Electronic Supplementary Information (ESI)

Iron(III)-bipyridine incorporated metal-organic frameworks for photocatalytic reduction of CO_2 with improved performance

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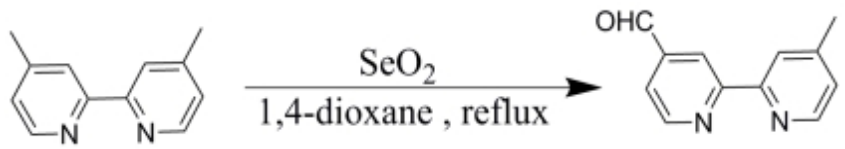
SECTION 1. Ligand synthesis

Materials and methods. Ligand amino-triphenyldicarboxylic acid (amino-TPDC) was prepared as reported previously.[1] 4,4'-Dimethyl-2,2'-bipyridine were purchased from Energy Chemical. SeO_2 was obtained from Alfa Chemical, other chemicals and solvents are of reagent grade obtained from Sinopharm Chemical Reagent Co., Ltd without further purification. ^{1}H-NMR spectra were measured on Bruker-DRX 400 MHz instruments at room temperature.

Synthesis of 4′-methyl-[2,2′-bipyridine]-4-carbaldehyde.



In accordance with a modified procedure reported previously,[2] a mixture of 4,4'-dimethyl-2,2'-bipyridine (1.00 g, 5.4 mmol), SeO_2 (660 mg, 5.9 mmol) and 1,4-dioxane (50 mL) was added to a round-bottom flask, which was heated to reflux for 2 days. After a time, the yellow suspension became a black precipitate. The reaction was hot filtered quickly. After cooled to room temperature, the solution was filtered again. The resulting residue was collected through a rotary evaporator from the yellow filtrate, then was dissolves in ethyl acetate and filtered again. The filtrate was extracted with 1.0 M NaOH and 0.3 M $Na_2S_2O_5$ successively, then the aqueous phase was extracted with $CHCl_3$ again. The organic phase was evaporated to yield pure 4′-methyl-[2,2′-bipyridine]-4-carbaldehyde (37%). IR (KBr pellet cm^{-1}) 3050 (m), 3023 (m), 1720 (s), 1620 (s), 1530 (m), 1285 (s), 1145 (m), 675 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3H), 7.21 (d, 1H), 7.74 (dd, 1H), 8.31 (s, 1H), 8.61 (d, 1H), 8.86 (s, 1H), 8.93 (d, 1H), 10.21 (s, 1H).

SECTION 2. UiO synthesis

Materials and methods. UiO-68-NH_2 was prepared as reported previously,[1] other chemicals and solvents are of reagent grade obtained from Sinopharm Chemical Reagent Co., Ltd and used without further purification. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu-Kα (λ = 1.5418 Å) radiation. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 5 kV. Thermogravimetric analyses (TGA) were performed by means of TGA-DSC1 thermal analyzer (Mettler-Toledo Instrumentation) in the temperature range of 30-800 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Fourier transform Infrared (FT-IR) spectra were recorded using KBr discs in the range of 400-4000 cm^{-1} on a Bruker Vector 22 FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on UIVAC-PHI 5000 VersaProbe using monochromatized Al Kα at hν = 1486.6 eV. The C 1s peak was used as the reference peak. ^{1}H-NMR spectra were measured on Bruker-DRX 400 MHz instruments at room temperature.

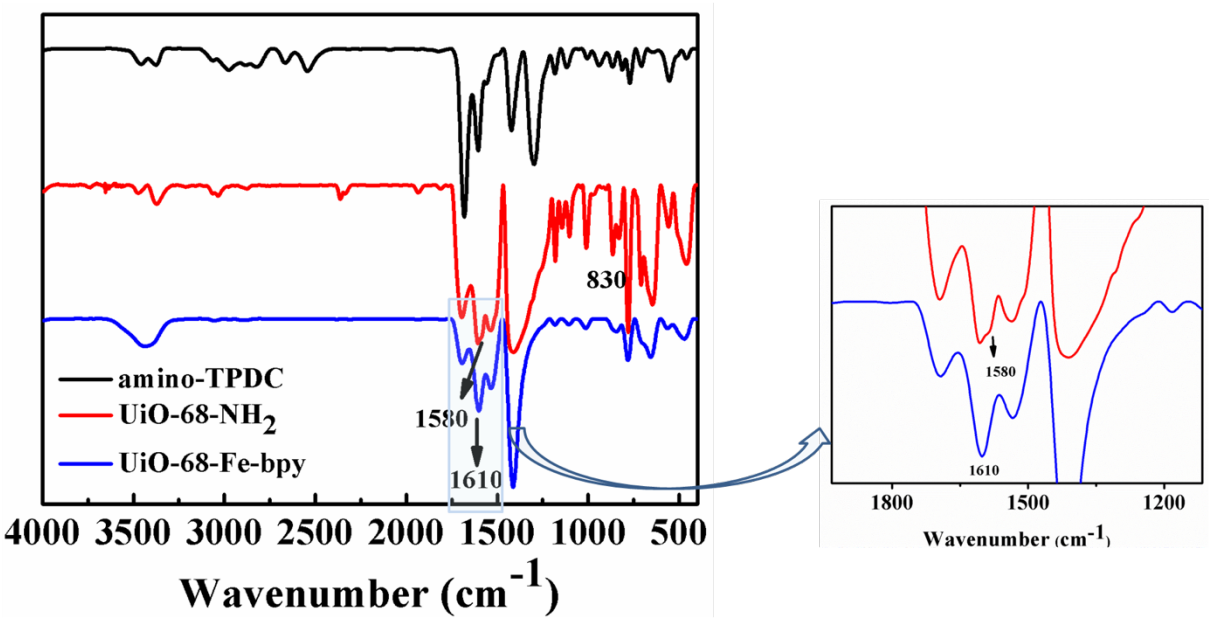


Fig. S1 IR spectra of amino-TPDC, UiO-68-NH_2 and UiO-68-Fe-bpy.

