

Electronic Supplementary Information (ESI)

Salen-Co(III) insertion in a multivariate cationic metal-organic framework for the enhanced cycloaddition reaction of carbon dioxide

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Physical characterization

The BET surface area measurement was performed with N₂ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2010 instrument. The IR were taken on a VERTEX70 by Bruker. The TEM images were taken on a FEI TECNAI G2 F20 microscope equipped EDS detector at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was conducted using a JEOL-6700F instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 10⁻⁹ Torr. PXRD patterns were recorded on a Rigaku-Dmax2500 diffractometer using CuKα radiation (λ = 0.154 nm). The NMR spectra were measured on an Avance III Bruker Biospin spectrometer. The crude product yield of the catalytic reaction was determined by using Agilent 7890A gas chromatograph (GC) equipped with FID detector and autosampler. When test conversion and epoxidation, HP-5 Column was used in GC.

Materials

All the solvents were obtained from Sinopharm without any further processing. High purity CO₂ (99.99%) was supplied by from gas trader. p-Hydroxybenzoic acid, urotropine, cyclohexanediamine, Co(CH₃COO)₂·6H₂O and all the reaction substrates (Allyl glycidyl ether, 1,2-Epoxyoctane, 1,2-Epoxyhexane, Styrene oxide and Glycidyl Phenyl Ether) were obtained from J&K. 2-(imidazol-1-yl)terephthalic acid (Im-BDC) was purchased from ligand synthesis company and purified according to the reported procedure.¹

Synthesis procedure

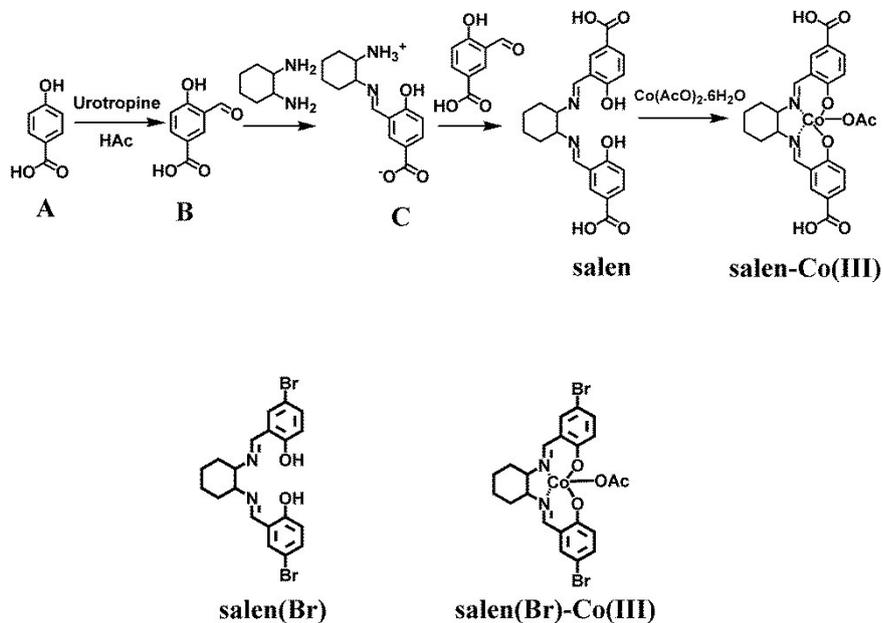


Fig. S1 Synthesis of salen-Co(III) and molecular structure of salen(Br) and salen(Br)-Co(III).

3-formyl-4-hydroxybenzoic acid (B),² 3-[(E)-[2-aminocyclohexyl]imino]methyl-4-hydroxybenzoic acid (C),³ ligand N,N'-Bis(3-carboxyl-salicylidene)-1,2-cyclohexanediamine (salen),³ N,N'-Bis(3-carboxyl-salicylidene)-1,2-cyclohexanediamino cobalt(III) acetate (salen-Co(III)),⁴ N,N'-Bis(3-Br-salicylidene)-1,2-cyclohexanediamine (salen(Br))⁵ and N,N'-Bis(3-Br-salicylidene)-1,2-cyclohexanediamino cobalt(III) acetate (salen(Br)-Co(III))⁵ were synthesized according to known procedure.

Synthesis of Salen-Co(23%)Clm-UiO-66

ZrCl₄ (196 mg), Im-H₂BDC·HCl·H₂O (134 mg), salen-Co(III) (179 mg), and acetic acid (2.38 mL) in 21 mL of DMF were ultrasonically dissolved in a 100 mL Teflon-lined autoclave. The mixture was heated in an oven at 120 °C for 12 h. After the mixture cooled to room temperature, light green precipitates were collected by centrifugation. The solids were washed with DMF three times to remove unreacted precursors and then solvent exchanged with acetone three times.

