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Photocatalytic CO_2 reduction by a mixed metal (Zr/Ti), mixed ligand metal-organic framework under visible light irradiation

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Supporting Information

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Experimental

*Synthesis of $Zr_6O_4(OH)_4(C_8H_7O_4N)_{5.17}(C_8H_8O_4N_2)_{0.83}$ **(1(Zr))**.* A solution of $ZrCl_4$ (0.3 mmol) and 80 equiv of acetic acid (as a modulator) were dissolved in 5 mL of DMF with the aid of sonication in a 20 mL scintillation vial. A separate solution of containing a mixture of NH_2-H_2bdc (0.255 mmol) and $(NH_2)_2$-H_2bdc (0.045 mmol) was dissolved in 5 mL of DMF with the aid of sonication in a 20 mL scintillation vial. The solution containing the organic linkers was rapidly poured into the solution containing $ZrCl_4$ and the resulting mixture was incubated in a preheated oven at 85 °C for 24 h. After cooling, the resulting brown powder was isolated by centrifugation (using a Beckman Coulter Allegra X-22R with a fixed-angle rotor (C0650), at 6000 rpm for 10 min) and washed with DMF (3×10 mL), then soaked in MeOH for 3 d with the solution replaced with fresh methanol every 24 h. The washed powders were isolated by centrifugation (see conditions above) and then dried under vacuum at room temperature.

Synthesis of UiO-66(Zr)-NH_2 ($Zr_6O_4(OH)_4(C_8H_7O_4N)_6$). UiO-66(Zr)-$NH_2$ was prepared by same methods as used for **1(Zr)**, but with NH_2-H_2bdc (0.3 mmol) as the sole organic linker.

*PSE between **1(Zr)** and Ti(IV).* Postsynthetic exchange for **1(Zr)** was performed following a reported procedure.[S1] $TiCl_4(THF)_2$ (0.1 mmol) was dissolved in 2 mL of DMF. This solution was added to **1(Zr)** (ca. 29.5 mg, 0.1 mmol equiv based on the organic linkers) and the mixture was incubated at 85 °C in a preheated oven for 5 d. After cooling, the solids were isolated by centrifugation (see conditions above) and washed with DMF (3×10 mL), then soaked in MeOH for 3 d with the solution replaced with fresh methanol every 24 h. The washed powders were isolated by centrifugation (see conditions above) and then dried under vacuum at room temperature.

PSE between UiO-66(Zr)-NH_2 and Ti(IV). Postsynthetic exchange for UiO-66(Zr)-NH_2 was performed by same method described for **1(Zr/Ti)**, but a different amount of MOF was used (ca. 29.2 mg, 0.1 mmol equiv based on NH_2-H_2bdc).

Synthesis of NH_2-MIL-125(Ti). NH_2-MIL-125(Ti) was prepared following a previously reported method.[S2] A mixture of tetrapropylorthortitanate (TPOT, 0.6 mL) and NH_2-H_2bdc (0.55 g) was dissolved in 10 mL of 9:1 (v/v) mixed solution of DMF-MeOH. After stirring for 30 min to achieve complete dissolution, the solution was transferred to a Teflon-lined stainless-steel autoclave, followed solvothermal reaction for 48 h at 150 °C. After cooling to room temperature, the yellow powders that precipitated were collected via centrifugation at 7000 rpm for 15 min using a Hettich Rotana 460R centrifuge equipped with as A5615 fixed-angle rotor, washed with copious amounts of DMF and MeOH, and dried under vacuum at 60 °C overnight.

Powder X-ray Diffraction (PXRD) analysis. PXRD patterns were collected on a Bruker D8 Advance diffractometer. 20-30 mg of MOF samples were loaded on glass holder and measured at 40 kV, 40 mA for Cu Kα (λ=1.5418 Å), with a scan speed of 2 deg/min in 2θ, and a 2θ range of 5° to 40°.

Scanning Electron Microscopy (SEM) and Energy-dispersed X-ray spectroscopy (EDX). SEM images were collected on a Phillips XL 30 ESEM instrument. 2-3 mg of MOFs were dispersed on carbon tape and sputtered by iridium for conductivity. The SEM was operated at 10 kV of acceleration voltage with spot size of 3. Oxford EDX and Inca software were used to perform elemental analysis using characteristic X-rays for each element of interest.

*Liquid ^{1}H NMR Analysis of **1(Zr)**.* The ratio between NH_2-bdc and $(NH_2)_2$-bdc in **1(Zr)** was calculated by digesting the MOF and measuring the ^{1}H NMR spectrum of the fully dissolved sample. ~10 mg of the MOF was dissolved in 1M NaOH/D_2O for 24 h and the solution was transferred to an NMR tube and measured on a 400 MHz NMR (Varian, Mercury 400). Integrated area of peaks at 7.02 ppm and 7.58 ppm were used for quantification of $(NH_2)_2$-bdc and NH_2-bdc, respectively.