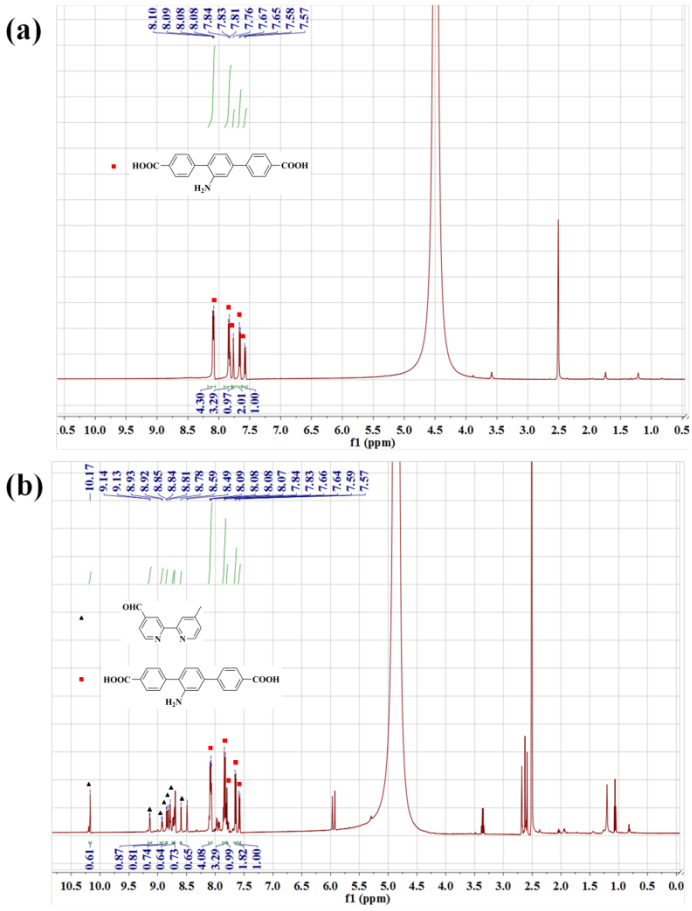


Fig. S2 ^{1}H NMR spectra of the digested (a) UiO-68-NH_2 and (b) UiO-68-bpy in HF/DMSO-d_6.

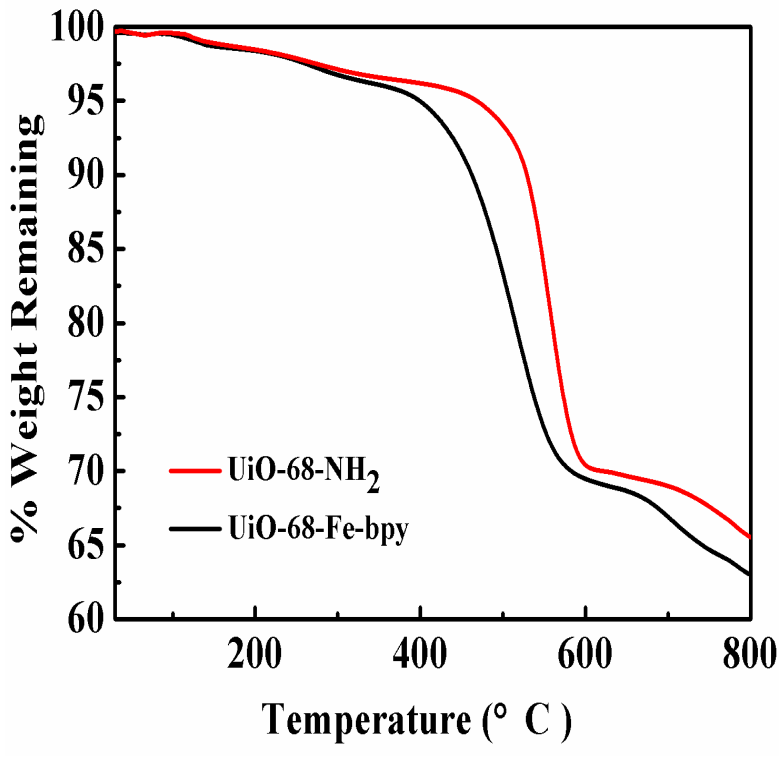


Fig. S3 TG traces of UiO-68-NH_2 and UiO-68-Fe-bpy.

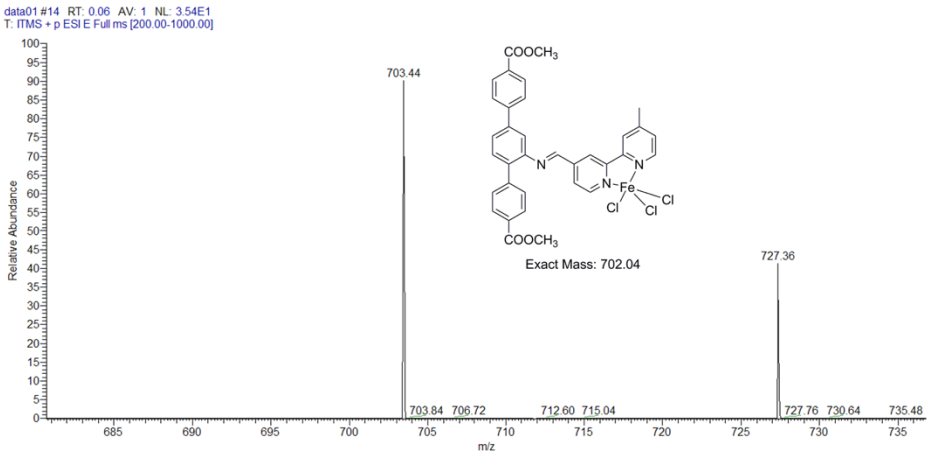


Fig. S4 MS spectrum of TPDC-Fe-bpy (TPDC-Fe-bpy was synthesized by the esterified amino-TPDC, 4′-methyl-[2,2′-bipyridine]-4-carbaldehyde, $FeCl_3$ using the method of UiO-68-Fe-bpy) (The weak coordinated DMF molecule is lost under acidic condition).

SECTION 3. Steady state X-ray absorption spectroscopy (XAS)

XAS measurements were performed at the beamline 12BM-B at the Advanced Photon Source of Argonne National Laboratory. The Extend X-ray Absorption Fine Structure spectra (EXAFS) were collected at room temperature by fluorescence mode using a 13-element germanium solid-state detector. One ion chamber is placed before the sample and used as the incident X-ray flux reference signal. Samples were scanned at the Fe edge. Fe foil was scanned at the same time for energy calibration.

