Electronic Supplementary information

Two Dimensional Covalent Organic Framework Materials for Chemical Fixation of Carbon Dioxide: Excellent Repeatability and High Selectivity

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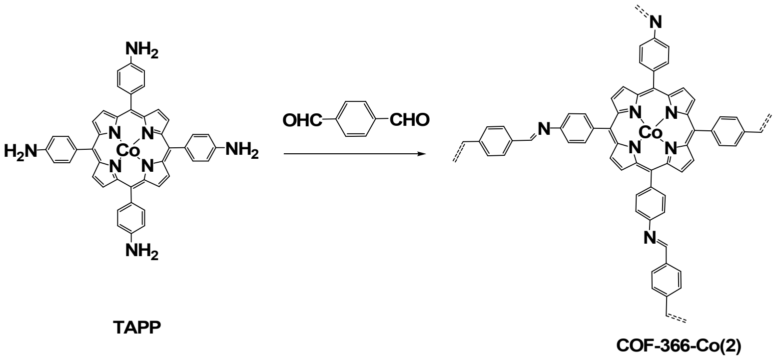
Section S1. Materials and methods

Materials

Unless otherwise stated, all chemicals in this research were commercial available and used without further purification. Propylene oxide (PO), zinc acetate $[Zn(OAc)_2 \bullet 2H_2O]$, cobalt acetate $[Co(OAc)_2 \bullet 2H_2O]$, propanoic acid (99 wt%), ehanol, methanol, dichoromethane, tetrahydrofuran (THF), N,N-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P. R. China). Terephthaldehyde, pyrrole, squaric acid tetraphenylposhonium bromide (TPPB), tetrabutyammonium bromide (TBAB), 4-dimethylaminopyridine (DMAP) Phenyltrimethylammonium tribromide (PTAT) were purchased from Energy Chemical. (Shanghai, P.R. China). Pyrrole was freshly distilled before use. Carbon dioxide (CO_2> 99.99%) was obtained from Hua Dong Te Qi Co. Ltd. (Nanchang, P. R. China). The Elem Anal for all the compounds were collected using Elementar EL III.

Synthesis methods

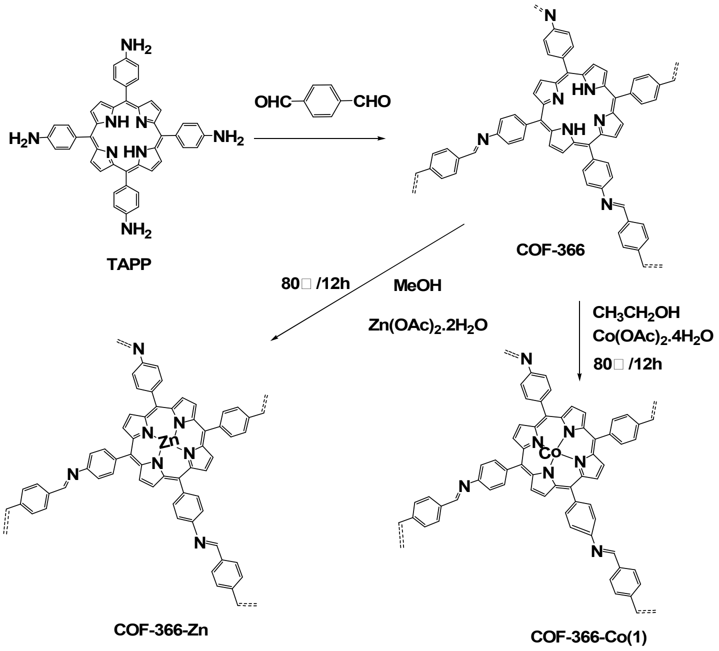
5,10,15,20-tetrakis (4-aminophenyl) porphrin and COF-366 and COF-366-Co(1) were synthesized accord to the reported references[1].



Scheme S1. The synthesis of COF-366-Co(2).

