

Supporting Information for

An insight into the reaction mechanism of CO₂ photoreduction catalyzed by atomically dispersed Fe atoms supported on graphitic carbon nitride

Zhengyan Zhao, Wei Liu, Yantao Shi*, Heming Zhang, Xuedan Song, Wenzhe Shang, Ce Hao**State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China*

***Corresponding authors.**

E-mail address: shiyantao@dlut.edu.cn (Y. Shi); haoce@dlut.edu.cn (C. Hao)

The formulas of the rate constants involved in the photophysical and photochemical processes

The rate constant of the fluorescence emission (k_F)¹ can be calculated by the integration of the emission spectra based on Fermi's golden rule and the time-dependent perturbation theory,

$$k_F(T) = \int \sigma_{em}(\omega, T) d\omega$$

the $\sigma_{em}(\omega, T)$ is written as¹⁻²

$$\sigma_{em}(\omega, T) = \frac{4\omega^3}{3\hbar c^3} \sum_{u,v} P_{iv}(T) |\langle \theta_{fu} | \mu_{fi} | \theta_{iv} \rangle|^2 \delta(\omega_{iv, fu} - \omega)$$

The rate constants of IC³ and ISC⁴ are calculated as follows:

$$k_{IC} = \frac{2\pi}{\hbar} \sum_{u,v} P_{iv}(T) \left| \sum_n \langle \Phi_f | \hat{P}_n | \Phi_i \rangle \langle \Theta_{fu} | \hat{P}_n | \Theta_{iv} \rangle \right|^2 \delta(E_{iv} - E_{fu})$$

$$k_{ISC} = \frac{2\pi}{\hbar} \sum_{u,v} P_{iv}(T) |\langle \Phi_f | \hat{H}^{SO} | \Phi_i \rangle|^2 |\langle \Theta_{fu} | \Theta_{iv} \rangle|^2 \delta(E_{iv} - E_{fu})$$

where ω is the circular frequency; T is the temperature; \hbar is the reduced Planck constant; c is the speed of light in vacuum; v and u are the vibrational quantum numbers of the initial state and the final state, respectively; P_{iv} is the Boltzmann distribution of the initial vibronic manifold; Θ is the vibrational wavefunction; i and f are the initial and the final state, respectively; μ_{fi} is the electric transition dipole moment from the initial electronic state to the final electronic state; and δ is the Dirac operator; Φ is the electronic state; \hat{P}_n indicates the momentum operator of the n th normal vibrational mode in the final state; n is the index of normal vibrational modes; E represents the energy; and \hat{H}^{SO} denotes the Hamiltonian operator of spin-orbit coupling.

The reaction rate constant k_R of the photochemical process is calculated based on the transition state theory:

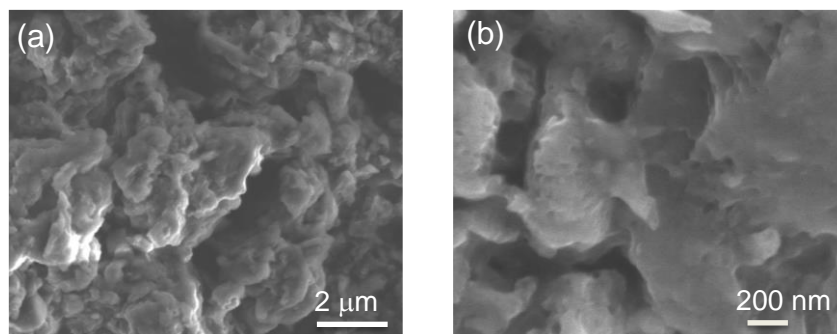
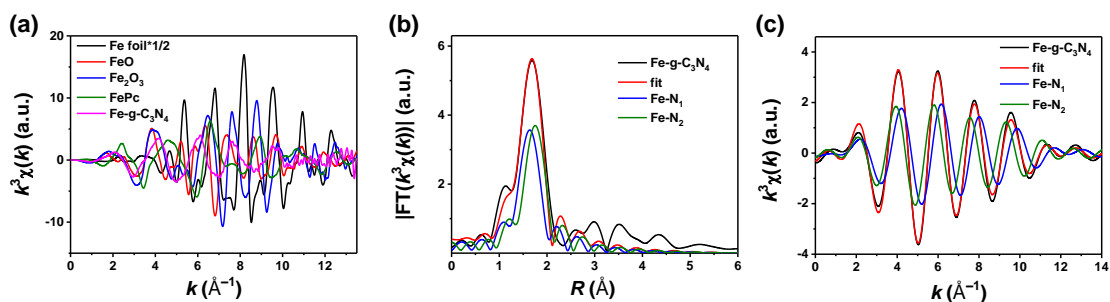
$$k_R = k_i \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right)$$

$$k_i = 1 + \frac{1}{24} \left(\frac{\hbar \nu_i}{k_B T}\right)^2$$

where k_B is the Boltzmann constant, ΔG^\ddagger is the Gibbs free energy, namely the difference in energies between the transition state and the reactant complex; R is the ideal gas constant; k_i is the transmission coefficient; and ν_i is the imaginary frequency of the transition state.