Diffuse Reflectance UV-Vis Spectroscopy. UV-Vis spectra were collected using a StellarNet, EPP 2000C spectrophotometer with a diffuse reflectance measurement system. A step size of 1 nm/sec and a wavelength range of 300 nm to 800 nm were used. F(R) values were calculated by Kubelka-Munk function of $(1\text{-}R)^2/2R$ for solid state samples. A polytetrafluoroethylene (PTFE) disk (StellarNet, RS-50), which reflects >97% of incident light (300 nm $< \lambda <$ 1700 nm), was used as a reference (R).

BET Surface Area Analysis. ~50 mg of **1(Zr)** and **1(Zr/Ti)** were evacuated on a vacuum line overnight at room temperature. The samples were then transferred to a pre-weighed sample tube and degassed at 105 °C on an adsorption analyzer (Micromeritics, ASAP 2020) for a minimum of 12 h or until the outgas rate was <5 mm Hg. The sample tube was re-weighed to obtain a consistent mass for the degassed exchanged MOF. BET surface area (m^2/g) measurements were collected at 77 K by liquid N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using the volumetric technique.

UV-light Photoelectron Spectroscopy (UPS) analysis. UPS was used to analyse valence band structure of MOFs and was collected on a Thermo VG Scientific instrument with a Sigma Probe using He light source of 21.2 eV. 2-3 mg of sample were dispersed on 1 cm^2 of copper tape attached to a silicon wafer with gold wire to give samples electric conductivity. Gold plate was used for calibration. The valance band maxima of the MOFs were obtained from the UPS measurement. The lowest binding energy indicates the value of valance band maximum at vacuum level and this value was converted to standard hydrogen electrode (SHE), $E_{vac} = E_{SHE} + 4.5$ eV. Bandgap energies of the MOFs were obtained from the absorption edge values from the F(R) trace of the MOFs (see UV-Vis spectroscopy above). The conduction band minimum of the MOF was calculated by sum of valence band maximum and bandgap energy of the MOF.

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Analysis. ICP-MS was used to determine the metal content of Zr and Ti in PSE MOFs. ICP-MS analysis was performd on an Agilent ICP-MS 7700S. Samples were dissolved in 7:3 (v/v) solution of HNO_3-HCl and heated to 200 °C with the aid of a microwave reactor for 30 min.

Photoluminescence (PL) Analysis. Light emission properties of MOFs were recorded on a Horiba LabRam HR PL photoluminescence spectrometer using a 325 nm laser as the excitation source. 2-3 mg of samples were placed in a hole at the center of plate-type cell, then MOFs were exposed to laser source. All parameters were same for precise comparison between Zr-based MOFs and Zr/Ti-based MOFs.

pH Measurements. pH of photocatalysis solutions were measured using a Thermo

Scientific Origon 3-starpH meter equipped with glass body combination electrode. The pH meter was calibrated by two points method using aqueous buffers of pH 4.01 (Orion pH buffer 910104) and pH 10.01 (Orion pH buffer 910110).

Photocatalytic CO_2 Reduction Experiments. 5 mg of photocatalyst was dispersed in 5 mL of 4:1 (v/v) mixed solution of acetonitrile (MeCN)-triethanolamine (TEOA), which contained 1-benzyl-1,4-dihydronicotiamide (0.1 M, BNAH). The suspension was purged by CO_2 gas at a pressure of 1 bar for 30 min. The resulting solution was placed under visible light irradiation using a 300 W Xe arc lamp (Newport, 6258, using a Newport 66983 power supply) equipped with two cut-off filters to ensure visible light irradiation (420 nm $< \lambda <$ 800 nm). Cooling water circulation was provided for heat dissipation. The distance between the reaction vessel and the visible light source was 5 cm and the intensity of incident light was 100 mW/cm^2 (measured by a radiometer (FieldMaxII equipped with PowerMax, Coherent). The reaction products, including formic acid, were extracted following reported procedure.[S3] After 6 h of photocatalysis, the suspension was subjected to centrifugation at 7000 rpm for 15 min using a Hettich Rotana 460R centrifuge equipped with as A5615 fixed-angle rotor to remove the photocatalyst. The products were extracted using 3 mL of ethyl acetate. The ethyl acetate solution was washed with 3 mL of 0.5 M H_2SO_4(aq) three times. 1 μL of the ethyl acetate solution containing the extracted products was injected into a GC-MS (Agilent, GC-7890A and MS-5975C) equipped with a capillary column (Supleco, 30m × 0.32mm) and MSD (Mass selective detector, inert triple-axis detector) to identify the reaction products. The initial temperature of oven was 130 °C and maintained for 5 min followed by ramping up to 230 °C at a rate of 10 °C/min. Finally, the oven was maintained at 230 °C for 25 min. Helium was used as the carrier gas. The MOFs collected after photocatalysis (see above) were washed with MeOH (3×10 mL) and dried under vacuum at 60 °C for analysis by

PXRD, ICP-MS, and for retesting for catalytic recyclability.

Liquid ^{13}C NMR of CO_2 Isotopes. ^{13}C NMR samples were prepared under the same photocatalysis reaction conditions described above section, but using a deuterated solvent and an isotope of CO_2. CD_3CN (Cambridge, 99.8% D) was used instead of CH_3CN as solvent and $^{13}CO_2$ (Aldrich, 99% ^{13}C, ~3% of ^{18}O) was used for purging gas instead of $^{12}CO_2$. After 13 h of photocatalysis, the MOFs were collected via centrifugation (as described above) and the supernatant was directly transferred to an NMR tube for analysis using a 400 MHz NMR (Agilent, 400MHz 54mm NMR DD2). $H^{13}COOH$ (Aldrich, 95 wt% in H_2O, 99% ^{13}C) was used to calibrate a chemical shift of $H^{13}COOH$ in CD_3CN and deprotonated $H^{13}COO^-$ in basic CD_3CN/TEOA solutions.