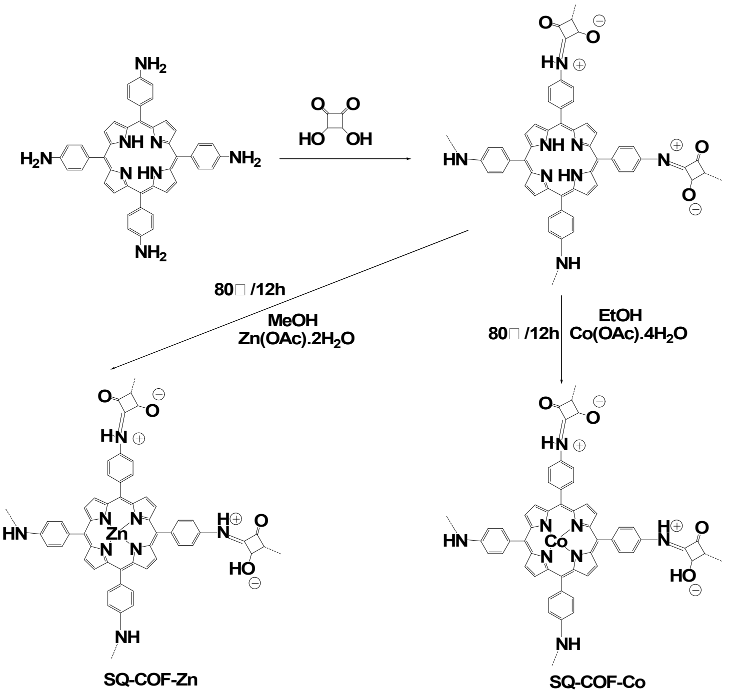
Synthesis of COF-366-Co(1): COF-366-Co(1) was synthesized by direct metallation of free base polymeric porphyrin COF-366 with $Co(OAc)_2$. COF-366 (150 mg) and $Co(OAc)_2 \bullet 4H_2O$ (1.0 g) were added to the ethanol (200 ml). After refluxing for 12 h，the solution was cooled down to room temperature and filtered. The filer cake was washed thoroughly with ethanol. The final filter cake was dried under vacuum overnight to remove absorbed ethanol. Elem. Anal. calcd (%) for COF-366-Co(1)：C，77.67; H, 3.88; N, 12.08. Found: C, 77.93.1; H, 3.79.; N, 11.84.

Synthesis of COF-366-Zn: COF-366-Zn was synthesized following the synthetic procedure used for COF-366-Co(1) except that $Co(OAc)_2{\bullet}2H_2O$ (1.0 g) was replaced by $Zn(OAc)_2{\bullet}2H_2O$ and ethanol was replaced by methanol. Elem. Anal. calcd (%) for COF-366-Zn：C, 77.17; H, 3.58; N, 12.00. Found: C, 77.45.1; H, 3.67.; N, 11.74.



Scheme S2.

Synthesis of COF-SQ：The mixture of TAPP (173.8 mg) and squaric acid (57.0 mg) in n-butanol/o-dichlorobenzene (10 ml, 1/1) was degassed in stainless steel autoclave (15 ml), and then heated at 120℃ for 3 days, The precipitate was collected by filtrated, washed with THF for 10 times and anhydrous acetone for 2 times, and dried at -60℃ under vacuum for 24 h, to give COF-SQ as a dark purple powder[2].



Scheme S3

Section S2. Thermal gravimetric analysis (TGA)

TGA analysis traces for the activated COF-366-Zn samples were collected on a TA Instruments METTLER TOLEDO thermal gravimetric analyzer with the sample held in a platinum pan under air atmosphere with the flow rate of 40 ml/min. Temperature was controlled by the furnace heating from 25℃ up to 900 °C with a ramp rate of 5℃/min.

Section S3. FT-IR spectral profiles

Fourier transform infrared (FT-IR) spectra (4000-400 cm^{-1}) were obtained from KBr pellets using a Bruker TENSORII FT-IR system.

Section S4. PXRD patterns

Powder X-ray diffraction data were collected using a XD-2 Purkinje multi crystal X-ray diffractometer in parallel beam geometry employing Cu Kαradiation at 40 kV, 30 mA. Diffraction intensity data for 2θ from 2 ~ 60° were collected at the scanning speed of 1.504 sec/step with 2θ step increment of 0.2°.

The Pawley PXRD refinements were performed using the Reflex module in the Materials Studio 7.0, in which the Thompson-Cox-Hastings profile function were used for the profile fitting (peak broadening, peak asymmetry and zero shift error were taken into account). Unit cell and sample parameter were refine at the meantime. Before the Pawley PXRD refinements, the unit cell and sample parameter was refined by DFT calculation by VASP.

Section S5. Gas Adsorption Measurements and Non-Local Pore Size Distributions for COF-366-Zn

N_2 adsorption desorption isotherm was tested on ASAP2020 type surface properties analyzer of Micromeritics, before the test, sample is degassing 24 h in vacuum at 130 ℃ .Testing process is carried out in liquid nitrogen at 77 K. The specific surface area of the sample is calculated according to the BET (Brunauer-Emmett-Teller).

Section S6. Catalyzing Reaction

In this reactions, Teraphenylphosphonium bromide (TPPB), tetrabutylammonium bromide (TBAB), Phenyltrimethylammonium bromide (PTAT) and 4-dimethylaminopyridine (DMAP) were selected as co-catalysts. The COF-366-M (M=Zn, Co), co-catalyst (TPPB, TBAB, PTAT or DMAP), epoxides and solvent were placed in a 25 mL stainless autoclave, then charged with CO_2 and the mixture was stirred to start the reaction. The product was analyzed by gas chromatography (GC) with a flame ionization detector (FID). In order to analyze the products qualitatively, the gas chromatography-mass spectrometer (GC-MS) (7890A-5975C Agilent Corporation) equipped with a HP-5 capillary column (Hewllett-Packard, USA, 30 m × 0.25 mm × 0.25 mm)) was also used to identify the components of the product.

Section S7. The reaction mechanism calculated by DFT method.

