Supporting Information

Photoinduced morphology transformation of a self-assembled iron(II) coordination polymer: non-precious, high-performance, and self-enhancing photocatalytic CO_2 reduction

Youting Fang, Xinyue Hong and Duobin Chao*

School of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 315211, Zhejiang, China

E-mail: chaoduobin@nbu.edu.cn

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. Ligand **N3tpy** was synthesized as we previously reported.[1] Scanning electron microscope (SEM) were obtained on a Hitachi S4800 Field-Emission Scanning Electron Microscope at an accelerating voltage of 15.0 kV. Powder X-ray diffraction (XRD) patterns were obtained using D8 Advance Xray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was carried out using Kratos Axis Ultra DLD with Al Kα X-ray source (hν = 1486.6 eV). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 670 FT-IR spectrometer with KBr. High-resolution Transmission Electron Microscopy (HRTEM) image was obtained on Tecnai F20 with an accelerating voltage of 200 kV. UV-Vis absorption studies were carried on a LAMBDA 850+ spectrophotometer. 1H-NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz). Photoluminescence studies were accomplished using Shimadzu RF-6000 Luminescence spectrometer. The UV-vis diffuse reflectance spectra (DRS) were recorded on Lambda 950 Scan Spectrophotometers (Perkin Elmer). Photoelectrochemical experiments were carried out on CHI660E in a one-compartment cell equipped with glassy carbon or samples loaded FTO glass as working electrode, Ag/AgCl reference electrode, and platinum plate counter electrode at room temperature. GC analysis for quantum yield calculation was performed on Shimadzu GC-2014 (packed column TDX-01, 2 m × 3 mm, FID detector with Shimadzu Methanizer MTN-1 for CO and TCD detector for H_2, N_2 as carrier gas). GC–MS experiment for $^{13}CO_2$ was carried out with Agilent 7890B–5977A. GC analysis for recyclable experiments were carried out on Agilent Technologies 7820 A gas chromatography (GC) system (TCD detector, CP-CarboPlot P7 capillary column, 27.46 m x 25 μm, argon carrier gas).

1.2 Synthesis of coordination polymer FeN3tpy

Ligand **N3tpy** (500 mg, 0.38 mmol) dissolved in DMF (30 mL) at room temperature. Then, $Fe(BF_4)_2$•$6H_2O$ (73 mg, 0.19 mmol) was carefully added into the solution. The mixed solution was further stirred with a magnetic stirrer at 100 °C overnight. Purple precipitate was generated and then collected by filtration and washing with CH_2Cl_2, C_2H_5OH, and H_2O, respectively. The collected precipitate was dried under vacuum to afford coordination polymer **FeN3tpy** (309 mg).

1.3 Photocatalytic CO_2 reduction

General procedure: **FeN3tpy** (2.0 mg), 4CzIPN (0.2 mM), and TEA (0.28 M) were mixed in 5.0 mL DMA/H_2O (v/v = 4:1) solution in a glass tube sealed up with a rubber septum. Before light irradiation, the mixed solution was bubbled with CO_2 for 20 min. Then, the reaction suspension was stirred with a stirrer under blue LED light irradiation for 6 h at room temperature. The light source is a blue LED instrument at 420 nm with a light intensity of 0.2 W (3STECH, Shanghai). Gaseous products (CO and H_2) were analyzed by injection of 250 μL aliquots from headspace to GC instrument. Liquid product was analyzed by recording ^{1}H NMR spectrum of reaction solution. For each recyclable catalytic cycle, reaction suspension was centrifuged and washed with CH_3CN for 3 times. The catalyst dried naturally at room temperature.

