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Electronic Supplementary Information

Salen(Co(III)) imprisoned within pores of metal-organic framework by postsynthetic modification and its asymmetric catalysis for CO_2 fixation under room temperature

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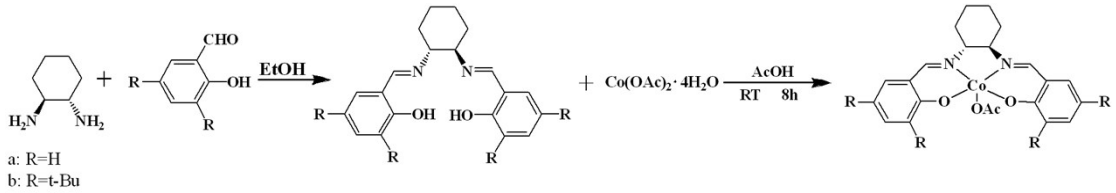
Section S1 Experiments

General. Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, TCI, ACROS etc.). DMF and chloroform were dried using molecular sieves.

General procedure for the preparation of (*R, R*)-Salen(Co(III)) and *tBu*-(*R, R*)-Salen(Co(III))



The complexes were synthesized as previous literature (*J. Am. Chem. Soc. 2004, 126, 1360-1362*). Typically, Salicylaldehyde derivative (2.0 equiv) is added to a 0.2 M solution of (*R, R*)-1,2-Diaminocyclohexane (1.0 equiv) in absolute ethanol. The mixture is heated to reflux for 6 h and then water is added dropwise to the cooled bright yellow solution (occasionally product begins to crystallize prior to addition of water). The resulting yellow crystalline solid is collected by filtration and washed with a small portion of ethanol. The Salen ligand was sufficiently pure to be taken on to the next step. Salen (2.0 mmol), $Co(OAc)_2 \bullet 4H_2O$ (2.14 mmol, 1.07 equiv), and 10 mL glacial AcOH were added to a 50 mL round-bottomed flask charged with a Teflon stir bar. The stirred mixture turned brown within a few minutes. After 20 min the flask was equipped with a vacuum adaptor and a dip tube so that air could be pulled through the reaction mixture (8h). Excess acetic acid was removed under high vac using a vacuum drying machine over night. The solid was dissolved and vigorously stirred in 10 mL ethanol and then precipitated by addition of 25 mL water. The catalyst was filtered, rinsed (3 x 15 mL water) and dried in a 70 °C oven.

General process for preparation of (*R, R*)-Salen(Co(III)@IRMOF-3-AM

IRMOF-3 was prepared as previously described (*J. Am. Chem. Soc. 2006, 128, 1304–1315*). The DMF trapped in the pore of the IRMOF-3 was exchanged by $CHCl_3$ by soaking the crystals in 10 mL of $CHCl_3$ for 3 days with fresh $CHCl_3$ added every 24 h.

Approximately 165 mg IRMOF-3 (ca. 0.6 mmol equiv of $-NH_2$) was evacuated at 50 ^oC for 6 h, and then dispersed in 4 mL of chloroform containing 48 mg of (*R, R*)- or (*S, S*)-Salen(Co(III)). After allowing the sample to stand at 55 ^oC for 12 h, 1.2 mmol of acetic anhydride was added into the reaction solution, and the mixture was heated for additional 12 h. The solution was decanted, and the crystals were washed with $CHCl_3$ for 3 times, and then soaked in 10 mL of $CHCl_3$ for 3 days with fresh $CHCl_3$ added every 24 h. After 3 days of soaking the crystals were stored in the last $CHCl_3$ solution until needed. The prepared catalyst was denoted as (*R, R*)-Salen(Co(III)@IRMOF-3-AM.

General process for preparation of *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM

UMCM-1-NH_2 was prepared as previously described (Inorg. Chem. 2009, 48, 296-306). The procedure of the preparation of *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM was similar with that of (*R, R*)-Salen(Co(III)@IRMOF-3-AM except that the acetic anhydride in the PSM step was replaced by n-Butyric anhydride.