All calculations were performed using Gaussian 09 package.[3] Theoretical calculations for the geometrical optimizations was performed by density functional theory (DFT) using B_3LYPmethod[4-5]. The 6-311G+ (d,p) basis sets were employed for C, H, O and N atoms, and LanL2dZ ECP used for Zn and Co atoms. We ascertained that all the transition states have only one imaginary frequency through vibrational analysis. Intrinsic coordinate calculations (IRC) were performed to ensure that the transition states led to the expected reactants and products. The vibrational frequency were calculated at the same level to characterize the nature of the stationary points as true minima (with no imaginary frequency) or transition states (with unique imaginary frequency). The zero-point vibrational energy (ZPE) and thermal corrections was also obtained by frequency calculations. The solvent effects have been considered using a relatively simple self-consistent reaction field (SCRF) method, based on the polarizable continuum model (PCM). The solvent used in this calculation is CH_3CN.

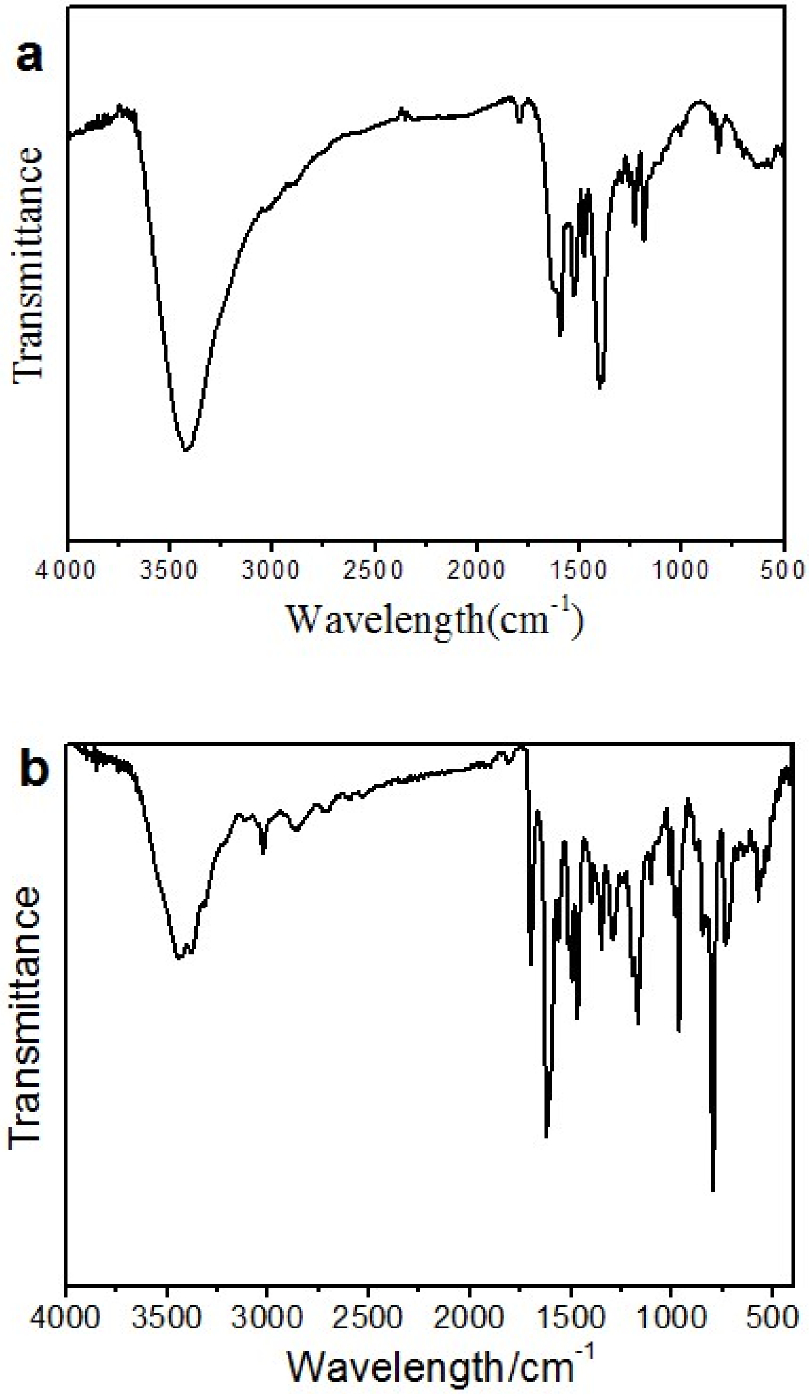


Figure S1. FT-IR spectra of COF-SQ (a) and COF-366 (b).