Table S1 The blank experiments of CO₂ photoreduction.

	Catalyst	Medium	Atmosphere	Irradiation time	CO
1	g-C ₃ N ₄	water	Ar	10 h	None
2	g-C ₃ N ₄	water	CO ₂	Dark	None
3	None	water	CO ₂	10 h	None

**Fig. S1** (a) (b) Scanning electron microscopy images of Fe-g-C₃N₄.**Fig. S2** (a) Fe K-edge k^3 -weighted EXAFS oscillations $k^3\chi(k)$ of Fe-g-C₃N₄ sample. The data of Fe foil, FeO, Fe₂O₃ and FePc are shown for reference (b) The fitting curves of k^3 -weighted EXAFS spectra and (c) $k^3\chi(k)$ oscillations of Fe-g-C₃N₄ sample using the ARTEMIS module of IFEFFIT.**Table S2** EXAFS fitting results for Fe-g-C₃N₄ sample using the ARTEMIS module of IFEFFIT.

Sample	Path	N	R (Å)	σ^2 (10^{-3}Å^2)	ΔE_0 (eV)	R -factor
Fe-g-C ₃ N ₄	Fe-N ₁	2.0	2.08	2.3	6.0	0.001
	Fe-N ₂	2.2	2.19	2.3	6.0	

N , R , σ^2 , and ΔE_0 are the coordination number, interatomic distance, Debye–Waller factor, and shift in the edge energy.

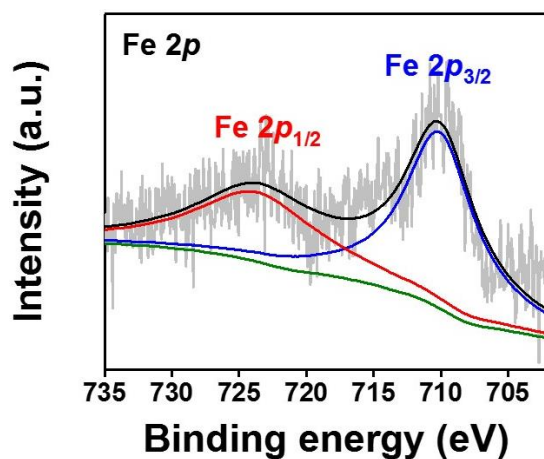


Fig. S3 Fe 2p XPS spectra of Fe-g-C₃N₄.

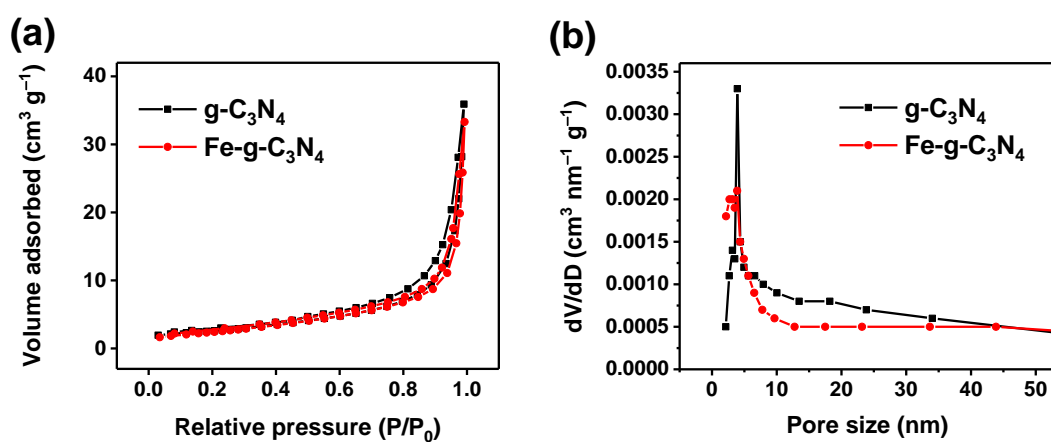


Fig. S4 (a) N₂ adsorption-desorption isotherms and (b) Barrett-Joyner-Halenda (BJH) pore size distribution curves of g-C₃N₄ and Fe-g-C₃N₄ samples

Table S3 The BET surface areas, total pore volumes, and pore size of g-C₃N₄ and Fe-g-C₃N₄ samples.