Asymmetric catalysis for the coupling reaction of CO_2 with racemic epoxides

All the cycloaddtion reaction experiments were conducted in a stainless steel pressure reactor with a shaker. The mixture of racemic epoxides (50 mmol), n-Bu_4NBr (0.0161 g, 0.05 mmol) and heterogeneous chiral catalysts (50mg of (*R, R*)-Salen(Co(III)@IRMOF-3-AM (ca. 0.05 mmol equiv of (*R, R*)-Salen(Co)), or 65 mg of *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM (ca. 0.05 mmol equiv of *tBu*-(*R, R*)-Salen(Co)) were sealed in the reactor. Then 2.0 MPa CO_2 was carefully charged into the reactor by slightly regulating the valve to replace the air. The reactor was put into a bath of 25 ^oC and shaked for 8 h. After the reaction was completed, the reactor was cooled to 5 ^oC in an ice-water bath, and excess gases were vented out slowly. After the catalyst was separated by filtration, the reaction mixtures were diluted 10-fold by ethyl acetate and analyzed by Agilent 7890 GC with Agilent J&W Cyclosil B Chiral capillary column (30m×0.25mm id ×0.25μm film).

Section S2 Material Characterizations

^{1}H NMR Digestion and Analysis. Approximately 5 mg of crystalline sample was dried under vacuum at 50 °C for 3 h and then digested by sonication in 500 µL of d_6-DMSO and 100 µL of dilute DCl (23 µL of 35% DCl in D_2O diluted with 1000 µL of d_6-DMSO). ^{1}H NMR spectra were recorded on a Bruck FT-NMR spectrometer (400 MHz).

Powder X-ray diffraction (PXRD) Analysis. Approximately 15 mg of crystalline sample (typically soaked in $CHCl_3$) was air dried before PXRD analysis. PXRD data were collected at ambient temperature on a Puxi DX-3 diffractometer at 40 kV, 40 mA for Cu *Kα* (*λ* = 1.5418 Å), with a scan speed of 1°/min, a step size of 0.02° in 2θ, and a 2θ range of 4-40°. The experimental backgrounds were corrected using the Jade 5.0 software package.

N_2 Sorption. BET surface area (m^2/g) measurements were collected at 77 K with dinitrogen on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique. Approximately 30-60 mg of activated samples were evacuated on a vacuum line for 12 h, then transferred to a preweighed sample tube and degassed at 85 °C for approximately 18 h or until the outgas rate was < 5 µmHg. The sample tube was reweighed to obtain a consistent mass for the degassed samples.

Thermal Gravimetric Analysis (TGA). Approximately 10 mg of sample was analyzed under a stream of dinitrogen using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 °C/min.

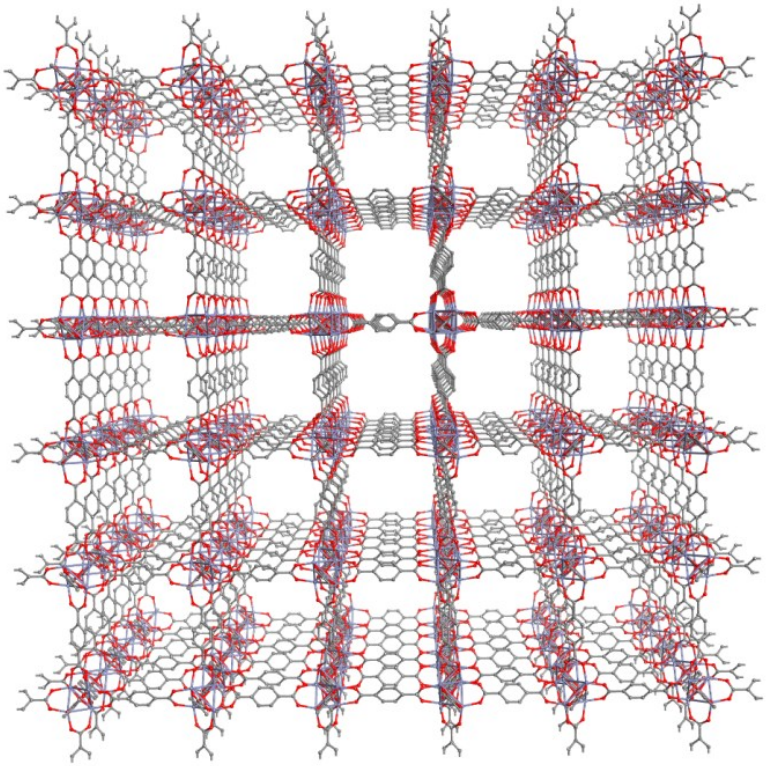
Solid-state Circular Dichroism (CD) analysis. The solid sample was sandwiched between two quartz disks, and measured on a J-820 (Jsco Co. Japan) spectrophotometer with integrating sphere. The scan rate was 500 nm/min, and all of the spectra were accumulated two times.

