

## Supporting Information

Coordination–driven discrete metallo–supramolecular assembly for rapid and selective photochemical CO<sub>2</sub> reduction in aqueous solution

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## 1. Experimental Section

### 1.1 Materials and instruments

All reagents including solvents and starting materials for synthesis were purchased from commercial suppliers and used as received. Terpyridine ligand **Phdtpy** was synthesized as reported.<sup>1</sup> ESI-MS spectra were recorded using a ThermoScientific Q Exactive instrument. ESI-TOF-MS was carried out with Triple TOF 600. UV-Vis-NIR absorption spectra were recorded on a G9 spectrophotometer. CV and SWV experiments were carried out on CHI660E in a one-compartment cell equipped with glassy carbon working electrode, Ag/AgCl reference electrode, and platinum plate counter electrode at room temperature. The potentials were referenced to SCE through an internal standard oxidation of ferrocene. GC analysis for CO<sub>2</sub> reduction was performed on Shimadzu GC-2014 (packed column TDX-01, 2 m x 3mm, FID detector with Shimadzu Methanizer MTN-1 for CO and TCD detector for H<sub>2</sub>, N<sub>2</sub> as carrier gas). HCOOH was analyzed with HPLC Shimadzu LC-20AD (SI-52 4E column and 3.6 mmol/L Na<sub>2</sub>CO<sub>3</sub> aqueous solution as the eluant). GC-MS experiment for <sup>13</sup>C was carried out with Agilent 7890B-5977A.

### 1.2 Synthesis of assembly Fe<sub>6</sub>L<sub>6</sub>

Ligand **Phdtpy** (0.3 mmol, 162 mg) was dissolved in 90 mL CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (V/V, 1:2) solution. Then FeCl<sub>2</sub>·4H<sub>2</sub>O (0.3 mmol, 60 mg) was added into the solution and the resulted purple solution was stirred at 40 °C for 24 hours. The reaction solution was further filtered through Celite and filtrate was collected. Excess NH<sub>4</sub>FP<sub>6</sub> (1.8 mmol, 294 mg) was added to the filtrate to afford purple precipitate. The precipitate was further purified by silica column chromatograph using CH<sub>3</sub>CN/saturated KNO<sub>3</sub> aqueous solution (V/V, 5:1). The assembly **Fe<sub>6</sub>L<sub>6</sub>** was obtained as purple solid. Yield: 37%. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 9.64(s, 24H), 9.37 (s, 6H), 8.91 (d, 24H, J= 6.4 Hz), 8.68 (d, 12H, J= 8.0 Hz), 8.25 (t, 6H, J = 8.0 Hz), 7.98 (t, 24H, J = 7.6 Hz), 7.37 (d, 24H, J = 5.2 Hz), 7.17 (m, 24H). <sup>13</sup>C NMR (CD<sub>3</sub>CN): 160.63, 158.20, 153.19, 149.80, 138.86, 138.45, 131.06, 129.88, 127.47, 124.20, 122.14. ESI-TOF-MS: m/z 445.7497[M-9(PF<sub>6</sub><sup>-</sup>)]<sup>9+</sup> (calcd. 445.7486), 519.5891 [M-8(PF<sub>6</sub><sup>-</sup>)]<sup>8+</sup> (calcd. 519.5879), 614.5240 [M-7(PF<sub>6</sub><sup>-</sup>)]<sup>7+</sup> (calcd. 614.5264), 741.1094 [M-6(PF<sub>6</sub><sup>-</sup>)]<sup>6+</sup> (calcd. 741.1054), 918.3211 [M-5(PF<sub>6</sub><sup>-</sup>)]<sup>5+</sup> (calcd. 918.3193), 1184.1429 [M-4(PF<sub>6</sub><sup>-</sup>)]<sup>4+</sup> (calcd. 1184.1402).

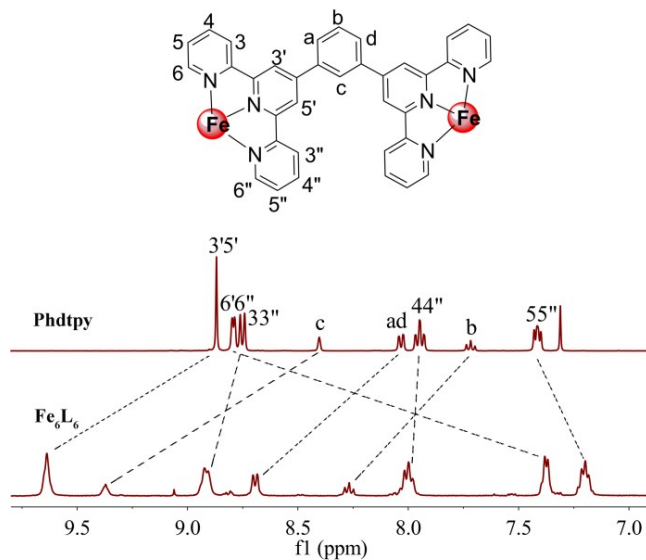
### 1.3 Photochemical CO<sub>2</sub> reduction

