

Supporting Information

Exploiting consecutive photoinduced electron transfer (ConPET) in CO₂ photoreduction

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Experimental section

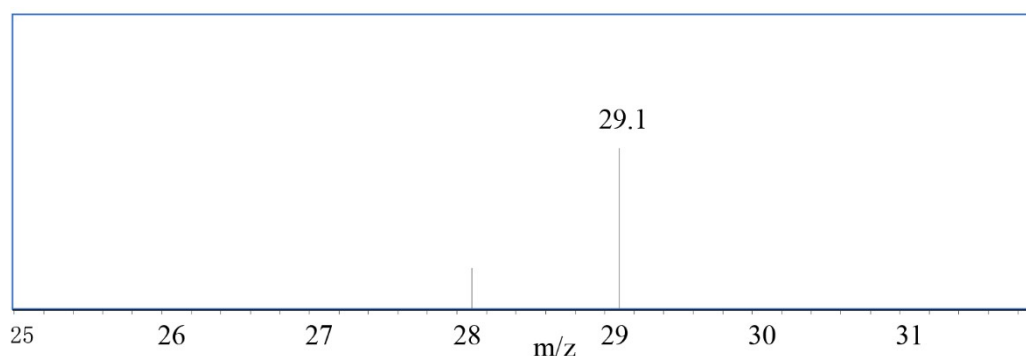
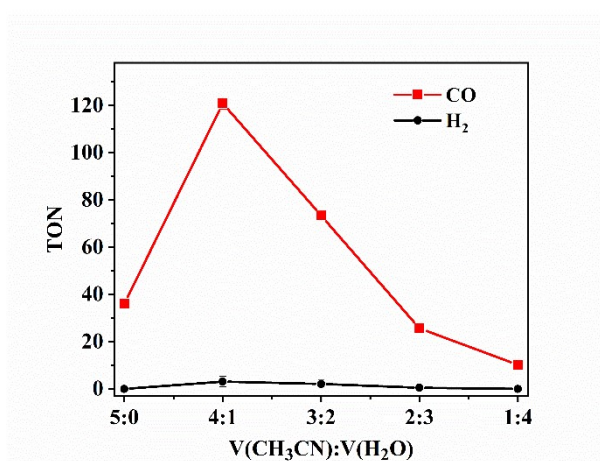
Materials and instruments. Chemicals and solvents are purchased from commercial suppliers and used as received. 4CzIPN^[1] and [Fe(tpy)₂](PF₆)₂^[2] were prepared as previously reported. EPR test was conducted with Bruker EMXnano. CV experiments were performed on CHI660E in a one-compartment cell using glassy carbon as working electrode, Ag/AgCl reference electrode, and platinum plate counter electrode at a scan rate of 0.1 V s⁻¹. GC analysis for gas samples of CO₂ photoreduction 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 H₂, N₂ as carrier gas). HCOOH and other liquid products were determined by ¹H NMR. UV-vis-NIR absorption spectra were recorded with a G9 spectrophotometer. Emission spectra were recorded with Shimadzu RF-6000. GC-MS experiment for ¹³CO₂ was carried out with Agilent 7890B-5977A. ¹H NMR spectra were obtained with Bruker AVANCE III (400MHz). Time-resolved emission decay plots were obtained with Edinburgh FLS980 spectrometer.

General procedure for photocatalytic CO₂ reduction with [Ru(tpy)₂]²⁺ and 4CzIPN. Typically, A 5 mL CH₃CN/H₂O (v/v, 4:1) solution containing catalyst [Ru(tpy)₂]²⁺, photosensitizer 4CzIPN and electron donor TEA was added slowly into a glass tube and then carefully sealed with a rubber stopper. The solution was bubbled with CO₂ through a needle for 15 min and further completely sealed again for visible light irradiation by a LEDs setup (SMPC-LVWT, 420-650 nm, 3 W LEDs) supplied by Technical Institute of Physics and Chemistry CAS. The whole setup was kept at room temperature during photocatalysis. To analyze gaseous products, 100 μL of headspace gas was directly injected the GC instrument with a gastight syringe. Moles of products (CO and H₂) were determined by corresponding calibration curves. Liquid products were analyzed by ¹H NMR spectra.

