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Different functional group modified zirconium frameworks for photocatalytic reduction of carbon dioxide

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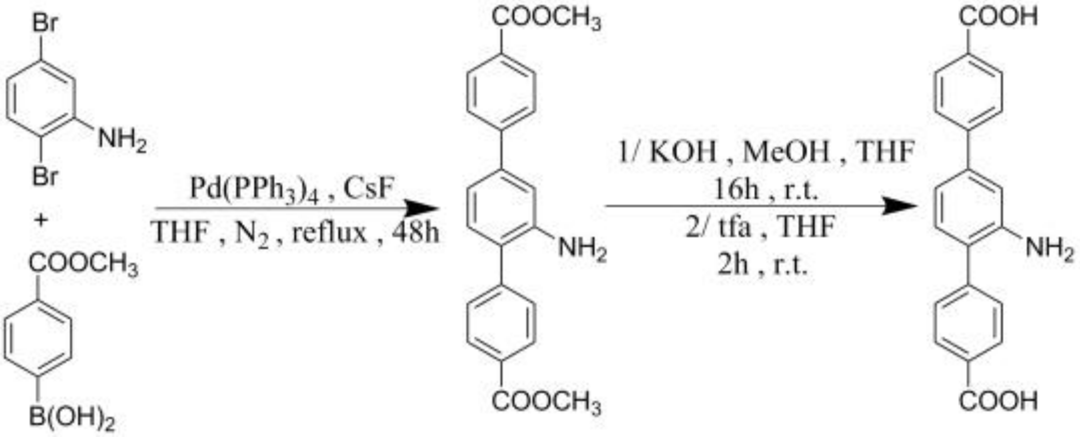
SECTION 1. Ligand synthesis

Materials and methods. 2,5-Dibromoaniline, 4-(methoxycarbonyl)-phenylboronic acid, tetrakis(triphenylphosphine)palladium, and CsF were purchased from Energy 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 amino-triphenyldicarboxylic acid (amino-TPDC)



Amino-TPDC was synthesized as reported previously.[1] A mixture of 2,5-dibromoaniline (2.00 g, 8.0 mmol), 4-(methoxycarbonyl)-phenylboronic acid (4.40 g, 24.5 mmol), tetrakis(triphenylphosphine) palladium (1.00 g, 0.87 mmol) and CsF (5.82 g, 38 mmol) were suspended in 50 mL of anhydrous tetrahydrofuran (THF) in a 100 mL round-bottom flask. The mixture was heated at 80 ℃ for 2 days under nitrogen atmosphere. After cooling to room temperature, The reaction mixture was poured into deionized water (30 mL) and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were concentrated in vacuo. The brown solid residue was purified by silica gel column chromatography (dichloromethane: ethyl acetate = 40:1) to give the esterified ligand as yellow solid. Yield: 58%. IR (KBr pellet cm^{-1}) 3423 (m), 3364 (m), 2934 (m), 1706 (s), 1600 (s), 1423 (s), 1276 (m), 1100 (w), 745 (s), 690 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15-8.09 (m, 4H), 7.67 (d, 2H), 7.60 (d, 2H), 7.24 (d, 1H), 7.12 (dd, 1H), 7.06 (d, 1H), 3.95 (s, 6H).

The methyl amino-triphenyldicarboxylate ester from above (1.68 g, 4.65 mmol) was dissolved into THF (200 mL) and heated to 40 ℃. KOH (30.8 g, 0.55 mol) in methanol (100 mL) was added into the above solution, which was stirred at 40 ℃ for 18 h. A white precipitate was collected by centrifugation and washed by THF. After that the solid was suspended into 100 mL THF. Then, trifluoroacetic acid (12 mL) was added into the mixture, which was stirred for 2 h at room temperature. The yellow solid product (amino-TPDC) was collected by vacuum filtration, washed with water and dried in vacuo. Yield: 80%. IR (KBr pellet cm^{-1}) 3456 (m), 3371 (m), 2967 (m), 1685 (s), 1617 (s), 1419 (s), 1299 (s), 1118 (w), 774 (m), 697 (m). ^{1}H NMR (DMSO-d_6): δ = 12.97 (br, 2H), 8.03 (m, 4H), 7.74 (d, 2H), 7.61 (d, 2H), 7.16 (d, 2H), 7.02 (dd, 1H), 5.12 (br, 2H).