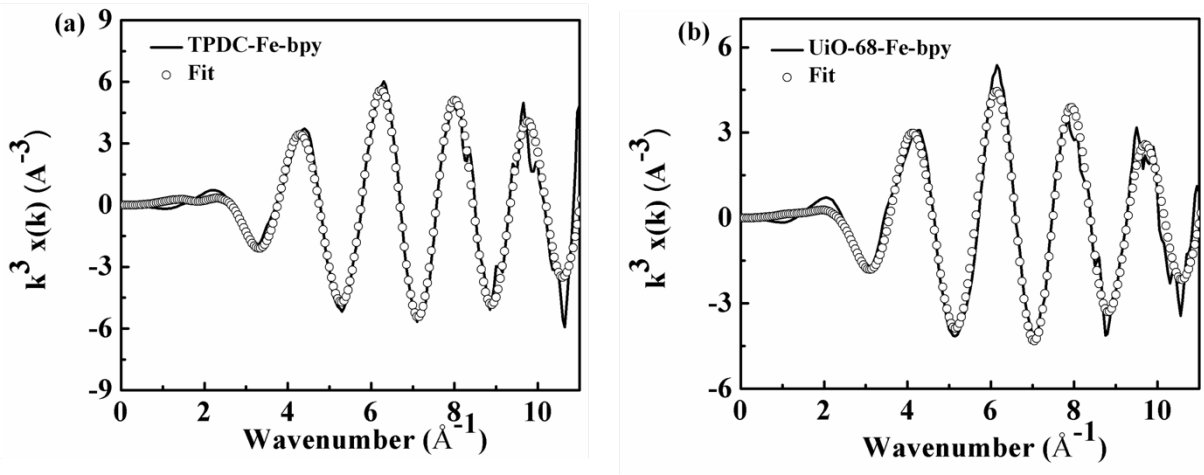


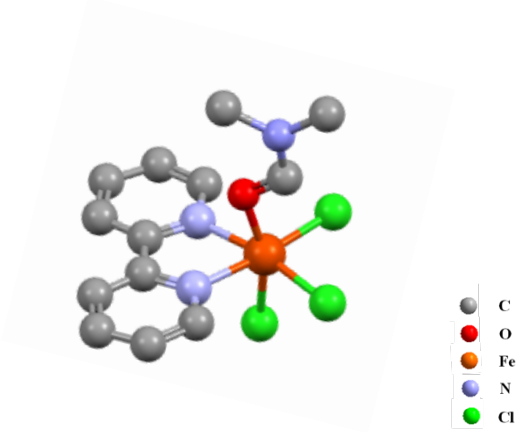
Fig. S5 The X-ray absorption spectra in k-space of (a) TPDC-Fe-bpy and (b) UiO-68-Fe-bpy at Fe K-edge. The solid lines and open circles are experimental and fitted results, respectively.

Table S1. Summary of EXAFS fitting parameters for TPDC-Fe-bpy.

	ΔE0 (ev)	**CN**	**R (Å)**	**σ^2x 10^{-3} (Å^2)**
Fe-N	-5.357	2	2.11	2
Fe-Cl		3	2.18	6

Table S2. Summary of EXAFS fitting parameters for UiO-68-Fe-bpy.

	ΔE0 (ev)	**CN**	**R (Å)**	**σ^2x 10^{-3} (Å^2)**
Fe-N	-7.569	2	2.07	2
Fe-Cl		3	2.18	10



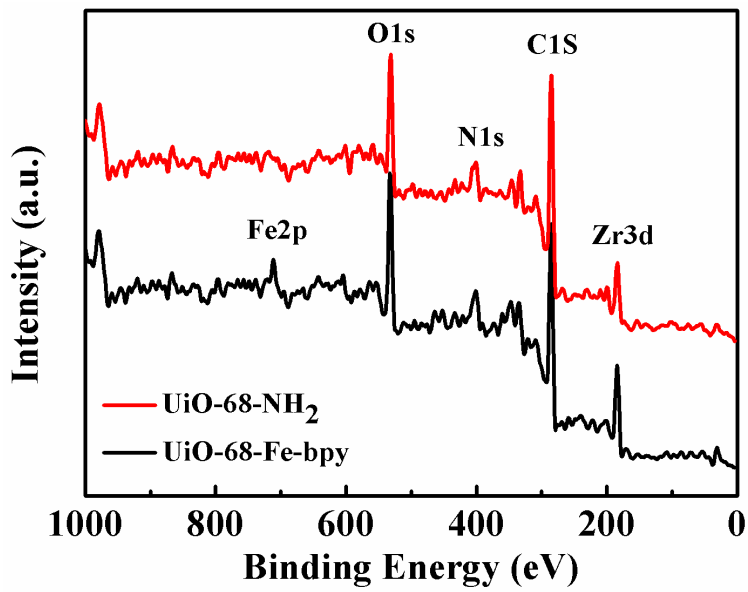


Fig. S6 XPS spectra of UiO-68-NH_2 and UiO-68-Fe-bpy.

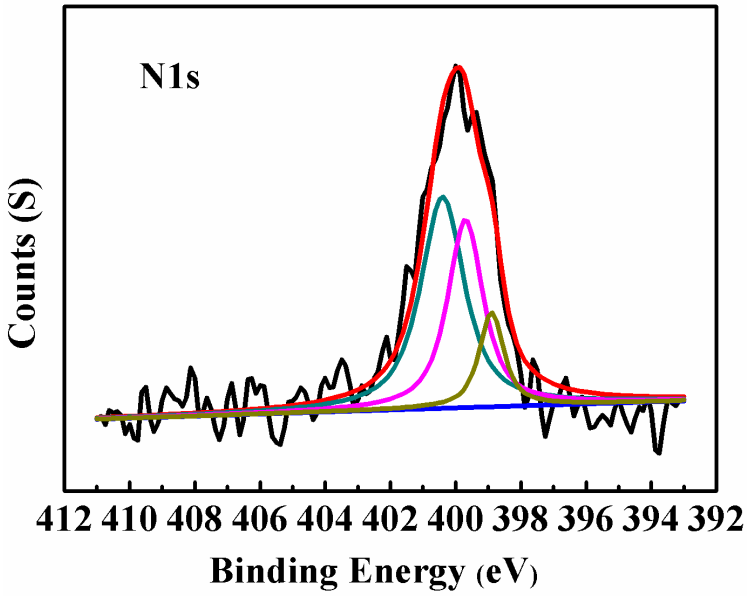


Fig. S7 N 1s spectrum of UiO-68-Fe-bpy.