Apparent quantum yiled (AQY) was determined by the following equation.

$$\text{AQY} = \frac{\text{Number of CO molecules x 2}}{\text{Number of incident photons}} \text{ x } 100\% \qquad \text{(eq S1)}$$

The number of incident photons was obtained using a chemical actinometer $K_3Fe(C_2O_4)_3$ as reported.[2, 3] Fe(II) can be generated when $K_3Fe(C_2O_4)_3$ irradiated in buffer solution (HAc/Ac^-). As

Fe(II) is easily coordinated to 1,10- phenanthroline (phen), a new complex $[Fe^{II}(phen)_3]^{2+}$ is therefore formed in buffer solution containing phen. The newly formed complex $[Fe^{II}(phen)_3]^{2+}$ is well-known and its amount is can be quantitatively determined through UV-vis absorption spectroscopy due to typical absorption at 510 nm. In our experiment, the $K_3Fe(C_2O_4)_3$ solution (5.0 mL) was irradiated for 5 seconds. Then the solution was diluted to 17.5 mL for UV-vis absorption measurement. The absorbance at 510 nm of the diluted solution (3.0 mL) was recorded to be 0.28. According to Beer-Lambert's equation $A = \varepsilon cl$, the moles of generated Fe(II) can be obtained. For Beer-Lambert's equation, ε (11100 L mol^{-1} cm^{-1}) is the molar coefficient of $[Fe^{II}(phen)_3]^{2+}$ at 510 nm, c is the concentration of generated $[Fe^{II}(phen)_3]^{2+}$ and l (1 cm) is the width of quartz cuvette.
Concentration of generated Fe(II) in the quartz cuvette: $c(Fe^{II}) = A/\varepsilon l$ = 0.28 / (11100 L mol^{-1} cm^{-1} x 1cm) = 2.52 x 10^{-5}mol L^{-1}.
Moles of generated Fe(II) every second in the irradiated solution: $n(Fe^{II})$ = $c(Fe^{II})$ x 17.5 mL / 5 s = 8.82 x 10^{-8} mol s^{-1}.
Numbers of generated Fe(II) every second: $n(Fe^{II})$ x N_A. N_A is 6.02 x 10^{23} mol^{-1}. As the quantum yield for Fe^{2+} generation at 420 nm is about 1.0, the incident photons are then calculated to be 1.91 x 10^{20} h^{-1}.

The AQY of **FeN3tpy** was determined to be 11.7% by using the generated amount of CO (73.6 μmol) in the first 4 hours at the fifth cycle.

1.4 Photoelectrochemical measurements

All photoelectrochemical measurements were conducted in a three–electrode electrochemical cell with a platinum plate as the counter electrode, Ag/AgCl as the reference electrode, and FTO glass loaded with sample **FeN3tpy** (nanoplate-like or and nanosphere-like) as the working electrode.

FTO glass working electrode was prepared as follows: **FeN3tpy** (2 mg) was added to C_2H_5OH (2 mL) solution containing Nafion (10 μL). The mixture was then treated by sonication for 20 min to obtain the ink of **FeN3tpy**. The ink (200 μL) was carefully dropped onto the conductive surface of FTO glass. Next, the FTO glass was left to dry naturally under air and used as a working electrode.

Mott-Schottky plots, transient photocurrent responses and electro-chemical impedance spectra were all obtained in the aqueous Na_2SO_4 solution (0.5 M). For Mott-Schottky plots, the open circuit voltage was 0.36 V. The initial potential was −1.5 V and the final potential is 0 V (at 800,1000,1200 Hz). The increment of potential was set as 0.05 V. For transient photocurrent responses, run time was 300 s with an interval of 20 s. The light source was white LEDs equipment (SMPC–LVWT, 420–650 nm, 3 W LEDs, Technical Institute of Physics and Chemistry & Chinese Academy of Sciences). The potential for transient photocurrent test was set at open circuit potential. For electrochemical impedance spectra, the potential was set at open circuit potential and the frequency was set from 0.1 Hz to 100 kHz.

Linear sweep voltammetry (LSV) curves were obtained in a H-cell with a platinum plate as the counter electrode, Ag/AgCl as the reference electrode, and carbon paper loaded with **FeN3tpy** (1 mg cm^{-2}). The electrolyte is aqueous $KHCO_3$ solution (0.5 M). The scan rate is 20 mV s^{-1}. The potentials vs Ag/AgCl are transformed to values vs RHE. E (vs RHE) = E (vs Ag/AgCl) + 0.197 V + 0.0591 V * pH.

