

Supporting Information

Merging an organic TADF photosensitizer and a simple terpyridine–Fe(III) complex for photocatalytic CO₂ reduction

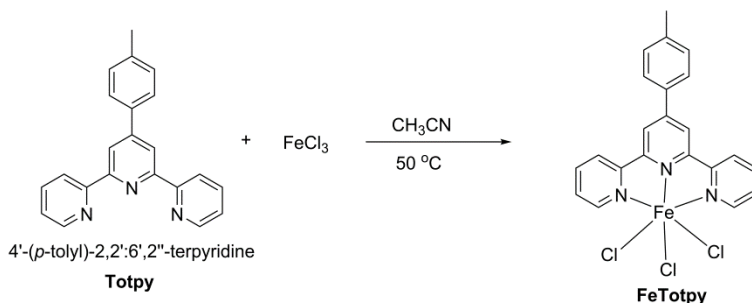
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1. Experimental Section

1.1 Materials and instruments

All starting materials were purchased from commercial suppliers and used as received. Terpyridine **Totpy**¹ and 4CzIPN² were synthesized as reported. High-resolution mass spectra HR-ESI-MS spectra were recorded using a ThermoScientific Q Exactive instrument. Emission spectra were measured by Shimadzu RF-6000 as the light source. UV-vis absorption spectra were obtained on a G9 spectrophotometer. Cyclic voltammetry (CV) was carried out on CHI660E in a one-compartment cell equipped with a glassy carbon working electrode, a Ag/AgCl reference electrode, and a platinum wire counter electrode at a scan rate of 0.1 V s⁻¹ at room temperature. The potentials were referenced to SCE through an internal standard oxidation of ferrocene. GC analysis for CO₂ reduction was performed on Shimadzu GC-2014 (packed column TDX-01, 2 m x 3mm, FID detector and N₂ as carrier gas). GC-MS test was carried out with Agilent 7890B-5977A.

1.2 Synthesis of Fe(Totpy)Cl₃



Scheme S1 Synthetic route for catalyst **FeTotpy**.

The ligand **Totpy** (0.2 mmol, 65 mg) was added into 10 mL CH₃CN solution containing FeCl₃•6H₂O (0.25 mmol, 68 mg) and stirred at 50 °C for 8 h. The precipitate was collected through filtration. Then the product was obtained as light green powder after drying in vacuum. Yield: 78 mg, 81%. HR-ESI-MS (m/z): found 449.0136 for [M-Cl]⁺ (calcd. 449.0143 for C₂₂H₁₇Cl₂FeN₃⁺). Elemental analysis: found C 54.72, H 3.26, N 8.39 (calcd. C 54.42, H 3.53, N 8.65).

1.3 Photocatalytic CO₂ reduction

General procedure: a 5 mL DMF or DMF/H₂O solution containing **FeTotpy**, 4CzIPN or [Ru(bpy)₃]²⁺ and TEA was degassed with CO₂ for 18 min before irradiation at room temperature 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. The generated CO and H₂

were analyzed by injection of 200 μL aliquots from reaction vial headspace into GC–2014 instrument equipped with TCD and FID detectors.

The quantum yield 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 was determined by GC–2014 and the number of incident photons was estimated by Newport Model 842–PE. The quantum yield estimated by this way seems to be relatively low because incident photons may not be fully used by the photosensitizer.

References

1. J. Wang and G. S. Hanan, *Synlett*, 2005, **2005**, 1251–1254.
2. J. Luo and J. Zhang, *ACS Catal.*, 2016, **6**, 873–877.

