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Electronic Supplementary Information

A Highly Active, Robust Photocatalyst Heterogenized in Discrete Cages of Metal-Organic Polyhedra for CO_2 Reduction

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Supplementary Information Table of Contents

Section S1. *Details for Sample preparation*

1. Materials

All reagents were obtained from Sigma-Aldrich and were used without further purification unless otherwise mentioned.

Synthesis of $[(CP_3Zr_3O(OH)_3)_4(BPDC_{0.85}ReTC_{0.15})_6]$, ReTC-MOP. The ReTC-MOP was prepared by two linkers of 2,2′-dibiphenyl-4,4′-dicarboxylic acid (H_2BPDC) and H_2ReTC ($Re^I(CO)_3(BPYDC)(Cl)$, BPYDC=2,2'-bipyridine-5,5'-dicarboxylate). H_2ReTC (6.3 mg, 0.012 mmol), H_2BPDC (13.9 mg, 0.058 mmol) and bis(cyclopentadienyl)zirconium dichloride (CP_2ZrCl_2, 40.3 mg, 0.138 mmol) were dissolved in a solution mixture of DMA (2 ml) and DI water (0.15 ml) in a 20 ml screw-capped vial and followed heating at 85 °C for 16 h. The orange precipitate were washed three times with DMA using a centrifuge (8000 rpm for 10 min) and sequentially immersed in methanol for 24 h. Finally, the samples were collected by removing the solvent under vacuum for 12 h at room temperature. The ReTC-MOP identified by the combination of inductively coupled plasma optical emission spectroscopy (ICP-OES) and ^1H NMR spectrum of a digested solution with HF. The ReTC contents in ReTC-MOP was determined by ICP-OES to 4.88 wt%. Molar ratio of ReTC to linkers $[mol_{ReTC}/(mol_{bpdc} + mol_{ReTC})]$ was calculated from the ICP-OES results, coordinating 0.9 ReTC to Zr in unit cell.

Synthesis of $[Zr_6O_4(OH)_4(BPDC_{0.9}\ ReTC_{0.1})_6]$, ReTC-MOF (nano): H_2ReTC (4.4 mg, 0.008 mmol), H_2BPDC (7.8 mg, 0.032 mmol) and $ZrCl_4$ (9.3 mg, 0.04 mmol) were dissolved in a solution mixture of DMF (10 ml)/ acetic acid (0.5 ml) in a 20 ml screw-capped vial and heating at 85 °C for 12 h. The orange suspensions was washed with DMF once and methanol three times using a centrifuge (8000 rpm for 10 min). The ReTC contents in ReTC-MOF (nano) was determined by ICP-OES to 5.45 wt%. Molar ratio of ReTC to linkers [$mol_{ReTC}/(mol_{BPDC} + mol_{ReTC})$] was calculated from the ICP-OES, coordinating 0.6 ReTC to Zr in unit cell.

Synthesis of ReTC-MOF (micro): H_2ReTC (1.80 mg, 0.003 mmol), H_2BPDC (2.907 mg, 0.012 mmol) and $ZrOCl_2{\cdot}8H_2O$ (3.040 mg, 0.009 mmol) were dissolved in a solvent mixture of DEF/ formic acid (1.6 mL/3.3 mL) in a 20 mL vial. The mixture was heated at 140 °C for 48 h. Orange octahedral crystals were collected and washed three times with fresh DMF.

Synthesis of BPDC-MOP. H_2BPDC (33.4 mg, 0.069 mmol) and CP_2ZrCl_2 (40.3 mg, 0.138 mmol) were dissolved in a solution mixture of DMA (2 ml) and DI water (0.15 ml) in a 20 ml screw-capped vial and followed heating at 85 °C for 16 h. The white precipitate was collected and washed three times with DMA using a centrifuge (8000 rpm for 10 min) and then sequentially immersed in methanol for 24 h. Finally, the samples were collected by removing the solvent under vacuum for 12 h at room temperature.