Table S1. Photocatalytic CO₂ reduction using [Ru(tpy)₂]²⁺ and 4CzIPN.^[a]

Entry	Catalyst	Photosensitizer	Electron donor	CO (μmol)	H ₂ (μmol)	TON _{CO} (Sel.)
1	[Ru(tpy) ₂] ²⁺	4CzIPN	TEA	12.4	0.45	124 (96.5%)
2	[Ru(tpy) ₂] ²⁺	-	TEA	0	0	0
3	-	4CzIPN	TEA	trace	0	N.D.
4	[Ru(tpy) ₂] ²⁺	4CzIPN	-	0	0	0
5 ^[b]	[Ru(tpy) ₂] ²⁺	4CzIPN	TEA	0	0	0
6 ^[c]	[Ru(tpy) ₂] ²⁺	4CzIPN	TEA	0	0	0

[a] Conditions: concentrations of [Ru(tpy)₂]²⁺, 4CzIPN and TEA are 20 μM, 100 μM and 0.28 M, respectively. The solution is CO₂-saturated CH₃CN/H₂O (v/v, 4:1) solution under visible light irradiation for 120 min. [b] Without light irradiation. [c] Without CO₂.

**Fig. S1** Isotopic labeling experiment using ¹³CO₂ to generate ¹³CO (m/z =29.1). The gas sample was directly injected into the GC-MS instrument for analysis.**Fig. S2** Photocatalytic CO₂ reduction using [Ru(tpy)₂]²⁺ (20 μM), 4CzIPN (100 μM) and TEA (0.28 M) in 5mL CH₃CN/H₂O solution under visible light irradiation for 120 min.

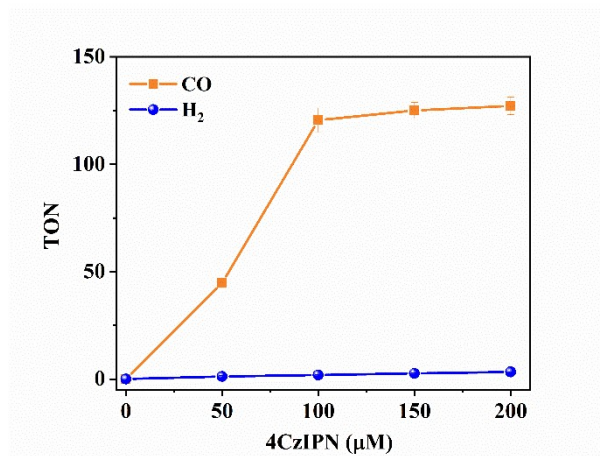


Fig. S3 Photocatalytic CO₂ reduction using [Ru(tpy)₂]²⁺ (20 μM), 4CzIPN (0 - 200 μM) and TEA (0.28 M) in 5mL CH₃CN/H₂O (v/v, 4:1) solution under visible light irradiation for 120 min.

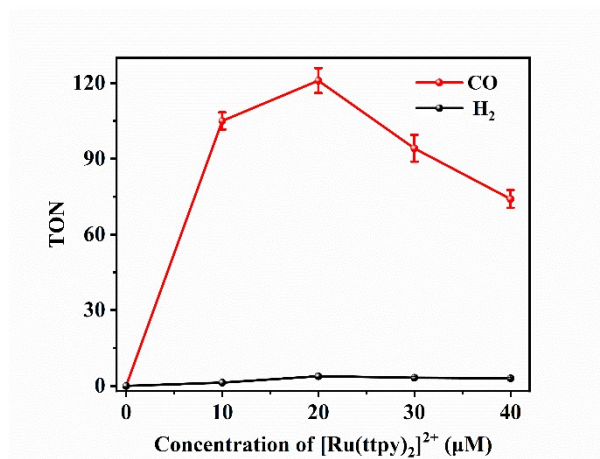


Fig. S4 Photocatalytic CO₂ reduction using [Ru(tpy)₂]²⁺ (0 - 40 μM), 4CzIPN (100 μM) and TEA (0.28 M) in 5mL CH₃CN/H₂O (v/v, 4:1) solution under visible light irradiation for 120 min.

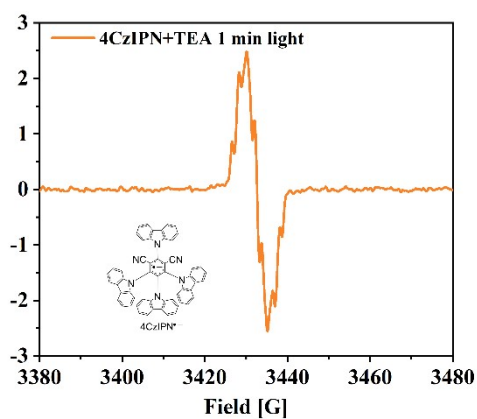


Fig. S5 EPR spectrum of 4CzIPN (2 mM) in CH₃CN/H₂O (v/v, 4:1) solution containing TEA (50 mM) upon visible light irradiation.

