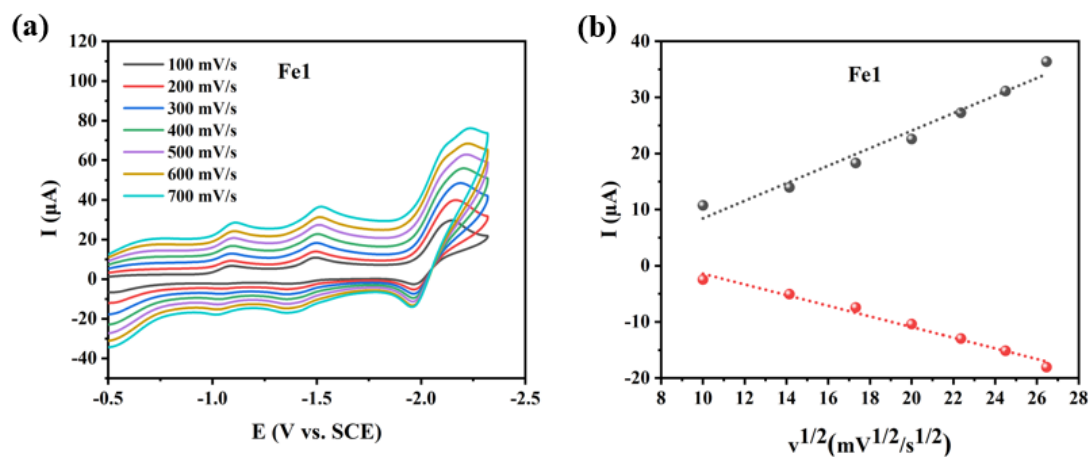


Fig. S9 (a) CVs of **Fe1** (1 mM) in DMF under a N₂ atmosphere at various scan rates (100-700 mV/s). (b) The square roots of currents (*i*_{pc} and *i*_{pa}) vs. scan rate (*v*^{1/2}) of **Fe1** at -1.43 V.

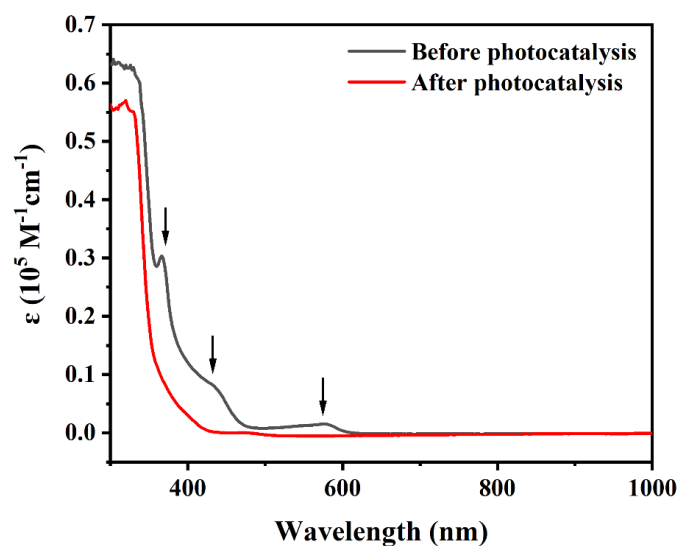


Fig. S10 UV-vis absorption spectra of photocatalytic reaction solution using **Fe1** before and after photocatalysis.

Table S1 Summary of photocatalysis experiments under different concentrations of **Fe1**, 4CzIPN, and different volume ratios of water.

Entry	Fe1 (μM)	4CzIPN(mM)	Volume of water (mL)	CO		H ₂	
				Products (μmol)	TON (Selectivity%)	Products (μmol)	TON
1	0	0.1	1	0.49	0	0	0
2	6	0.1	1	11.13	371	0	0
3	10	0.1	1	20.31	406(95.5)	0.96	19
4	20	0.1	1	31.05	311(98.1)	0.61	12
5	40	0.1	1	35.09	175(97.8)	0.78	16
6	10	0	1	0	0	0	0
7	10	0.01	1	9.59	192(96.6)	0.34	7
8	10	0.05	1	20.31	406	0	0
9	10	0.1	1	29.03	581(98.8)	0.35	7
10	10	0.2	1	41.05	821(99.4)	0.26	5
11	10	0.3	1	43.60	872(98.7)	0.57	11
12	10	0.4	1	43.96	879(99.4)	0.26	5
13	10	0.1	0	8.05	161	0	0
14	10	0.1	0.5	19.34	387(98.8)	0.23	5
15	10	0.1	1	20.31	406(95.5)	0.96	19
16	10	0.1	1.5	14.31	286(98.0)	0.29	6
17	10	0.1	2	14.53	291(99.5)	0.08	2
18	10	0.1	2.5	15.08	302(97.4)	0.41	8
19	10	0.1	3	0	0	0	0
20	10	0.1	3.5	0	0	0	0