Synthesis of Salen-Co(12%)@Im-UiO-66

ZrCl₄ (196 mg), Im-H₂BDC·HCl·H₂O (202 mg), salen-Co(III) (45 mg), and acetic acid (2.38 mL) in 21 mL of DMF were ultrasonically dissolved in a 100 mL Teflon-lined autoclave. The mixture was heated in an oven at 120 °C for 12 h. After the mixture cooled to room temperature, light green precipitates were collected by centrifugation. The solids were washed with DMF three times to remove unreacted precursors and then solvent exchanged with acetone three times.

Synthesis of Salen-Co(23%)@Br-Etim-UiO-66

A CH₃CN (15 mL) suspension of Salen-Co(23%)@Im-UiO-66 (392 mg) and bromoethane (1 mL) was heated at 80 °C for 48 h under N₂ atmosphere. The product was collected by centrifugation, washed with EtOH (10 mL × 2), acetone (10 mL × 2), and ether (10 mL × 2) to generate Salen-Co(23%)@Br-Etim-UiO-66 as light green powder solids after drying at 70 °C under vacuum for 12 h.

Synthesis of Salen-Co(12%)@Br-Etim-UiO-66

A CH₃CN (15 mL) suspension of Salen-Co(12%)@Im-UiO-66 (392 mg) and bromoethane (1 mL) was heated at 80 °C for 48 h under N₂ atmosphere. The product was collected by centrifugation, washed with EtOH (10 mL × 2), acetone (10 mL × 2), and ether (10 mL × 2) to generate Salen-Co(12%)@Br-Etim-UiO-66 as light green powder solids after drying at 70 °C under vacuum for 12 h.

The typical catalytic reaction procedure

In a thick-walled reaction tube, 30 mg of salted MTV-MOF and 5 mmol substrate reacts for 12 h in 120 °C and 0.1 MPa CO₂ atmosphere. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

In a typical procedure, Salen-Co(23%)@Br-Etim-UiO-66 (30 mg) and 5 mmol allyl glycidyl ether were placed in a 15 mL thick-walled reaction tube equipped with a magnetic stirrer. After being sealed, the tube was purged thrice with CO₂. The reaction was carried out at 120 °C for 12 h and constant 1 bar CO₂. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

The recyclability test procedure

After reaction, Salen-Co(23%)@Br-Etim-UiO-66 was separated by centrifugal, and washed by acetone two times. After dried in vacuum, it can be used in next catalytic reaction.

Table S1. The amount of salen-Co(III) based on ICP results and the name of cationic MTV-MOFs.

Molar ratio of the start material Im-BDC to salen-Co(III)	Co (wt%) in cationic MTV-MOF	Zr (wt%) in cationic MTV-MOF	The molar ratio of salen-Co(III) / % ^a	Denoted as ^b
6:4	3.10	21.34	23	Salen-Co(23%)@Br-Etim-UiO-66
9:1	1.58	21.36	12	Salen-Co(12%)@Br-Etim-UiO-66

^a The molecular formula of UiO-66 is [Zr₆O₄(OH)₄][BDC]₆.⁶ So our MTV-MOFs can be expressed as [Zr₆O₄(OH)₄][Im-BDC]_x[(Br)Etim-BDC]_y[salen-Co(III)]_z and the total molar of ligands in MTV-MOFs equal to the molar of Zr. So the molar ratio of salen-Co(III) to all the ligands can be calculated by the formula as below; ^b Im-UiO-66 represents for UiO-66 topology-based MOFs that synthesized by Im-BDC and ZrCl₄, (Br)Etim-UiO-66 represents for Br- and imidazolium based MOFs that obtained from the reaction of Im-UiO-66 and bromoethane and Salen-Co(X%)@ represents for X% molar ratio of salen-Co(III) was inserted in the MOFs.

$$\text{The molar ratio of salen - Co(III)} = \frac{z}{x + y + z} = \frac{(\text{wt}\% \text{ of Co})/M_{\text{Co}}}{(\text{wt}\% \text{ of Zr})/M_{\text{Zr}}} * 100\%$$

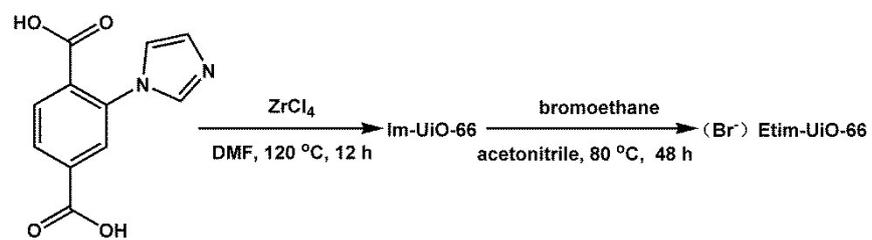


Fig. S2 Synthesis of (Br⁻)Etim-UiO-66.