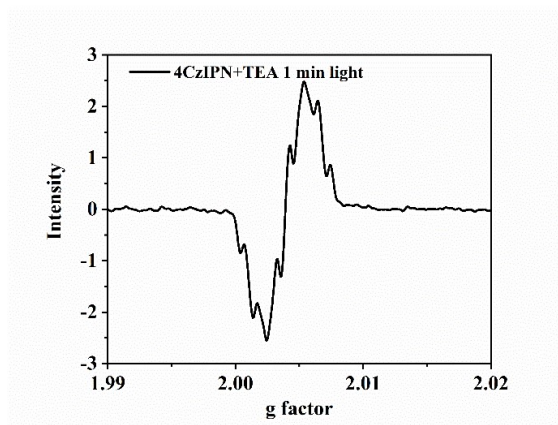


Fig. S6 The g factor of generated radical anion $4\text{CzIPN}^{\cdot-}$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v, 4:1) solution containing 4CzIPN (2 mM) and TEA (50 mM) under a N_2 atmosphere upon visible light irradiation.

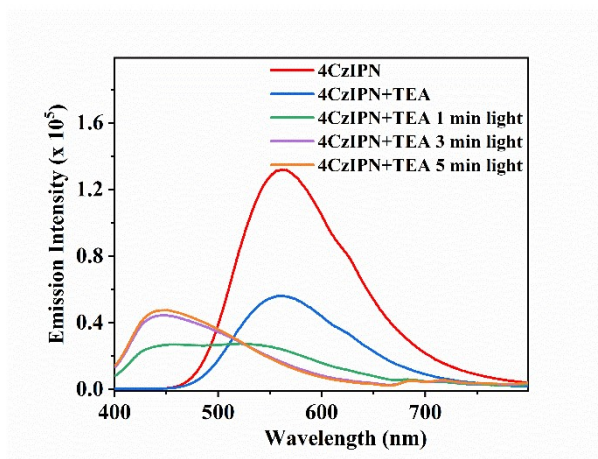


Fig. S7 Emission spectra of 4CzIPN (50 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v, 9:1) solution upon visible light irradiation under a N_2 atmosphere. The concentration of TEA is 50 mM.

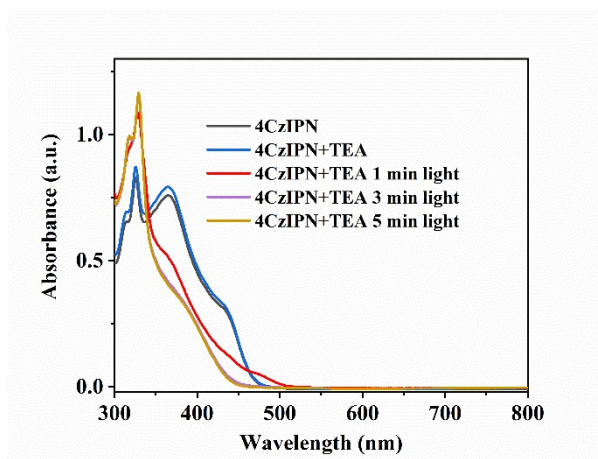


Fig. S8 UV-vis absorption spectra of 4CzIPN (50 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v, 9:1) solution upon visible light irradiation in the presence of TEA (50 mM) under a N_2 atmosphere.

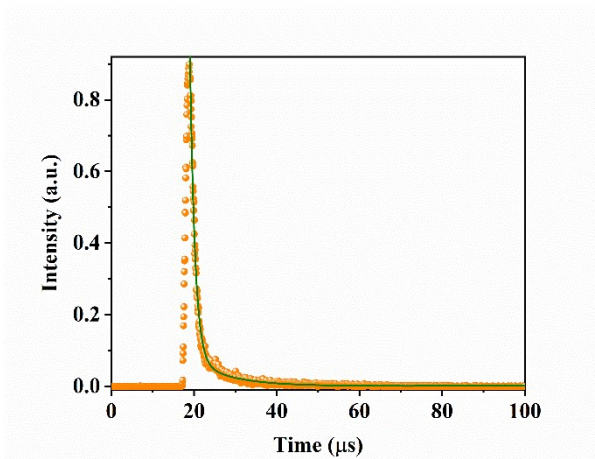


Fig. S9 Emission decay plots at 445 nm for the solution containing 4CzIPN (50 μM) and TEA (50 mM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v, 9:1) after 5 min of visible light irradiation under a N_2 atmosphere.