	g-C ₃ N ₄	Fe-g-C ₃ N ₄
S_{BET} (m ² g ⁻¹)	9.17	9.07
V_{pore} (cm ³ g ⁻¹)	0.06	0.05
Pore size (nm)	17.31	16.03

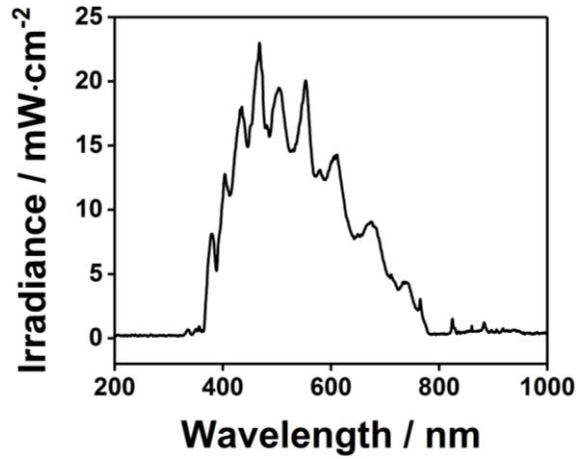


Fig. S5 Spectrum of the 300 W xenon lamp used in this work.

The calculation of quantum efficiency of CO₂ reduction is given as follows. A fiber optic spectrometer (CEL-P4000, Ceaulight) was used for light source spectrum. The light intensity was characterized by an optical power meter (CEL-NP2000, Ceaulight, Beijing). The irradiated area for the reaction is 35.26 cm² (6.7 cm radius). The calculation of the apparent quantum yield (AQY) is defined as:

$$\text{AQY}(\%) = \frac{2 \times \text{the number of produced CO molecules}}{\text{the number of incident photons}} \times 100\% = \frac{Ne}{Nq}$$

$$Ne = 2 \times N_A \times n$$

$$Nq = S \times t \times \int_{200}^{1000} Nd\lambda$$

$$N = \frac{P \times \lambda}{h \times c}$$

Ne is the total number of transfer electrons in the reaction, N_A is the Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), n (in mol) is the amount of products produced by 1 g photocatalyst. Nq is the number of integrated photons with a wavelength from 200 nm to 1000 nm, S is the irradiation area, t is the photo-irradiation time (s), N is the number of incident photons, P is the irradiation energy, λ is the wavelength (nm), h is the planck constant ($h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), c is the speed of light ($c = 3 \times 10^8 \text{ m}\cdot\text{s}^{-1}$). The calculated

AQY of $g\text{-C}_3\text{N}_4$ and $\text{Fe-}g\text{-C}_3\text{N}_4$ are $2.0 \times 10^{-5}\%$ and $3.8 \times 10^{-5}\%$, respectively.