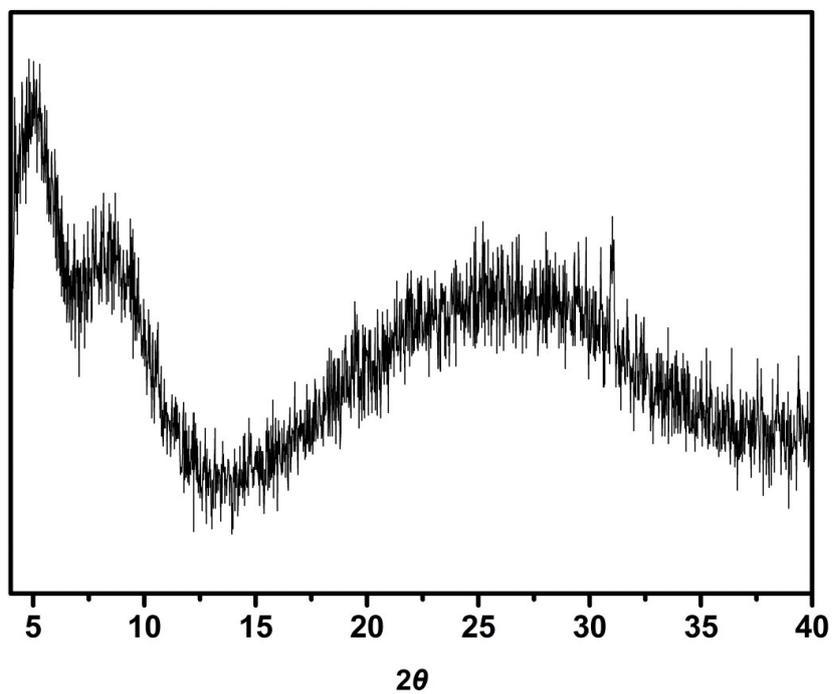


Fig. S3 PXRD of solid obtained from the direct reaction of salen-Co(III) and ZrCl₄.

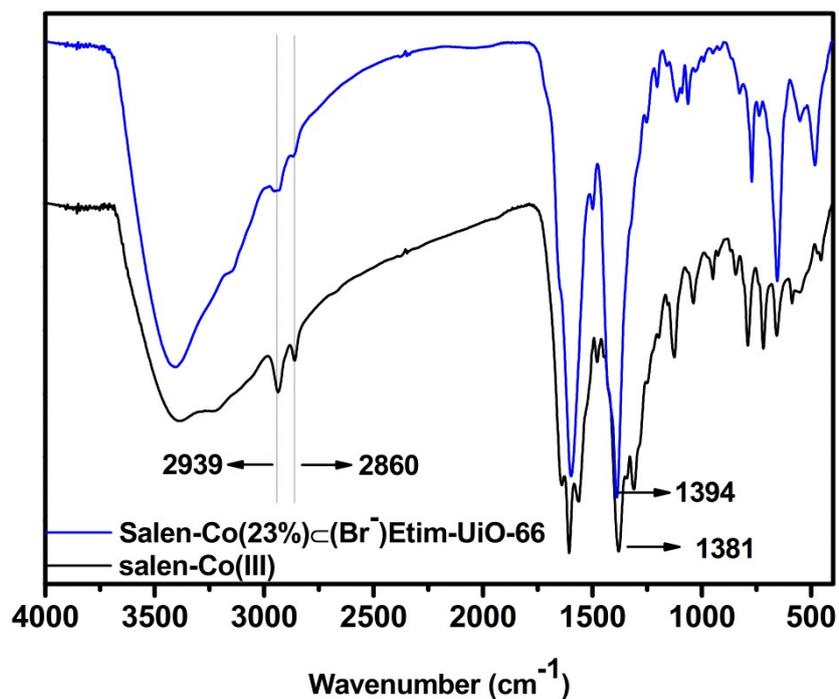


Fig. S4 IR of salen-Co(III) ligand (black line) and Salen-Co(23%)-(Br⁻)Etim-UiO-66 (blue line). The two peaks at 2939 cm^{-1} and 2860 cm^{-1} attributed to the methylene in 1,2-aminocyclohexane.