Supporting Information Tables

	Initial	After 1 cycle	After 2 cycles	After 3 cycles
1(Zr/Ti)	2.52	2.86	3.13	3.42
UiO-66(Zr/Ti)-NH_2	3.03	4.15	5.42	7.06

Table S1. The ratio between Zr and Ti in **1(Zr/Ti)** and UiO-66(Zr/Ti)-NH_2 after each round of photocatalysis.

	Zr (experimental)	Zr (theoretical)	Ti (experimental)	Ti (theoretical)
1(Zr)	30.1 wt%	31.0 wt%	-	-
1(Zr/Ti)	23.3 wt%	-	4.8 wt%	-
Ti@**1(Zr)**[a]	-	29.2 wt%	-	6.1 wt%

[a] Ti@**1(Zr)** = $Zr_6O_4(OH)_4(C_8H_7O_4N)_{5.17}(C_8H_8O_4N_2)_{0.83}\bullet Ti_{2.37}$, model for **1(Zr)** with non-specific Ti loading where Zr(IV) is not replaced by Ti(IV) in SBUs of **1(Zr)**.

Table S2. ICP-MS results for **1(Zr)** and **1(Zr/Ti)**. These results indicate that Zr(IV) in inorganic clusters in MOF was substituted by Ti(IV) during PSE.

Name	Photosensitizer	Solvent	TOF (h^{-1})	Reference
TiO_2/Graphene	None	1M NaOH	0.004	*J. Air Waste Manag. Assoc.*, **2014**, 64, 578
TiO_2	Cu porphyrin	$H_3PO_{4(aq)}$	0.0024	*Molecules*, **2015**, 20, 396
ZnS	None (UV light)	Water Isopropanol	0.02	*Appl. Catal. B*, **2015**, *in press*
MWCNT/TiO_2	None (UV light)	Water	0.002	*Carbon*, ***2007***, *45, 717*
1(Zr/Ti)	None	MeCN/TEOA BNAH	1.04	This work

Table S3. Photocatalytic ability of MOFs compared to non-MOF, heterogeneous systems for the reduction of CO_2 to HCOOH. **1(Zr/Ti)** showed much higher TOF values when compared to various heterogeneous systems.

Name	Photosensitizer	Solvent	TOF (h^{-1})	Reference
MOF-253-Ru(CO_2)Cl	None	MeCN/TEOA	0.363	*Chem. Commun.* **2015**, 2645
MOF-253-Ru(CO_2)Cl	Ru(bpy)$_3$Cl$_2$	MeCN/TEOA	4.475	*Chem. Commun.* **2015**, 2645
Y-Ir(bpy)(ppy)$_2$(COOH)$_2$	None	MeCN/TEOA	0.095	*Chem. Sci.* **2014**, *5*, 3803
NH_2-MIL-125(Ti)	None	MeCN/TEOA BNAH	0.253	This work
1(Zr/Ti)	None	MeCN/TEOA BNAH	1.04	This work

Table S4. Photocatalytic ability of **1(Zr/Ti)** compared to other MOF-based photocatalytic systems reported in the literature. **1(Zr/Ti)** showed higher TOF number than MOF photocatalytic systems that do not utilize noble metals. The photocatalytic systems containing noble metal light sensitizers showed better efficiency than **1(Zr/Ti)**.