2. Supplementary Figures

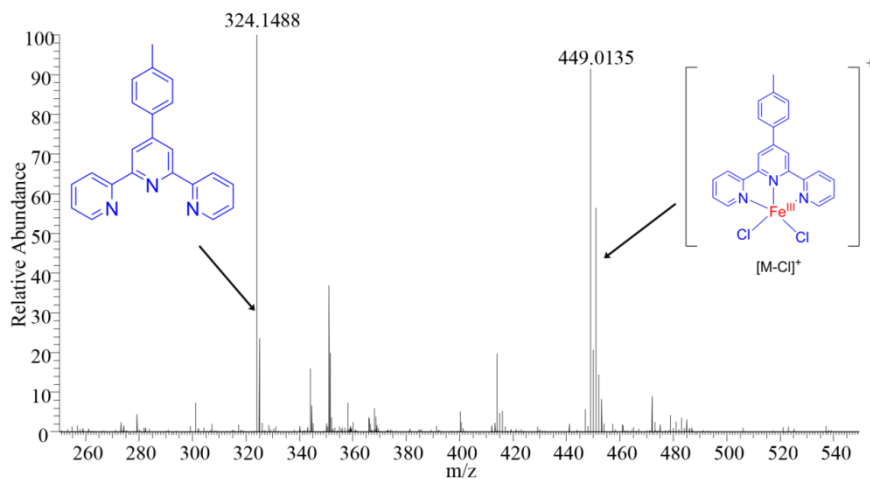


Fig. S1 HR–ESI–MS spectrum of **FeTotpy**. The m/z signal at 449.0135 is due to release of one Cl^- from **FeTotpy**.

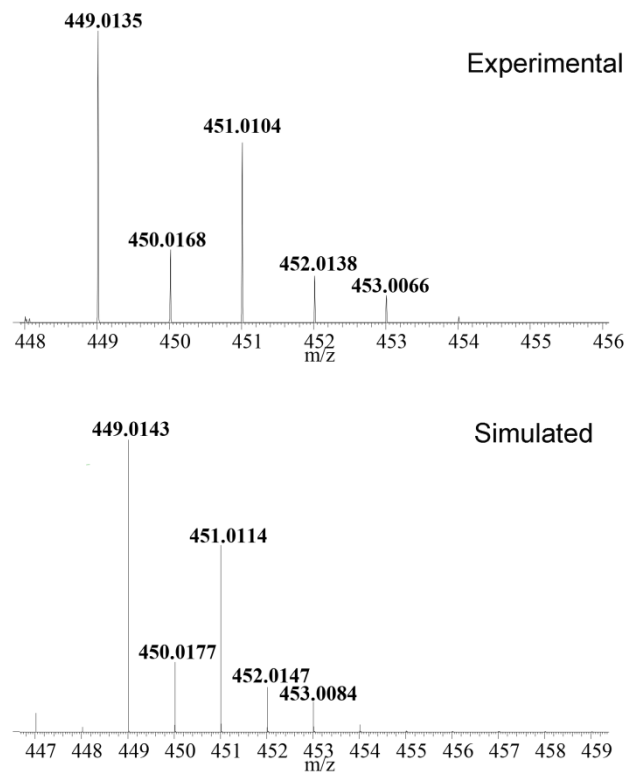


Fig. S2 Comparison of experimental MS spectrum and simulated result of $[M-Cl]^{+}$.

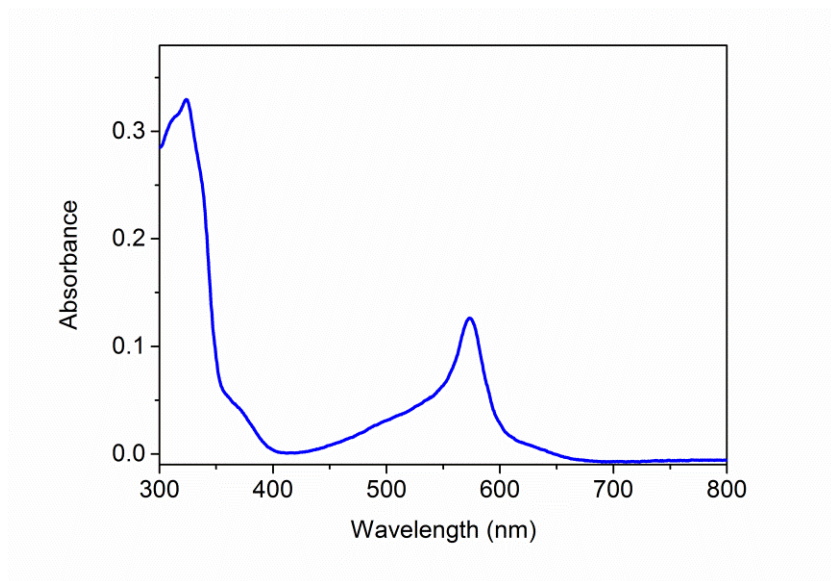


Fig. S3 UV-vis absorption spectrum of **FeTotpy** (10 μ M) in DMF solution.