General procedure: a 5 mL DMF or DMF/H<sub>2</sub>O solution containing Fe<sub>6</sub>L<sub>6</sub>, 4CzIPN and TEA was degassed with CO<sub>2</sub> for 15 min in a reaction tube and then the tube was sealed. The reaction solution was irradiated with a white LED light equipment (SMPC–LVWT, 420–650 nm, 3 W LEDs) supplied by Institute of Physics and Chemistry & Chinese Academy of Sciences. Unless otherwise stated, all photochemical experiments were conducted with this equipment. The generated CO and H<sub>2</sub> were analyzed through external standard method by injection of 100 μL aliquots of headspace gas into Shimadzu GC–2014 instrument equipped with TCD and FID detectors. All photochemical CO<sub>2</sub> reduction reactions were carried out at least in duplicate.

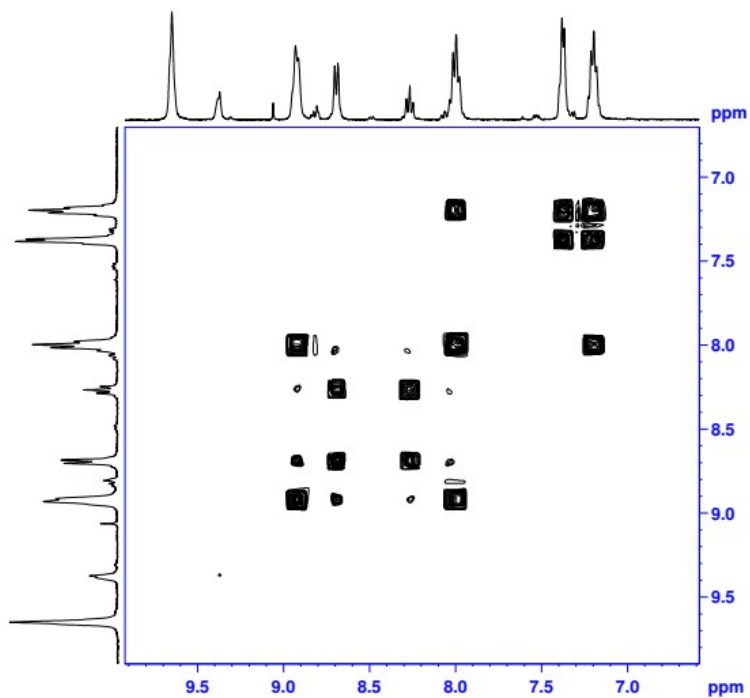
The apparent quantum yield (AQY) of the photocatalytic reaction is calculated according to the following equation:

$$\Phi = (\text{number of CO molecules}) \times 2 / (\text{number of incident photons}) \times 100\%$$

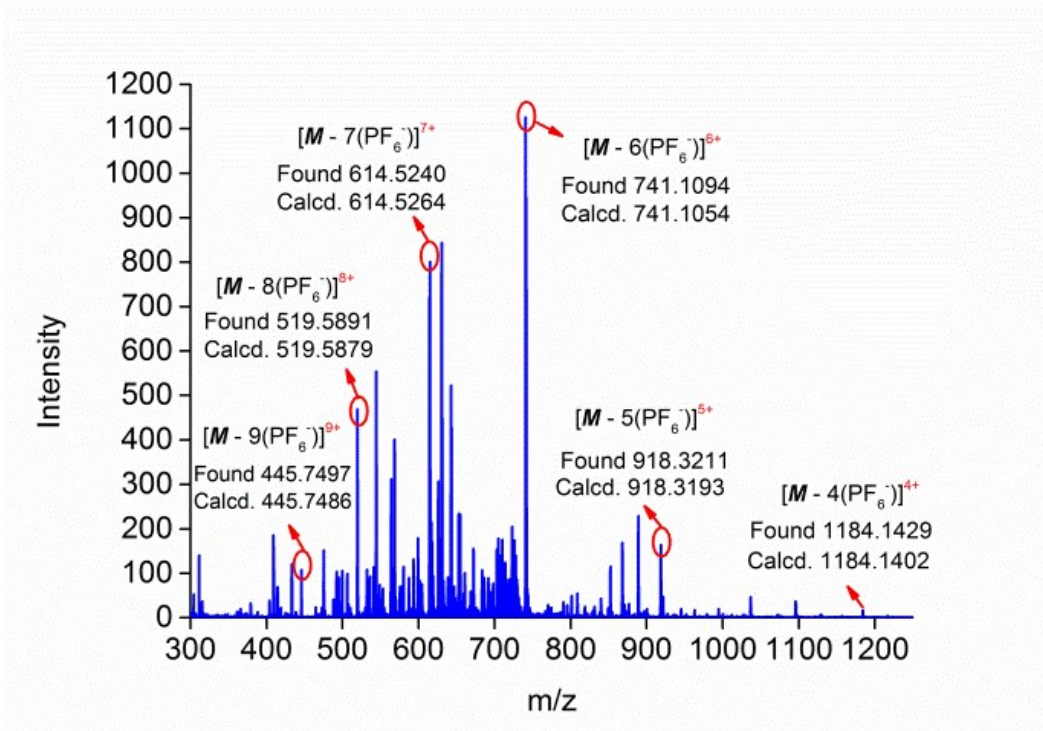
The moles of CO molecules were determined by GC–2014. The light sources for AQY test are blue LEDs (440 nm, 180 mW cm<sup>-2</sup>). The number of incident photons was estimated based on power of LEDs and irradiation time. The power of blue LEDs is probably too large for this photocatalytic system and photons might be not completely used for photochemical reactions.