2. Supplementary Figures and tables

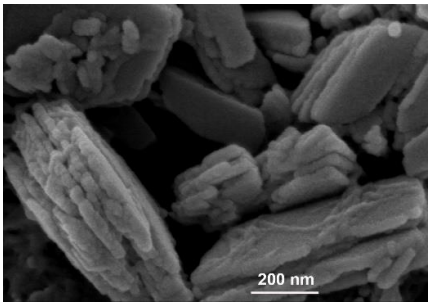

Fig. S1 SEM image of **FeN3tpy** with a scale bar of 200 nm.

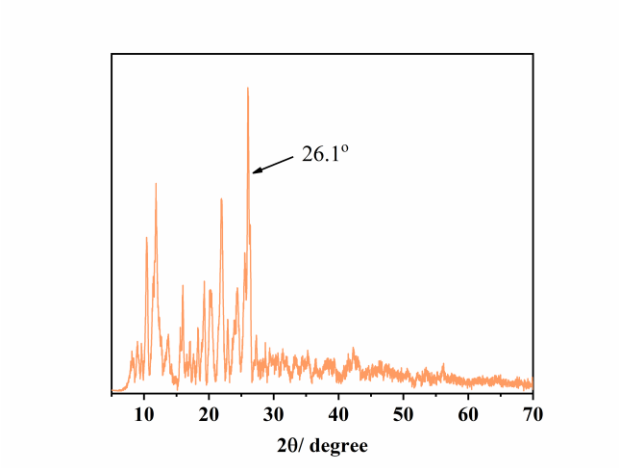

Fig. S2 PXRD result of **FeN3tpy**.

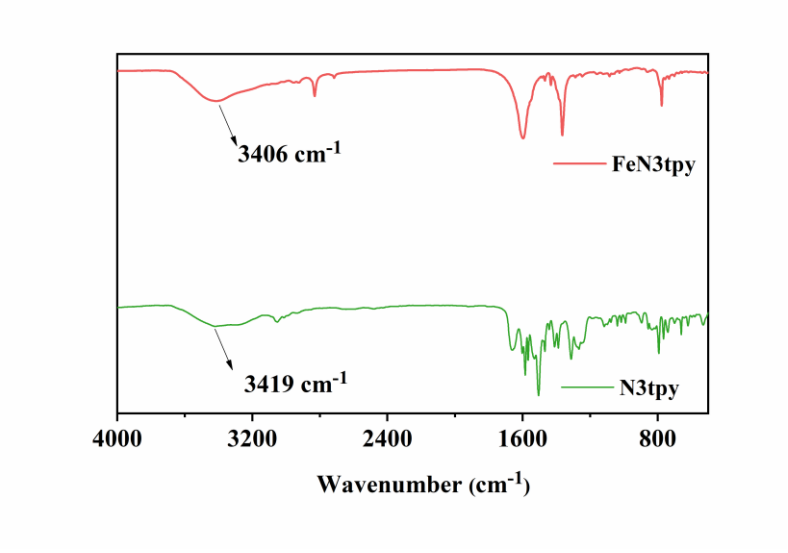

Fig. S3 FT-IR spectra of **FeN3tpy** and ligand **N3tpy**.

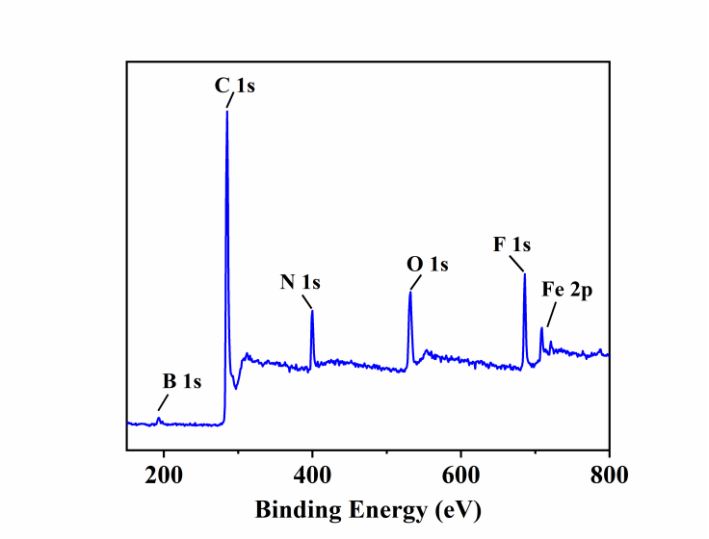

Fig. S4 XPS survey spectrum of **FeN3tpy**.