2. Characterization

For high-angular dark-filed (HAADF) scanning transmission electron microscope observation, samples were first dispersed in an organic solvent by sonication and dropped onto a TEM grid. Additionally, iodine treatment was followed up for obtaining the higher image. HAADF was carried out at 200 kV using a JEOL JEM-2100F. Inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer OTIMA 8300DV) was used to detect the components of ReTC-MOP and ReTC-MOF (nano). It should be enacted the microwave reaction (40 MHz) before detection. Samples (100 mg) were digested using a mixture of nitric acid (0.5 mL), hydrochloric acid (1.5 mL), and hydrofluoric acid (30 μL) and then diluted with 2 vol % of nitric acid solution (10 mL) before measurement. The powder x-ray diffraction spectra (PXRD) were obtained by the Bruker D8 Advance (TRIO/TWIN) at (40 kV, 40 mA). The scanning condition was set up 4 °/min scan rate from 3° to 45° with a silicon holder. Electrospray ionization mass (ESI-MASS) was conducted on Triple Quadrupole LC-Mass spectrometry (Finnigan TSQ Quantum Ultra EMR) with diluted samples in MeOH. The ^{1}H nuclear magnetic resonance (NMR) data was obtained by Bruker Advance III HD500. Samples were digested and dissolved by sonication in a mixture of DMSO-d_6 (dimethyl sulfoxide-d_6, 800 μl) and HF (10 μl). The digested solution was used directly for ^{1}H NMR. For IR, samples were prepared with 1 mg the well-grinded H_2ReTC (ReTC-MOP or BPDC-MOP) and 100 mg of KBr via compression moulding under 2 torr during 1 minute. The pellets were placed in an infrared gas cell equipped with CaF_2 windows and treated under the vacuum of 10 torr at 298 K for 1 h. And IR spectra were recorded at a resolution of 1 cm^{-1} and 100 scans. Gas phase Fourier transform infrared (FT-IR) spectroscopy was performed on a Bruker VERTEX 80V spectrometer equipped with Schlenk flask and an infrared gas cell with CaF_2 windows and recorded at the resolution of 0.25 cm^{-1} and 100 scans. *In situ* Attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy was performed on a Bruker VERTEX 80V spectrometer equipped with a single reflection silicon ATR module and the high energy broadly tunable lasers EKSPLA NT340. The solutions for photocatalytic CO_2 conversion were irradiated with 320 nm laser emission at 2600 mJ. And to prevent evaporation of solvent, liquid samples kept covered. The ATR FT-IR spectra every 30 min were recorded at the resolution of 1 cm^{-1} and 100 scans.

Section S2. *Details for photocatalytic measurement*

Photocatalytic CO_2 reduction experiment was conducted in CO_2-saturated acetonitrile (MeCN) with triethylamine (TEA) as a sacrificial reducing agent. (MeCN/TEA = 20/1, v/v; CO_2 gas = 99.999 % high purity) Samples were prepared in 50 ml septum-sealed glass vial with the mixture of 20 ml of MeCN and 1 ml of TEA. In cases of ReTC-MOP and ReTC-MOF, these samples typically contained 0.24 μmol of the fixed ReTC linker in the specific structures of ReTC-MOF and ReTC-MOP, whereas the free molecular catalyst of H_2ReTC involved 0.5 μmol of H_2ReTC in solution. Prepared glass vials were capped and saturated with CO_2 at the flow rate of 100 cc/min for 10 min. The vials were placed 43 cm in front of a 300 W Xe-lamp with the cutoff filter with magnetic stirring. The CO_2 reduction lasted for 24 h. And the gas in the headspace of the vial was analyzed by GC to determine the amount of the converted CO from CO_2. The turnover numbers (TON) was defined as the molar amount of generated CO to the molar amount of the catalyst. And, the turnover frequencies (TOF) was derived from the turnover number per the reaction time.

* Turnover number and turnover frequence calculation

For the CO_2 conversion, the turnover number (TON) and turnover frenquency (TOF) are calculation using the equations below.

TON = (the molar amount of CO production) **/** (the molar amount of catalyst)

TOF = (the molar amount of CO production) **/** [(the molar amount of catalyst) × (reaction time)]

* GC analysis conditions for photocatalytic CO_2 reduction experiments

- GC model: Agilent Technologies, 7890B
- Carrier gas: Ar
- Column: Agilent Porapak Q, G3591-80013
- Detector: FID
- Temperature program (total analysis time: 23min): 1) keep at 40 ℃ for 3 min, 40 ℃, 2) 200 ℃ with 8 ℃/ min
- Retention times (min) of the products: 1.03 min for CO, 1.60 min for CH_4, 3.36 min for CO_2

*** Ion chromatography (IC) analysis conditions for formic acid**

- IC model: Dionex Aquion
- Conductivity detector
- Column: Dionex IonPac AS 22 (4 mm × 150 mm)
- Flow rate: 0.6 mL/min
- Eluent solvent: a mixture of 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$