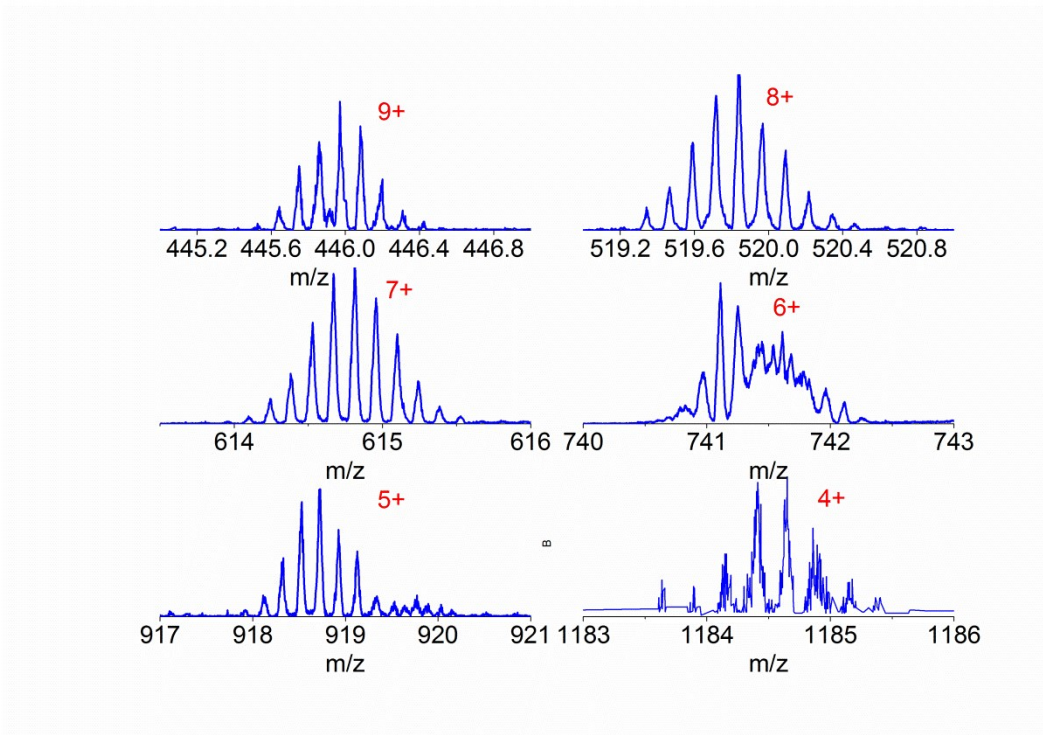
**Fig. S1** Partial <sup>1</sup>H NMR spectra (400 MHz) of ligand **Phdtpy** in CDCl<sub>3</sub> and assembly **Fe<sub>6</sub>L<sub>6</sub>** in CD<sub>3</sub>CN.



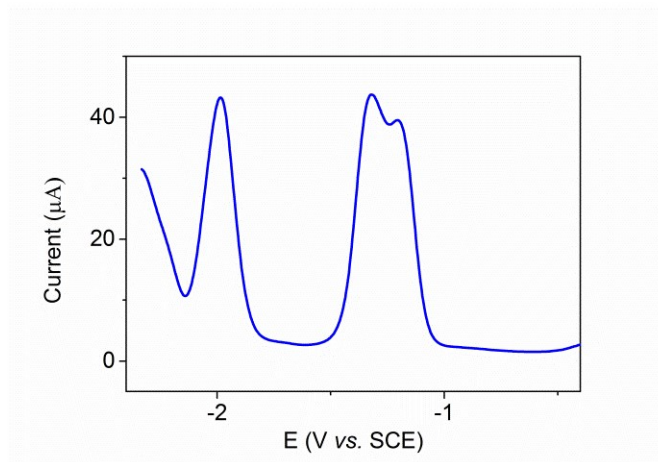
**Fig. S2** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of assembly **Fe<sub>6</sub>L<sub>6</sub>** in CD<sub>3</sub>CN.