Supporting Information Figures

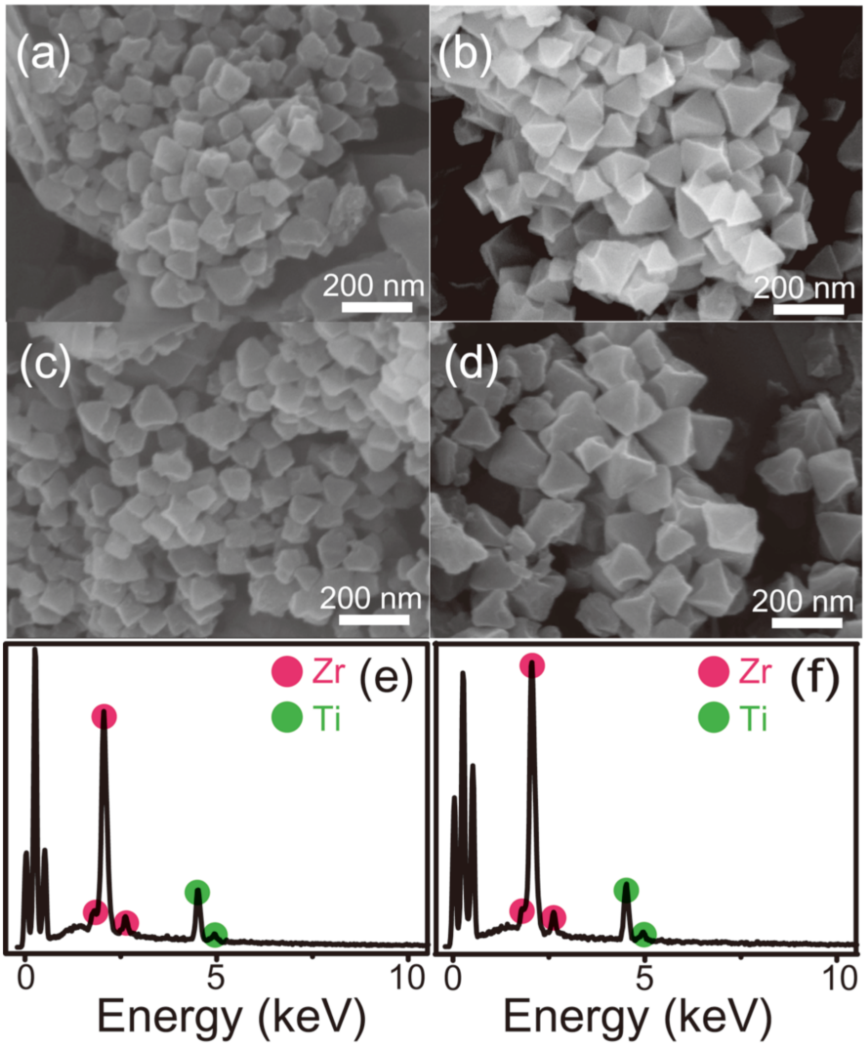

Fig. S1. Scanning electron microscope images of (a) **1(Zr)**, (b) UiO-66(Zr)-NH_2, (c) **1(Zr/Ti)**, (d) UiO-66(Zr/Ti)-NH_2. Energy-dispersed X-ray analysis results of (e) **1(Zr/Ti)** and (f) UiO-66(Zr/Ti)-NH_2.

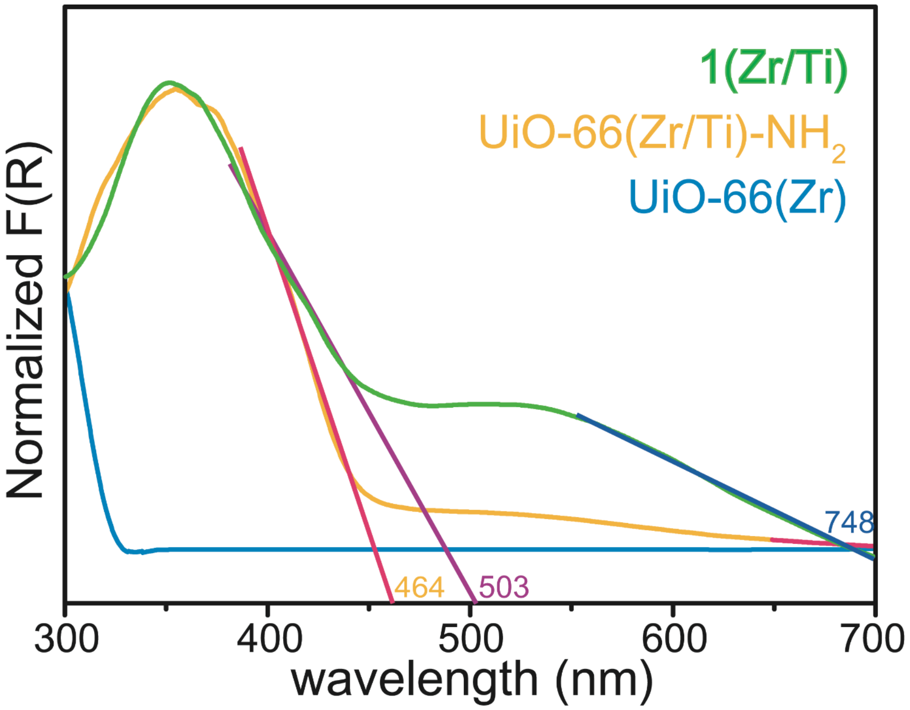

Fig. S2. Diffuse reflectance spectra of UiO-66 materials. Two band edges were obtained for **1(Zr/Ti)** at 503 nm and 748 nm, and the band edge for UiO-66(Zr/Ti)-NH_2 was 464 nm (tangent lines shown).