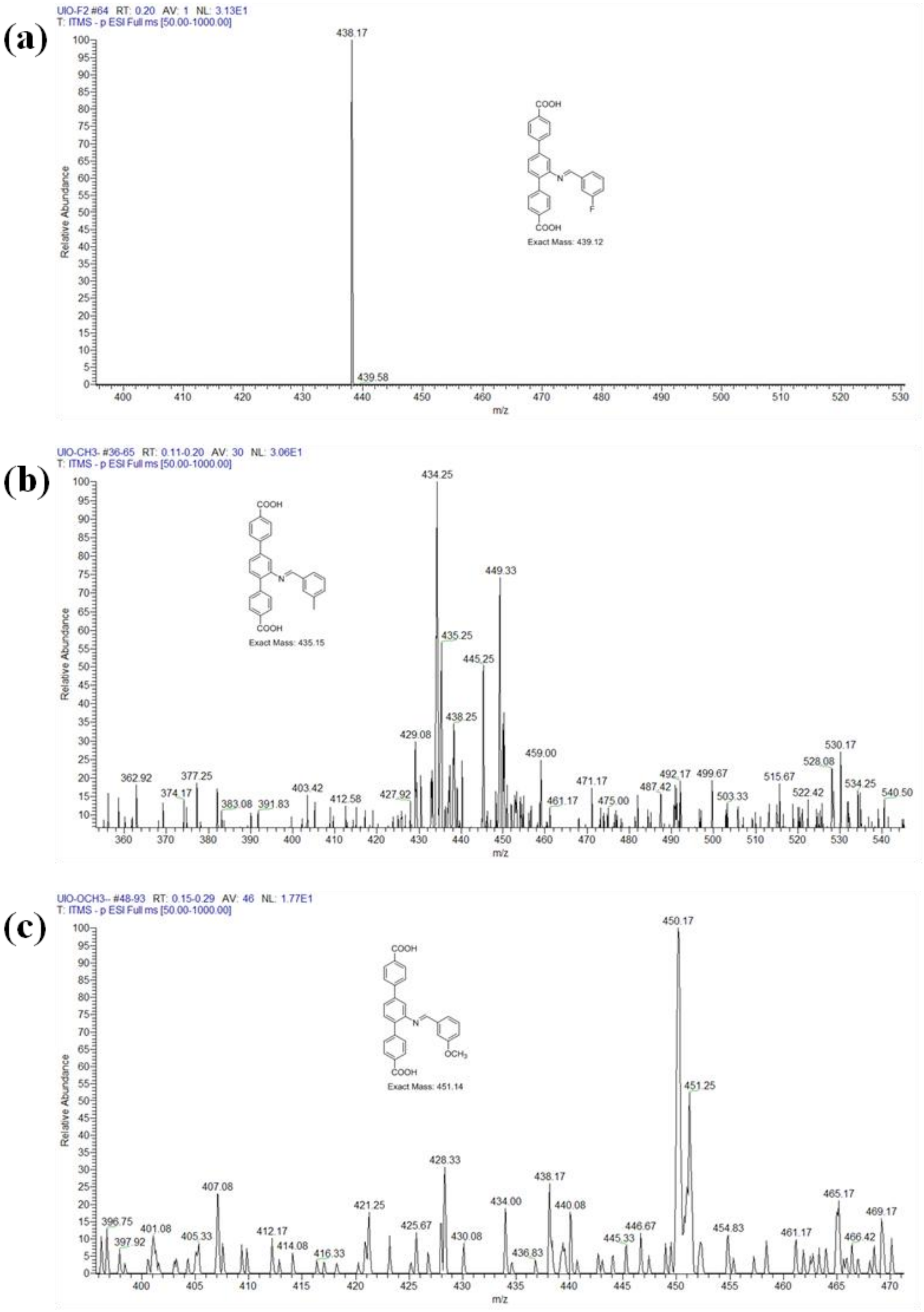


Fig. S1 ESI-MS (negative mode) of 438.17, 434,25, 450.17 corresponding to [M-H]$^-$ of the ligand after digestion of (a) UiO-68-F, (b) UiO-68-CH$_3$ and (c) UiO-68-OCH$_3$.