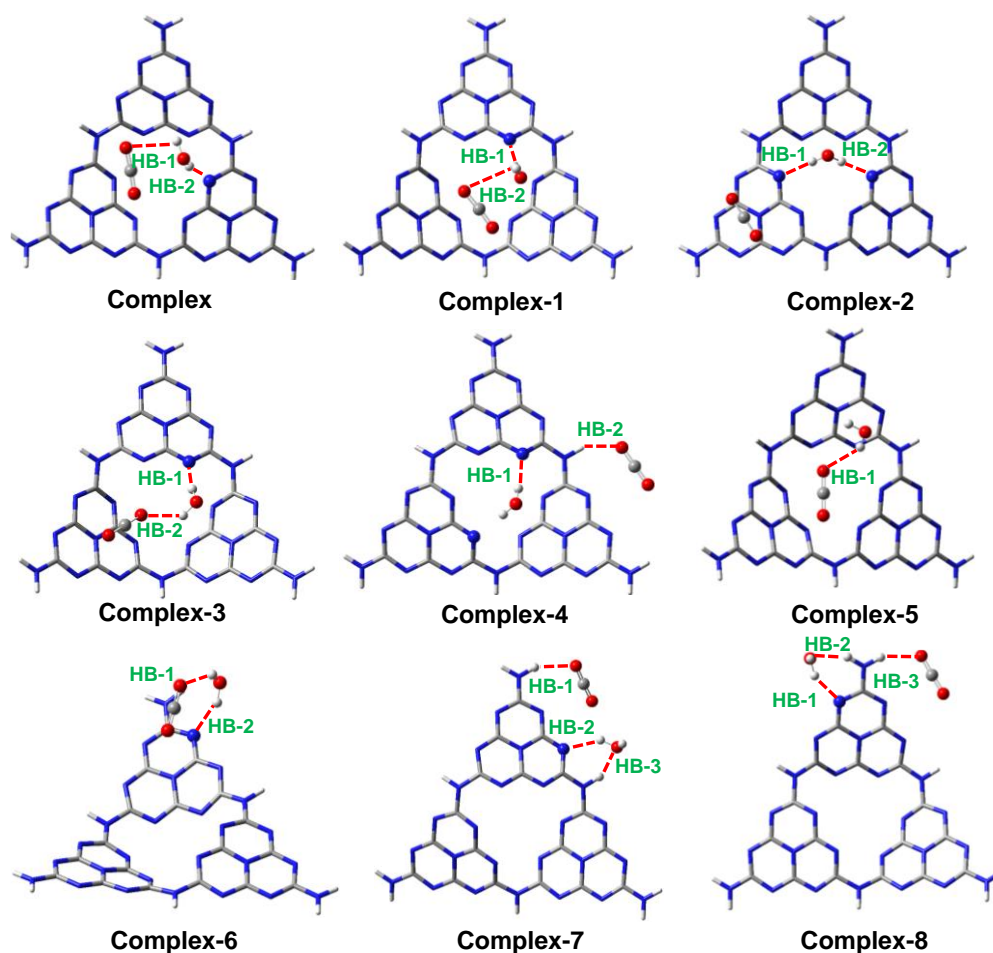


Fig. S6 $g\text{-C}_3\text{N}_4$, CO_2 and H_2O formed different hydrogen-bonded complexes at different binding sites, the optimized structures of the nine hydrogen-bonded complexes were given.

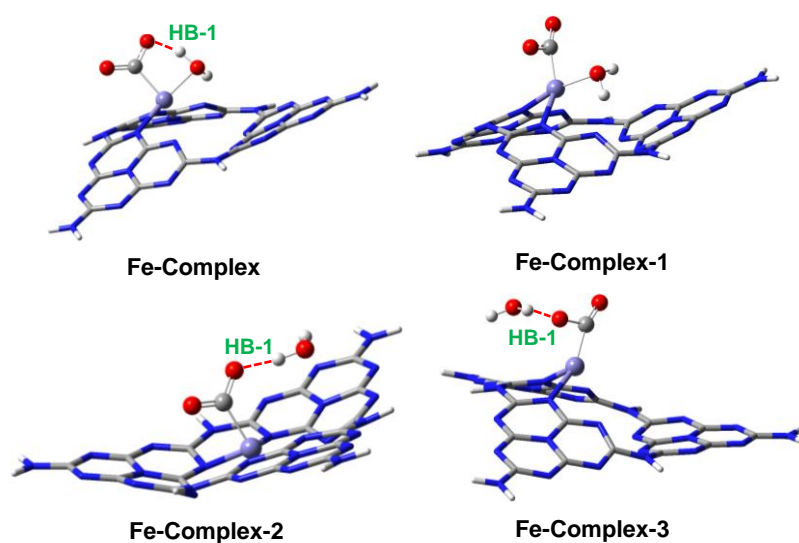


Fig. S7 $\text{Fe-}g\text{-C}_3\text{N}_4$, CO_2 and H_2O formed different hydrogen-bonded complexes at different binding sites, the optimized structures of the four hydrogen-bonded complexes were given.

Table S4 The relative energies of the different hydrogen-bonded complexes.

Structures	Relative energies (kal/mol)	Structures	Relative energies (kal/mol)
Complex	0.0	Fe-Complex	0
Complex-1	0.4	Fe-Complex-1	5.6
Complex-2	2.2	Fe-Complex-2	14.5
Complex-3	2.4	Fe-Complex-3	16.4
Complex-4	3.8		
Complex-5	4.6		
Complex-6	5.9		
Complex-7	6.8		
Complex-8	8.5		