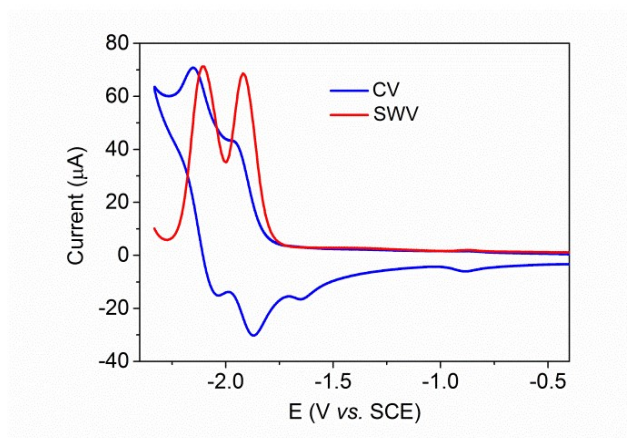
**Fig. S3** ESI-TOF-MS spectrum of assembly  $\text{Fe}_6\text{L}_6$ . The instrument is Triple TOF 4600.



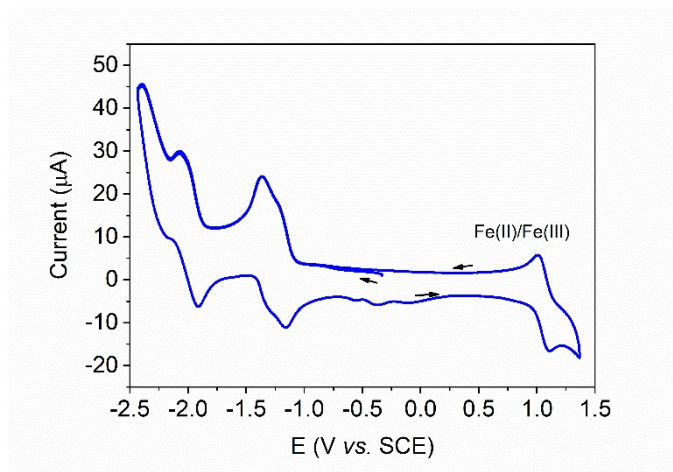
**Fig. S4** Partial experimental ESI-TOF-MS spectra of cations derived from  $\text{Fe}_6\text{L}_6$ .



**Fig. S5** SWV result of assembly  $\text{Fe}_6\text{L}_6$  in DMF.



**Fig. S6** CV and SWV results of ligand  $\text{Phdtpy}$  in DMF.



**Fig. S7** CV result of assembly  $\text{Fe}_6\text{L}_6$ .

**Table S1.** Photochemical CO<sub>2</sub> reduction using assembly **Fe<sub>6</sub>L<sub>6</sub>** with various water fractions.

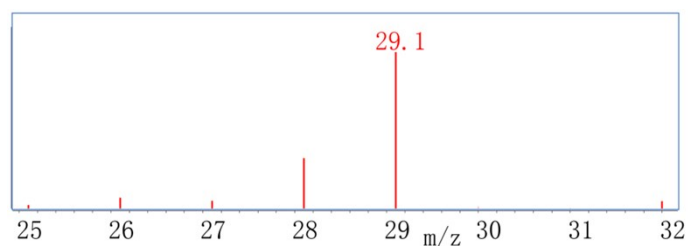
Water fraction (%)	CO (μmol)	H <sub>2</sub> (μmol)	TON (CO)	TON (H <sub>2</sub> )
0	5.87±0.98	0	294±49	0
10	68.33±9.05	1.45±0.21	3417±453	73±11
20	75.49±2.65	1.35±0.07	3775±133	68±4
30	106.68±11.65	1.4±0.28	5334±582	70±14
40	299±4.24	1.1±0.14	14956±222	55±7
50	34.62±0.98	0	1732±48	0
60	0	0	0	0
70	0	0	0	0

Conditions: catalyst [**Fe<sub>6</sub>L<sub>6</sub>**] = 4 μM, photosensitizer [4CzIPN] = 50 μM, [TEA] = 0.28 M in CO<sub>2</sub> saturated DMF/H<sub>2</sub>O solution with water fractions from 0 to 70% at room temperature upon visible light irradiation for 2 h.

**Table S2.** Control experiments for photochemical CO<sub>2</sub> reduction.

Entry	Catalyst	Photosensitizer	Sacrificial Donor	Atmosphere	TON(CO)	TON(H <sub>2</sub> )
1	<b>Fe<sub>6</sub>L<sub>6</sub></b>	–	TEA	CO <sub>2</sub>	0	0
2	<b>Fe<sub>6</sub>L<sub>6</sub></b>	4CzIPN	TEA	N <sub>2</sub>	0	76
3	–	4CzIPN	TEA	CO <sub>2</sub>	0	0
4	<b>Fe<sub>6</sub>L<sub>6</sub></b>	4CzIPN	–	CO <sub>2</sub>	0	0
5	<b>Fe<sub>6</sub>L<sub>6</sub></b>	Ru(bpy) <sub>3</sub> <sup>2+</sup>	TEA	CO <sub>2</sub>	55	0

Conditions: [**Fe<sub>6</sub>L<sub>6</sub>**] = 4 μM, [4CzIPN] = 50 μM, [TEA] = 0.28 M, [Ru(bpy)<sub>3</sub><sup>2+</sup>] = 50 μM in DMF/H<sub>2</sub>O (v/v, 3:2) solution at room temperature upon visible light irradiation for 2 hours.