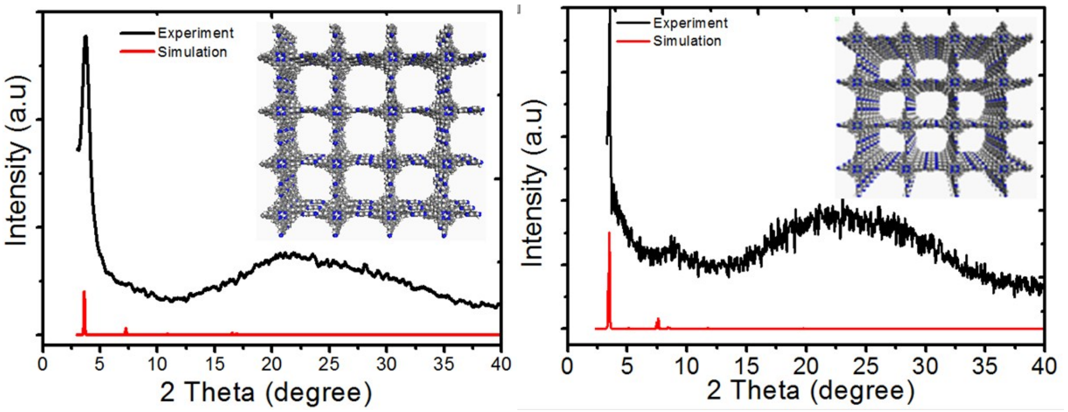


Figure S2. Stack plot of PXRD patterns COF-366 (left) and COF-366-Zn (right).

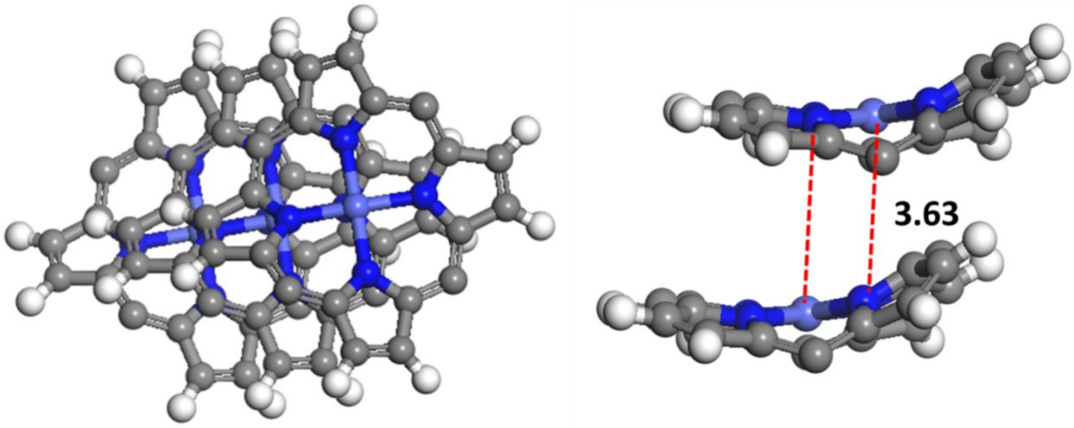


Figure S3. The the coordination between Co^{2+} and N atom of imine of adjacent layer in COF-366-Co (2).

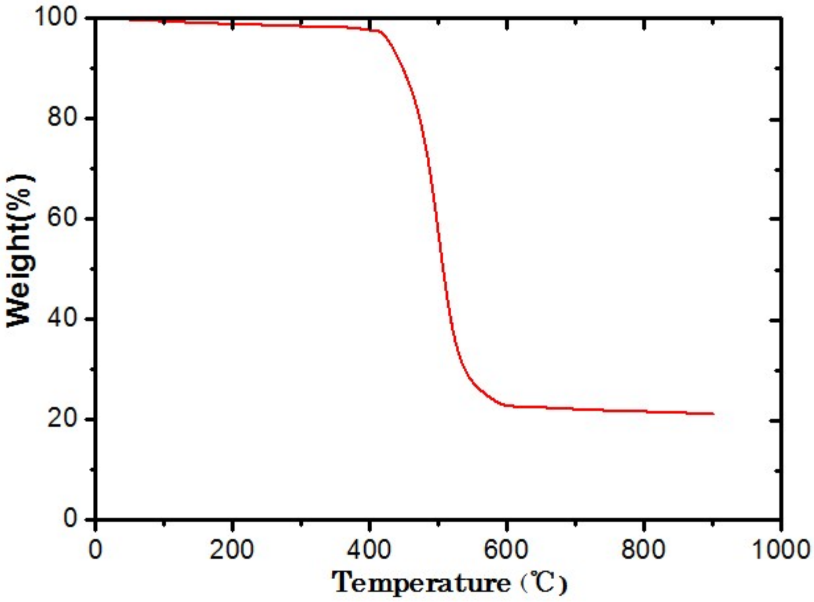


Figure S4. TGA trace for the activated sample of COF-366-Co under air atmosphere (under air).