Section S3. *Structural scheme of ReTC-MOP, ReTC-MOFs and BPDC-MOP*

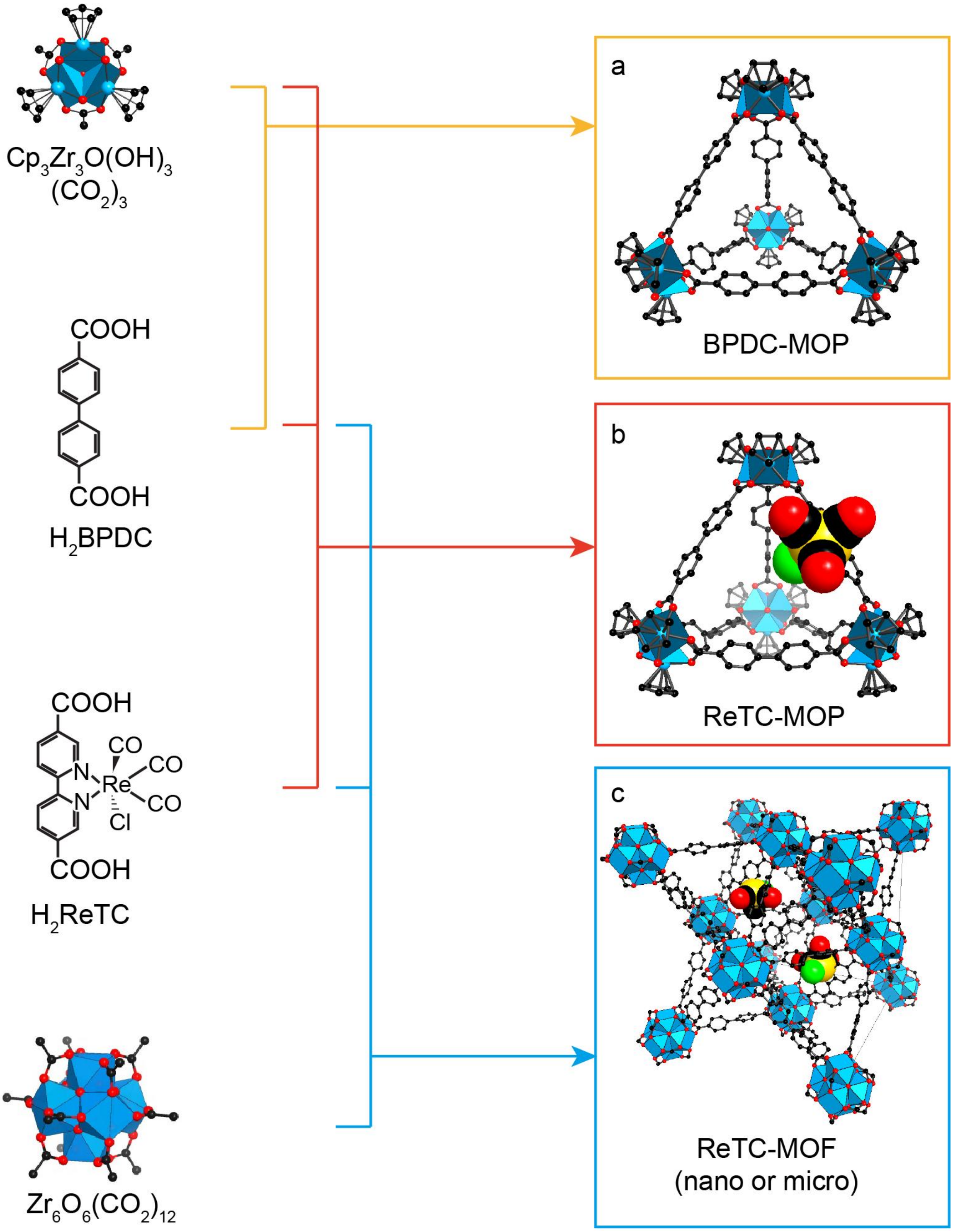

Fig. S1. Structural scheme of photocatalysts for CO_2-CO conversion. a) BPDC-MOP, b) ReTC-MOP, c) ReTC-MOF (nano or micro). Atom labeling scheme: C, black; O, red; Zr, blue polyhedra; Re, yellow; Cl, green; H atoms are omitted.