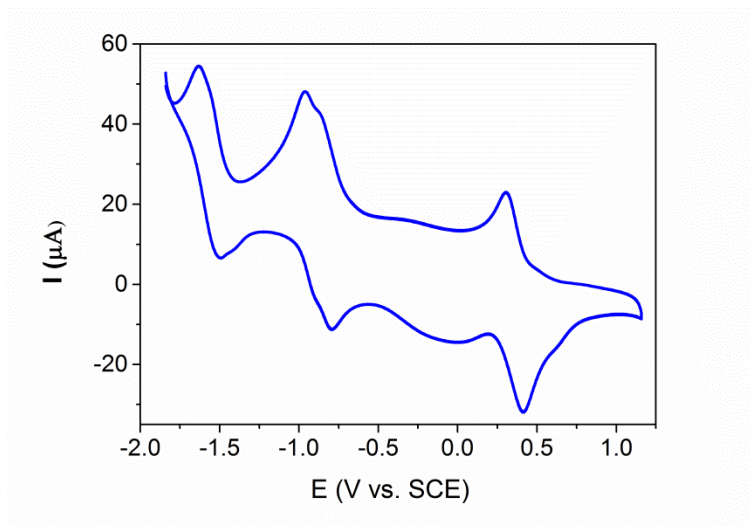


Fig. S4 CV of complex **FeTotpy** in DMF at room temperature.

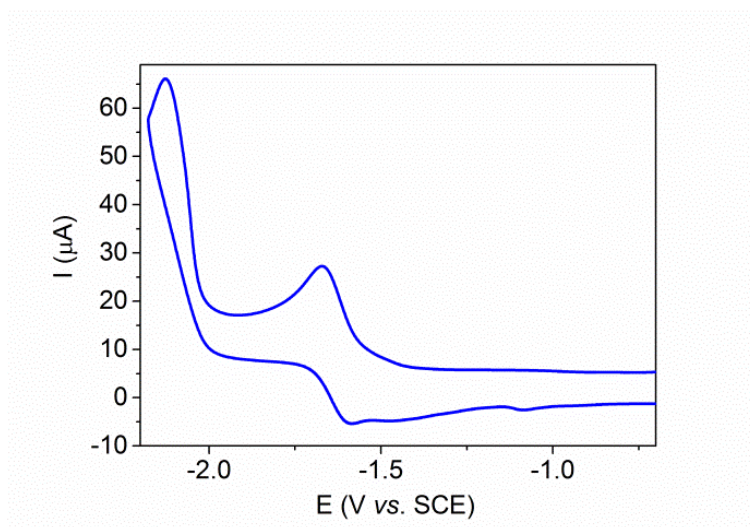


Fig. S5 CV of ligand **Totpy** in DMF at room temperature.