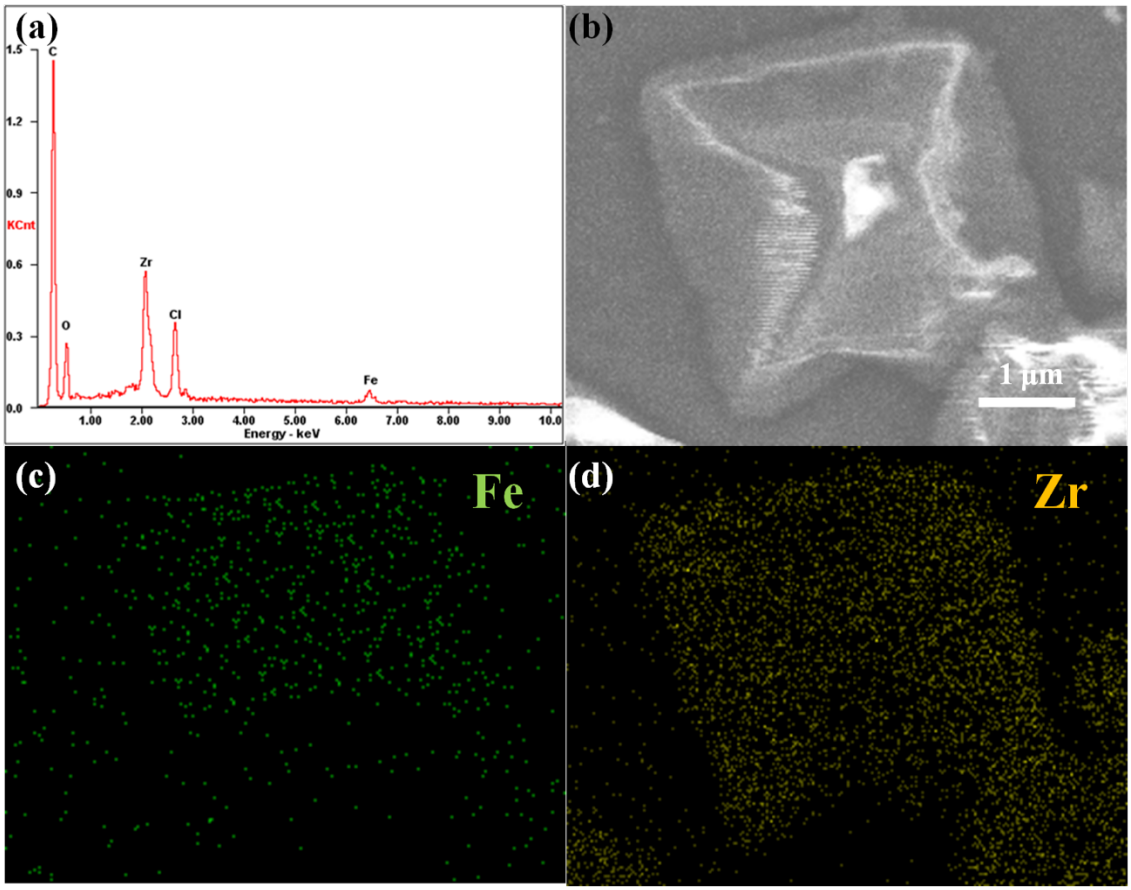


Fig. S8 (a) EDS spectrum and (b) SEM image of UiO-68-Fe-bpy. SEM-mapping images of (c) Fe and (d) Zr in UiO-68-Fe-bpy.

SECTION 4. Gas adsorption experiments

Materials and methods. N_2 and CO_2 used in adsorption experiments were 99.999% grade obtained from Tianhong Gas. Prior to gas adsorption experiments, the samples were soaked in acetone to exchange DMF, followed by evacuation under a dynamic vacuum at 120 ºC for 10 h. The TG traces (Fig. S14, ESI†) and PXRD patterns (Fig. S15, ESI†) indicated that the structures of UiO-68-NH_2 and UiO-68-Fe-bpy were well maintained after the removal of solvent. All the gas adsorption isotherms were measured on a Belsorp-max volumetric gas sorption analyzer by employing a standard volumetric technique up to saturated pressure. The N_2 adsorption isotherms were monitored at 77 K, while CO_2 adsorption isotherms were obtained at 273 and 298 K.

1) N_2 adsorption isotherms

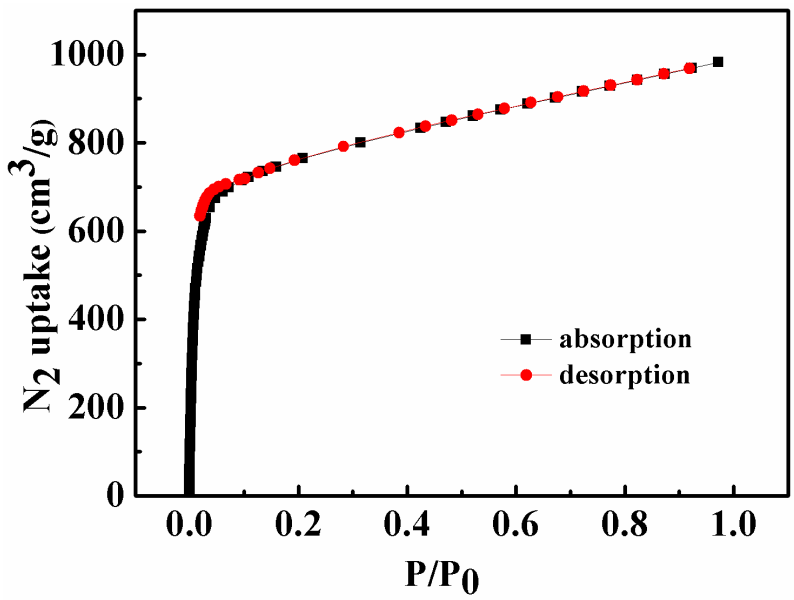


Fig. S9. Nitrogen adsorption isotherms (at 77 K) of UiO-68-NH_2. UiO-68-NH_2 has the BET surface area of 2589.7 m^2/g.

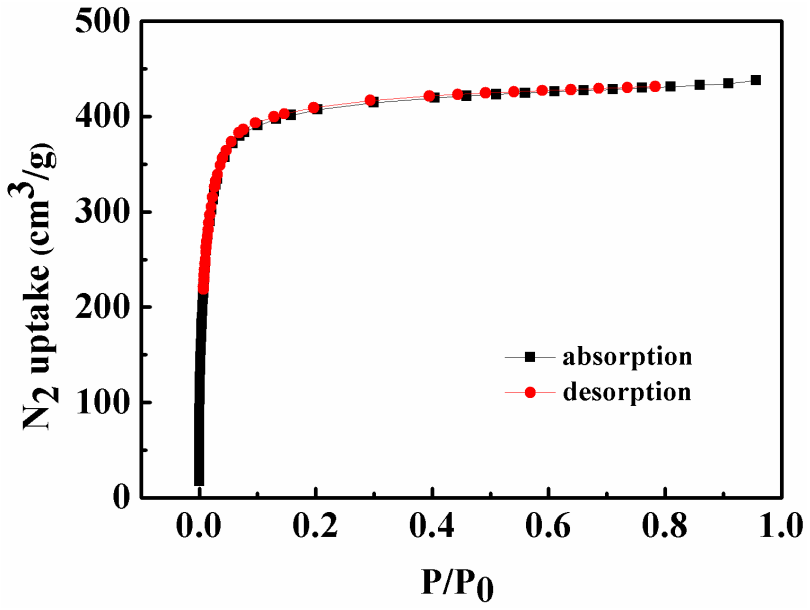


Fig. S10 Nitrogen adsorption isotherms (at 77 K) of UiO-68-Fe-bpy. UiO-68-Fe-bpy has the BET surface area of 1372.1 m^2/g.

2) CO_2 adsorption isotherms

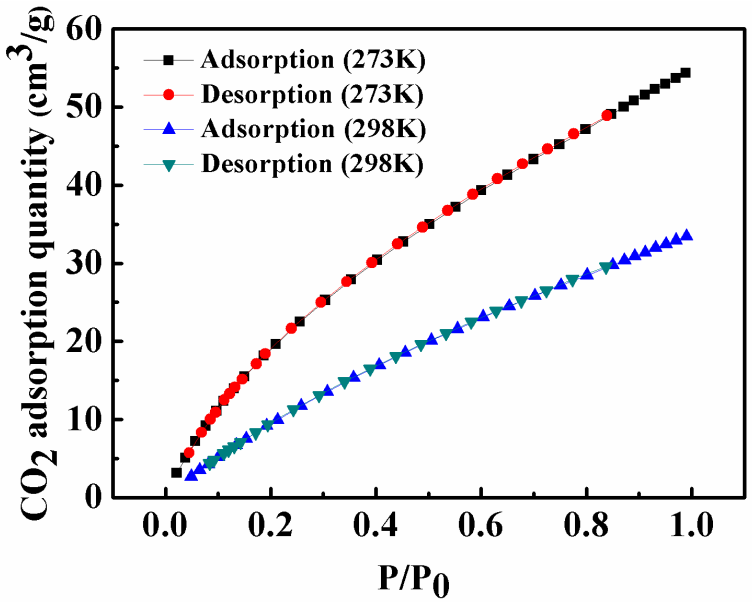


Fig. S11 CO_2 adsorption and desorption isotherms for UiO-68-NH_2 at 273 and 298 K.