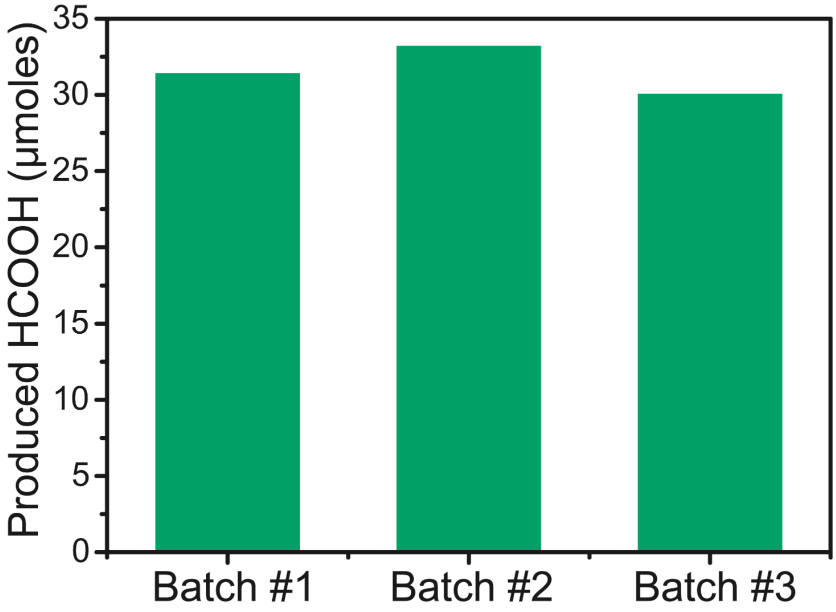

Fig. S3. Amounts of photocatalytically generated HCOOH from CO_2 by different three batches of **1(Zr/Ti)**.

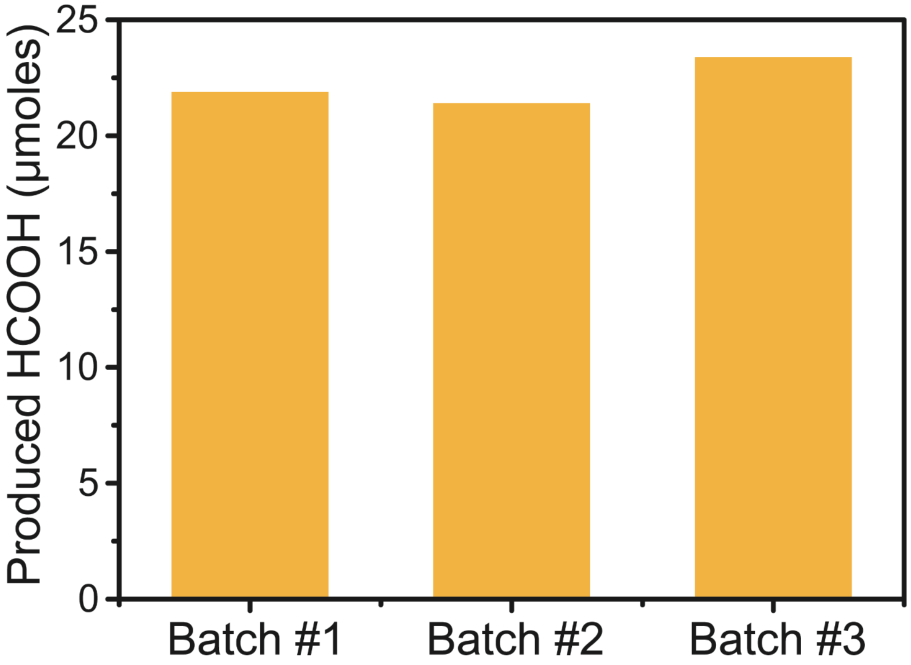

Fig. S4. Photocatalytic ability of UiO-66(Zr/Ti)-NH_2. UiO-66(Zr/Ti)-NH_2 produced 22.23 μmoles of HCOOH (average of three independent samples).

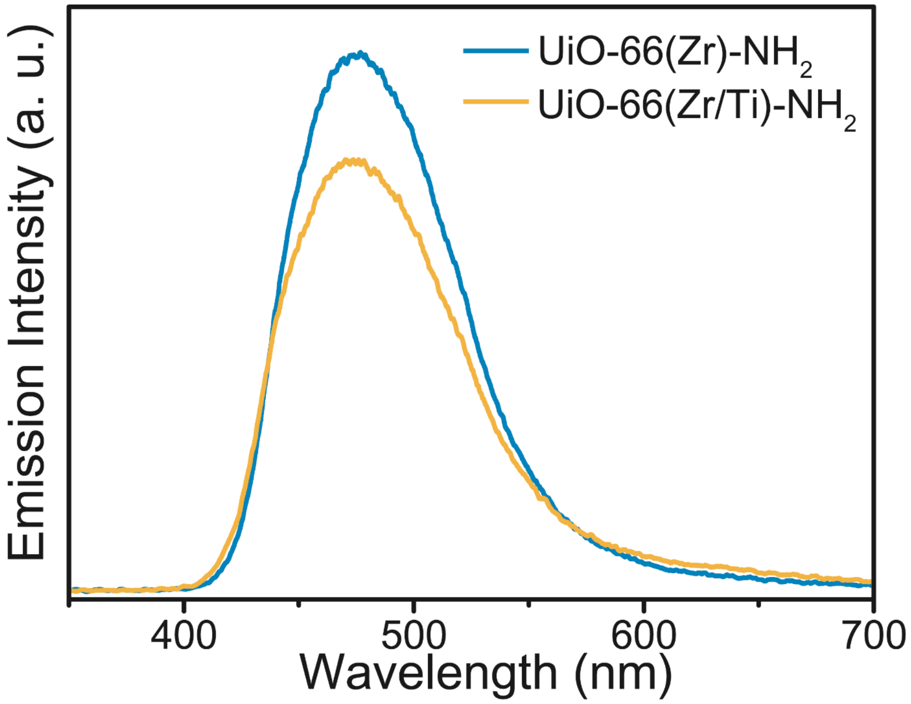

Fig. S5. Photoluminescence spectrum of UiO-66(Zr)-NH_2 and UiO-66(Zr/Ti)-NH_2.