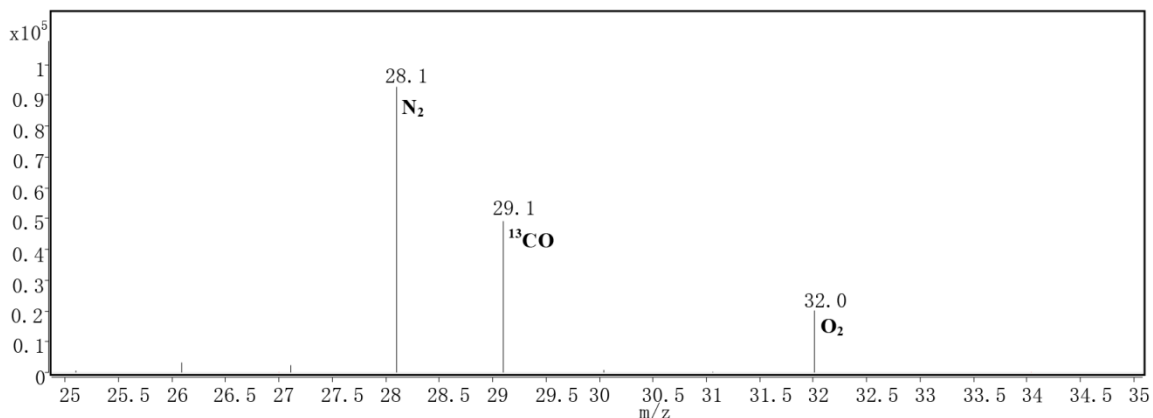


Fig. S6 Isotopic labeling experiment with $^{13}\text{CO}_2$ was conducted by injection 25 mL $^{13}\text{CO}_2$ into pre-degassed reaction solution with N_2 . The 200 μL aliquots of headspace with a syringe were analyzed directly by GC-MS Agilent 7890B-5977A. Therefore, signals of N_2 and O_2 are observed.

Table S1. Photophysical properties and redox potentials of photosensitizers

Dyes	Absorption /Emission $\lambda_{\text{max}}(\text{nm})$	τ	Excited State		Ground State		Ref.
			$E_{\text{Red}}(\text{P}^*/\text{P}^-)$ (V vs. SCE)	$E_{\text{Ox}}(\text{P}^+/\text{P}^*)$ (V vs. SCE)	$E_{\text{Red}}(\text{P}/\text{P}^-)$ (V vs. SCE)	$E_{\text{Ox}}(\text{P}^+/\text{P})$ (V vs. SCE)	
4CzIPN	435/550	5.1 μs	+1.35	-1.04	-1.21	+1.52	Angew. Chem. Int. Ed. 2014, 53, 6993–6996
$\text{Ru}(\text{bpy})_3^{2+}$	452/620	1.1 μs	+0.77	-0.81	-1.33	+1.29	J. Org. Chem. 2012, 77, 1617–1622
Eosin Y	520/553	2.1 ns	+0.83	-1.11	-1.06	+0.78	Chem. Commun., 2014, 50, 6688
FL	437/545	4.2 ns	+0.77	-1.07	-1.17	+0.87	Photochemistry and Photobiology, 2010, 86, 492–498
TEA						+0.69	C. R. Chimie, 2017, 20, 283–295

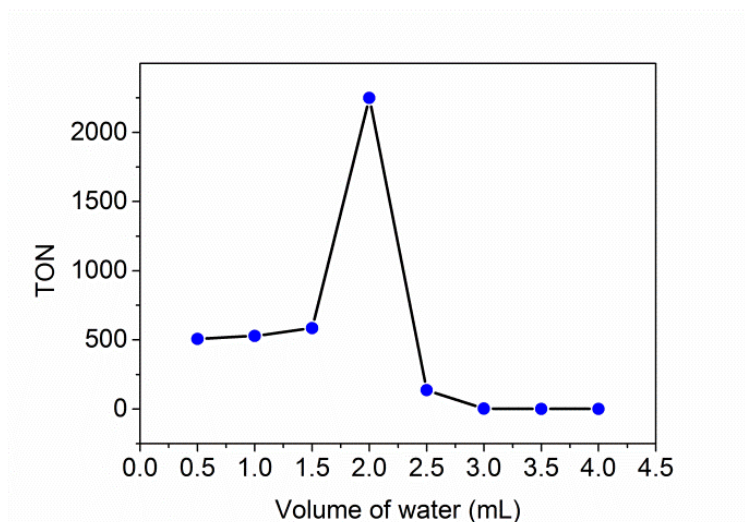


Fig. S7 TONs of photocatalytic CO₂ reduction reaction using **FeTotpy**, 4CzIPN and TEA in mixed DMF/H₂O solution (5 mL). The ratio of DMF/H₂O is 9:1, 4:1, 7:3, 3:2, 1:1, 2:3, 3:7 and 1:4, respectively.