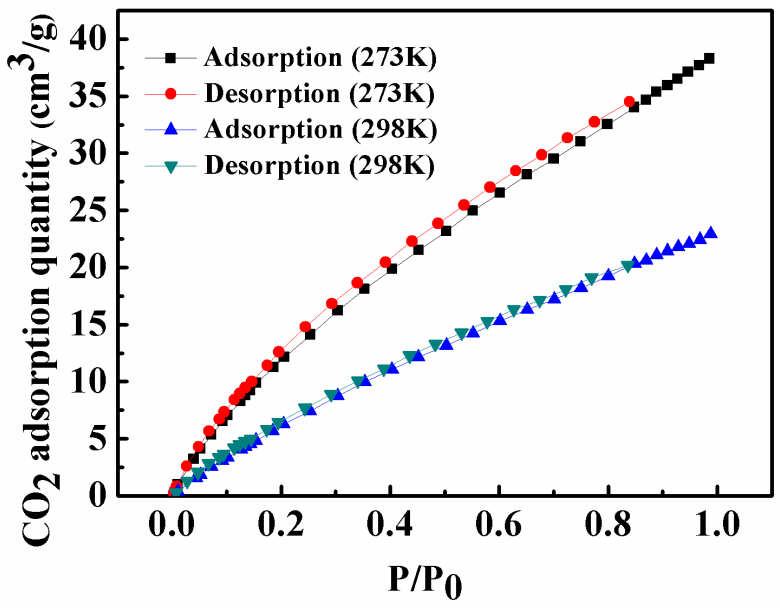


Fig. S12 CO_2 adsorption and desorption isotherms for UiO-68-Fe-bpy at 273 and 298 K.

3) Pore size distribution

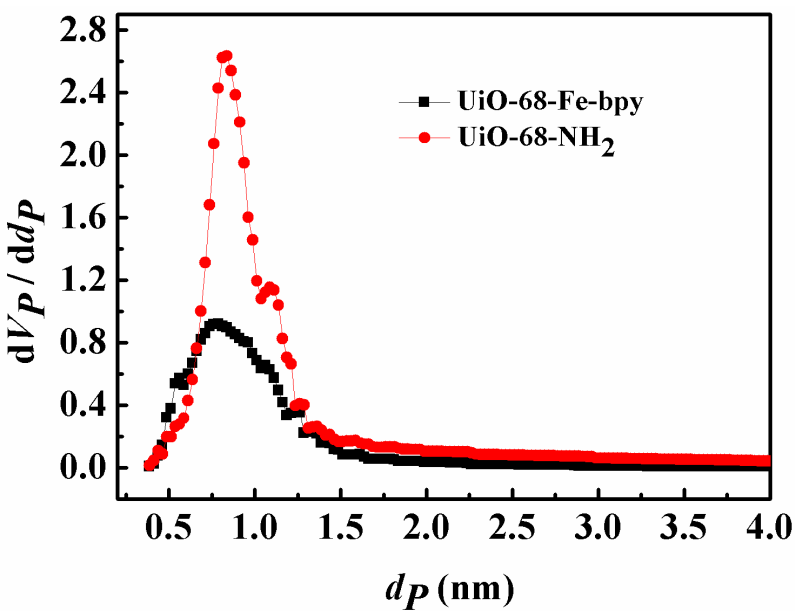


Fig. S13 Pore size distribution for UiO-68-NH_2 and UiO-68-Fe-bpy evaluated by using N_2 adsorption data measured at 77 K.

SECTION 5. UV-Vis diffuse reflectance spectrum

Materials and methods. $BaSO_4$ for UV-Vis diffuse reflectance spectrum was purchased from Sigma-Aldrich. UV-Vis diffuse reflectance data were recorded on a Shimadzu UV-3600 spectrophotometer in the wavelength range of 200-1200 nm, a white standard of $BaSO_4$ was used as reference.

Evaluate the band gaps of MOFs by UV-Vis diffuse reflectance spectrum. As most of the literatures have mentioned, MOFs can act as semiconductor during the photochemical CO_2 conversion process, we tried to determine the band gap (E_g) of the MOFs by UV-Vis diffuse reflectance spectra. Tauc plot was employed to determine the E_g of the materials, we adopted

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

to evaluate the band gap.

Notations:

α	absorption coefficient, dimensionless
h	Planck constant, $h = 4.136\times10^{-15}$ eV s
ν	frequency, s^{-1}
A	constant, $eV^{-1/2}$
E_g	band gap, eV

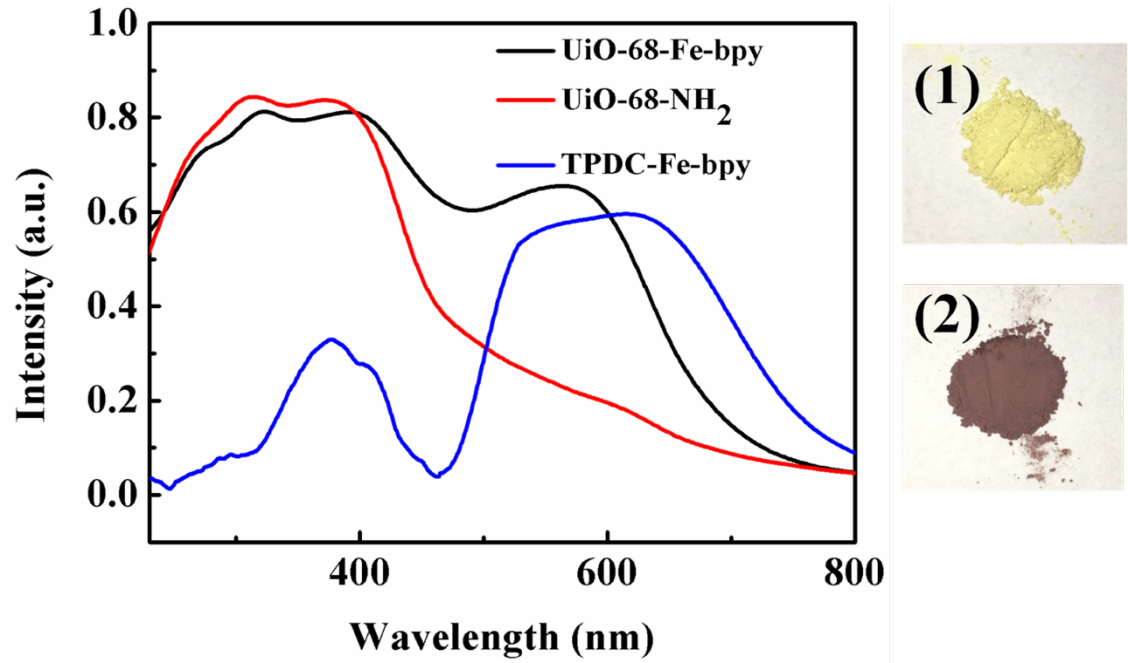


Fig. S14 UV-vis spectra of UiO-68-NH_2, TPDC-Fe-bpy and UiO-68-Fe-bpy (right: photograph of (1) UiO-68-NH_2 and (2) UiO-68-Fe-bpy).