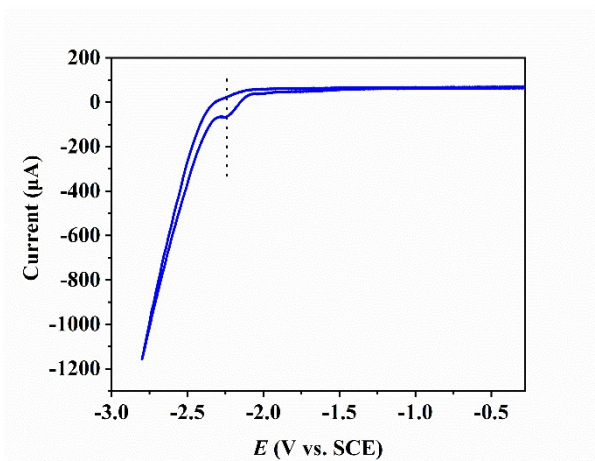


Fig. S10 CV of 1,4-dichlorobenzene in CH_3CN solution with NBu_4PF_6 (0.1 M) as supporting electrolyte at a scan rate of 100 mV s^{-1} at room temperature.

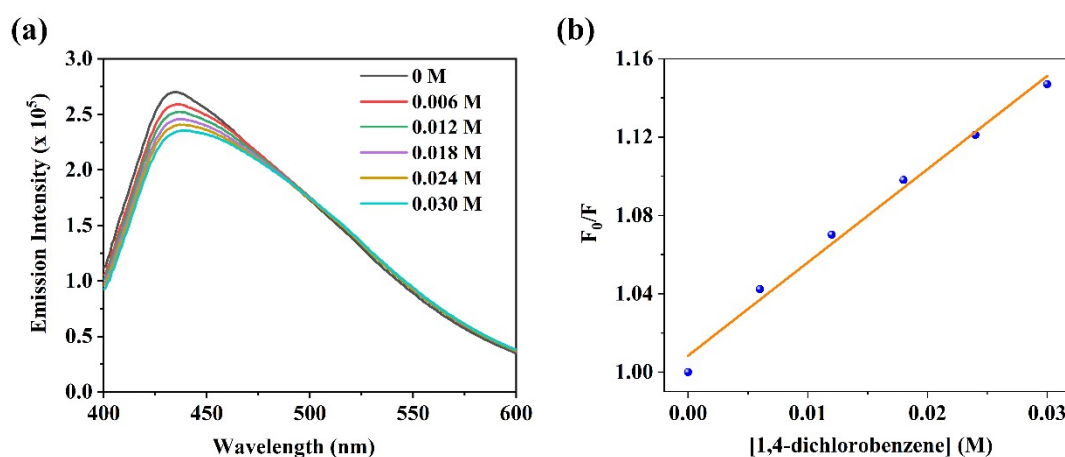


Fig. S11 (a) Emission quenching upon addition of 1,4-dichlorobenzene (0-30 mM) under a N_2 atmosphere. (b) Corresponding plots (F_0/F vs concentration of 1,4-dichlorobenzene). The Stern-Volmer quenching rate constant (k_q) is estimated to be $1.26 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.
Stern-Volmer equation

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

where F_0 and F are the emission intensity in the absence and presence of quenching agent TEA, τ_0 is the emission lifetime of radical anion $4\text{CzIPN}^{\bullet-}$, K_q is the bimolecular quenching rate constant, K_D is the Stern-Volmer quenching constant, and $[Q]$ is the molar concentration of 1,4-dichlorobenzene.