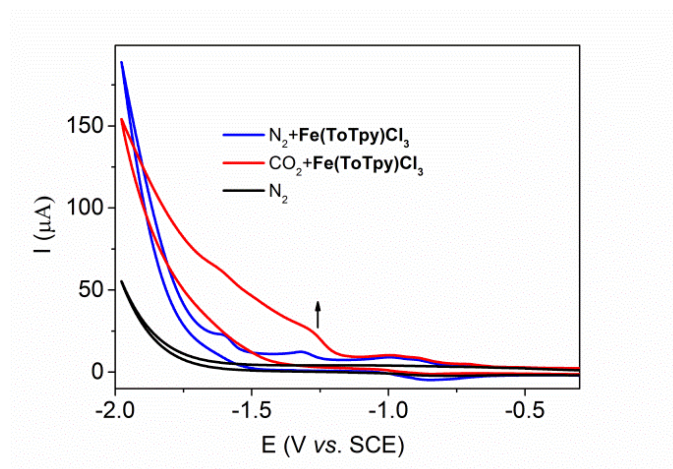


Fig. S8 Cyclic voltammograms (CV) of **FeTotpy** (0.5 mM) in DMF/H₂O (5:1) solution containing 0.1 M Bu₄NPF₆ at 0.1 V s⁻¹ under N₂ (blue) and CO₂ (red) atmosphere at room temperature. The black line is the blank result of DMF/H₂O (5:1) solution containing 0.1 M Bu₄NPF₆ without **FeTotpy**.

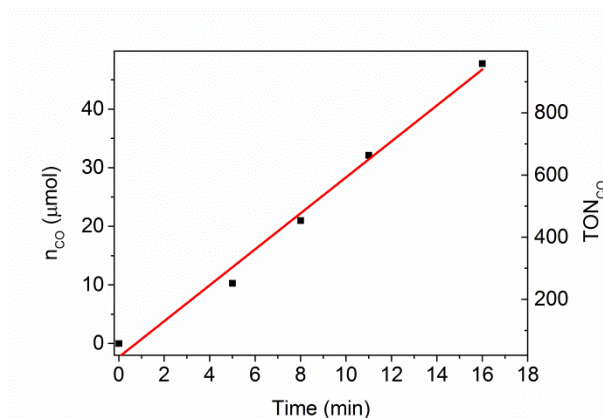


Fig. S9 TOF determination for photocatalytic CO_2 reduction with **FeTotpy**. Reaction conditions: **FeTotpy** ($10 \mu\text{M}$), 4CzIPN ($50 \mu\text{M}$) and TEA (0.28 M) in $5 \text{ mL DMF/H}_2\text{O}$ ($3:2$) solution.

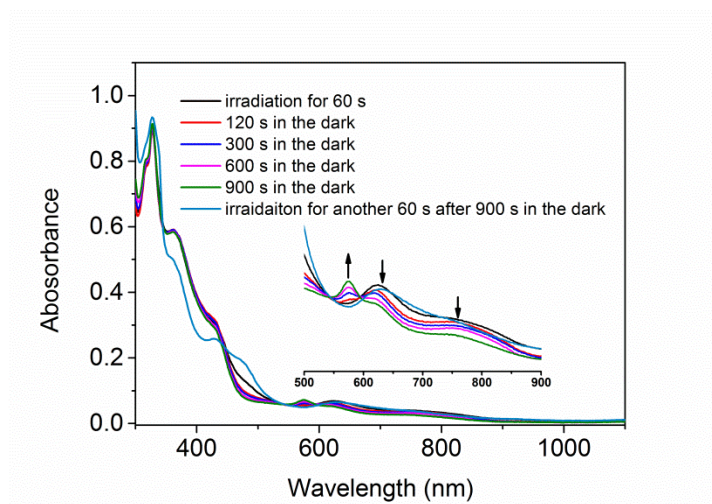
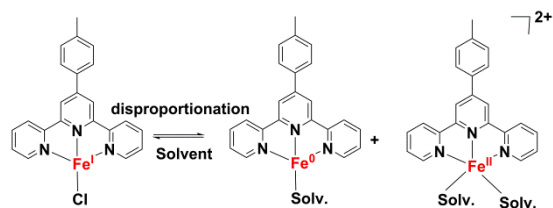


Fig. S10 UV-vis absorption spectra of the solution containing **FeTotpy** ($10 \mu\text{M}$), 4CzIPN ($25 \mu\text{M}$) and TEA (0.1 M) in 3 mL DMF at room temperature under N_2 atmosphere upon visible-light irradiation for 60 s and then in the dark for 900 s . The gray blue line shows the formed Fe(II) species through disproportionation of Fe(I) species could also be reduced by the photosensitizer 4CzIPN in the presence of TEA upon light irradiation for another 60 s . There is no complete overlap between yellow line and black line probably due to generation of Fe(0) species and minor decomposition.