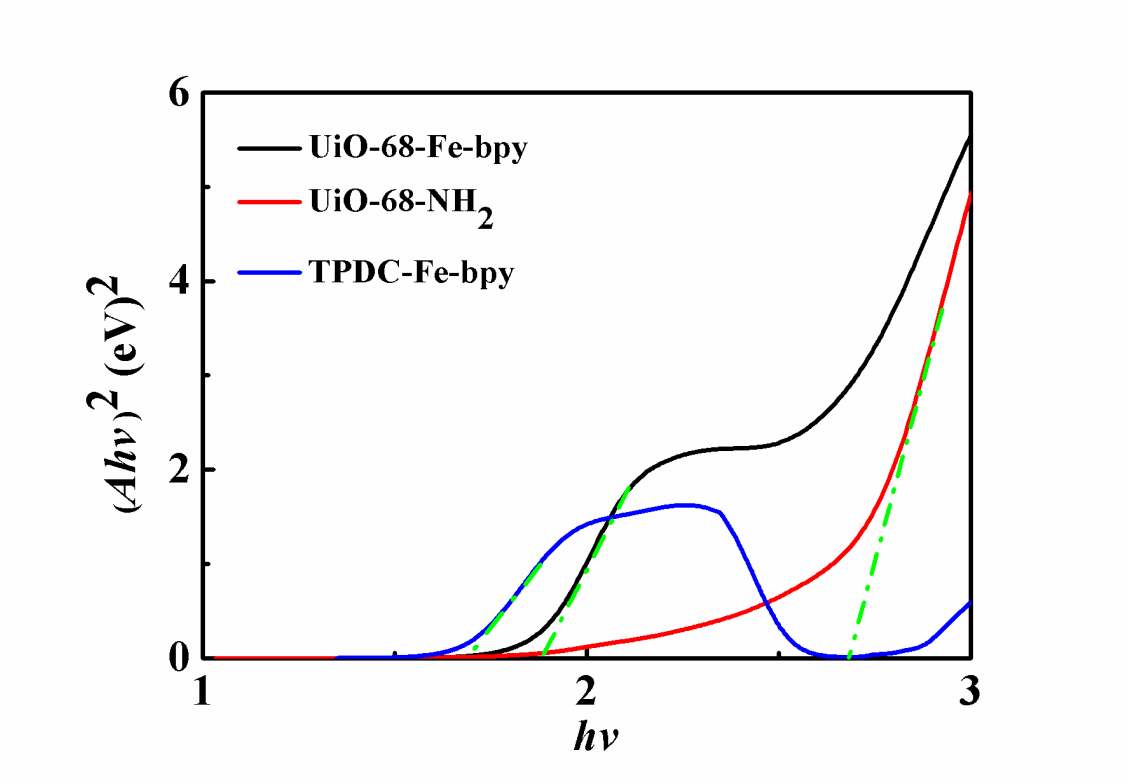


Fig. S15 Tauc plots of UiO-68-NH_2, TPDC-Fe-bpy and UiO-68-Fe-bpy.

SECTION 6. Electrochemical characterization

Materials and methods. MeOH (99.9%, Extra Dry, with molecular sieves, water ≤ 30 ppm (by K.F.)), Na_2SO_4 was purchased from Energy Chemical. ultrapure water (18 MΩ) used in the experiments was supplied by a Millipore System (Millipore Q), argon (99.999%) was obtained from Tianhong gas, other chemicals and solvents are of reagent grade obtained from Sinopharm Chemical Reagent Co., Ltd without further purification. The as-synthesized sample (2 mg) was dispersed into 1 mL MeOH, and then 10 μL Nafion was added.

Cyclic voltammetry. Cyclic voltammetry was performed on a CHI 730E electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode system with DMF + 0.1 M *n*-Bu_4NPF_6 used as the electrolyte at 0.1 V s^{-1}. The working electrode was glassy carbon electrode (3mm-diameter, Gaoss Union, Wuhan). The counter-electrode was a platinum wire and the reference electrode was an aqueous SCE electrode.

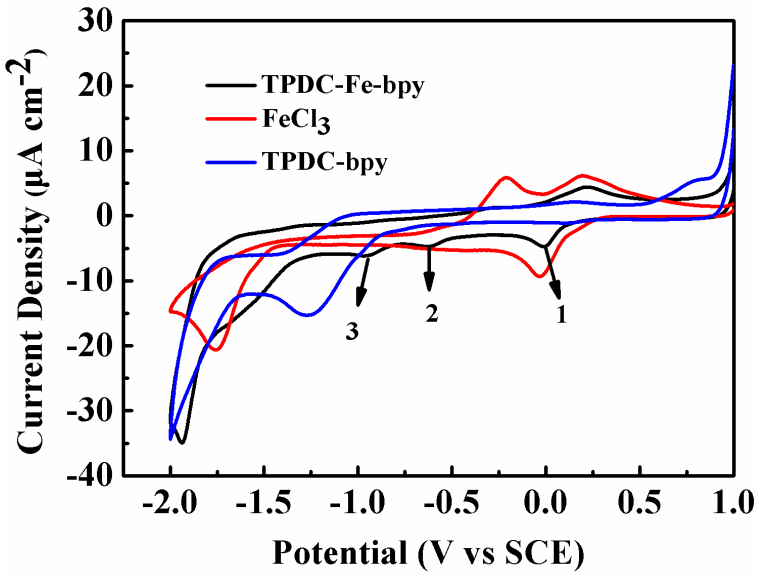


Fig. S16 Cyclic voltammograms of TPDC-Fe-bpy (black), TPDC-bpy (blue) and $FeCl_3$ (red) in CO_2 saturated solutions. (TPDC-Fe-bpy was synthesized by the esterified amino-TPDC, 4′-methyl-[2,2′-bipyridine]-4-carbaldehyde, $FeCl_3$ using the method of UiO-68-Fe-bpy).