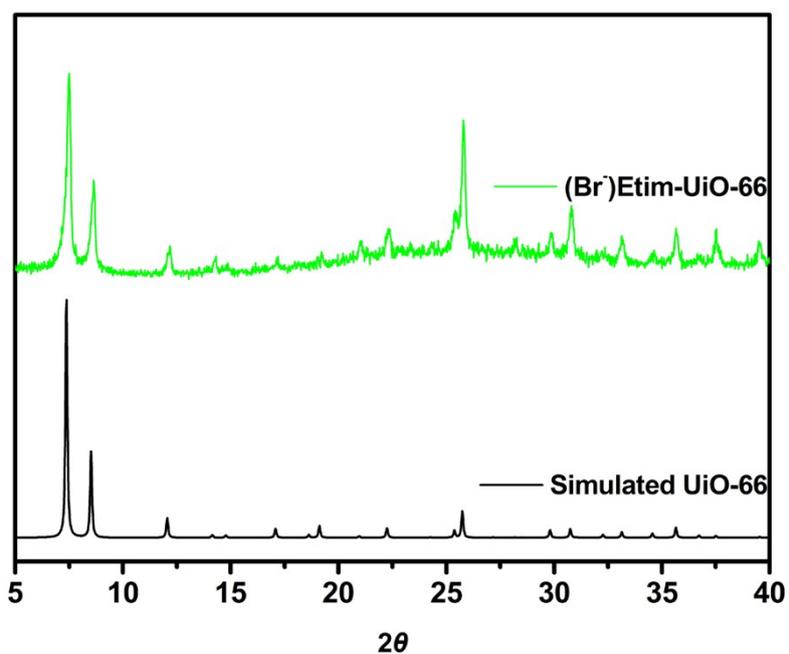


Fig. S5 PXRD of simulated UiO-66 (black) and UiO-66 topology-based (Br)Etim-UiO-66 (green) obtained from the reaction of Im-BDC and salen(Br)-Co(III).

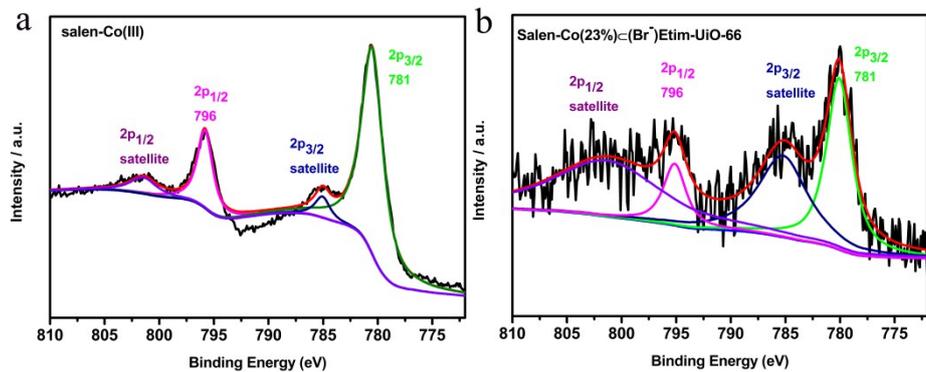


Fig. S6 XPS of Co in a) salen-Co(III) ligand and b) Salen-Co(23%)-(Br⁻)Etim-UiO-66.

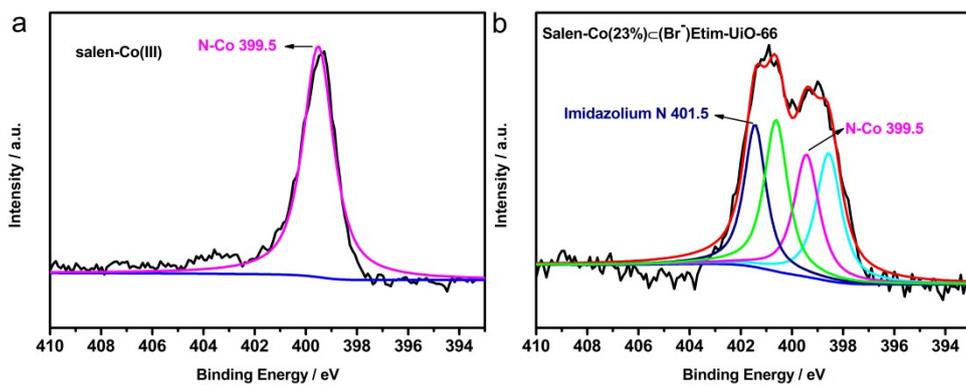


Fig. S7 XPS of N in a) salen-Co(III) ligand and b) Salen-Co(23%)-(Br⁻)Etim-UiO-66.