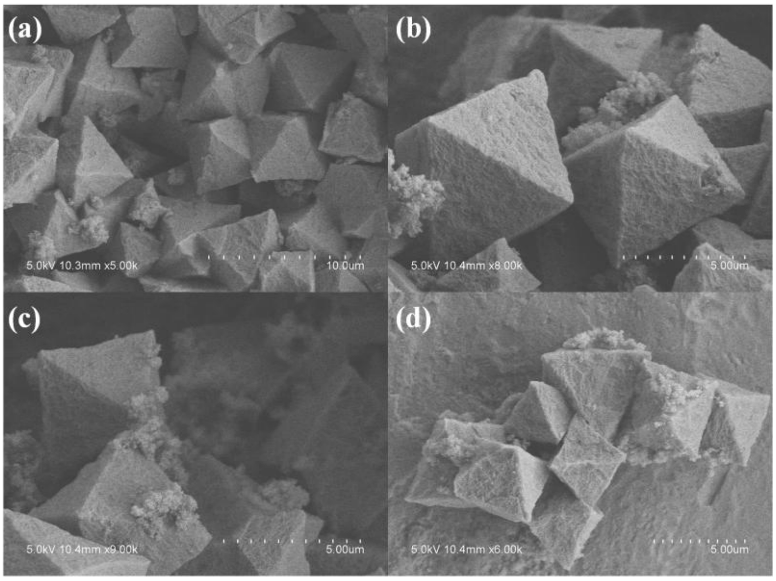


Fig. S2 SEM images of (a) UiO-68-NH_2, (b) UiO-68-F, (c) UiO-68-CH_3 and (d) UiO-68-OCH_3.

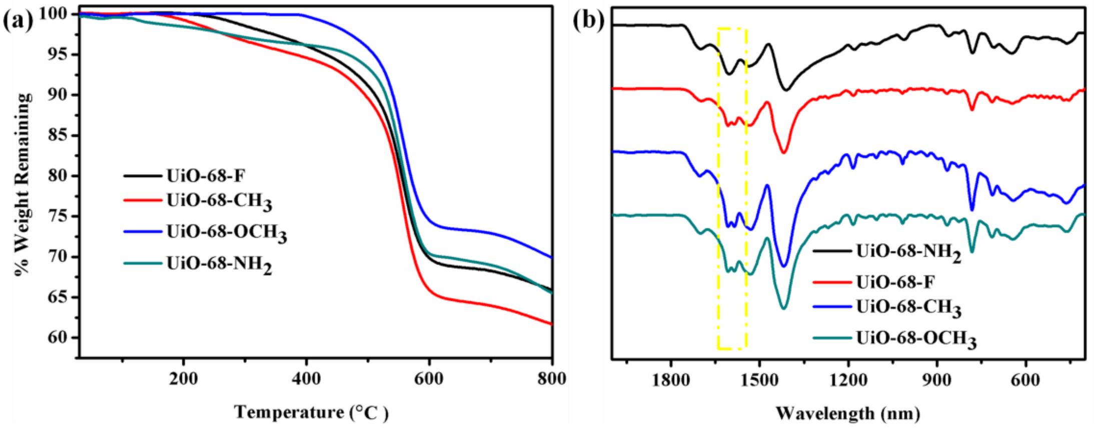


Fig. S3 (a) TG traces and (b) IR spectra of UiO-68-NH_2, UiO-68-F, UiO-68-CH_3 and UiO-68-OCH_3.

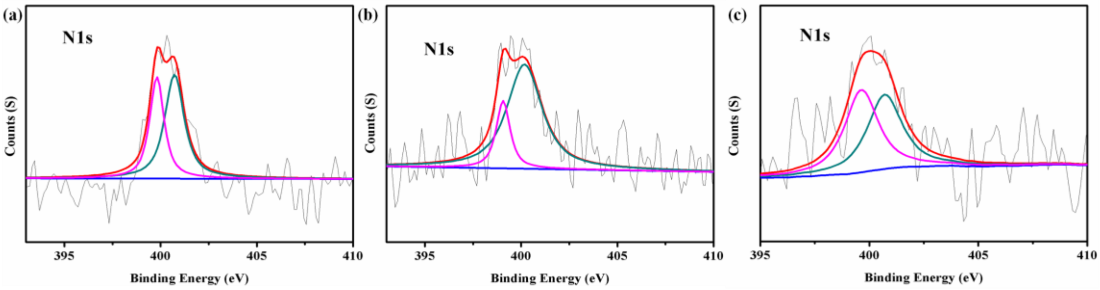


Fig. S4 N 1s XPS spectra of (a) UiO-68-F, (b) UiO-68-CH_3 and (c) UiO-68-OCH_3.