Table S1. Binding energy (BE) of C 1s, O 1s, N 1s, B 1s, F 1s, and Fe 2p for **FeN3tpy** and **N3tpy**

	C 1s BE (eV)			O 1s BE (eV)	N 1s BE (eV)			B 1s BE (eV)	F 1s BE (eV)	Fe $2p_{1/2}$ BE (eV)	Fe $2p_{3/2}$ BE (eV)
Sample	C=C	C=N-	C=O	O=C	=N-	NH-					
N3tpy	284.6 (75)	285.2 (21)	284.5 (4)	531.7	398.4 (70)	399.6 (23)	397.5 (7)				
FeN3tpy	284.7 (76)	285.6 (21)	284.5 (3)	531.8	399.8 (66)	400.1 (25)	398.6 (9)	194.0	685.9	721.2	708.4

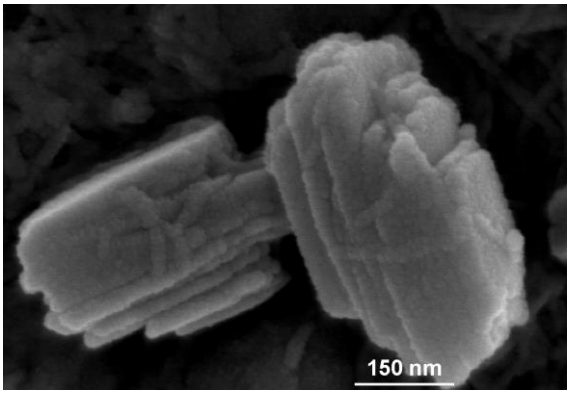

Fig. S5 SEM image of **FeN3tpy** with a scale bar of 150 nm.

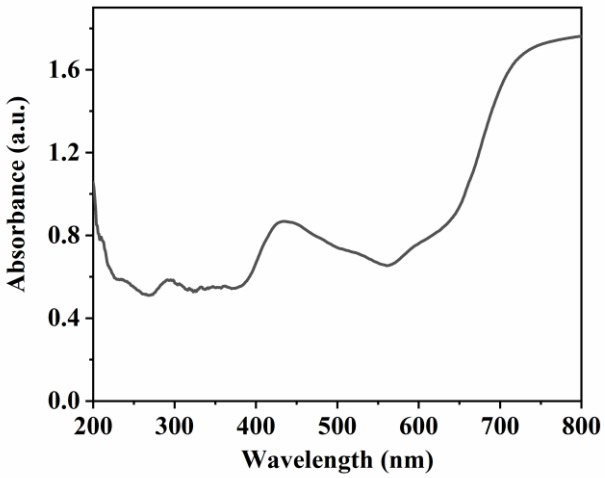

Fig. S6 UV-vis-DRS spectrum of **FeN3tpy**.

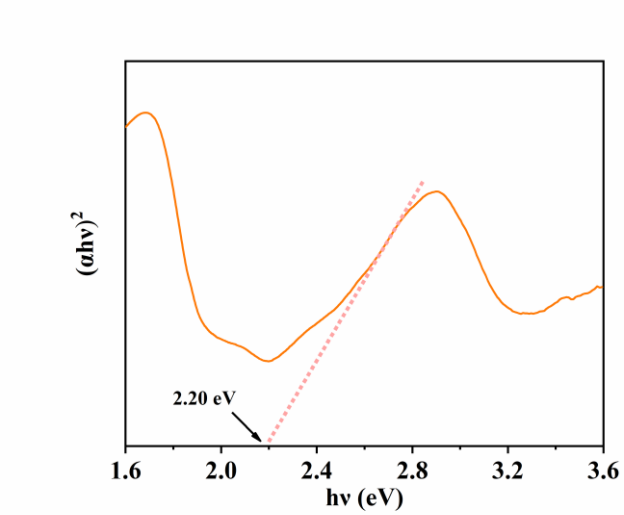

Fig. S7 Tauc plot of **FeN3tpy**.