Section S4. *Supplementary characterization of ReTC-MOP, ReTC-MOFs and BPDC-MOP*

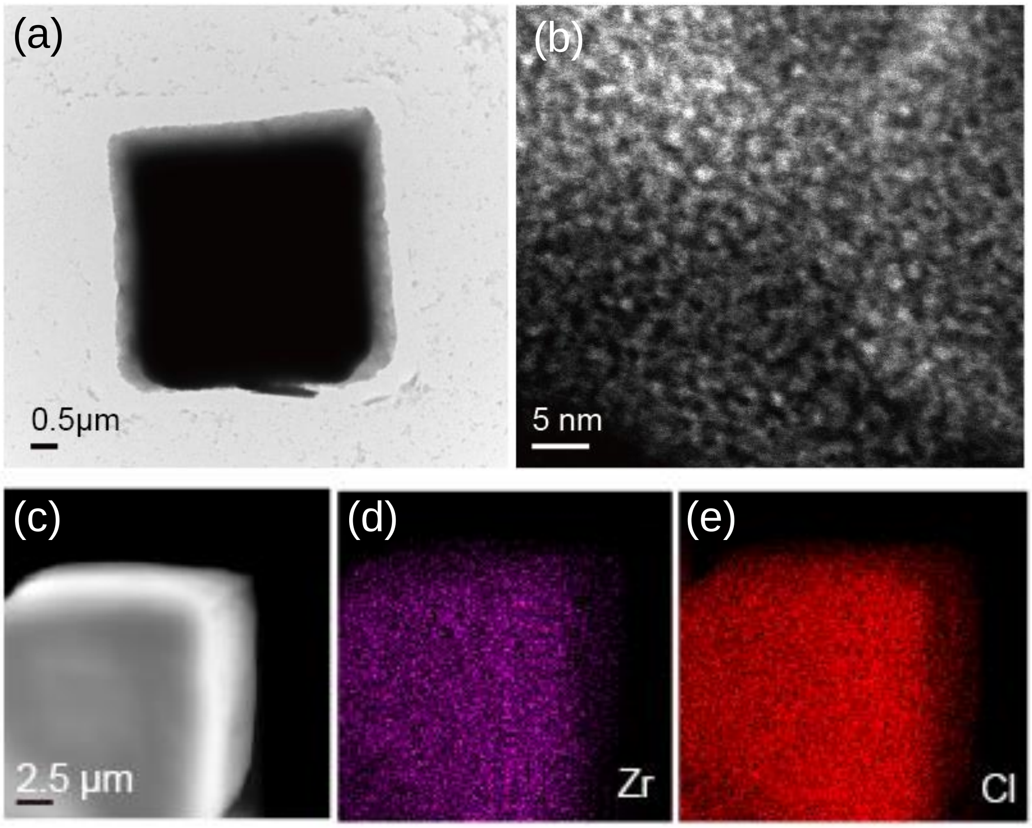

Fig. S2. STEM images of (a) “BPDC-MOP crystal” and (b) BPDC-MOP; additionally treated with iodine for 2h to improve image quality. (c-e) EDX elemental mapping image of BPDC-MOP.

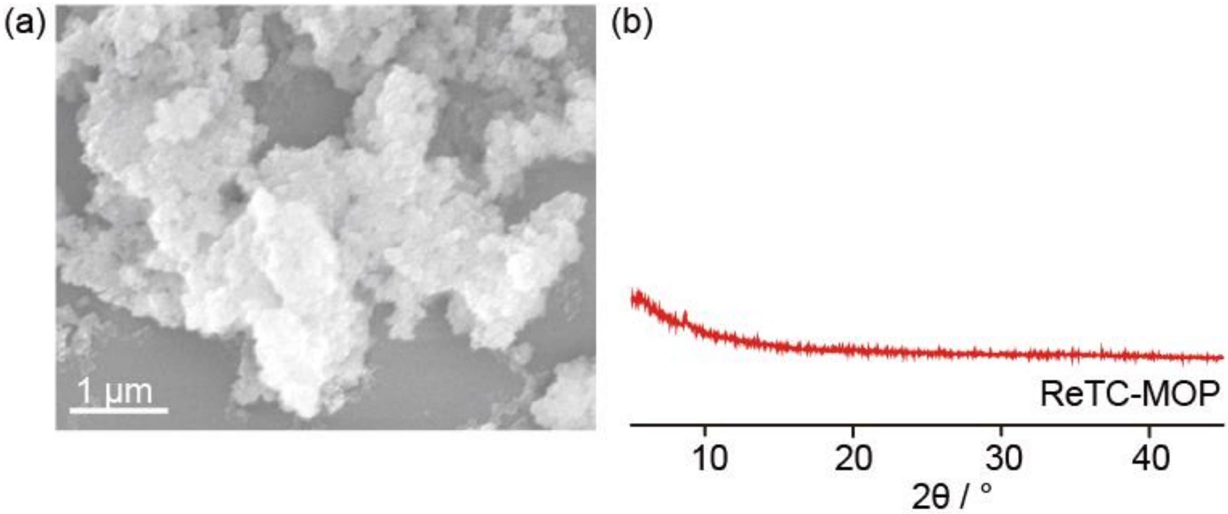

Fig. S3. (a) SEM image and (b) XRD pattern of unpacked ReTC-MOP.