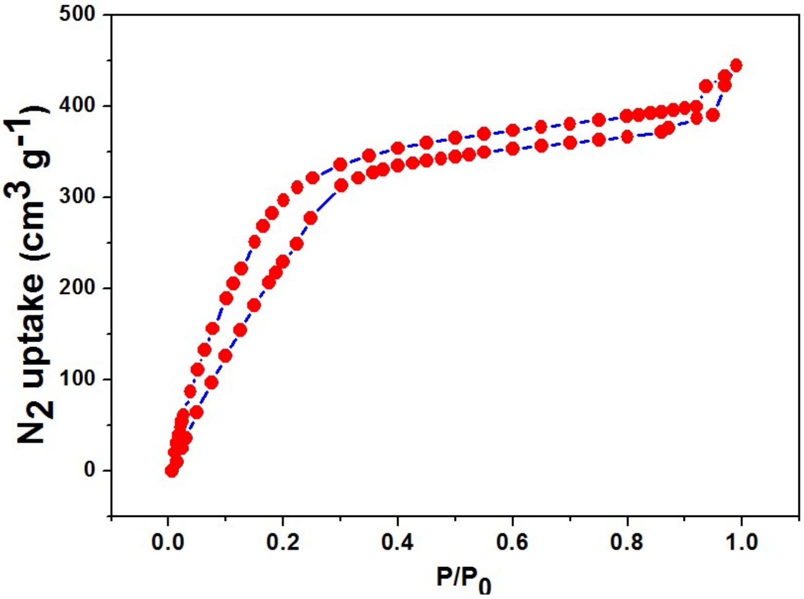


Figure S5. Nitrogen sorption isotherm of COF-366-Zn.

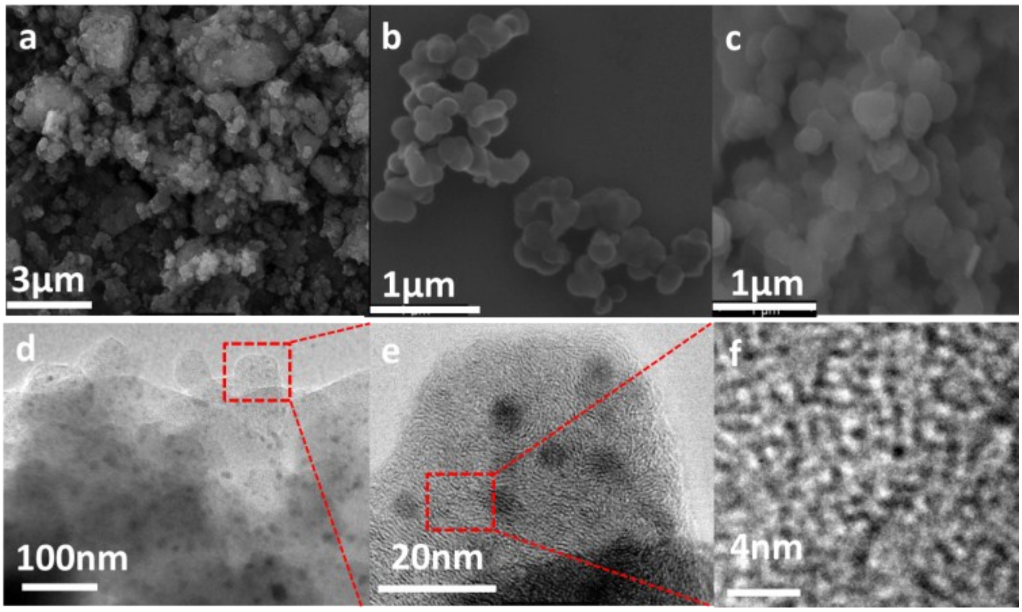


Figure S6. SEM images of COF-366-Co(1) (a), COF-366-Co(2) (b), COF-366-Zn (c) and TEM images of COF-366-Zn (d, e and f).