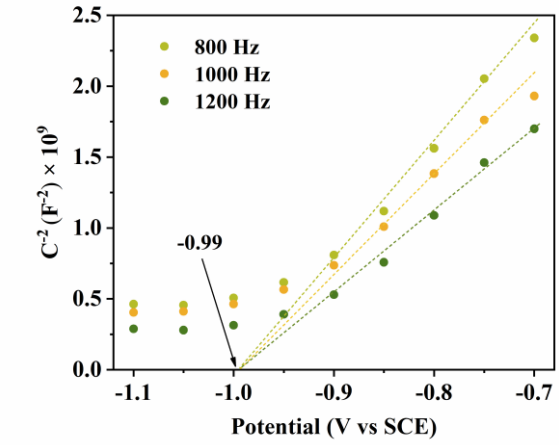

Fig. S8 Mott-Schottky plots of **FeN3tpy**.

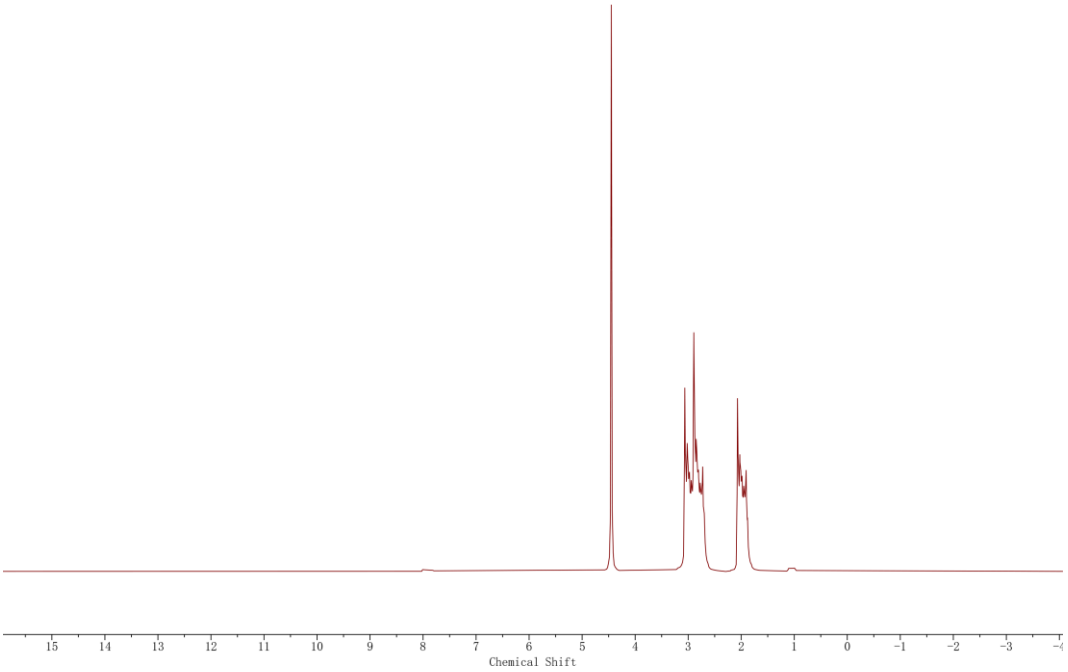

Fig. S9 ^{1}H NMR spectrum of reaction solution (400 μL) by addition of D_2O (100 μL) and DMSO (15 μL) as the internal standard.