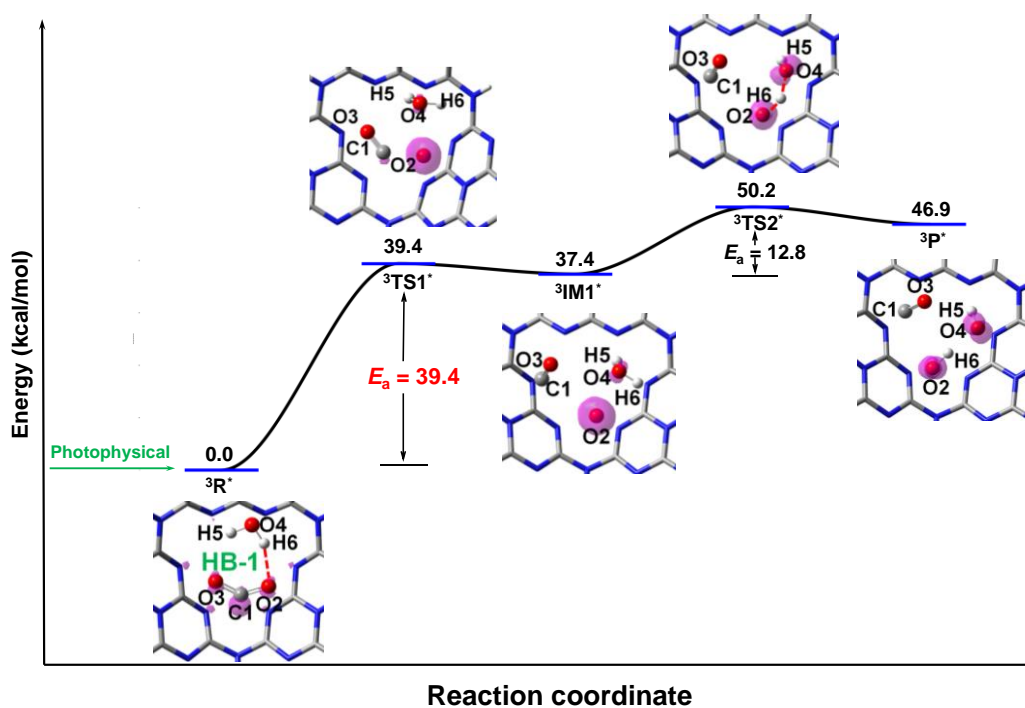


Fig. S8 The photochemical reaction path (Path-2) of CO₂ reduction for Complex.

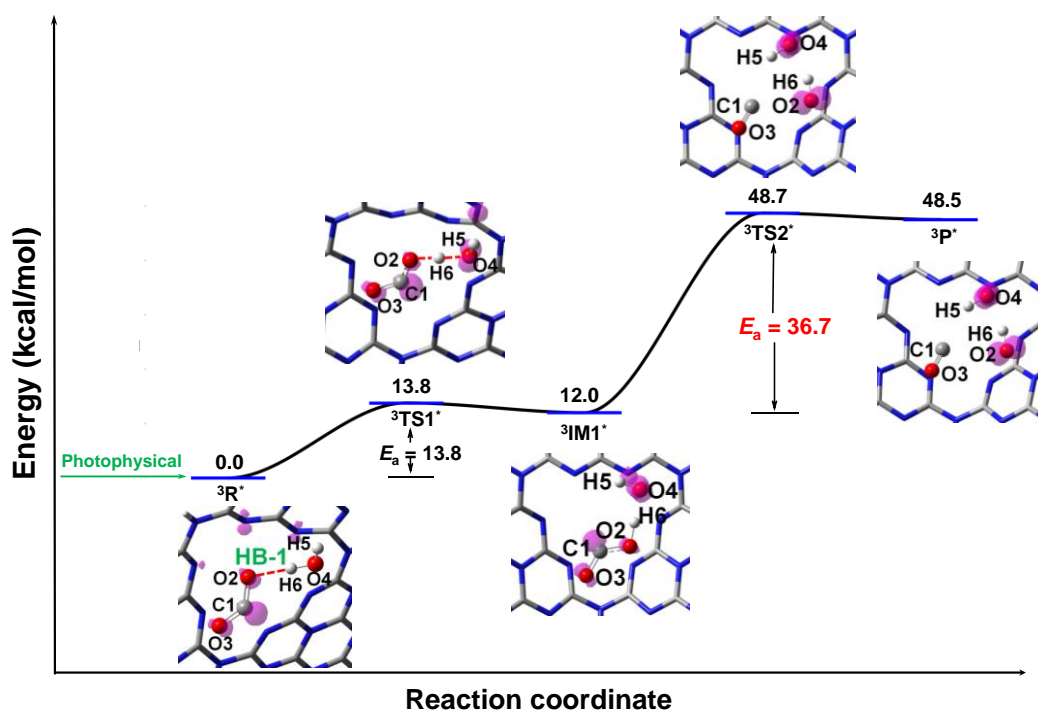


Fig. S9 The photochemical reaction path (Path-3) of CO₂ reduction for Complex.

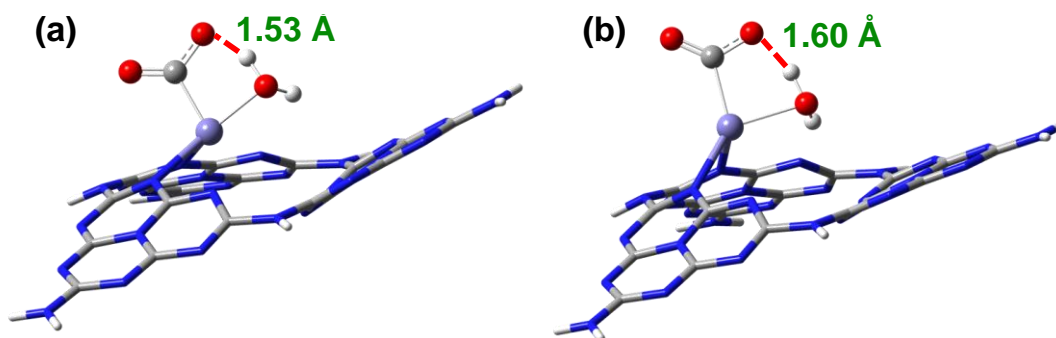


Fig. S10 The optimized structures of Fe-Complex in the (a) triplet state and (b) quintet state.