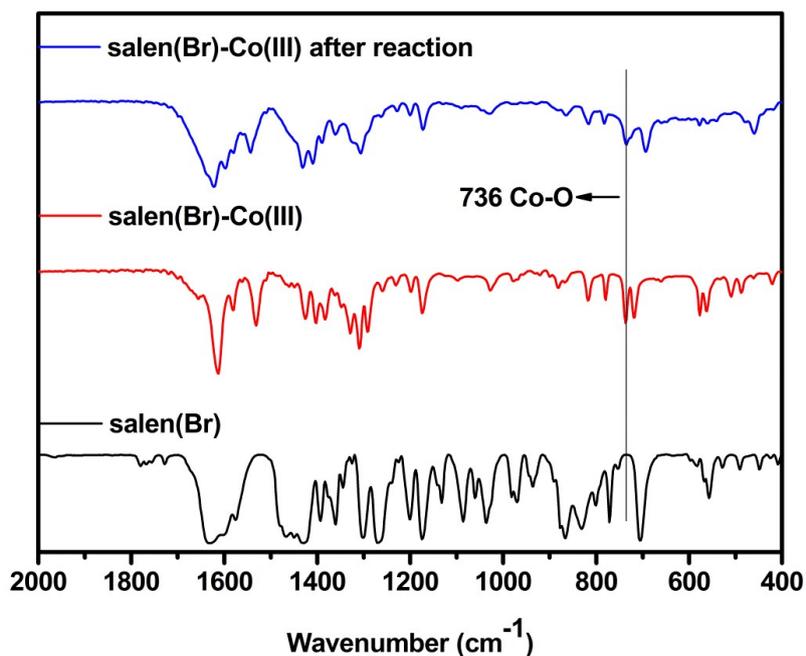


Fig. S8 a) control experiment based on salen(Br)-Co(III), b) IR of salen(Br) (black line), salen(Br)-Co(III) (red line) and salen(Br)-Co(III) after reaction (blue line).

Reaction procedure: ZrCl_4 (196 mg), salen(Br)-Co(III) (448 mg), and acetic acid (2.38 mL) in 21 mL of DMF were ultrasonically dissolved in a 100 mL Teflon-lined autoclave. The mixture was heated in an oven at 120 °C for 12 h. After the mixture cooled to room temperature, 100 mL deionized water was added to the mixture and wine red precipitates were collected by centrifugation. The solids were washed with water three times and then dried at 70 °C under vacuum for 12 h.

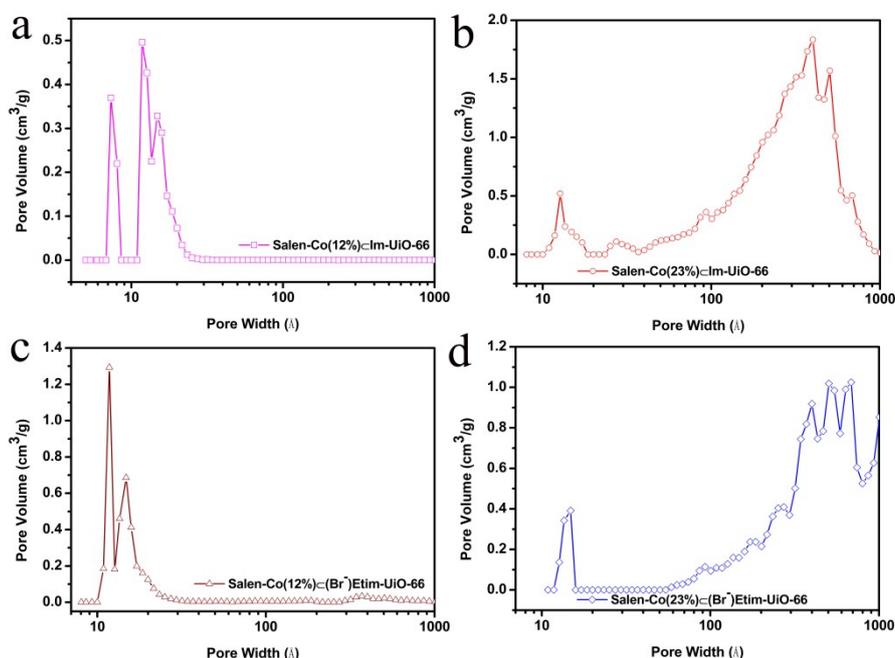


Fig. S9 Pore size distribution of a) Salen-Co(12%)@Im-UiO-66, b) Salen-Co(23%)@Im-UiO-66, c) Salen-Co(12%)@-(Br)Etim-UiO-66 and d) Salen-Co(23%)@-(Br)Etim-UiO-66 based on DFT method.