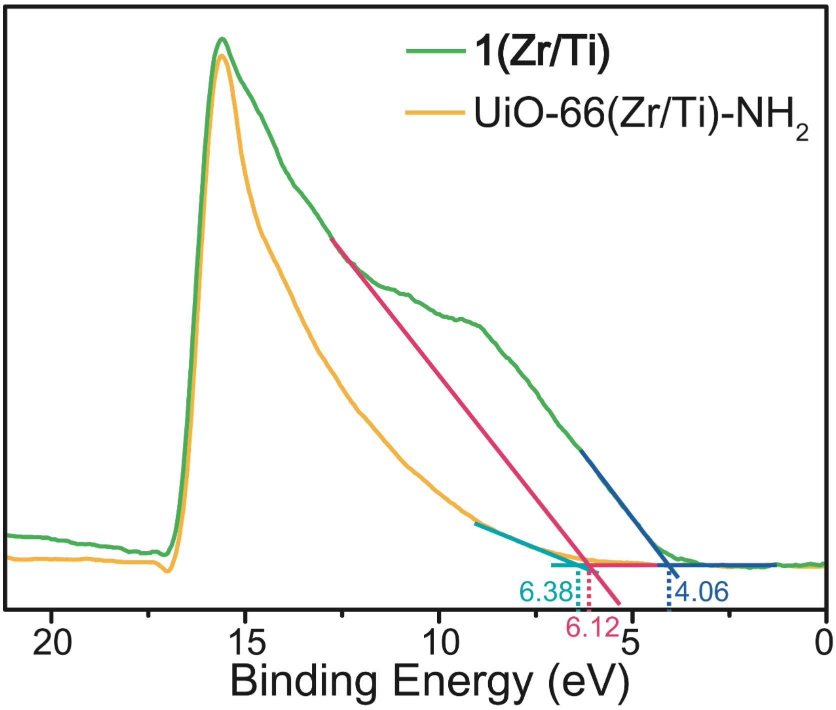

Fig. S6. UV-light Photoelectron spectrum of **1(Zr/Ti)** and UiO-66(Zr/Ti)-NH_2. Edge values for valence band maxima of MOFs were calculated using double tangents (shown).

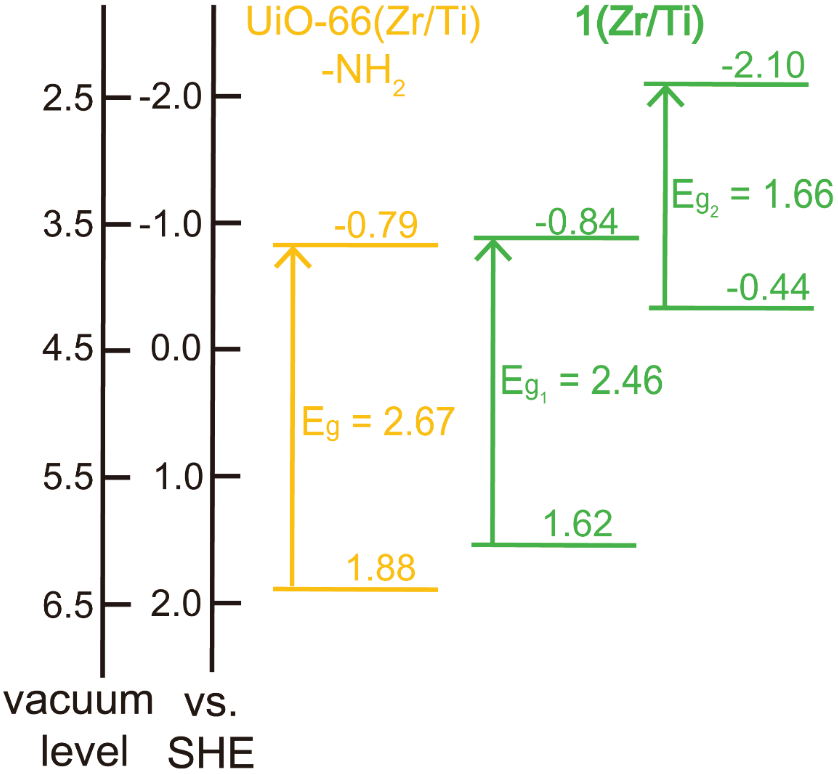

Fig. S7. Energy band structure of both **1(Zr/Ti)** and UiO-66(Zr/Ti)-NH_2.