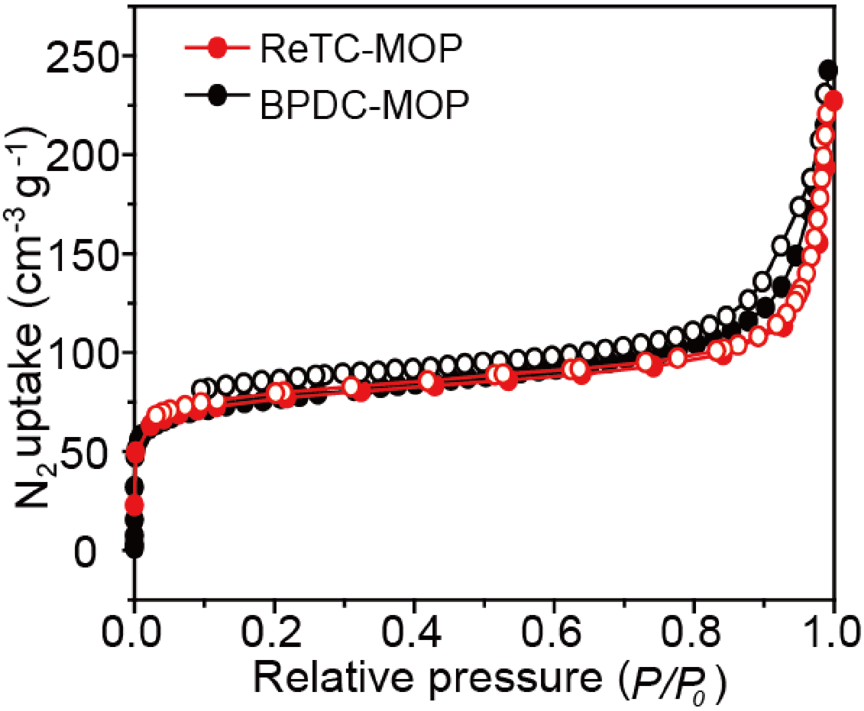

Fig. S4. N_2 adsorption-desorption isotherms for BPDC-MOP and ReTC-MOP. Solid and open circles represent adsorption and desorption branches, respectively.

Gas adsorption analysis was performed on a Quntachrome Instrument Quadrasorb-SI automatic volumetric gas adsorption analyzer. A liquid nitrogen bath (77 K) and ultra-high purity grade N_2 and He (99. 999%, Praxair) were used for the N_2 adsorption–desorption isotherms. Samples were prepared and measured after evacuating at 100 °C for 24 h.

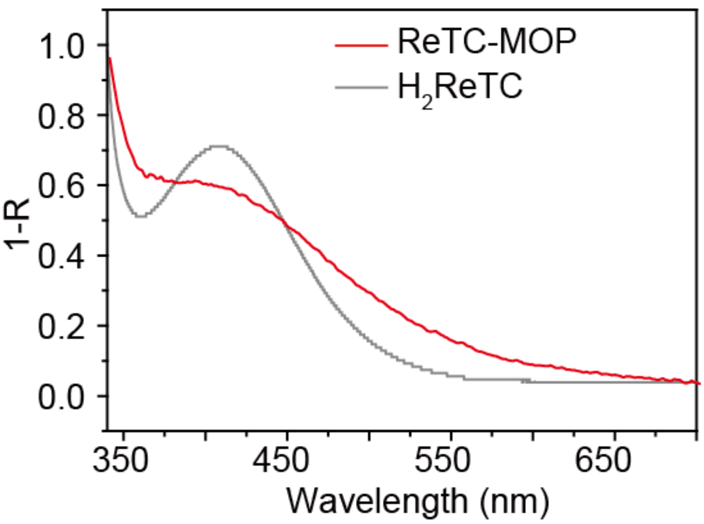

Fig. S5. N_2 adsorption-desorption isotherms for BPDC-MOP and ReTC-MOP. Solid and open circles represent adsorption and desorption branches, respectively.