Solid-state UV-Vis Analysis. Approximately 50 mg of crystalline sample (typically soaked in $CHCl_3$) was air dried before analysis. Then, the solid sample was sandwiched between two quartz disks, and measured on a Agilent Cary 60 UV-Vis, with a scan speed of 500 nm/min, and range of 300-800 nm.

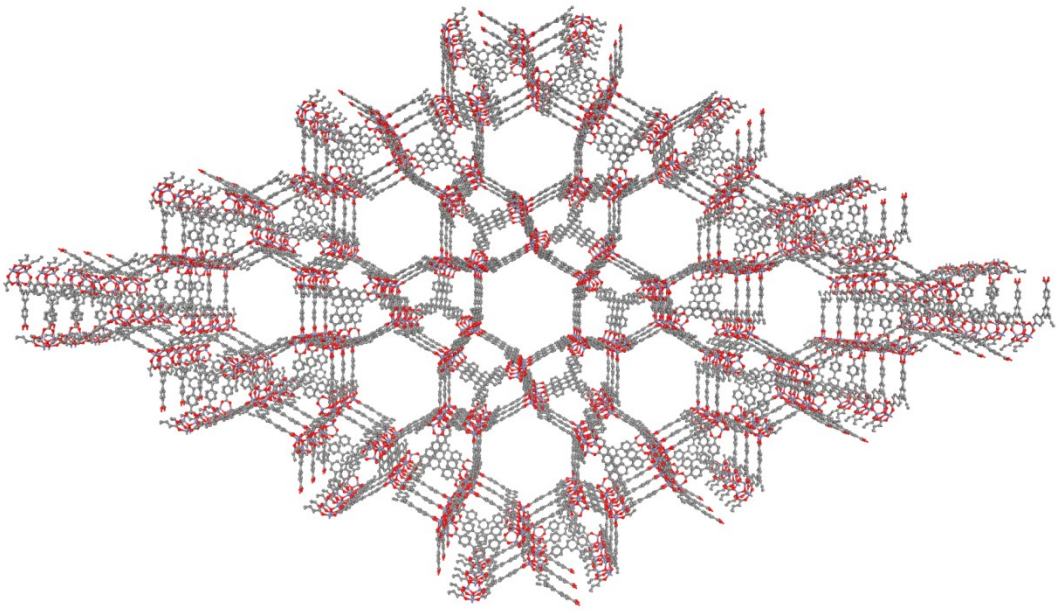
Inductive Coupled Plasma Emission Spectrometer Analysis (ICP). Approximately 5 mg of crystalline sample was dried in a 50 °C oven for 3 h, and the sample was digested by sonication in 2 mL of H_2O and 1 mL of concentrated nitric acid. Then the solution is collected by filtration and diluted to 10 mL. Metal Co and Zn content were analysed on a Aglient 5100 ICP-OES.

Section S3 Figures

Fig. S1 Schematic representation of IRMOF-3 **(a)** and UMCM-1-NH_2 **(b).** The amino group on the benzene 1,4-dicarboxylic linker and hydrogen atoms are omitted for clearne



(a)



(b)

Fig. S2 Schematic dimension representation of the maximal cross-sections for the window of IRMOF-3, UMCM-1-NH_2, (*R, R*)-Salen(Co(III)), *tBu*-(*R, R*)-Salen(Co(III)) and n-Bu_4NBr. Note that both (*R, R*)-Salen(Co(III)) and n-Bu_4NBr with smaller molecular size can penetrate into IRMOF-3 but *tBu*-(*R, R*)-salen(Co(III)) cannot.