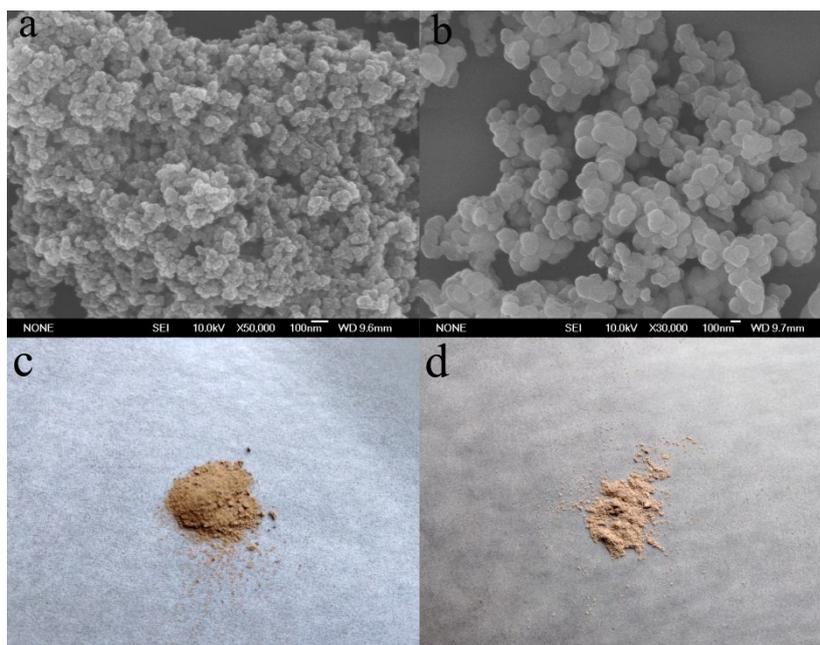


Fig. S10 SEM of a) Salen-Co(23%)@Im-UiO-66, b) Salen-Co(12%)@Im-UiO-66, color of c) the low crystallinity powder that obtained from the reaction of salen-Co(III) and ZrCl₄ and d) the mixture of the low crystallinity powder and (Br⁻)Etim-UiO-66.

Table S2. Energy Dispersive Spectrometer.

Catalyst	The content of Br in MTV-MOFs / Atomic%
Salen-Co(23%)@Br ⁻ Etim-UiO-66	0.44
Salen-Co(12%)@Br ⁻ Etim-UiO-66	1.44