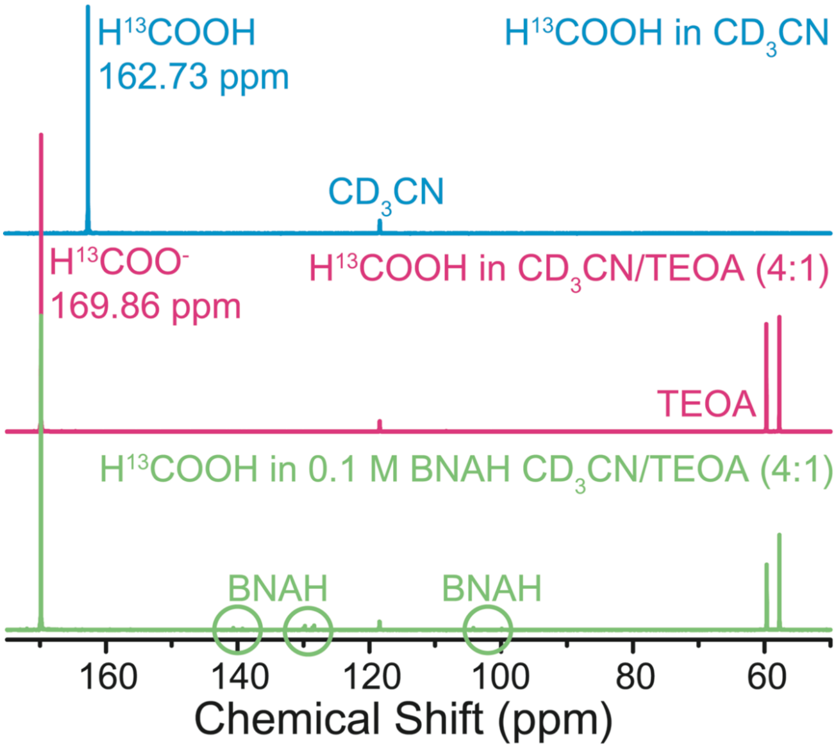

Fig. S8. ^{13}C liquid NMR reference spectra for assigning $H^{13}COO^-$, TEOA, and BNAH.

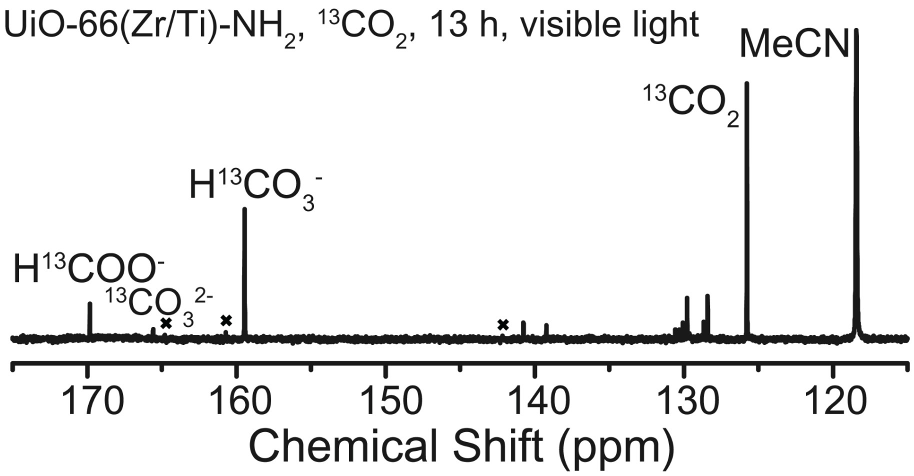

Fig. S9. ^{13}C liquid NMR spectrum of product from CO_2 photocatalysis by UiO-66(Zr/Ti)-NH_2. ✖ = possible impurities produced by decomposition of MOFs.

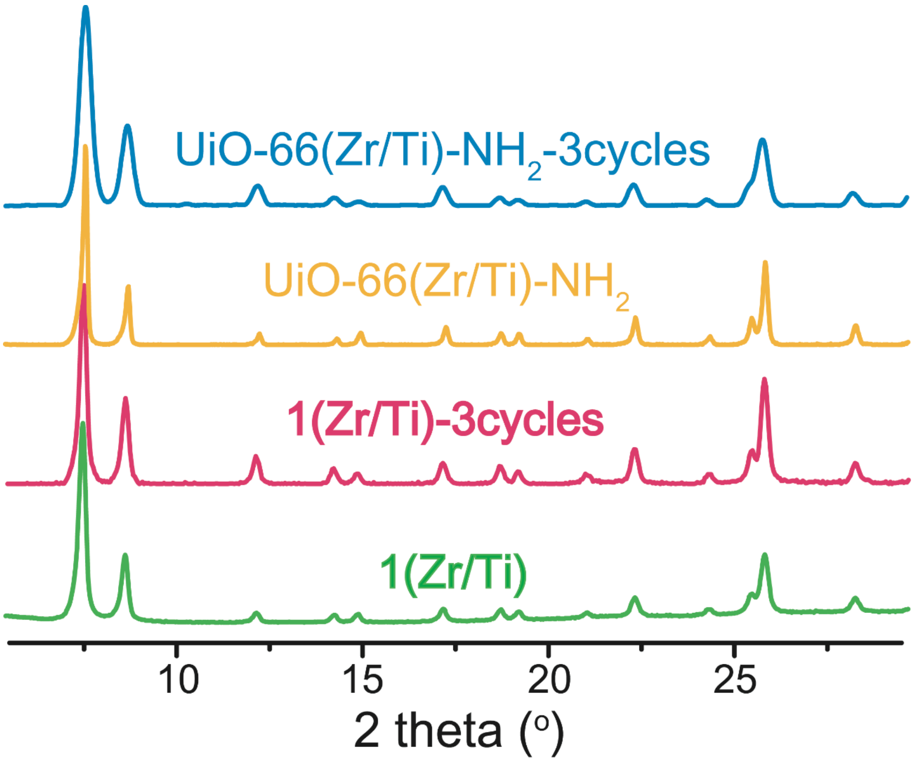

Fig. S10. PXRD patterns of **1(Zr/Ti)** and UiO-66(Zr/Ti)-NH$_2$ before and after three photocatalytic cycles.