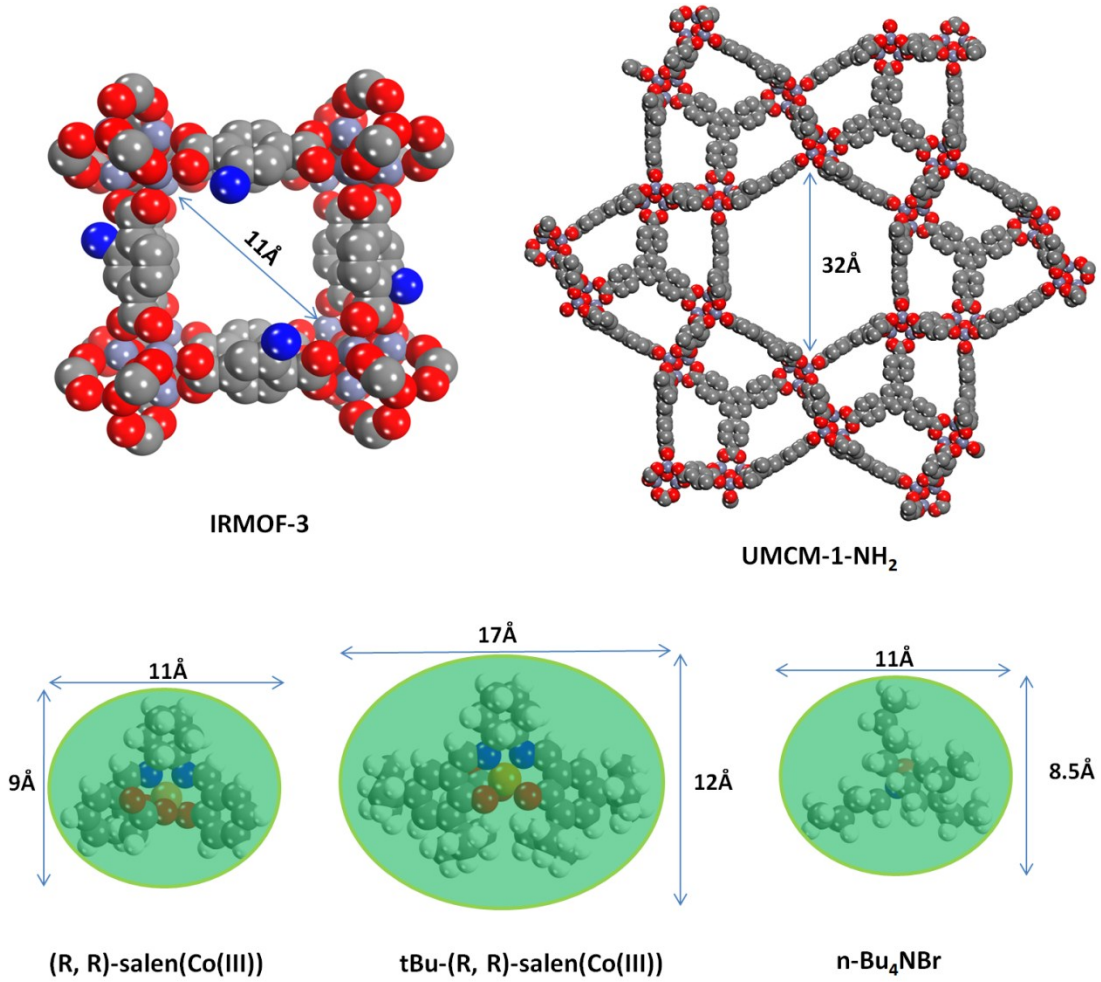


Fig. S3 Crystal photographs of IRMOF-3(a), (*R, R*)-Salen(Co(III))@IRMOF-3-AM, and (*R, R*)-Salen(Co(III))@IRMOF-3-AM after asymmetricly catalytic reaction for CO_2 fixation.