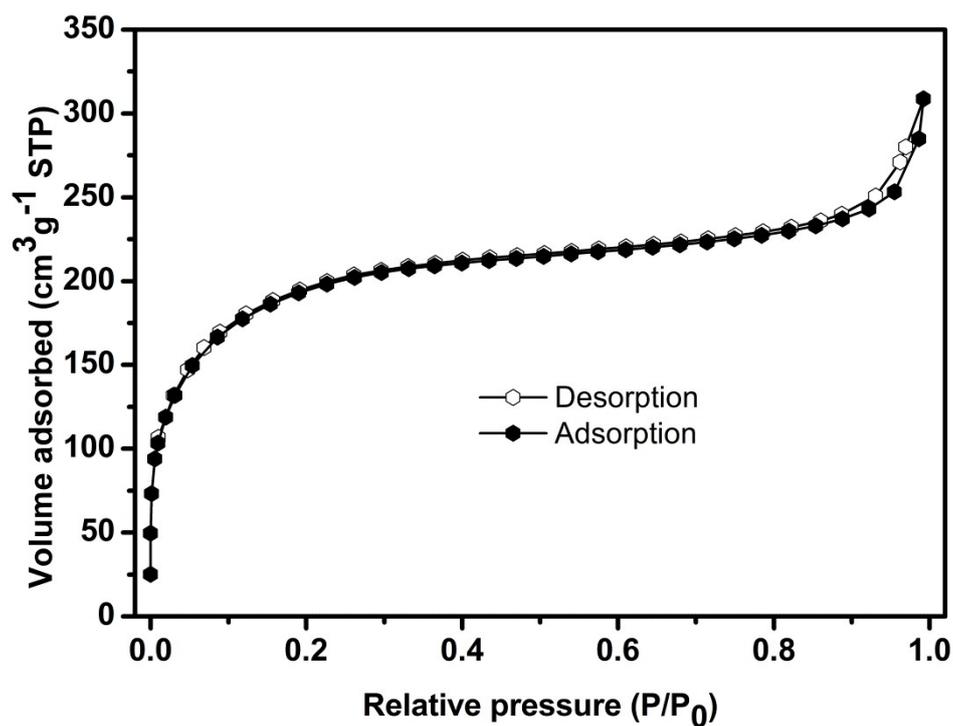


Fig. S11 Nitrogen sorption curves of (Br)Etim-UiO-66 at 77 K.

Table S3 Catalytic cycloaddition reaction of allyl glycidyl ether with CO₂ by different catalysts.^a

Entry	Catalyst	T / °C	Conv / % ^b	Selec / % ^b
1	Salen-Co(23%)-(Br)Etim-UiO-66	60	8	98
2	Salen-Co(23%)-(Br)Etim-UiO-66	90	44	97
3	Salen-Co(23%)-(Br)Etim-UiO-66	120	92	96
4	none	120	0	--
5	Salen-Co(12%)-(Br)Etim-UiO-66	120	72	96
6	(Br)Etim-UiO-66	120	70	82
7	salen-Co(III) ligand	120	64	93
8	Salen-Co(23%)-(Im-UiO-66	120	65	90
9	(Br)Etim-UiO-66+salen-Co(III) ligand	120	62	89

^a Reaction conditions: 0.1 MPa CO₂, 5 mmol allyl glycidyl ether, 30 mg catalyst, 12 hours. ^b Determined by GC.

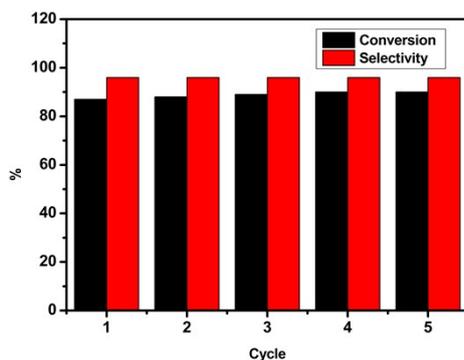


Fig. S12 Recycling of Salen-Co(23%)-(Br-)Etim-UiO-66 for the cycloaddition of CO₂ with allyl glycidyl ether at 0.1 MPa, 120 °C for 12 h.

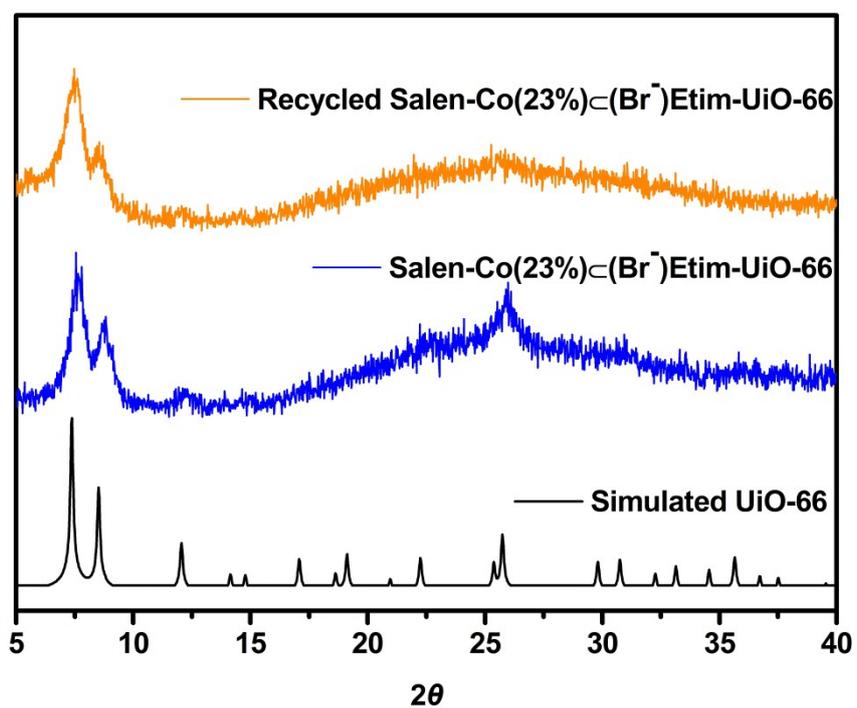


Fig. S13 PXRD of recycled Salen-Co(23%)-(Br-)Etim-UiO-66 (orange line), Salen-Co(23%)-(Br-)Etim-UiO-66 (blue line) and simulated UiO-66 (black line).