Table S5 The relative energies of the structures for Fe-Complex in the triplet and quintet states. (unit: kcal/mol).

	Triplet state	Quintet state
Relative energies	9.75	0.00

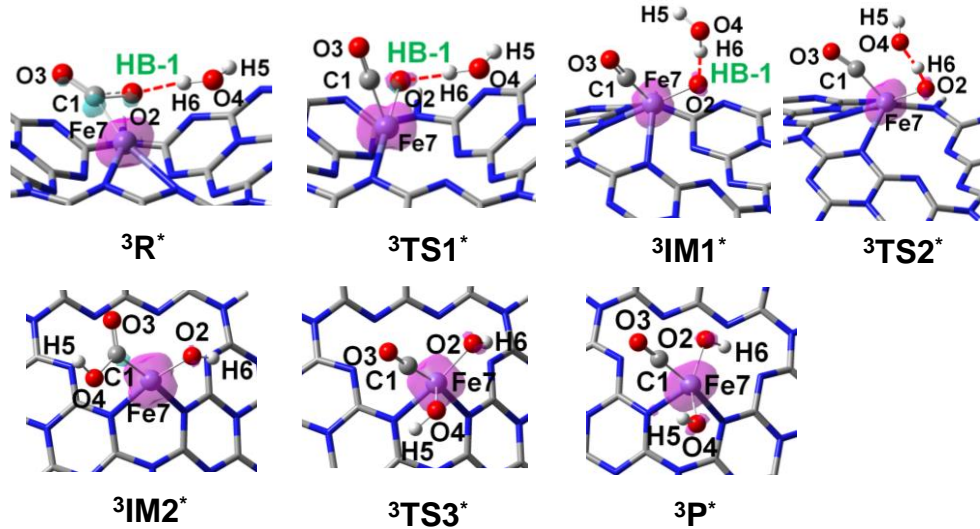
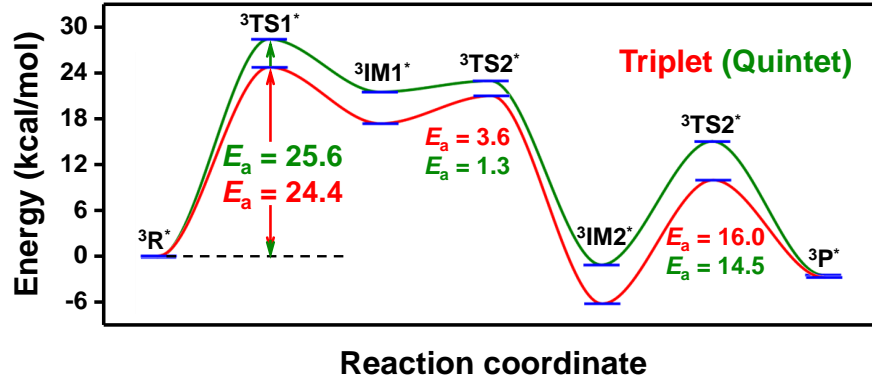


Fig. S11 The photochemical reaction path (Path-2) of CO₂ reduction for Fe-Complex in the triplet (red) and quintet (green) states.

The reaction order is derived as follows:

The total reaction rate is determined by the rate of the rate-limiting step:

$$r = -dc(^3[g-C_3N_4 \cdots OH \cdots H_2O-C(=O)O]^{*})/dt = k_5 c(^3[g-C_3N_4 \cdots OH \cdots H_2O-C(=O)O]^{*}) \quad (1)$$

For the absorption equilibrium formed by CO₂, H₂O and the catalyst:

$$K_1 = k_1/k_{-1} = c(^1[g-C_3N_4 \cdots H_2O \cdots O=C=O])/c(^1[g-C_3N_4]) c(H_2O) c(CO_2) \quad (2)$$

For the equilibrium between $^1[g-C_3N_4 \cdots H_2O \cdots O=C=O]^{*}$ and $^1[g-C_3N_4 \cdots H_2O \cdots O=C=O]$:

$$K_2 = c(^1[g-C_3N_4 \cdots H_2O \cdots O=C=O]^{*})/c(^1[g-C_3N_4 \cdots H_2O \cdots O=C=O])$$

$$\text{Then, } c(^1[g-C_3N_4 \cdots H_2O \cdots O=C=O]^{*}) = K_1 K_2 c(^1[g-C_3N_4]) c(H_2O) c(CO_2) \quad (3)$$