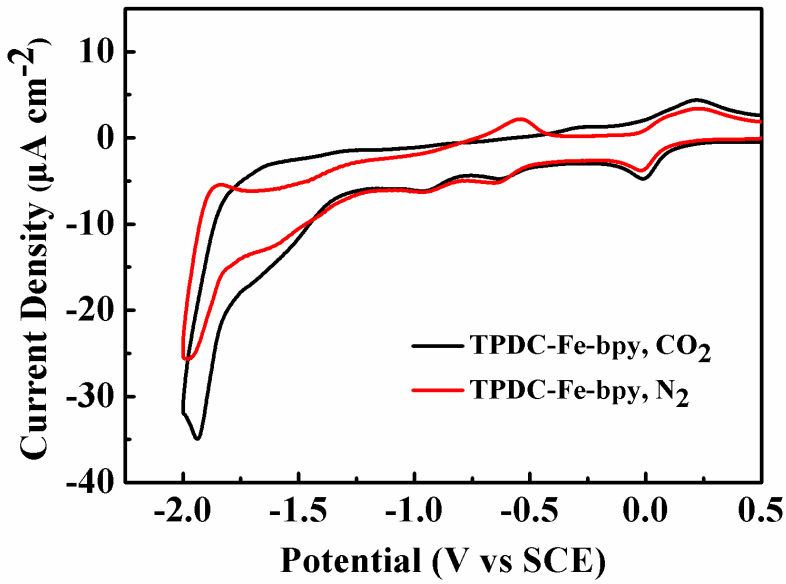


Fig. S17 Cyclic voltammograms of TPDC-Fe-bpy in CO_2 (black) and N_2 (red) saturated solutions.

SECTION 7. Photochemical CO_2 conversion experiments

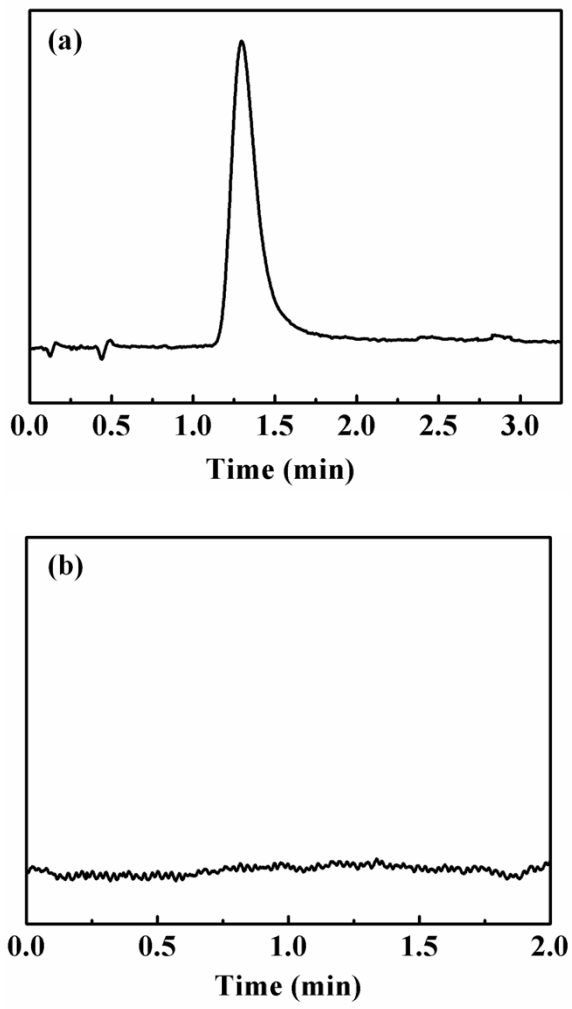


Fig. S18 Typical gas chromatogram observed during long-term irradiation: (a) FID detector for CO and CH_4 monitoring, CO was detected with retention time of about 1.290 min, however, no CH_4 (retention time: 2.540 min) was detected; (b) TCD detector for H_2 detecting, which showed no H_2 (retention time: 0.578 min) was detected.

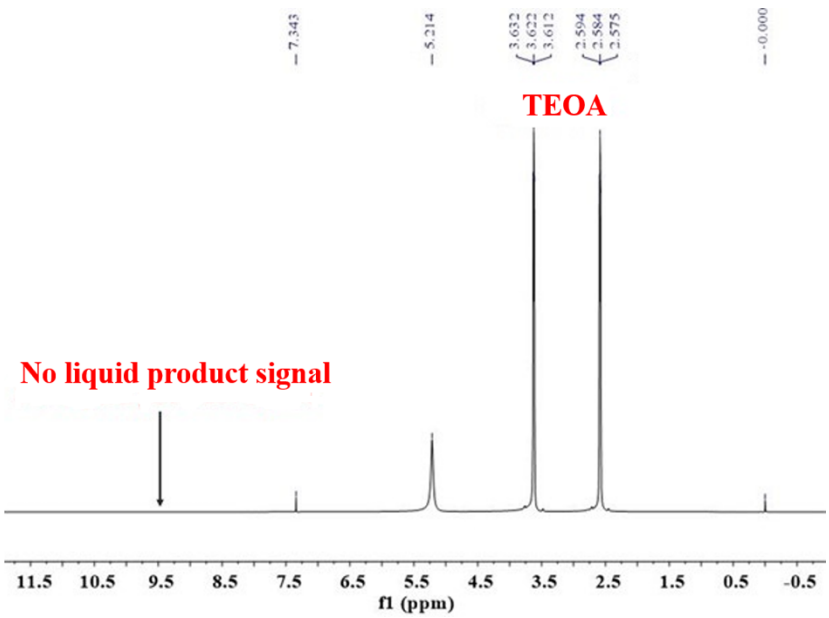


Fig. S19 ^{1}H-NMR spectrum used to detect the liquid product from the photocatalytic reaction.

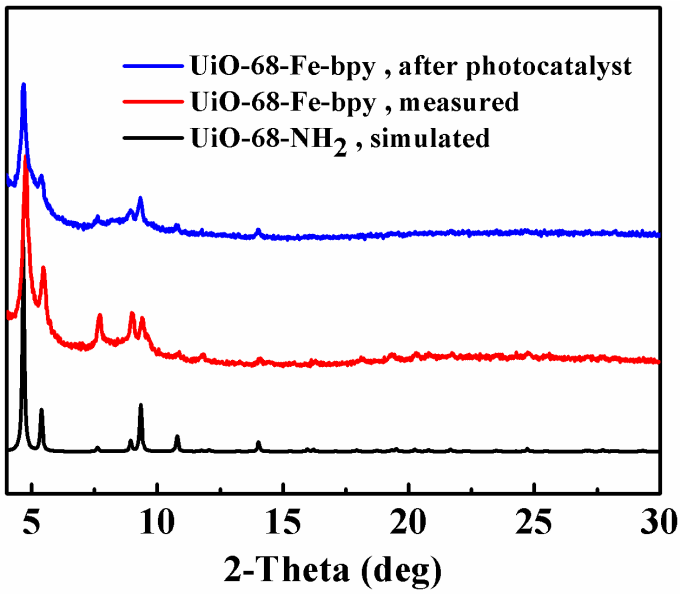


Fig. S20 XRPD patterns of simulated UiO-68-NH_2, UiO-68-Fe-bpy before and after 18 h photocatalysis.