Section S5. *Supplementary data for photocatalytic performances*

Fig. S6. Image of the ReTC-MOP containing solution for photocatalytic reaction.

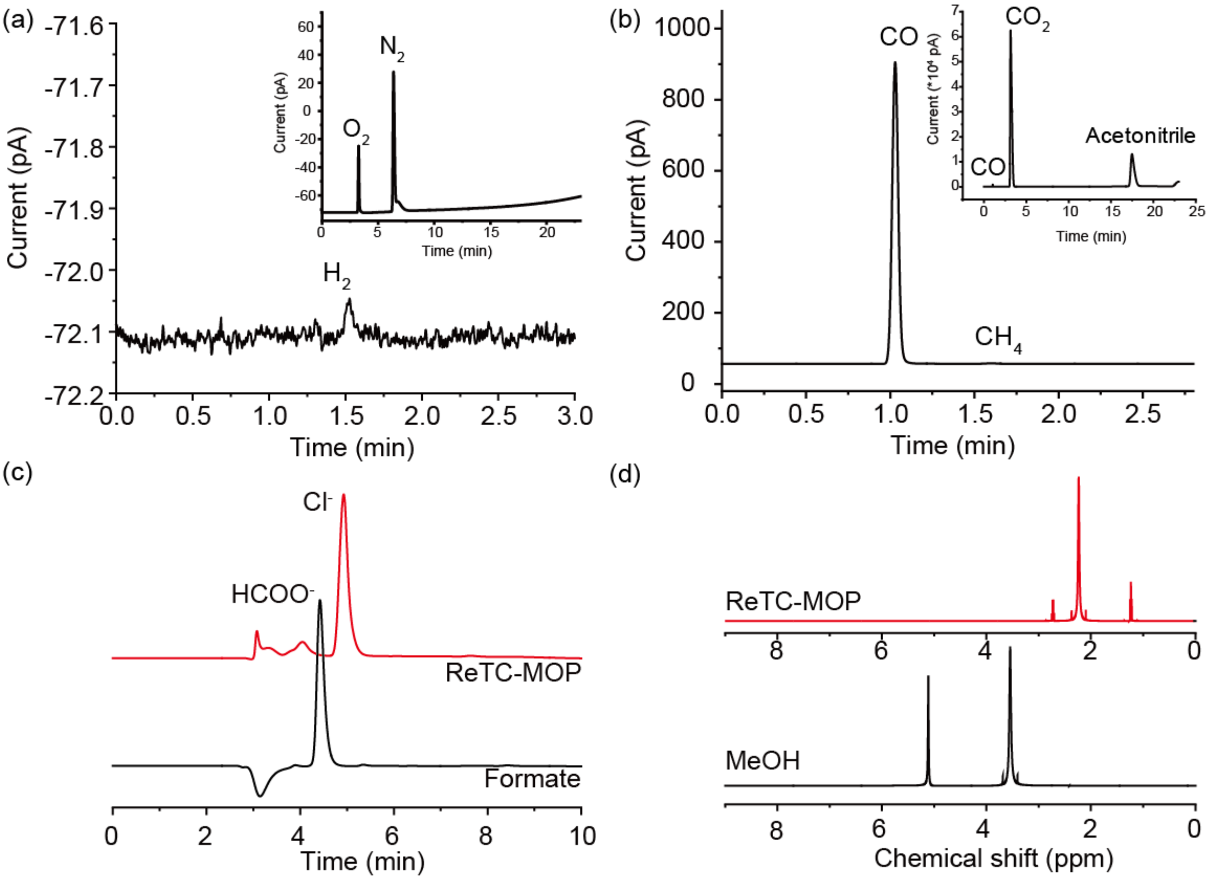

Fig. S7. GC results for confirming the produced (a) H_2 and (b) CH_4 (inset: GC results for full analysis time) (c) Ion chromatography results for the derived formate from ReTC-MOP (top) and formate stock solution (bottom). (d) NMR results for the derived methanol from ReTC-MOP (top) and methanol (bottom).