For $^3[g-C_3N_4 \cdots H_2O \cdots O=C(=O)O]^{*}$:

$$dc(^3[\text{g-C}_3\text{N}_4^+ \cdots \text{H}_2\text{O} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^-]^*)/dt = k_2 c(^1[\text{g-C}_3\text{N}_4 \cdots \text{H}_2\text{O} \cdots \text{O}=\text{C}=\text{O}]^*) - k_3 c(^3[\text{g-C}_3\text{N}_4^+ \cdots \text{H}_2\text{O} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^-]^*) = 0$$

$$\text{Then, } k_2 c(^1[\text{g-C}_3\text{N}_4 \cdots \text{H}_2\text{O} \cdots \text{O}=\text{C}=\text{O}]^*) = k_3 c(^3[\text{g-C}_3\text{N}_4^+ \cdots \text{H}_2\text{O} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^-]^*) \quad (4)$$

For $^3[\text{g-C}_3\text{N}_4\text{-H}^{\delta+} \cdots \text{OH} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^{\delta-}]^*$:

$$dc(^3[\text{g-C}_3\text{N}_4\text{-H}^{\delta+} \cdots \text{OH} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^{\delta-}]^*)/dt = k_3 c(^3[\text{g-C}_3\text{N}_4^+ \cdots \text{H}_2\text{O} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^-]^*) - k_4 c(^3[\text{g-C}_3\text{N}_4\text{-H}^{\delta+} \cdots \text{OH} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^{\delta-}]^*) = 0$$

$$\text{Then } k_3 c(^3[\text{g-C}_3\text{N}_4^+ \cdots \text{H}_2\text{O} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^-]^*) = k_4 c(^3[\text{g-C}_3\text{N}_4\text{-H}^{\delta+} \cdots \text{OH} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^{\delta-}]^*) \quad (5)$$

For $^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*$:

$$dc(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*)/dt = k_4 c(^3[\text{g-C}_3\text{N}_4\text{-H}^{\delta+} \cdots \text{OH} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^{\delta-}]^*) - k_5 c(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*) = 0$$

$$\text{Then, } k_4 c(^3[\text{g-C}_3\text{N}_4\text{-H}^{\delta+} \cdots \text{OH} \cdots \text{O}=\overset{\cdot}{\text{C}}=\text{O}^{\delta-}]^*) = k_5 c(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*) \quad (6)$$

Combining (4), (5) and (6),

$$k_5 c(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*) = k_2 c(^1[\text{g-C}_3\text{N}_4 \cdots \text{H}_2\text{O} \cdots \text{O}=\text{C}=\text{O}]^*) \quad (7)$$

Substitute (3) into (7):

$$k_5 c(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*) = k_2 K_1 K_2 c(^1[\text{g-C}_3\text{N}_4] c(\text{H}_2\text{O}) c(\text{CO}_2)) \quad (8)$$

For $^3[\text{g-C}_3\text{N}_4 \cdots 2\text{OH} \cdots \text{CO}]^*$:

$$dc(^3[\text{g-C}_3\text{N}_4 \cdots 2\text{OH} \cdots \text{CO}]^*)/dt = k_5 c(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*) - k_6 c(^3[\text{g-C}_3\text{N}_4 \cdots 2\text{OH} \cdots \text{CO}]^*) + k_{-6} c(^3[\text{g-C}_3\text{N}_4] c(\text{OH})^2 c(\text{CO})) = 0$$

$$\text{Then, } k_5 c(^3[\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O}-\overset{\cdot}{\text{C}}=\text{O}]^*) = k_6 c(^3[\text{g-C}_3\text{N}_4 \cdots 2\text{OH} \cdots \text{CO}]^*) - k_{-6} c(^3[\text{g-C}_3\text{N}_4] c(\text{OH})^2 c(\text{CO})) \quad (9)$$

For the desorption of the product CO:

$$K_6 = c(^3[\text{g-C}_3\text{N}_4] c(\text{OH})^2 c(\text{CO})) / c(^3[\text{g-C}_3\text{N}_4 \cdots 2\text{OH} \cdots \text{CO}]^*) \quad (10)$$

Substitute (10) into (9):

$$k_5 c(^3\text{g-C}_3\text{N}_4 \cdots \text{OH} \cdots \text{H} \backslash \text{O} - \dot{\text{C}} = \text{O})^* = (k_6/K_6 - k_{-6}) c(^3\text{g-C}_3\text{N}_4^*) c(\text{OH}\cdot)^2 c(\text{CO}) \quad (11)$$