Table S2. Control experiments of photocatalytic CO_2 reduction using **FeN3tpy**

Entry	Conditions	CO (μmol)	H_2 (μmol)
1[a]	**FeN3tpy**, 4CzIPN, TEA, light irradiation, and CO_2	55	0.4
2	Without **FeN3tpy**	-	-
3	Without 4CzIPN	-	-
4	Without TEA	-	-
5	Ar instead of CO_2	-	-
6	In the dark	-	-

[a] Conditions: **FeN3tpy** (2.0 mg), 4CzIPN (0.2 mM), TEA (0.28 M), light irradiation at 420 nm, DMA (4.0 mL), H_2O (1.0 mL), 6 h, under CO_2.

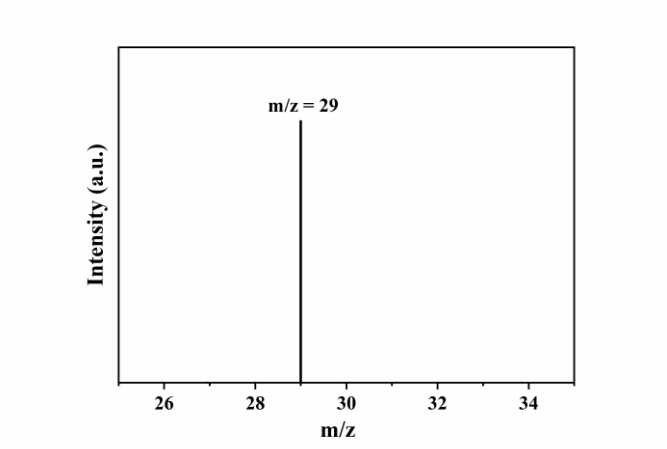

Fig. S10 GC-MS result of labeling experiment with $^{13}CO_2$.

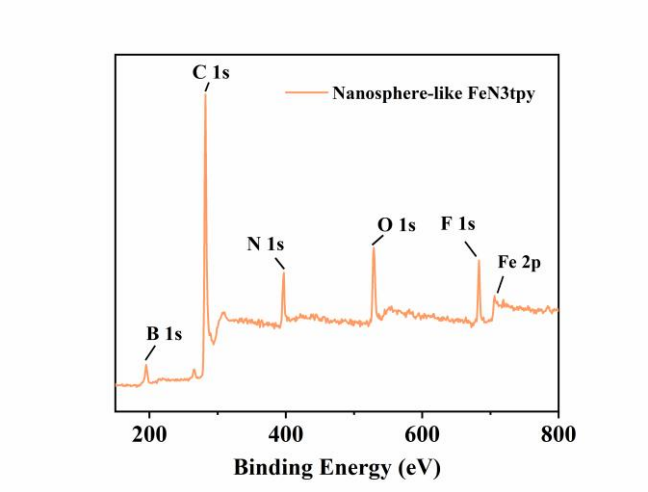

Fig. S11 XPS survey spectrum of nanosphere-like **FeN3tpy**.

Table S3. Binding energy (BE) of C 1s, O 1s, N 1s, B 1s, F 1s, and Fe 2p for nanosphere-like **FeN3tpy**

	C1s BE (eV)			O1s BE (eV)	N1s BE (eV)			B1s BE (eV)	F1s BE (eV)	$Fe2p_{1/2}$ BE (eV)	$Fe2p_{3/2}$ BE (eV)
Sample	C=C	C=N-	C=O	O=C	=N-	NH-					
Nanosphere-like **FeN3tpy**	284.8 (75)	285.8 (22)	284.5 (3)	531.2	399.7 (69)	400.4 (23)	398.5 (8)	194.0	685.8	721.5	708.7