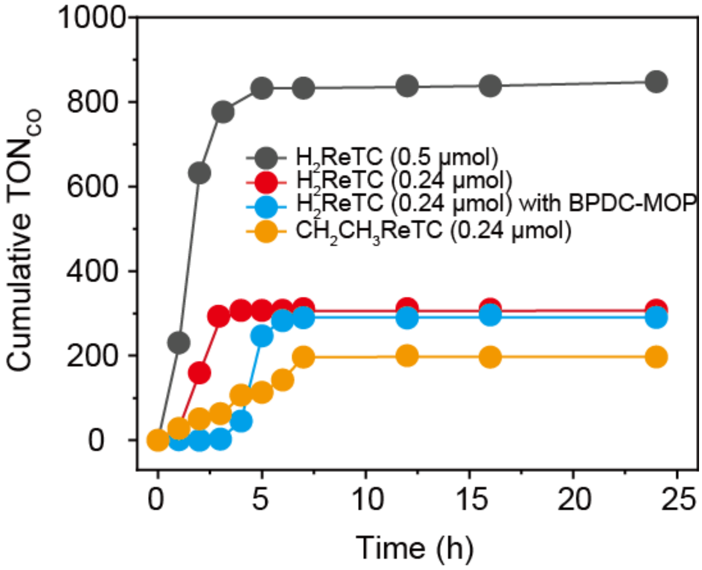

Fig. S8. Cumulative TON values of molecular photocatalysts over 24 h.

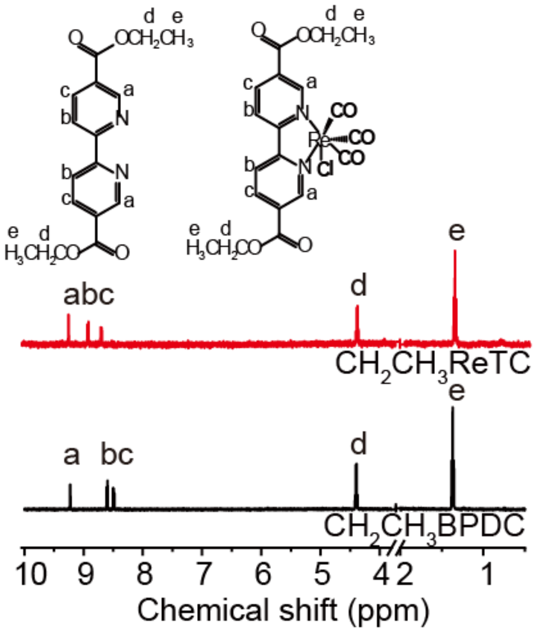

Fig. S9. ^{1}H NMR spectrum for CH_2CH_3BPDC (diethyl [2,2-bipyridyl]-5,5-dicarboxylate is termed as CH_2CH_3BPDC) and CH_2CH_3ReTC.

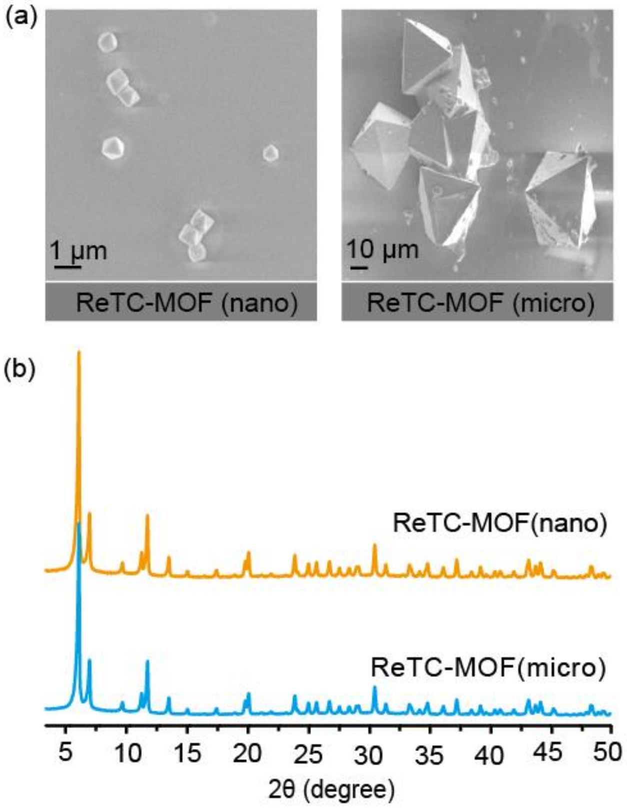

Fig. S10. Characterization of ReTC-MOF (nano) and ReTC-MOF (micro). (a) SEM images. (b) PXRD patterns.