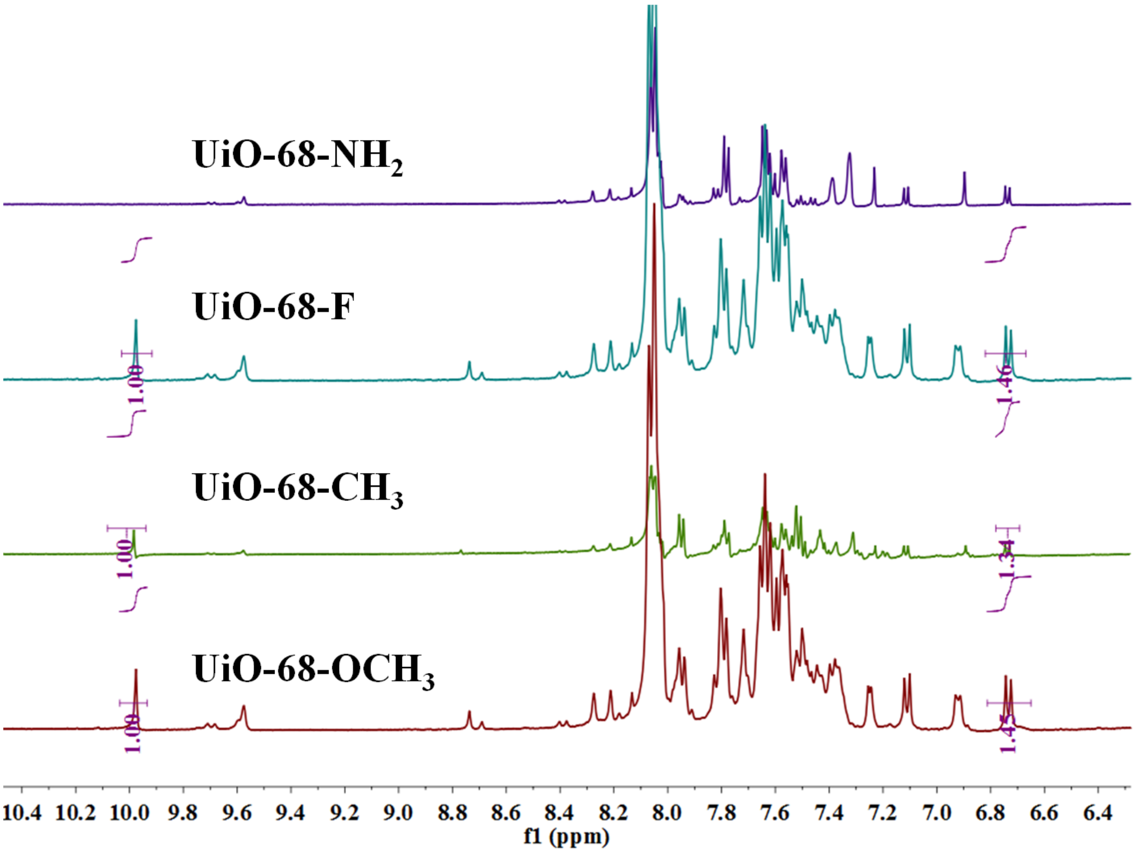


Fig. S5 ^1H NMR spectra of the digested UiO-68-NH_2, UiO-68-F, UiO-68-CH_3 and UiO-68-OCH_3 in HF/DMSO-d_6.

SECTION 2. Gas adsorption experiments

Materials and methods. N_2 used in adsorption experiments was 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 ℃ for 10 h. The

TG traces (Fig. S3a, ESI†) and PXRD patterns (Fig. 1a) indicated that the structures of UiO-68-F, UiO-68-CH3 and UiO-68-OCH3 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.