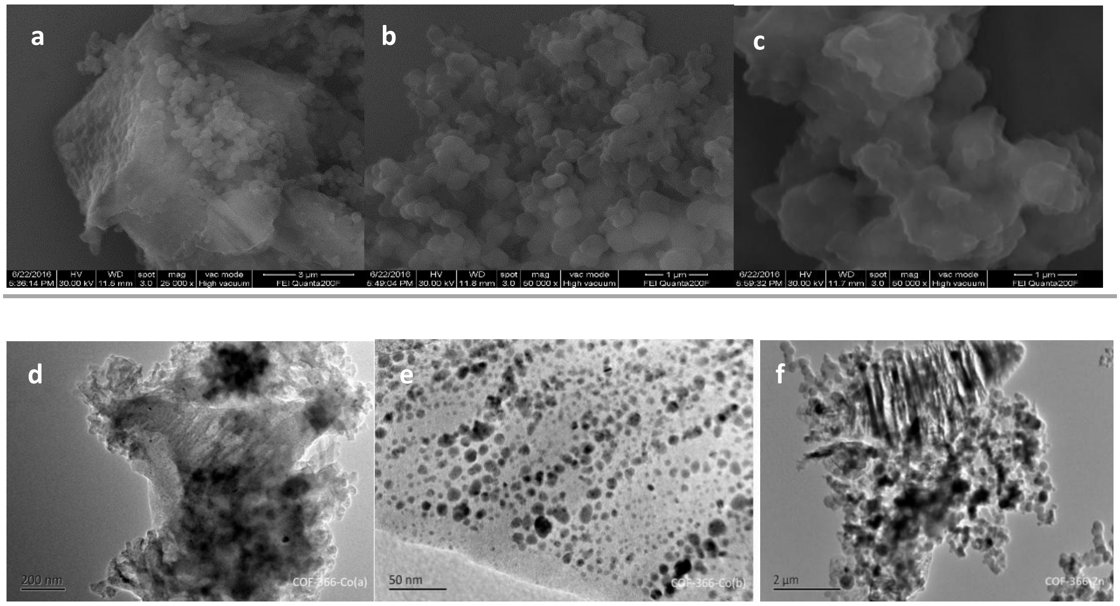


Figure S7. SEM image of COF-366(a), COF-366-Co(1) (b) and COF-366-Co(2) (c). TEM image of COF-366-Co(1) (d), COF-366-Co(2) (e) and COF-366-Zn (f).

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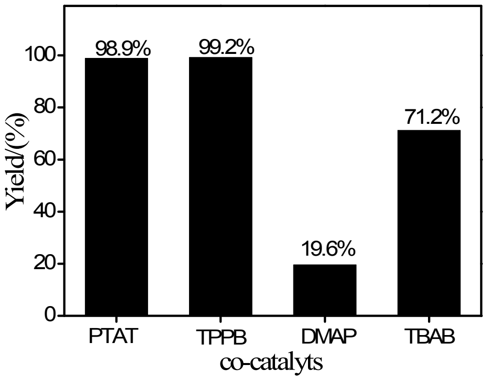


Figure S8. The influence of co-catalysts on the catalytic performance of COF-366-Zn in terms of yield for PC synthesis. Reaction conditions: 1.2 mL of 1, 2-epoxybutane, 40 mg of catalyst, 0.2 mmol (1.0 mol% relative to 1, 2-epoxybutane) of co-catalysts, acetonitrile as solvent. *T*= 120°C，*t*= 4h, P(CO_2)= 1.5MPa.

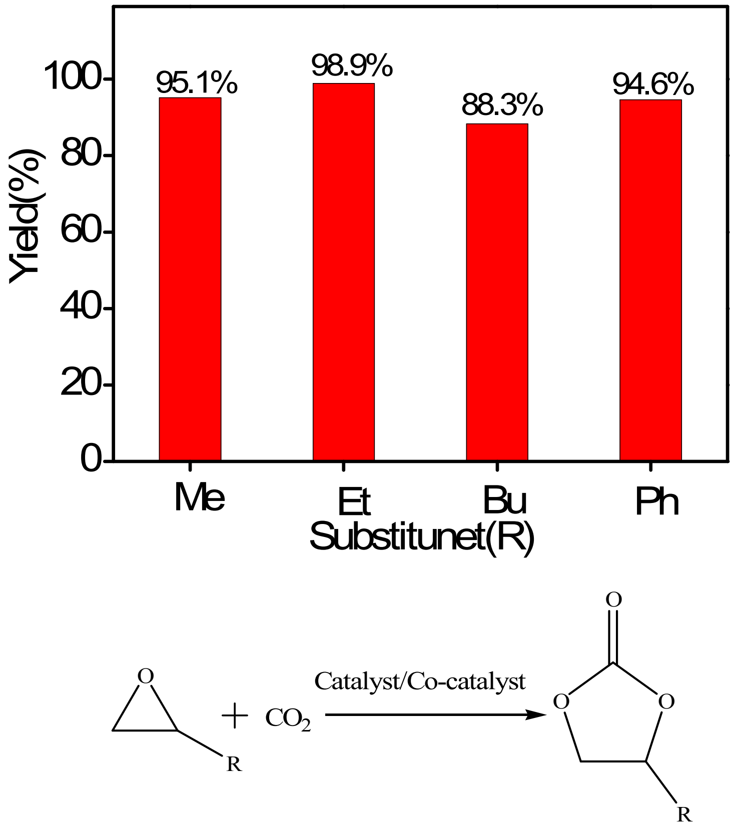


Figure S9. The influence of substituent of epoxides on the catalytic performance of COF-366-Zn in terms of yield for cyclic carbonate synthesis. Reaction conditions: 1.2

mL of epoxides, 40 mg of catalyst, 0.2 mmol (1.0 mol% relative to epoxides) of co-catalysts, acetonitrile as solvent. *T*= 120℃，*t*= 4h, P(CO_2)= 1.5 MPa