**Fig. S8** GC–MS result of isotopic labeling experiment with  $^{13}\text{CO}_2$  instead of  $\text{CO}_2$  for photochemical reduction reaction. The signal at 28.1 was also observed due to  $\text{N}_2$  in air when the sample was injected to GC–MS instrument.

**Table S3.** Product  $\text{H}_2$  of photochemical  $\text{CO}_2$  reduction with various concentrations of  $\text{Fe}_6\text{L}_6$ .

Concentration of $\text{Fe}_6\text{L}_6$ Time (min)	1 $\mu\text{M}$	2 $\mu\text{M}$	4 $\mu\text{M}$	8 $\mu\text{M}$
0	0 $\mu\text{mol}$	0 $\mu\text{mol}$	0 $\mu\text{mol}$	0 $\mu\text{mol}$
15	trace	trace	0.07 $\pm$ 0.014 $\mu\text{mol}$	0.12 $\pm$ 0.028 $\mu\text{mol}$
40	trace	trace	0.54 $\pm$ 0.036 $\mu\text{mol}$	0.83 $\pm$ 0.13 $\mu\text{mol}$
80	0.1 $\pm$ 0.014 $\mu\text{mol}$	0.36 $\pm$ 0.021 $\mu\text{mol}$	0.95 $\pm$ 0.028 $\mu\text{mol}$	1.79 $\pm$ 0.59 $\mu\text{mol}$
120	0.17 $\pm$ 0.028 $\mu\text{mol}$	0.52 $\pm$ 0.042 $\mu\text{mol}$	1.25 $\pm$ 0.018 $\mu\text{mol}$	2.29 $\pm$ 0.78 $\mu\text{mol}$

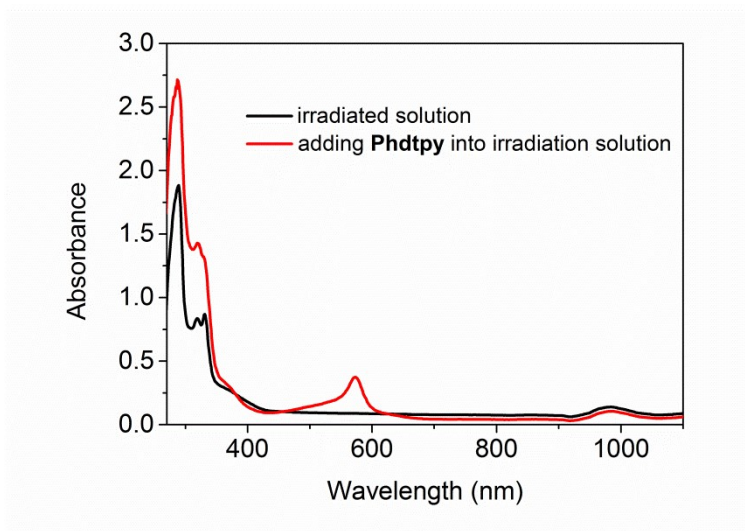
Conditions: Photosensitizer [4CzIPN] = 50  $\mu\text{M}$ , [TEA] = 0.28 M in DMF/ $\text{H}_2\text{O}$  (V/V, 3:2) solution with various concentrations of  $\text{Fe}_6\text{L}_6$  (1  $\mu\text{M}$ , 2  $\mu\text{M}$ , 4  $\mu\text{M}$ , 8  $\mu\text{M}$ ) at room temperature upon visible light irradiation.