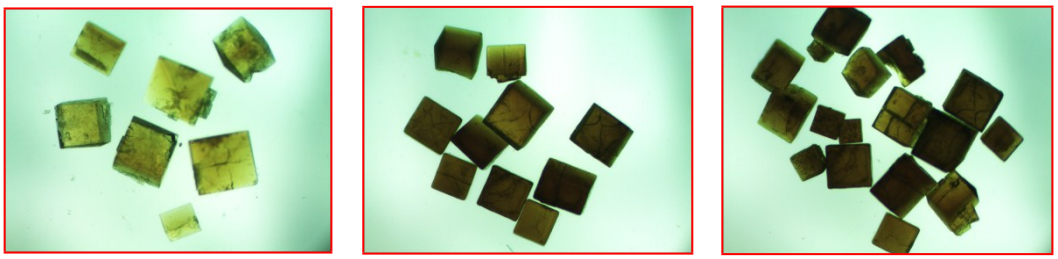
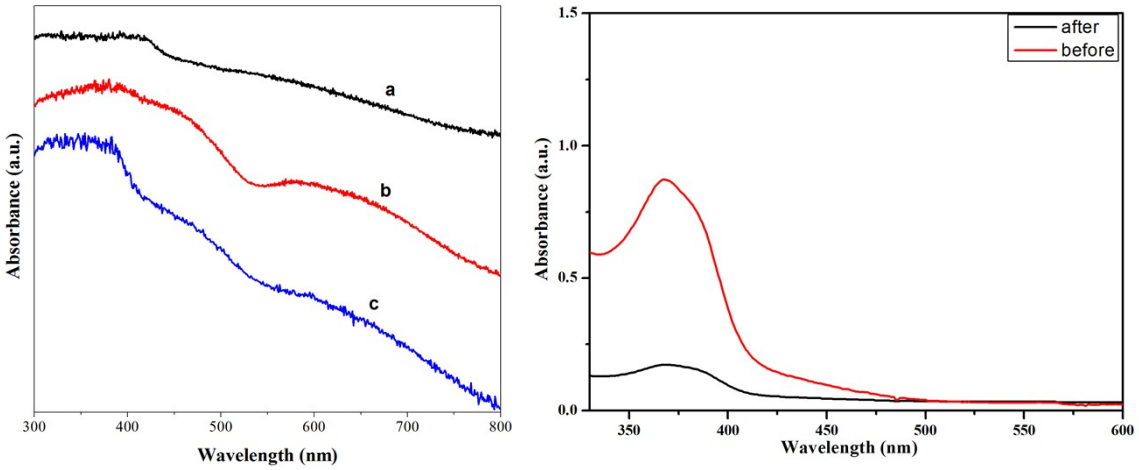


Fig. S4 (a) Solid-state UV-Vis diffuse reflectance spectra of IRMOF-3 (black line), (*R, R*)-Salen(Co(III)) (red line), and (*R, R*)-Salen(Co(III))@IRMOF-3-AM (blue line);
(b) UV-Vis spectra of (*R, R*)-Salen(Co(III)) in the filtrate before (red line) and after (black line) the adsorption.



(a) **(b)**

Fig. S5 ^{1}H NMR spectrum of the sample (*R, R*)-Salen(Co(III))@IRMOF-3-AM digested in DCl/D_2O/DMSO-d_6 solution. The peaks labeled as (•) and (°) were attributed the signals of ligands BDC-NH(CO)Me (amide) and BDC-NH_2, respectively. And the exact distribution for the peaks was labeled in letters a-g, respectively. The aromatic resonances of the benzene dicarboxylate of starting material (BDC-NH_2) and product (amide) were used to calculate the yield for the PSM conversion (80% conversion herein).

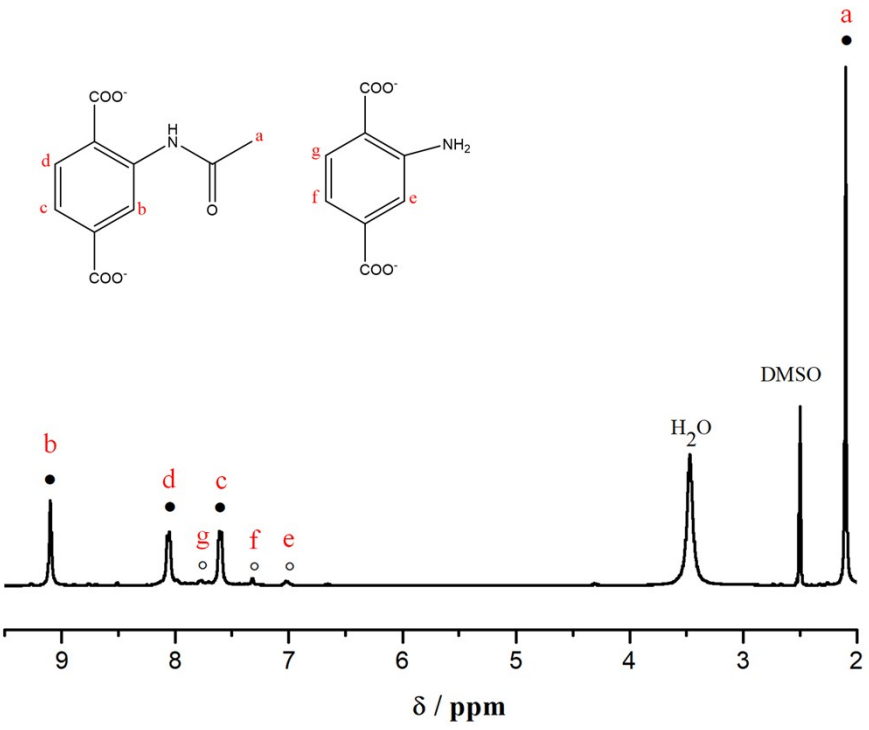


Fig. S6 TGA curves of IRMOF-3 (black) and (*R, R*)-Salen(Co(III))@IRMOF-3-AM (blue).