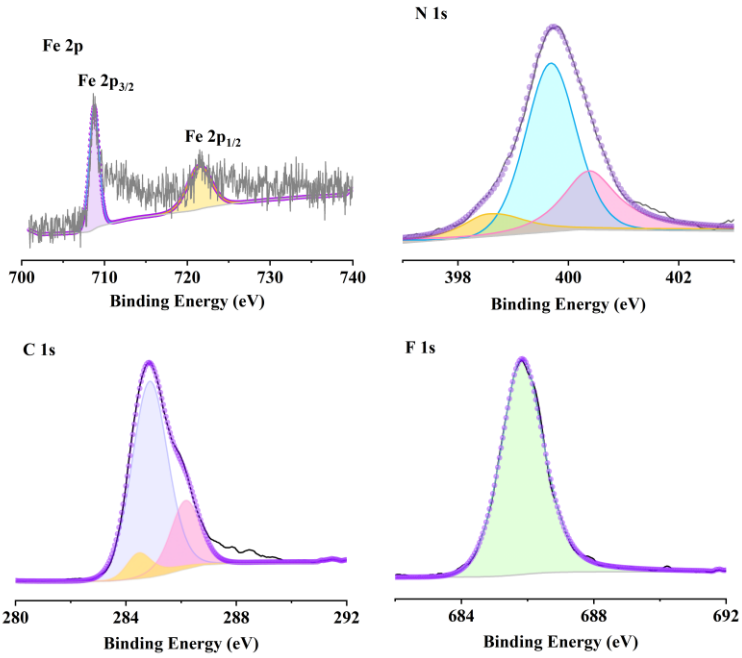

Fig. S12 High resolution XPS spectra of Fe 2p, N 1s, C 1s, and F 1s for nanosphere-like **FeN3tpy**.

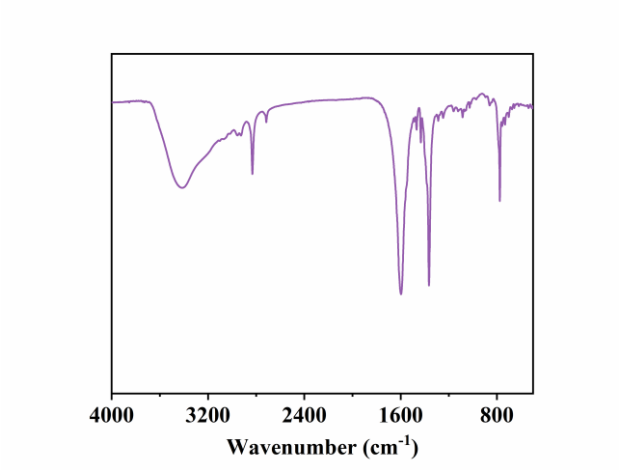

Fig. S13 FT-IR spectrum of nanosphere-like **FeN3tpy**.

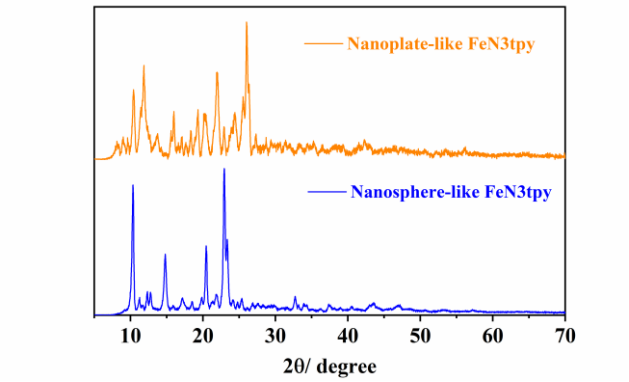

Fig. S14 Comparison of PXRD patterns of nanoplate-like **FeN3tpy** and nanosphere-like **FeN3tpy**.