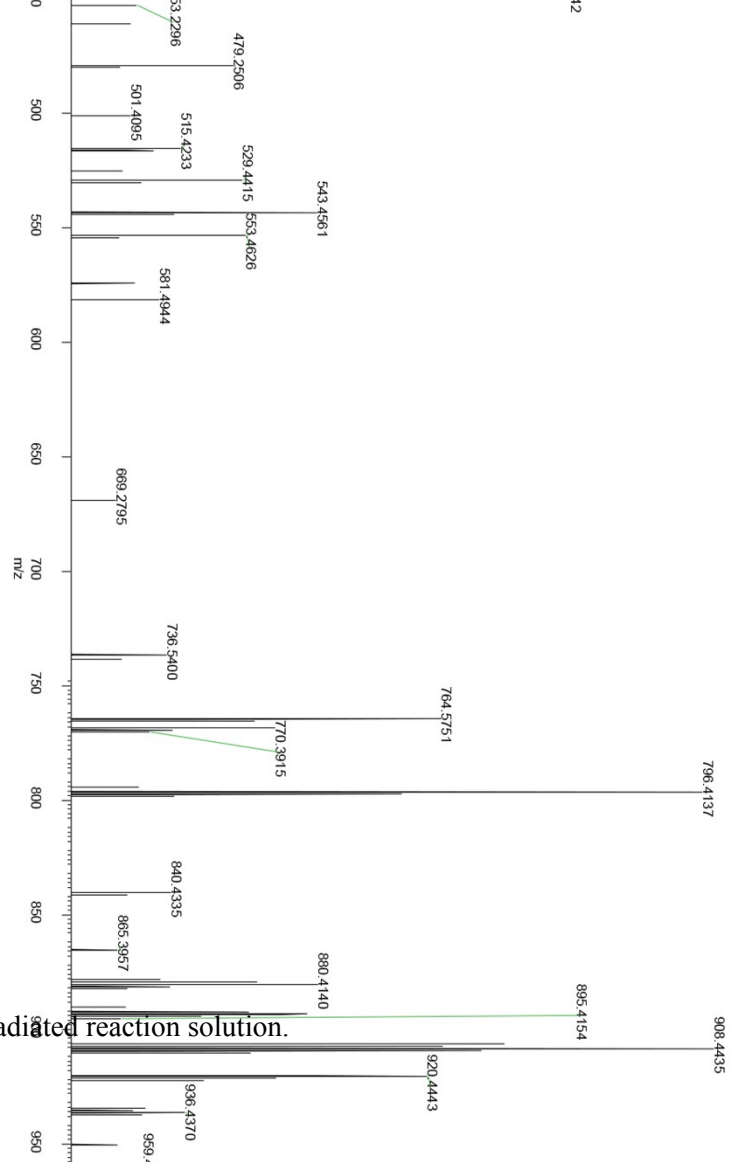
**Table S4.** Photochemical CO<sub>2</sub> reduction by adding various reagents into irradiated reaction solution.

Additives	CO (μmol)	H <sub>2</sub> (μmol)	TON (CO)	TON (H <sub>2</sub> )
Fe <sup>2+</sup>	2.05±0.66	trace	102±33	trace
<b>Phdtpy</b>	19.61±1.68	0.07±0.04	980±84	4±2
4CzIPN	3.11±1.27	0.82±0.36	155±63	41±18
4CzIPN, <b>Phdtpy</b>	215±1.89	0.81±0.14	10750±95	41±7
Fe <sup>2+</sup> , 4CzIPN	7.17±0.75	0.77±0.25	359±37	39±13

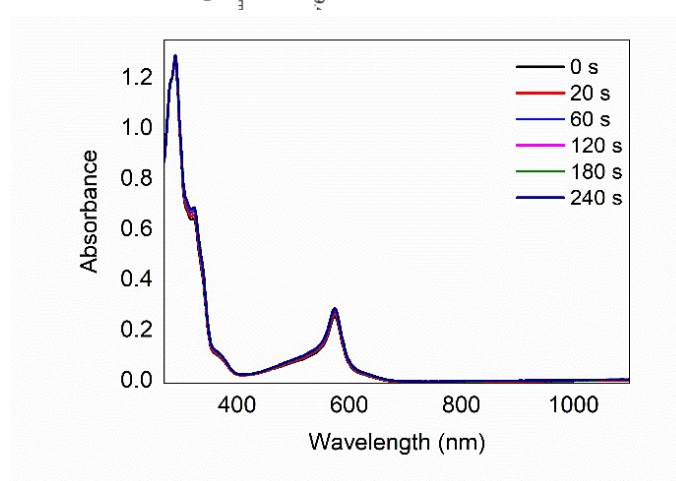
Conditions: The solution containing **Fe<sub>6</sub>L<sub>6</sub>** (4 μM), 4CzIPN (50 μM) and TEA (0.28 M) in DMF/H<sub>2</sub>O (v/v, 3:2) solution under a CO<sub>2</sub> atmosphere was irradiated for 2 h. Then additives including Fe<sup>2+</sup> (24 μM), **Phdtpy** (24 μM), 4CzIPN (50 μM), 4CzIPN (50 μM) plus **Phdtpy** (24 μM) and Fe<sup>2+</sup> (24 μM) plus 4CzIPN (50 μM) were added into the irradiated solution for another catalytic cycle, respectively.