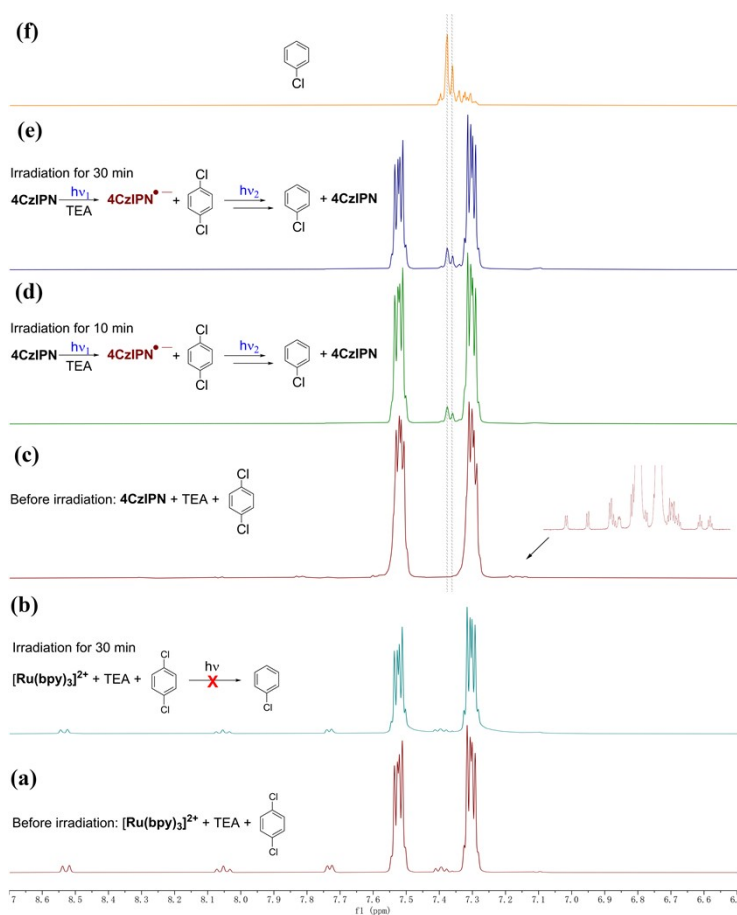


Fig. S12 ^1H NMR spectra of (a) $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (v/v, 10:1) solution containing $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.8 mg), TEA (15.8 mg) and 1,4-dichlorobenzene (17.8 mg) before irradiation. (b) solution (a) after 30 min of irradiation. (c) $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (v/v, 10:1) solution containing 4CzIPN (0.8 mg), TEA (15.8 mg) and 1,4-dichlorobenzene (17.8 mg) before irradiation. (d) solution (c) after 10 min of irradiation. (e) solution (c) after 30 min of irradiation. (f) chlorobenzene (10.8 mg) in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (v/v, 10:1) solution. The samples were prepared in a glovebox under a He atmosphere.

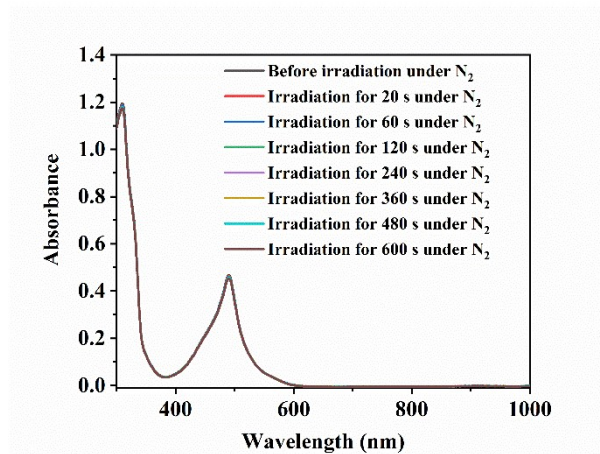


Fig. S13 UV-vis-NIR absorption spectra of $[\text{Ru}(\text{tpy})_2]^{2+}$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution containing TEA upon visible light irradiation under a N_2 atmosphere.

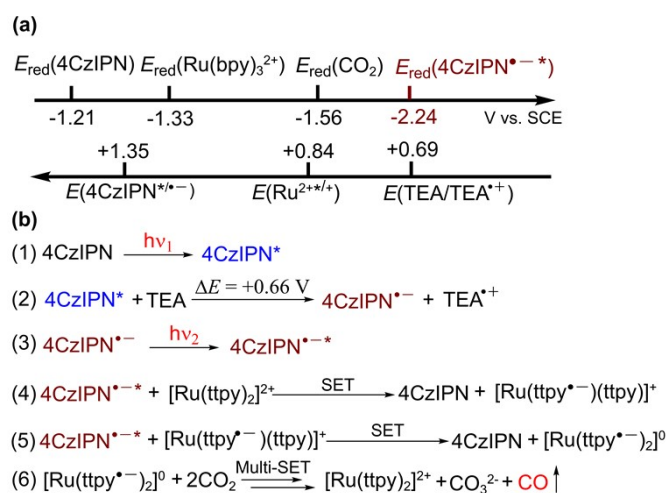


Fig. S14 (a) Redox potentials of various species and processes in this work. (b) A probable mechanism for CO_2 photoreduction using 4CzIPN and $[\text{Ru}(\text{tpy})_2]^{2+}$.

References:

- [1] J. Luo, J. Zhang, *ACS Catal.* **2016**, *6*, 873-877.
- [2] M. T. Indelli, F. Scandola, J.-P. Collin, J.-P. Sauvage, A. Sour, *Inorg. Chem.* **1996**, *35*, 303-312.