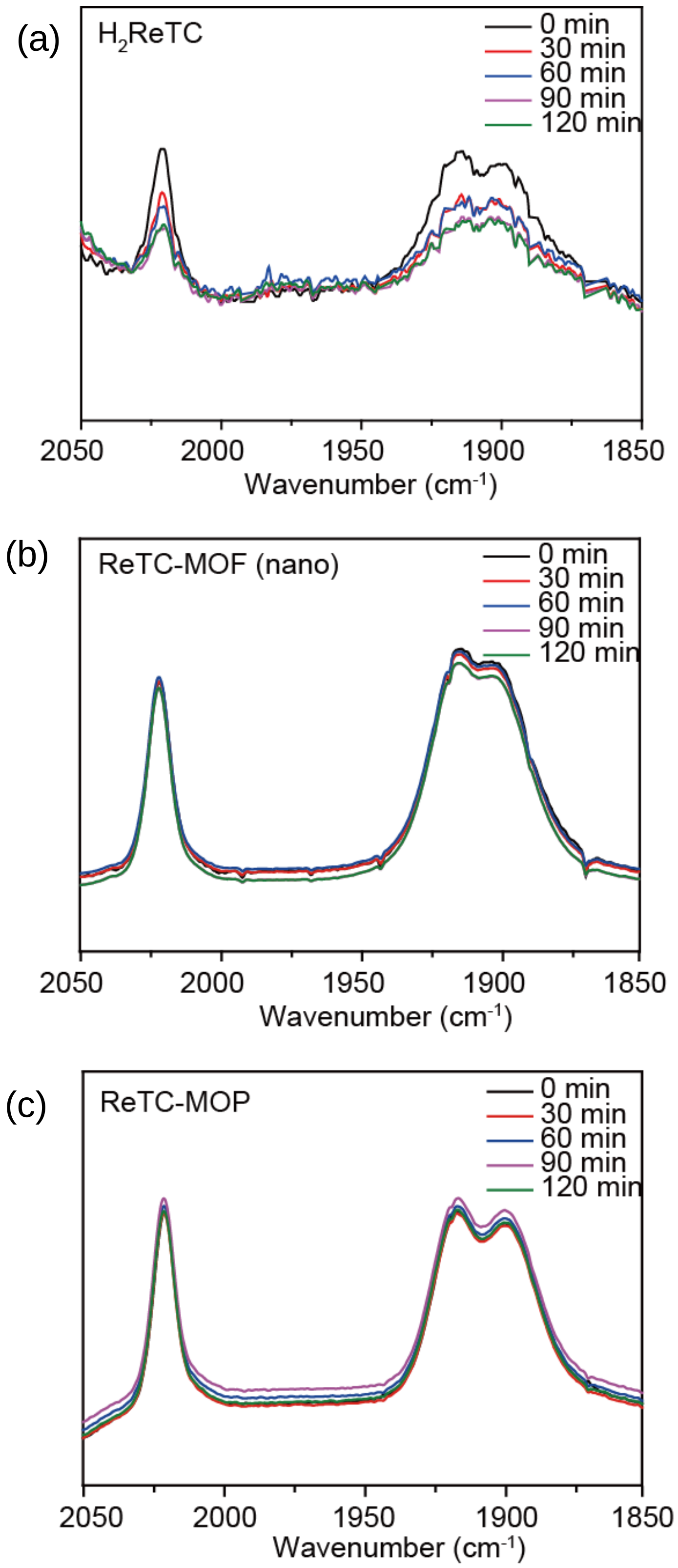

Fig. S11. *In-situ* ATR FT-IR spectra of (a) H_2ReTC, (b) ReTC-MOF (nano) and (c) ReTC-MOP after photocatalytic CO_2 to CO conversion in different time interval (measured every 30 min).

In situ Attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy was performed on a Bruker VERTEX 80V spectrometer equipped with a single reflection silicon ATR module and the high energy broadly tunable lasers EKSPLA NT340. The solutions were irradiated with 320 nm laser emission at 2600 mJ for 120 min. And to prevent evaporation of solvent, liquid samples kept covered. The ATR FT-IR spectra every 30 min were recorded at the resolution of 1 cm^{-1} and 100 scans. H_2ReTC, ReTC-MOF (nano) and ReTC-MOP for photocatalytic reaction were prepared at the concentration of 66 μM with acetonitrile and TEA (20/1, v/v). The 60 μl of the solutions was dropped onto the plate of a single reflection silicon ATR module and then immediately covered to prevent evaporation of solvent. And then, these solutions were saturated with $^{12}CO_2$ of 99.999 % purity at the flow rate of 10 cc/min for 1 min and followed the photocatalytic reaction with the aligned laser for 120 min.