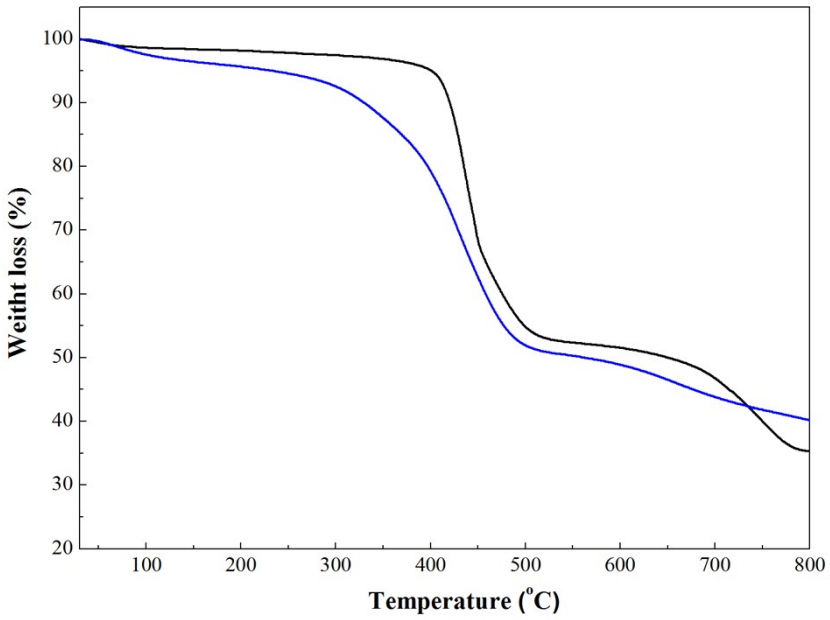


Fig. S7 Dinitrogen isotherms of IRMOF-3 (black), and (*R, R*)-Salen(Co(III))@IRMOF-3-AM (blue). The BET surface areas for them were 2982 and 475 m^2/g, respectively.

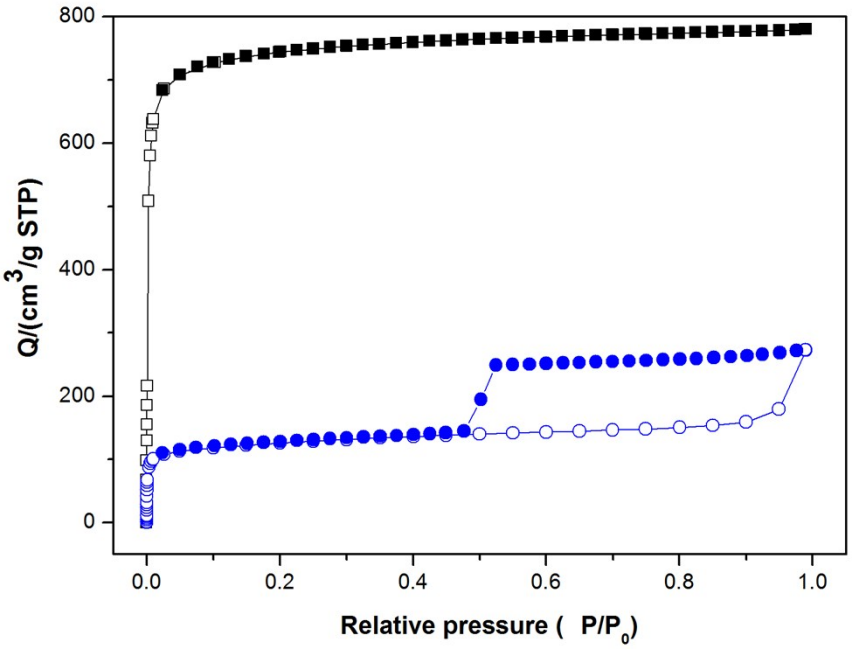


Fig. S8 ^{1}H NMR spectrum of the sample *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM digested in DCl/D_2O/DMSO-d_6 solution. The exact distribution for the peaks of ligands BDC-NH(CO)C_3H_7 (amide) and BTB was labeled in letters a-i, respectively. The PSM conversion calculated by the ratio of aromatic resonances of the product (amide) and starting material BDC-NH_2) is > 99%..