Conditions: use a visible light (3 W white LEDs, $\lambda = 420\text{-}650\text{ nm}$) to irradiate the CO₂-saturated reaction solution for 120 min at room temperature. TON = $n(\text{product})/n(\text{Fe1})$. **entry 1-5:** TONs of CO and H₂ with different concentrations of **Fe1** (0-40 μM) in 5 mL DMF/H₂O (v/v = 4/1) solution containing 4CzIPN (0.1 mM), and TEA (0.28 M); **entry 6-12:** TONs of CO and H₂ with different concentrations of 4CzIPN (0-0.4 mM) in 5 mL DMF/H₂O (v/v = 4/1) solution containing **Fe1** (10 μM), 4CzIPN and TEA (0.28 M); **entry 13-20:** TONs of CO and H₂ with different volumes of water in 5 mL DMF/H₂O solutions containing **Fe1** (10 μM), 4CzIPN (0.3 mM), and TEA (0.28 M).

Table S2 Time-dependent generation of CO in a 5 mL CO₂-saturated DMF/H₂O (v/v = 4/1) solution containing 10 μM **Fe1** (entry 1-5), **Fe2** (entry 6-10) or **Zn1** (entry 11-15), 0.28 M TEA, and 0.3 mM 4CzIPN.

Entry	Cat	Irradiation time (min)	CO		H ₂	
			Products (μmol)	TON (Selectivity%)	Products (μmol)	TON
1	Fe1	0	0	0	0	0
2		15	20.48	410(99.8)	0.04	1
3		30	35.64	713(99.1)	0.34	7
4		60	39.03	781(98.1)	0.77	15
5		120	43.91	878(99.2)	0.37	7
6	Fe2	0	0	0	0	0
7		15	2.19	44(98.6)	0.03	1
8		30	3.07	61(95.0)	0.16	3
9		60	3.17	63(94.9)	0.17	3
10		120	3.17	63(94.6)	0.18	4
11	Zn1	0	0	0	0	0
12		15	0.83	17	0	0
13		30	1.05	21	0	0
14		60	1.33	27	0	0
15		120	2.630	53	0	0

Table S3 Comparison of CO₂ photoreduction with recent molecular complexes.

Catalyst	Photosensitizer	[Catalyst]/ [Photosensitizer]	TON(selectivity %)		Reaction conditions	Reference
			CO	H ₂		
Fe1	4CzIPN	10 μM / 0.3 mM	878(99.2)	7(0.8)	0.28 M TEA in DMF/H ₂ O (v/v = 4/1), white LEDs (3 W, λ = 420-650 nm), 2h	This work
Zn1	4CzIPN	10 μM / 0.3 mM	53(~100 %)	0(0)	0.28 M TEA in DMF/H ₂ O (v/v = 4/1), white LEDs (3 W, λ = 420-650 nm), 2h	This work
Fe(qnpy)(H ₂ O) ₂] ²⁺	Ru(phen) ₃ ²⁺	50 μM / 0.2 mM	14095(98)	360(2)	0.11 M BIH in MeCN/H ₂ O (1:1, v/v), blue LED (460 nm), 68h	<i>Chem. Commun.</i> , 2020, 56 , 6249-6252. ³
CoZn	Ru-PS	0.1 μM / 0.4 mM	6680(98)	136(2)	0.3 M TEOA in H ₂ O/MeCN (v/v = 1/4) LED light (450 nm), 10h	<i>ACS Sustain. Chem. Eng.</i> , 2021, 9 , 9273-9281. ⁴
Re-THEA	-	0.4 mM	43(> 99)	< 1	0.3 mL TEOA in DMF, 500 W long-arc Xenon lamp (λ ≥ 400 nm), 12h	<i>ChemSusChem</i> , 2020, 13 , 6284-6289. ⁵
Ni-IDC	Ru(bpy) ₃ ²⁺	10 μM / 0.45 mM	2264.8(95)	119.2(5)	0.029 mM BIH in DMF/TEOA (v/v = 5/1), LED blue light (460 nm), 12h	<i>Inorg. Chem. Commun.</i> , 2020, 122 , 108269. ⁶
Co(bpy) ₂ Cl ₂	Acridine (Acr)	2 μM / 0.4 mM	100(~100 %)	0(0)	0.3 M TEOA in H ₂ O/MeCN (v/v = 1/4), 300 W Xe lamp (λ ≥ 400 nm), 5h	<i>Mol. Catal.</i> , 2021, 500 , 111299. ⁷

Notes and references

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