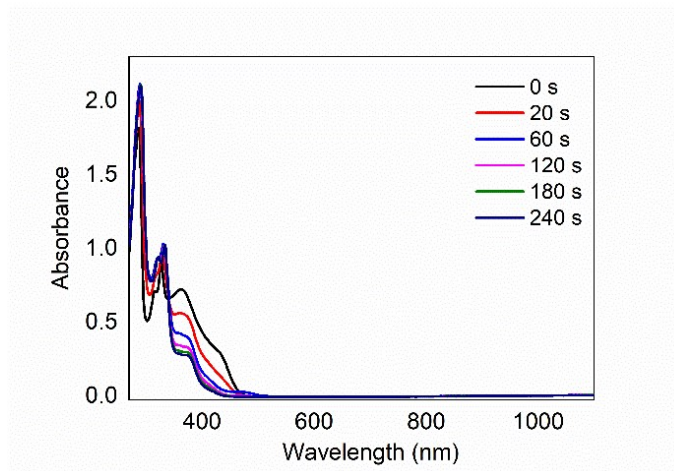
**Fig. S9** UV–Vis–NIR absorption spectra of irradiate reaction solution before (blank line) and after addition of ligand **Phdtpy** (24 μM). The reaction solution contained **Fe<sub>6</sub>L<sub>6</sub>** (4 μM), 4CzIPN (50 μM) and TEA (0.28 M) in DMF/H<sub>2</sub>O (v/v, 3:2) solution under a CO<sub>2</sub> atmosphere for 2 h of visible light irradiation.



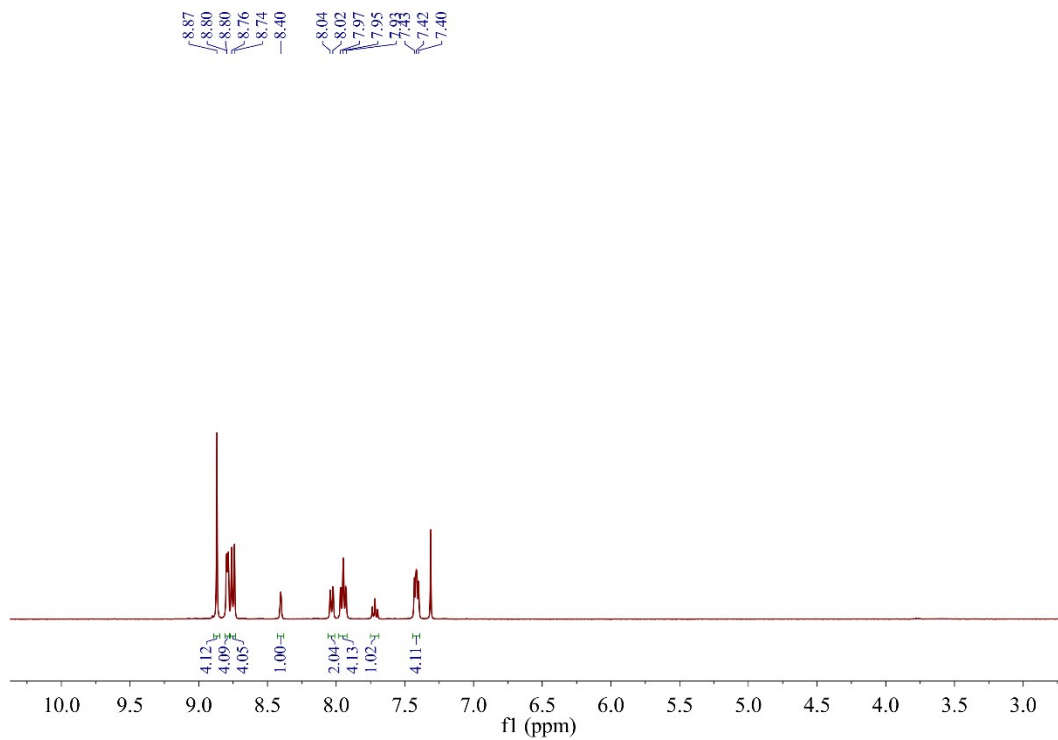
**Fig. S10** ESI-MS spectrum of irradiated reaction solution.



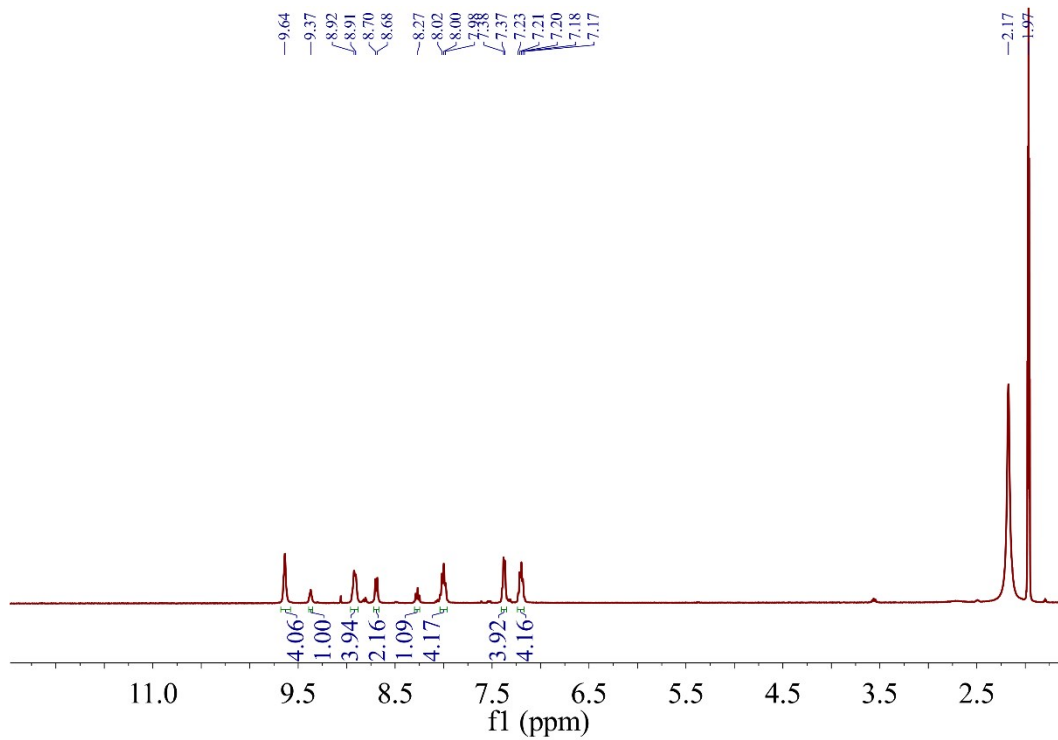
**Fig. S11** UV-Vis-NIR absorption spectra of assembly  $\text{Fe}_6\text{L}_6$  in the presence of TEA upon visible light irradiation under a  $\text{N}_2$  atmosphere.