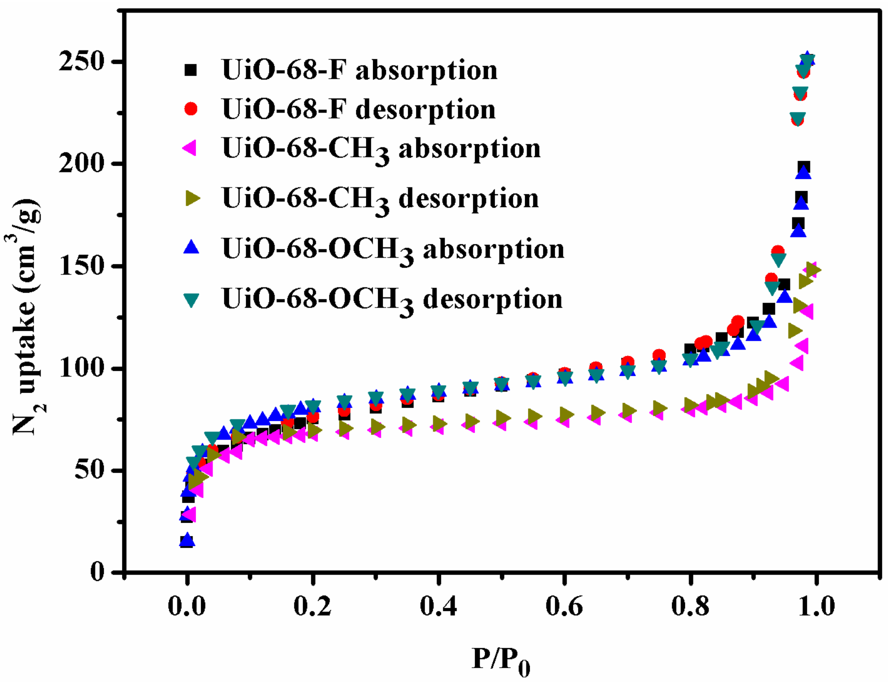


Fig. S6 Nitrogen adsorption isotherms of UiO-68-F, UiO-68-CH_3 and UiO-68-OCH_3 at 77 K.

SECTION 3. 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. It has been reported that MOFs can act as semiconductor during the photochemical CO_2 conversion process,[2] 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

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

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, $\mathrm{eV}^{-1/2}$
E_g	band gap, eV

SECTION 4. 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.

1) Electrochemical impedance spectroscopy. The electrochemical impedance spectroscopy was performed on the Zahner Zennium electrochemical workstation in a standard three-electrode system with a bias potential of -0.5 V. The working electrode was prepared by dropping the suspension (10 μL) onto the surface of the glassy carbon electrode (3mm-diameter, Gaoss Union, Wuhan). The counter-electrode was a platinum wire and the reference electrode was an aqueous SCE electrode. Then, EIS measurement was performed at room temperature in 0.1 M Na_2SO_4 deoxygened using an argon steam.

2) Photocurrent measurements. Photocurrent measurements were performed on a CHI 730E electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode system with a 0.1 M Na_2SO_4 solution as the electrolyte. The working electrode was prepared by dropping the suspension (250 μL) onto the surface of the photocatalyst-coated ITO (1 cm^2). The counter-electrode was a platinum plate and the reference electrode was an aqueous SCE electrode. And then, the photo-responsive signals of the samples were measured under chopped light at 0.1 V.

3) Mott-Schottky measurements. The Mott-Schottky measurements were performed on the Zahner Zennium electrochemical workstation in a standard three-electrode system with a 0.1 M Na_2SO_4 solution as the electrolyte. The working electrode was prepared by dropping the suspension (10 μL) onto the surface of the glassy carbon electrode (3mm-diameter, Gaoss Union, Wuhan). The counter-electrode was a platinum wire and the reference electrode was an aqueous SCE electrode.