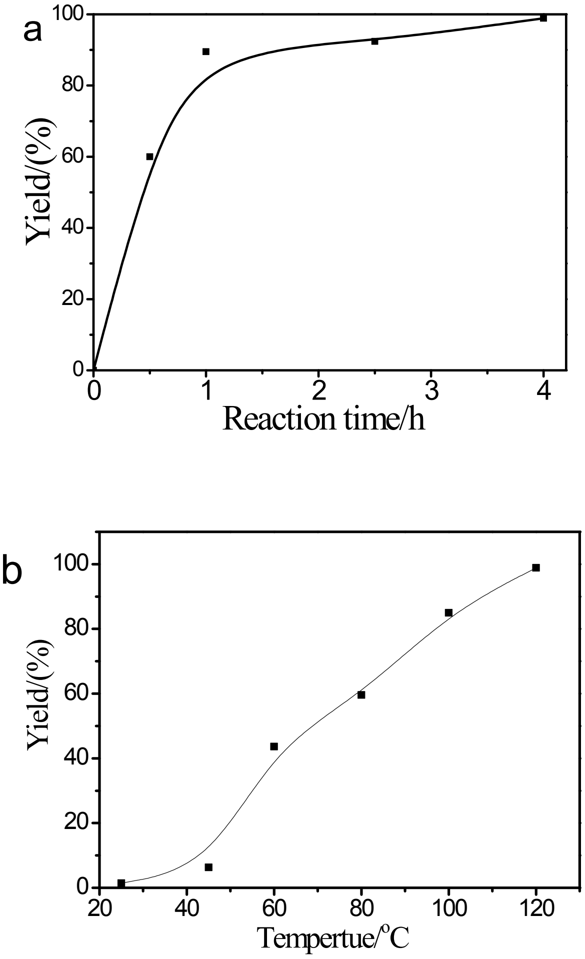


Figure S10. Effects of the reaction time (a) and temperature (b) on the cycloaddition reaction of CO_2. Fixed reaction conditions: 1.2 mL of 1, 2-epoxybutane, 40 mg of catalyst, 0.2 mmol (1.0 mol% relative to 1, 2-epoxybutane) of co-catalyst, acetonitrile as solvent. P(CO_2)= 1.5MPa. (a) *T*=120 ℃ and (b) *t*= 4h.

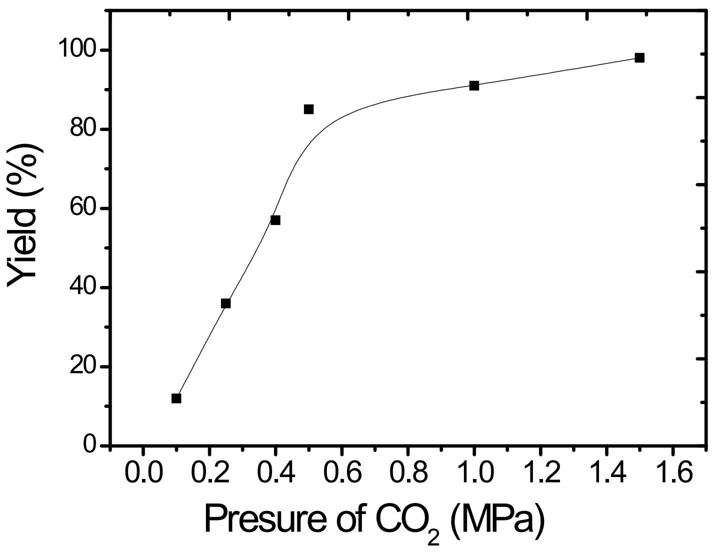
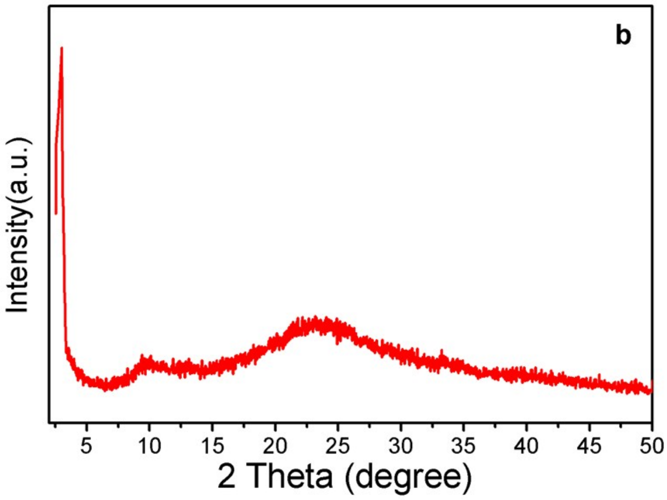


Figure S11. Effect of the reaction pressure of CO_2 on the cycloaddition reaction. Reaction conditions: 1.2 mL of 1, 2-epoxybutane, 40 mg of catalyst, 0.2 mmol (1.0 mol% relative to 1, 2-epoxybutane) of co-catalyst, acetonitrile as solvent. *T*= 120℃, *t*=4 h.