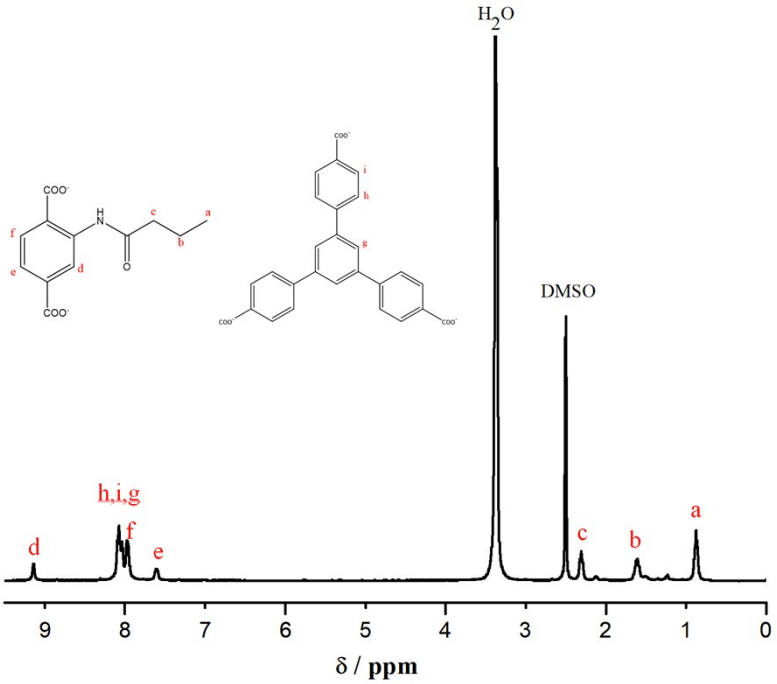


Fig. S9 Solid-state CD spectra of UMCM-1-NH_2 (black line) and *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM (red line), indicating that the *tBu*-(*R, R*)-Salen(Co(III)) complex has been confined in the cage of UMCM-1-NH_2.

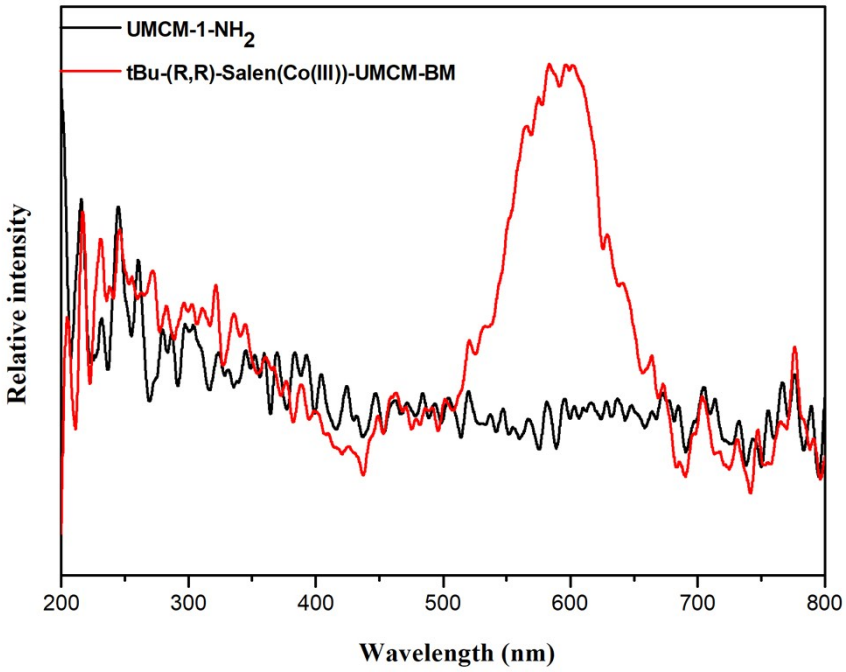


Fig. S10 PXRD patterns of simulated UMCM-1-NH_2 on the basis of the single crystal structure (a), fresh UMCM-1-NH_2 (b), *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM (c), and used *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM after three cycles for catalysis (d).