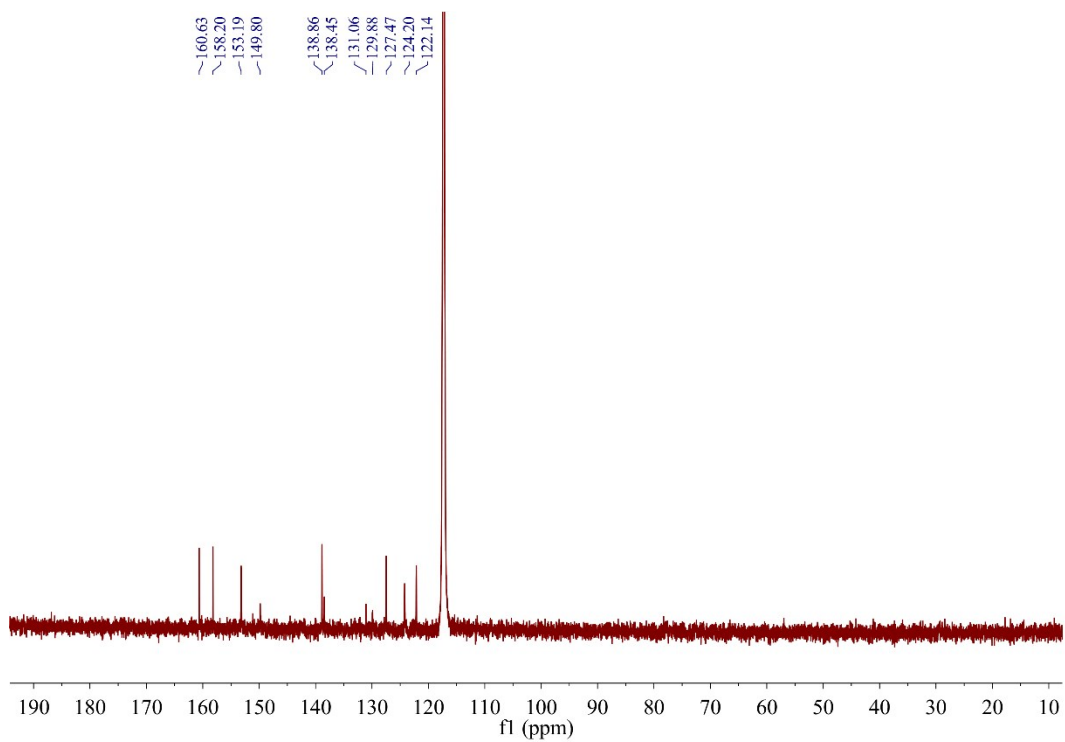
**Fig. S12** UV–Vis–NIR absorption spectra of 4CzIPN in the presence of TEA upon visible light irradiation under a  $N_2$  atmosphere.



**Fig. S13**  $^1\text{H}$  NMR spectrum of ligand **Phdtpy** in  $\text{CDCl}_3$ .



**Fig. S14**  $^1\text{H}$  NMR spectrum of assembly  $\text{Fe}_6\text{L}_6$  in  $\text{CD}_3\text{CN}$ .



**Fig. S15**  $^{13}\text{C}$  NMR spectrum of assembly  $\text{Fe}_6\text{L}_6$  in  $\text{CD}_3\text{CN}$ .

#### References:

- (1) Matias, T. A.; Mangoni, A. P.; Toma, S. H.; Rein, F. N.; Rocha, R. C.; Toma, H. E.; Araki, K., Catalytic Water–Oxidation Activity of a Weakly Coupled Binuclear Ruthenium Polypyridyl Complex. *Eur. J. Inorg. Chem.* **2016**, 5547–5556.