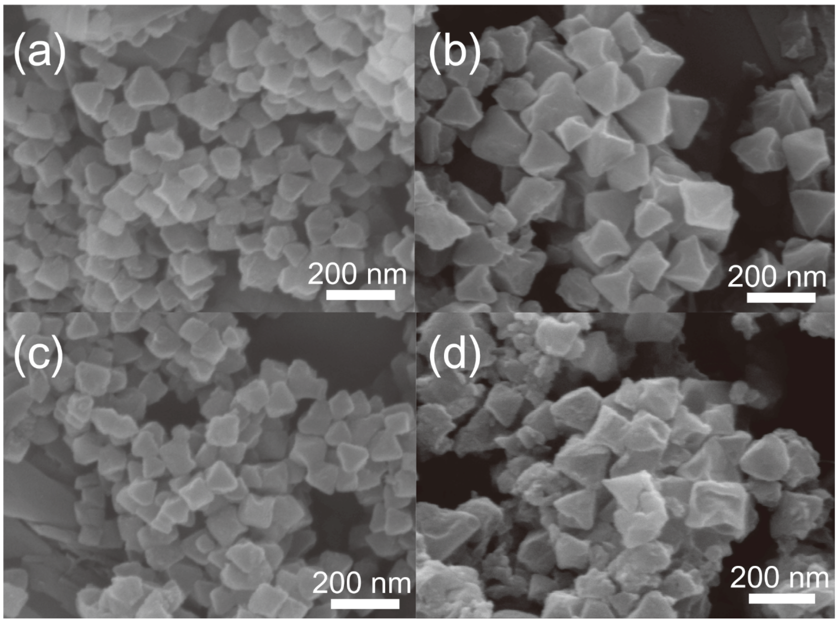

Fig. S11. SEM images of (a) **1(Zr/Ti)**, (b) UiO-66(Zr/Ti)-NH$_2$ before and (c) **1(Zr/Ti)**, (d) UiO-66(Zr/Ti)-NH$_2$ after three photocatalytic cycles.

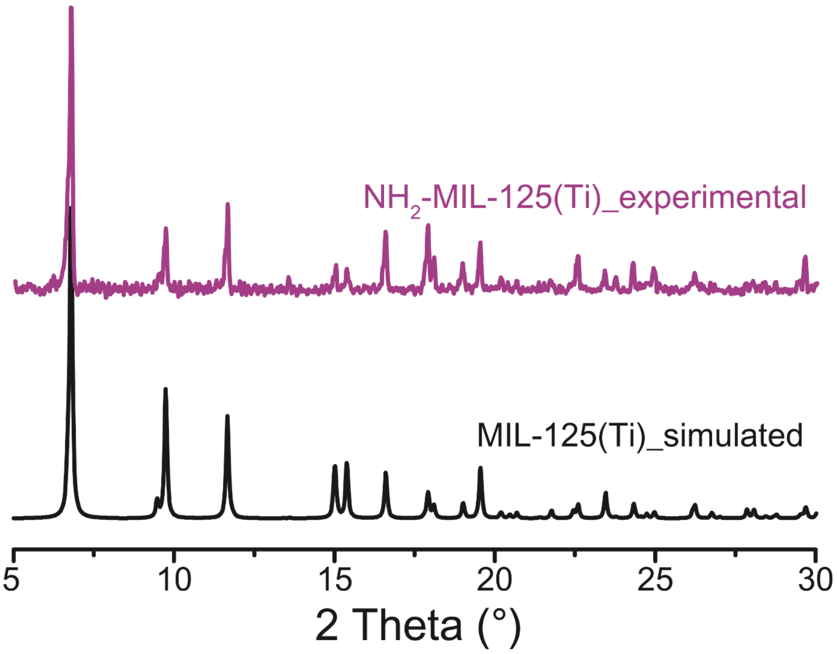

Fig. S12. PXRD pattern from NH$_2$-MIL-125(Ti) and calculated PXRD pattern of MIL-125(Ti) based on a reported crystal structure in the literature.[S4]

Reference

S1) M. Kim, J. F. Cahill, H. Fei, K. A. Prather and S. M. Cohen, *J. Am. Chem. Soc.* **2012**, *134*, 18082-18088

S2) Y. Horiuchi, T. Toyao, M. Saito, K. Mochizuki, M. Iwata, H. Higashimura, M. Anpo and M. Matsuoka, *J. Phys. Chem. C* **2012**, *116*, 20848-20853

S3) H. Takeda, H. Koizumi, K. Okamoto and O. Ishitani, *Chem. Commun.* **2014**, *50*, 1491-1493

S4) M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Férey, *J. Am. Chem. Soc.* **2009**, *131*, 10857-10859