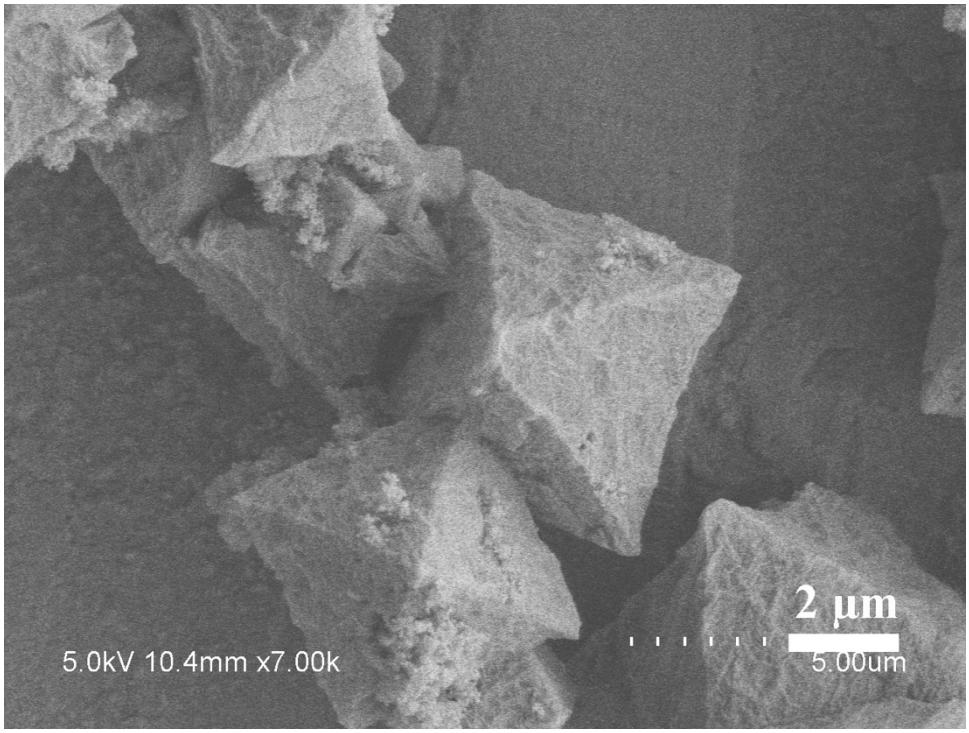


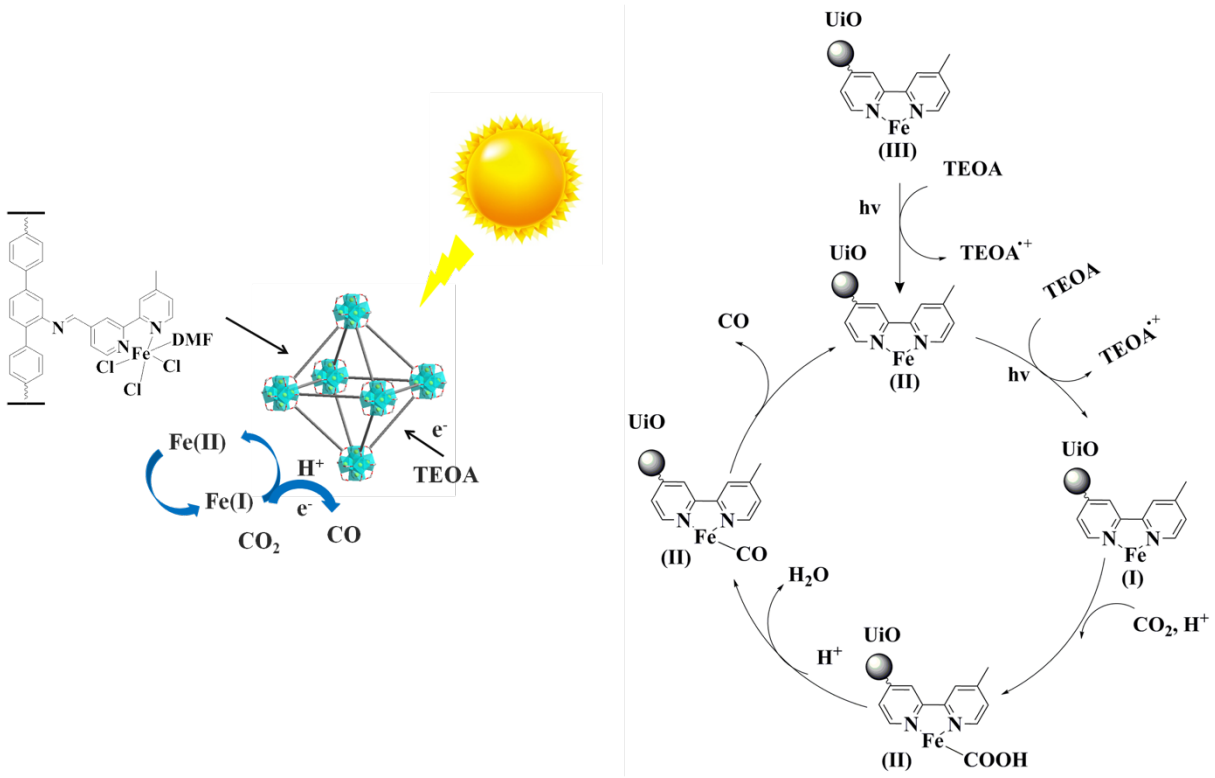
Fig. S21 SEM image of UiO-68-Fe-bpy after 18 h photocatalysis.

Table S3. Summary of photocatalytic CO_2 reduction performances over various visible light response photocatalysts

Photocatalyst	Products	CO Evolution for 6 h (μmol)	Light source Xe lamp (W)	Ref.
UiO-68-Fe-bpy	CO	10	300	This work
UiO-68-NH_2	CO	106	300	This work
TPDC-Fe-bpy	CO	21	300	This work
NH_2-MIL-53(Fe)	CO	15	300	3
NH_2-MIL-88B(Fe)	CO	50	300	3
CdS/TiO_2	CO	50	300	4

Table S4. ICP measurement for UiO-68-Fe-bpy after every run of photocatalysis

run (reaction for 6 h)	Fe content [wt%]	Selection [%]	CO Evolution [μmol/g]
1	0.58	100	106
2	0.57	100	103
3	0.51	100	105



Scheme S1. Proposed mechanism for photocatalytic CO_2 reduction over the as-prepared UiO-68-Fe-bpy under visible light.

SECTION 8. References

(1) Y. Wei, Y. Liu, F. Guo, X. Dao, W. Sun, *Dalton Trans*. 2019, **48**, 8221-8226.

(2) M. Brain, T. Glennt, E. Stephen, J. Gerald, J. Thomas, *Int. J. Pept. Protein Res*. 1991, **38**, 114-123.

(3) X. Y. Dao, J. H. Guo, Y. P. Wei, F. Guo, Y. Liu, W. Y. Sun, *Inorg. Chem*. 2019, **58,** 8517–8524.

(4) X. Pan, Y. Xu, *J. Phys. Chem. C* 2015, **119**, 7184-7194.