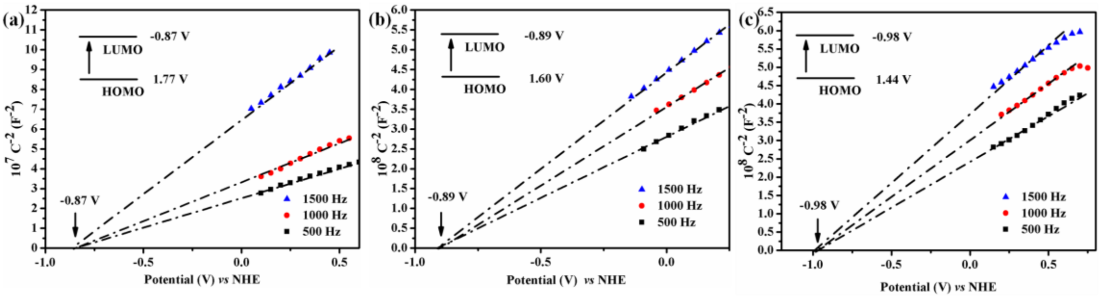


Fig. S7. Mott-Schottky plots for (a) UiO-68-F, (b) UiO-68-CH_3 and (c) UiO-68-OCH_3 in a 0.1 M Na_2SO_4 aqueous solution (inset: energy-band digram of (a) UiO-68-F, (b) UiO-68-CH_3 and (c) UiO-68-OCH_3).

4) Linear sweep voltammetry (LSV) measurements. Linear sweep voltammetry (LSV) measurements were performed on a CHI 730E electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode system with a 0.5M $KHCO_3$ (pH = 7.3) solution as the electrolyte. A volume of 10 mg as-synthesized sample, 10 mg acetylene black (AB), and 1 mL Nafion solution were mixed to form uniform catalyst ink. After sonication for 30 min, the ink was directly dropped onto the surface of the carbon cloth (1 cm

×1 cm). The counter-electrode was a platinum wire and the reference electrode was Ag/AgCl electrode.

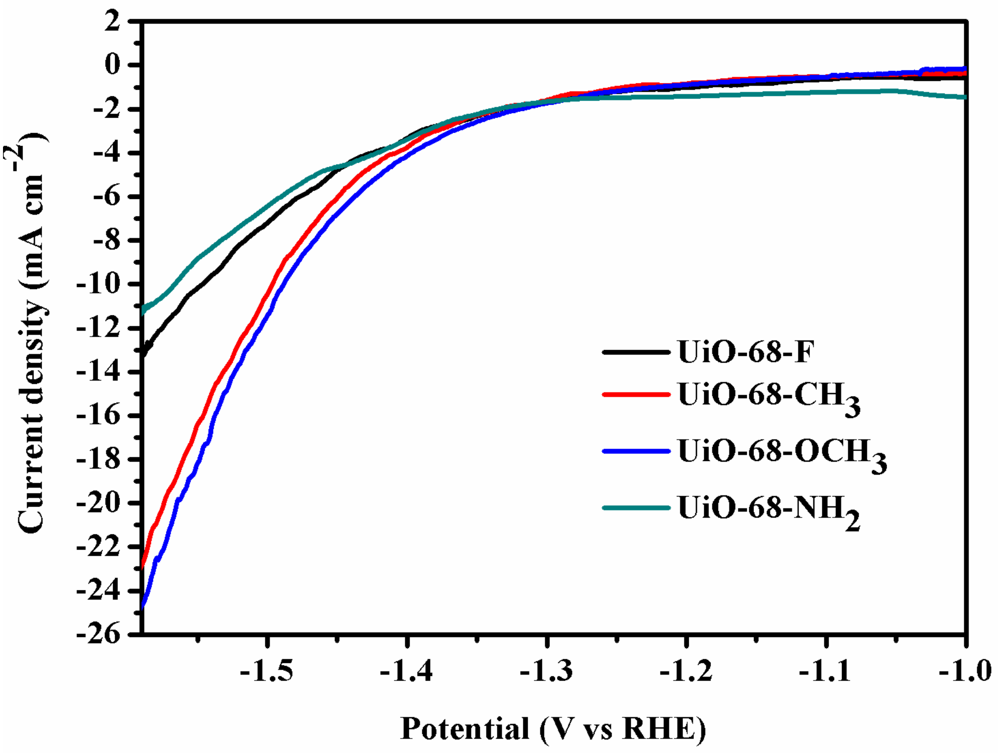


Fig. S8 Linear sweep voltammetric curves of UiO-68-NH$_2$ and UiO-68-PSMs.