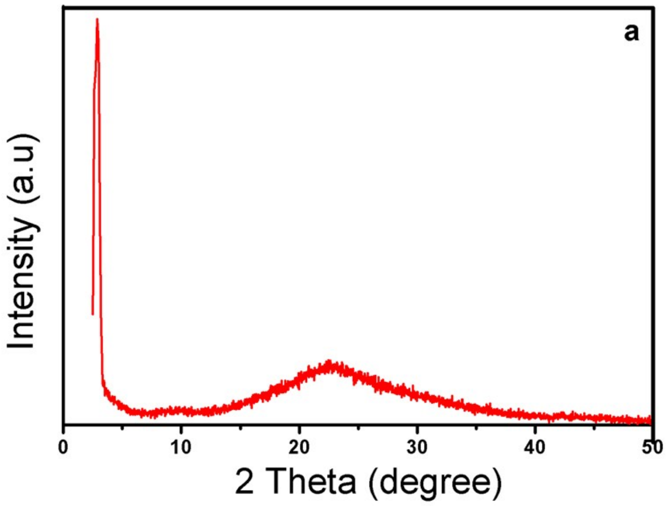


Figure S12. PXRD patterns of COF-366-Co and COF-366-Zn after **6 catalytic cycles.**

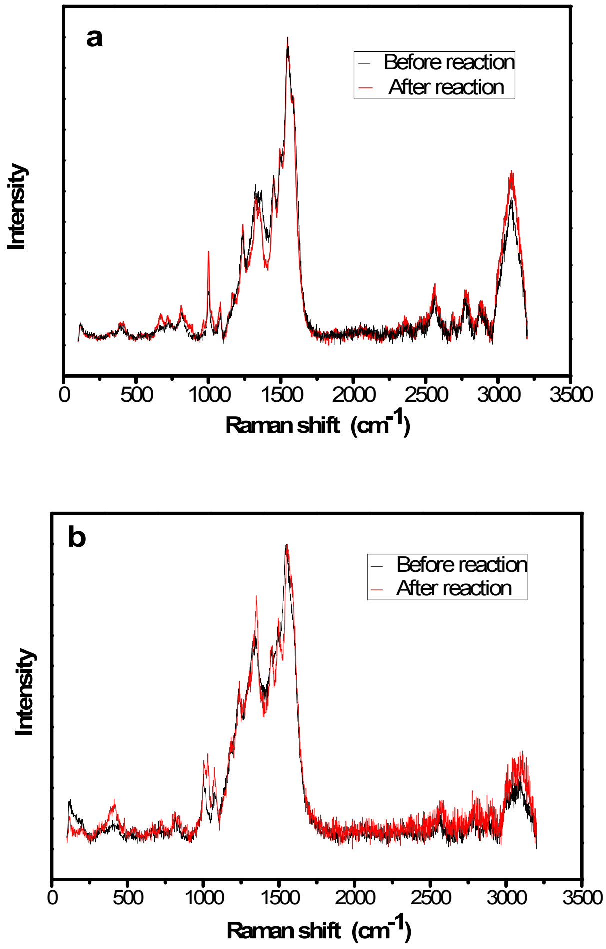


Figure S13 Raman spectra of COF-366-Co(a) and COF-366-Zn(b) before and after 6 catalytic cycles.

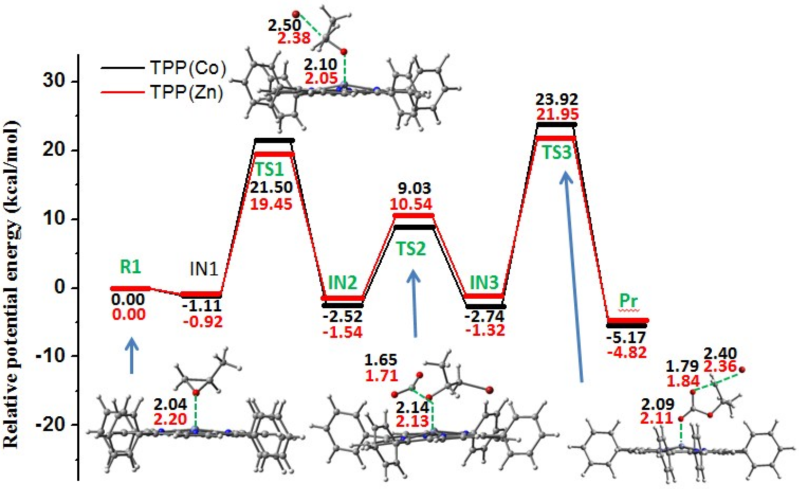


Figure S14. Potential energy profiles for the TPPZn and TPPCo catalyzed reaction of epoxide with CO_2 to give propylene carbonate (PC) at present of Br- as co-catalyst. Computations were performed at the B_3LYP/6-311gG+ (d, p) level with the SCRF method (CH_3CN). The relative free energies are given in kcal/mol. The energy of CO_2 is included in the former steps in which CO_2 does not appear explicitly

Table S1. Elemental atomic composition of the surface of the catalysts determined by XPS.

	C/Zn atomic ratio		C/Co atomic ratio	
	Experiment	Stoichiometric ratio	Experiment	Stoichiometric ratio
COF-366-Zn	79:1	72:1	/	
COF-366-Zn[a]	86:1		/	
COF-366-Co(1)	/		82:1	72:1
COF-366-Co(1)[a]	/		89:1	

[a] After 6 catalytic cycles.

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