Scheme 2 Disproportionation route of reduced Fe(I) species.

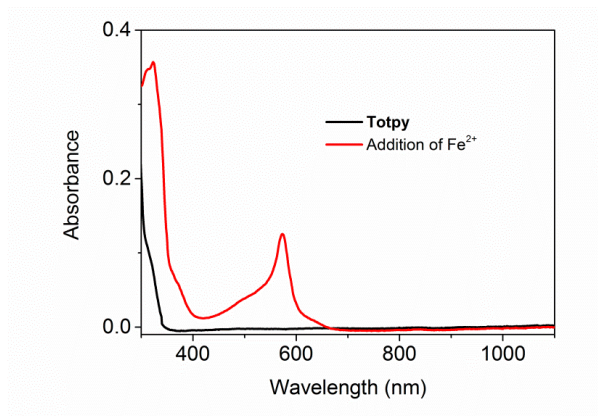


Fig. S11 UV-vis absorption spectra of **Totpy** (10 μM) in DMF upon addition of excess Fe^{2+} (60 μM , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) under N_2 atmosphere. It should be noted that the spectrum is similar to that of **FeTotpy**.

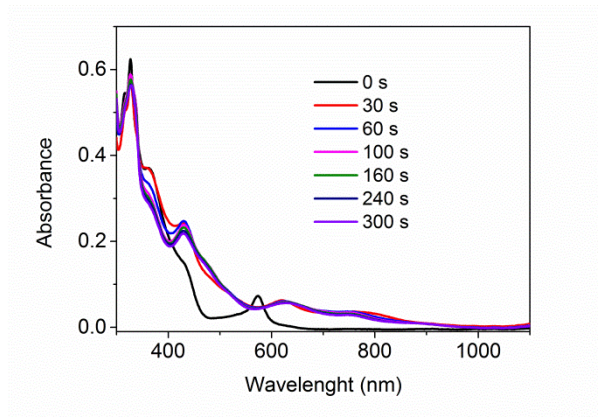


Fig. S12 UV-vis absorption spectra of the solution containing **FeTotpy** (10 μM), 4CzIPN (25 μM) and TEA (0.1 M) in 3 mL DMF at room temperature under CO_2 atmosphere upon visible-light irradiation for 0 s, 30 s, 60 s, 100s, 160s, 240 s and 300s, respectively.

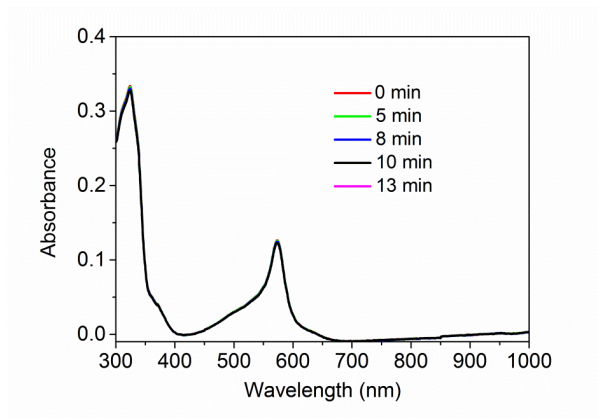


Fig. S13 UV-vis absorption spectrum of **FeTotpy** (10 μM) in DMF solution upon visible-light irradiation.