SECTION 5. Electron Paramagnetic Resonance (EPR) spectra

Materials and methods. UiO-68-NH$_2$, UiO-68-PSMs of UiO-68-F, UiO-68-CH$_3$ and UiO-68-OCH$_3$ in presence of TEOA were added to the EPR resonator, and degassed by several freeze-pump-thaw procedures and sealed. The same Xe lamp was used in this measurement at room temperature. The EPR spectra were obtained using a Bruker EMX plus-6/1 variable temperature X-band apparatus at 110 K and simulated with the software of WINEPR SimFonia.

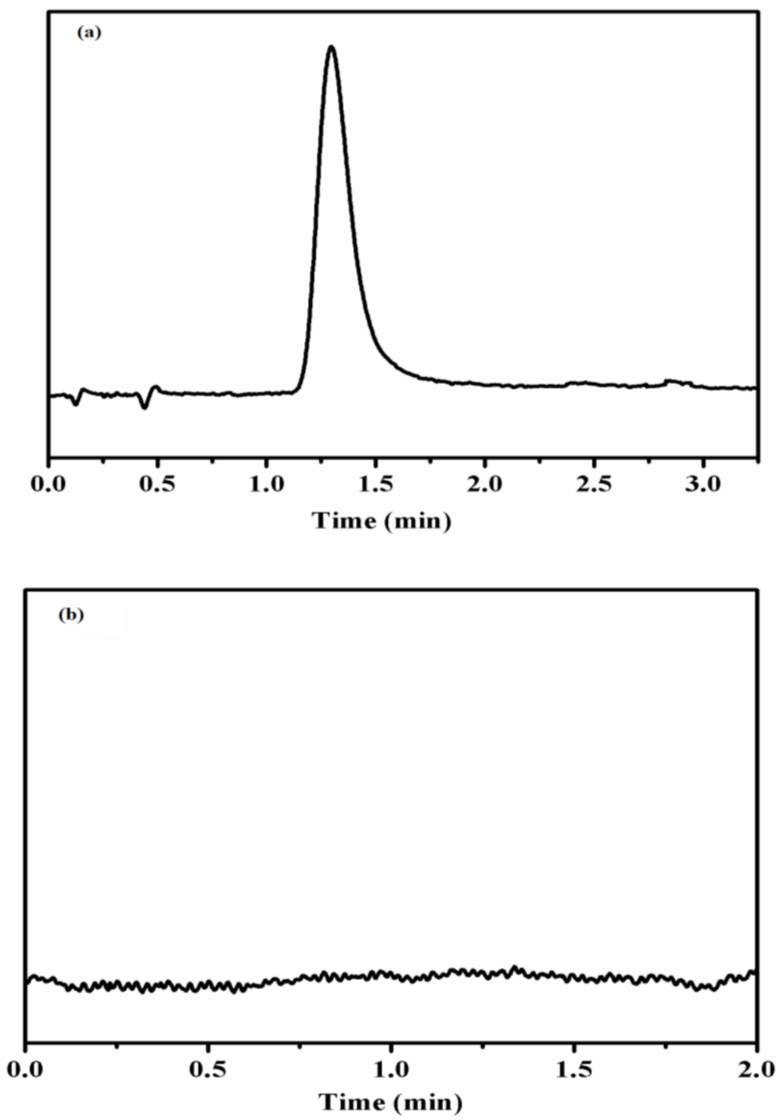


Fig. S9 Typical gas chromatogram observed during long-term irradiation: (a) FID detector for CO and CH_4 monitoring, CO was detected with retention time of about 1.290 min, however, no CH_4 (retention time: 2.540 min) was detected; (b) TCD detector for H_2 detecting, which showed no H_2 (retention time: 0.578 min) was detected.

SECTION 6. References

(1) A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17,** 6643.

(2) (a) H.-Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S.-H. Yu and H.-L. Jiang, *J. Am. Chem. Soc.* 2015, **137,** 13440; (b) H. Zhang, J. Wei, J. Dong, G. Liu, L. Shi, P. An, G. Zhao, J. Kong, X. Wang, X. Meng, J. Zhang and J. Ye, *Angew. Chem. Int. Ed.* 2016, **55,** 14310; (c) Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu and Z. Li, *Angew. Chem. Int. Ed.*, 2012, **51,** 3364; (d) D. Wang, R. Huang, W. Liu, D. Sun and Z. Li, *ACS Catal.*, 2014, **4,** 4254.