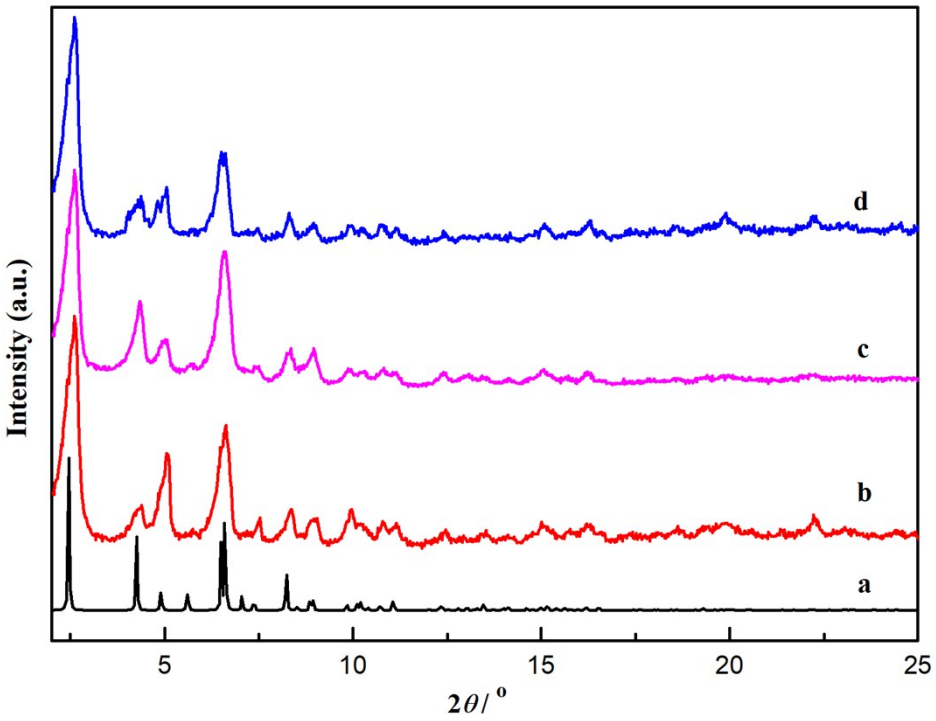


Fig. S11 TGA curves of UMCM-1-NH_2 (black) and *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM (red).

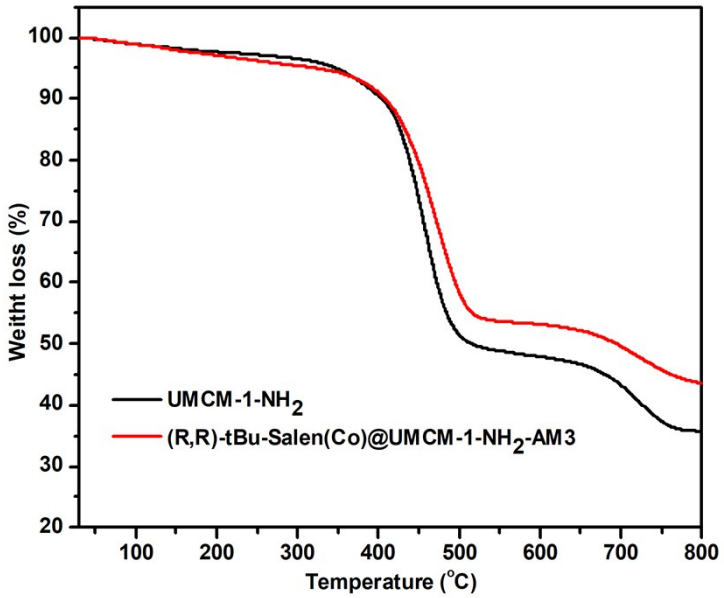


Fig. S12 Dinitrogen isotherms of UMCM-1-NH_2 (black), and *tBu*-(*R, R*)-Salen(Co(III))@UMCM-BM (blue). The BET surface areas for them were 4200 and 1660 m^2/g, respectively. It indicated that the bulky *tBu*-(*R, R*)-Salen(Co(III)) and amide substituent had trapped into the pore.