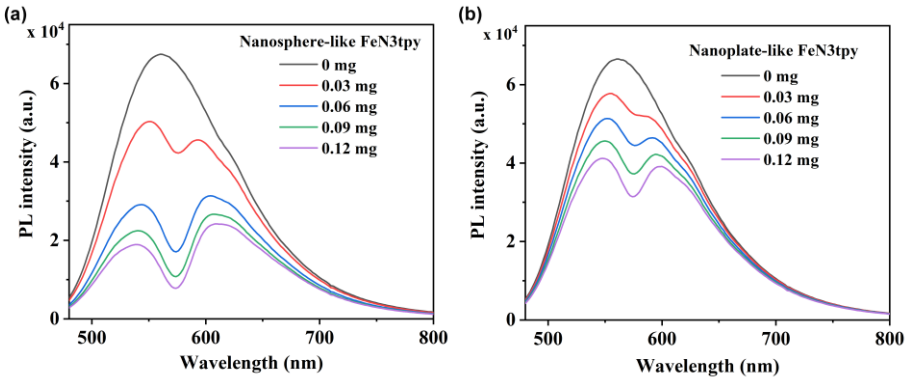

Fig. S15 PL quenching of 4CzIPN (5 μM) by (a) nanosphere-like **FeN3tpy**, (b) nanoplate-like **FeN3tpy** in DMF (λ_{ex} = 450 nm). Excitation and emission slits are 5 and 10 nm, respectively.

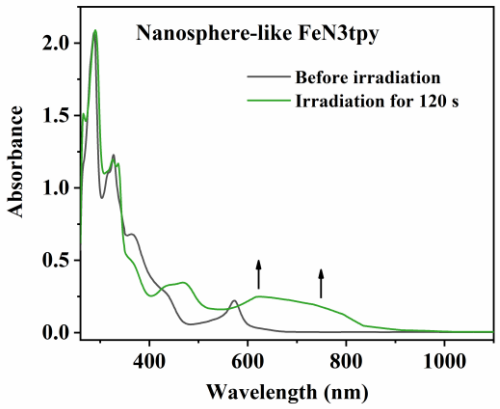

Fig. S16 UV-vis absorption spectra of nanosphere-like **FeN3tpy** (0.1 mg mL^{-1}) in DMF/H_2O (v/v = 4:1) solution containing 4CzIPN (50 μM) and TEA (70 mM) before and after irradiation of 120 s under N_2 at room temperature.

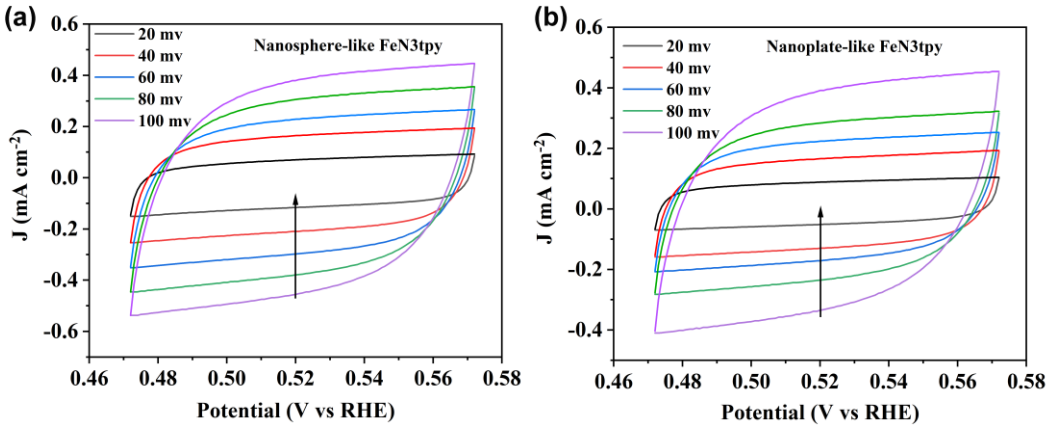

Fig. S17 (a) CVs of nanosphere-like **FeN3tpy** at different scan rates. (b) CVs of nanoplate-like **FeN3tpy** at different scan rates. Experiments were conducted in aqueous $KHCO_3$ solution (0.5 M).

References

[1] Y. Fang, T. Liu, L. Chen, D. Chao, *ACS Catal.* **2023**, *13*, 2086-2093.

[2] P. G. Alsabeh, A. Rosas-Hernández, E. Barsch, H. Junge, R. Ludwig, M. Beller, *Catal. Sci. Technol.* **2016**, *6*, 3623-3630.

[3] A. Bahamonde, P. Melchiorre, *J. Am. Chem. Soc.* **2016**, *138*, 8019-8030.