For $^1\text{g-C}_3\text{N}_4$:

$$\begin{aligned} -dc(^1\text{g-C}_3\text{N}_4)/dt &= k_1 c(^1\text{g-C}_3\text{N}_4) c(\text{H}_2\text{O}) c(\text{CO}_2) \\ &\quad - k_{-1} c(^1\text{g-C}_3\text{N}_4 \cdots \text{H}_2\text{O} \cdots \text{CO}_2) + k_7 c(^3\text{g-C}_3\text{N}_4^*) = 0 \end{aligned}$$

Then,

$$k_7 c(^3\text{g-C}_3\text{N}_4^*) = -k_1 c(^1\text{g-C}_3\text{N}_4) c(\text{H}_2\text{O}) c(\text{CO}_2) + k_{-1} c(^1\text{g-C}_3\text{N}_4 \cdots \text{H}_2\text{O} \cdots \text{CO}_2) \quad (12)$$

Substitute (2) into (12):

$$k_7 c(^3\text{g-C}_3\text{N}_4^*) = (k_1 - K_1 k_{-1}) c(^1\text{g-C}_3\text{N}_4) c(\text{H}_2\text{O}) c(\text{CO}_2) \quad (13)$$

For H_2O_2 :

$$dc(\text{H}_2\text{O}_2)/dt = k_8 c(\text{OH}\cdot)^2 - k_9 c(\text{H}_2\text{O}_2) + k_{-9} c(\text{O}_2)^{1/2} c(\text{H}_2\text{O}) = 0 \quad (14)$$

For the equilibrium between H_2O_2 and O_2 :

$$k_9 c(\text{H}_2\text{O}_2) = k_{-9} c(\text{O}_2)^{1/2} c(\text{H}_2\text{O}) \quad (15)$$

Substitute (15) into (14):

$$k_8 c(\text{OH}\cdot)^2 = (k_9/K_9 - k_{-9}) c(\text{O}_2)^{1/2} c(\text{H}_2\text{O}) \quad (16)$$

Substitute (8) and (11) into both sides of (1):

$$-k_2 K_1 K_2 c(^1\text{g-C}_3\text{N}_4) dc(\text{H}_2\text{O}) dc(\text{CO}_2)/dt = (k_6/K_6 - k_{-6}) c(^3\text{g-C}_3\text{N}_4^*) c(\text{OH}\cdot)^2 c(\text{CO})$$

Then,

$$-dc(\text{H}_2\text{O}) dc(\text{CO}_2)/dt = (k_6/K_6 - k_{-6})/K_1 K_2 k_2 c(^3\text{g-C}_3\text{N}_4^*) c(\text{OH}\cdot)^2 c(\text{CO})/c(^1\text{g-C}_3\text{N}_4) \quad (17)$$

(The concentration of the catalyst $c(^1\text{g-C}_3\text{N}_4)$ is constant)

Substitute (13) into (17):

$$-dc(\text{H}_2\text{O}) dc(\text{CO}_2)/dt = (k_1/K_1 - k_{-1})(k_6/K_6 - k_{-6})/K_2 k_2 k_7 c(\text{CO}) c(\text{H}_2\text{O}) c(\text{CO}_2) c(\text{OH}\cdot)^2 \quad (18)$$

Then,

$$-dc(\text{CO}_2)/dt = (k_1/K_1 - k_{-1})(k_6/K_6 - k_{-6})/K_2 k_2 k_7 c(\text{CO}) c(\text{CO}_2) c(\text{OH}\cdot)^2$$

(The concentration of H_2O ($c(\text{H}_2\text{O})$) is a constant)

Substitute (16) into (18):

$$-dc(\text{CO}_2)/dt = (k_1/K_1 - k_{-1})(k_6/K_6 - k_{-6})(k_9/K_9 - k_{-9})/K_2 k_2 k_7 k_8 c(\text{CO}) c(\text{CO}_2) c(\text{H}_2\text{O}) c(\text{O}_2)^{1/2} \quad (19)$$

Combined $c(\text{CO}_2)$ and $c(\text{H}_2\text{O})$ into the constant term:

$$-dc(\text{CO}_2)/dt = k' c(\text{CO}) c(\text{O}_2)^{1/2}$$

The CO₂RR is a first order reaction for the product CO.

References 1 Y. L. Niu, Q. Peng, C. M. Deng, X. Gao and Z. G. Shuai, *J. Phys. Chem. A*, 2010, **114**, 7817–7831. 2 Q. Peng, Y.P. Yi, Z.G. Shuai and J.S. Shao, *J. Am. Chem. Soc.*, 2007, **129**, 9333–9339. 3 Y.L. Niu, Q. Peng and Z.G. Shuai, *Sci. China, Ser. B*, 2008, **51**, 1153–1158.
4 Q. Peng, Y.L. Niu and Q. H. Shi, *J. Chem. Theory. Comput.*, 2013, **9**, 1132–1143.