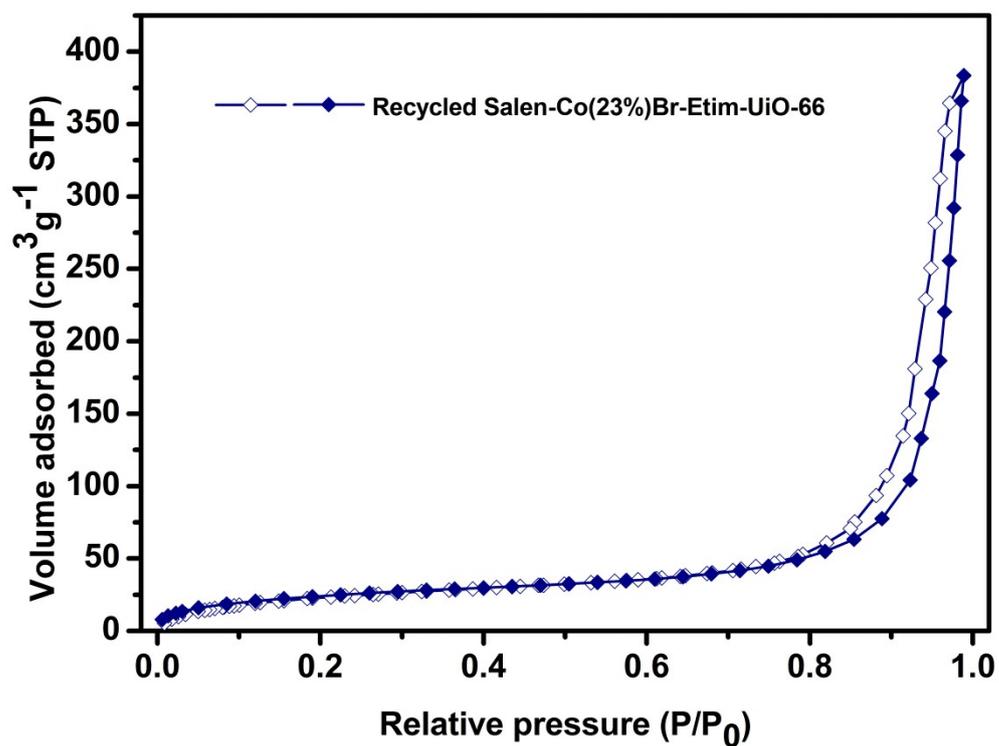


Fig. S14 Nitrogen sorption curves at 77 K of recycled Salen-Co(23%)-(Br)Etim-UiO-66.

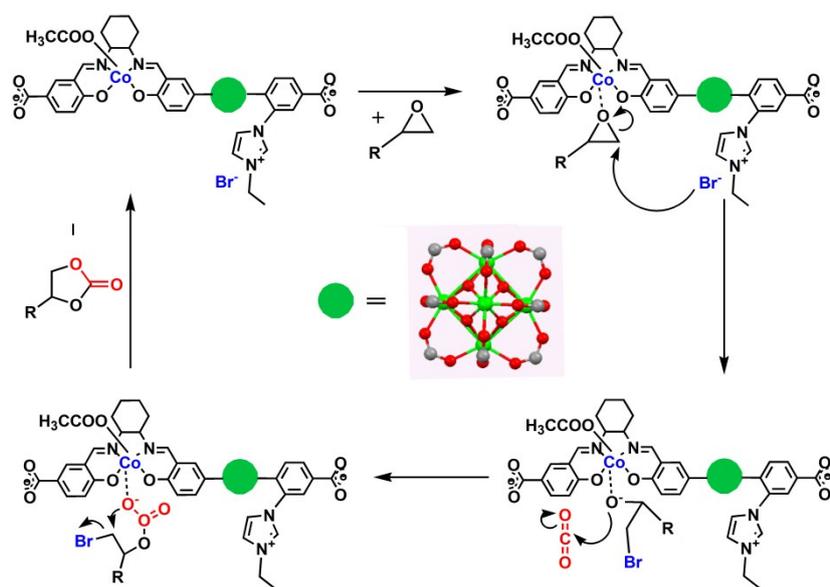


Fig. S15 The proposed pathway of the conversion of epoxide to cyclic carbonate.

Notes and references

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