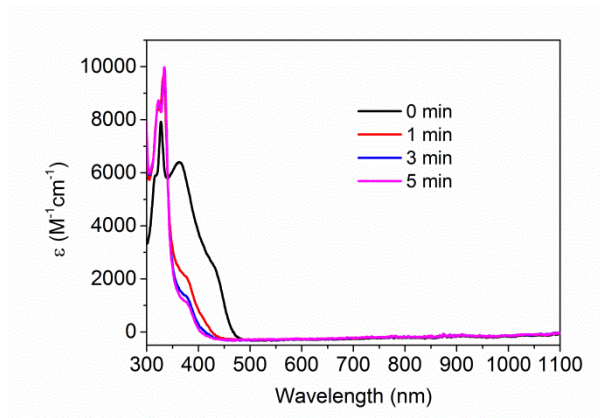


Fig. S14 UV-vis absorption spectrum of 4CzIPN (25 μM) and TEA (0.1 M) in DMF solution upon visible-light irradiation.

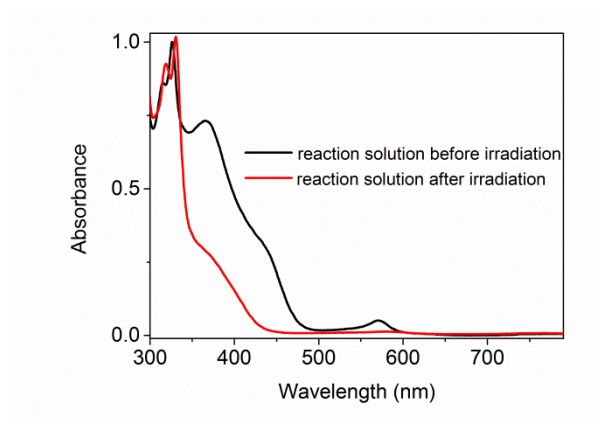


Fig. S15 UV-vis absorption spectra of reaction solution before and after light irradiation for 180 min.

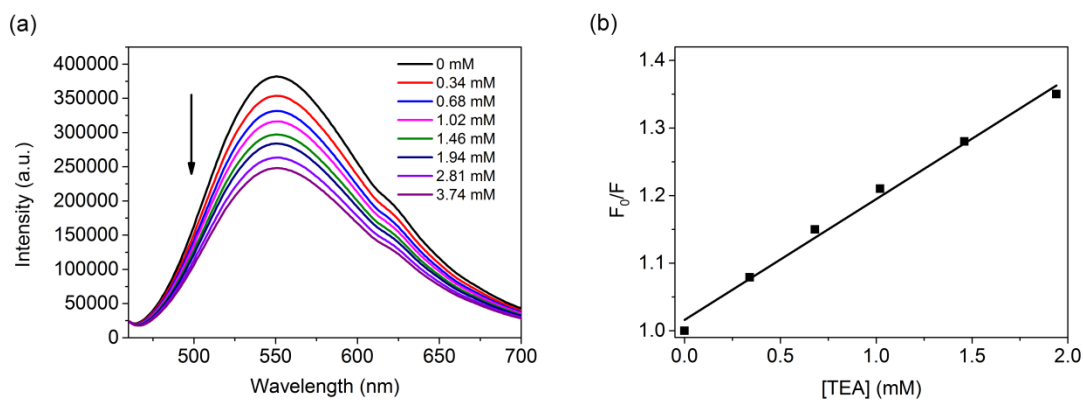


Fig. S16 (a) Fluorescence titration experiments of 4CzIPN (10 μM) upon addition of TEA (0 – 3.74 mM) in DMF ($\lambda_{\text{ex}} = 450 \text{ nm}$). (b) Corresponding plots (F_0/F vs concentrations of TEA). The Stern-Volmer constant and quenching rate constant are estimated to be $6.1 \times 10^7 \text{ Lmol}^{-1}$ and $1.2 \times 10^7 \text{ Lmol}^{-1}\text{s}^{-1}$.

Stern–Volmer equation

$$F_0/F_n = 1 + K_D[Q] = 1 + k_q\tau_0[Q]$$

where F_0 and F_n are the emission intensity in the absence and presence of quenching agent TEA, τ_0 is the emission lifetime of 4CzIPN in the absence TEA, k_q is the bimolecular quenching rate constant, K_D is the Stern–Volmer quenching constant, and $[Q]$ is the molar concentration of TEA.