*Electronic supplementary information*

# Robust high-connected rare-earth MOFs as efficient heterogeneous catalysts for $CO_2$ conversion

Na Wei,[a] Rong-Xia Zuo,[a] Yu-Yang Zhang,[a] Zheng-Bo Han*[a] and Xue-Jun Gu*[b]

[a]College of Chemistry, Liaoning University, Shenyang 110036, P. R. China.

[b]Institude of Rare and Scattered Elements, College of Chemistry, Liaoning University, Shenyang 110036, P. R. China.

## Materials and Methods

All chemicals for synthesis were commercially available reagents of analytical grade and were used without further purification. The C, H, and N microanalyses were carried out with Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000-400 $cm^{-1}$ range on a Nicolet 5DX spectrometer. Thermogravimetric analyses (TGA) were taken on a Perkin-Elmer Pyrisl (25-800 °C, 5 °C $min^{-1}$, flowing $N_2$ (g)). Powder X-ray diffraction was recorded with a Bruker AXS D8 advanced automated diffractometer with Cu-K$\alpha$ radiation. The products of catalysis reaction are monitored by Gas chromatography with a SP-2100A Gas chromatograph (GC). Inductively coupled plasma-optical emission spectroscopy (ICP) was performed using a 700 Series ICPOES (Agilent Technologies). $^1$H-NMR spectra were recorded on a Varian-300 MHz NMR spectrometer. Pyridine adsorption fourier-transform infrared (Py-IR) spectra were collected on a PE FT-IR Frontier spectrometer.

## Preparation

Synthesis of **$[(CH_3)_2NH_2][RE_3(\mu_3\text{-}OH)(BDC)_3(HCOO)_3]$ (RE-BDC, RE=Y, Tb, Er)**: A mixture of $H_2BDC$ (9.4 mg, 0.057 mmol), $RE(NO_3)_3\cdot 6H_2O$ (0.04 mmol), 2-FBA (48.2 mg) were dissolved in 3 mL mixed solvents of DMF (2.2 mL), $H_2O$ (0.5 mL) and $HNO_3$ (0.3 mL) in a screw-capped vial. The resulting mixture was kept in an oven at 105 °C for 48h. After cooling the vial to room temperature, the as-synthesized sample was purified through repeated washings with DMF to yield transparent polyhedral crystals.

**$[(CH_3)_2NH_2][Y_3(\mu_3\text{-}OH)(BDC)_3(HCOO)_3]$ (Y-BDC).** Yield: 68 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{29}H_{24}O_{19}NY_3$: C 36.39, H 2.53, N 1.46, Y 27.86 %. Found: C 36.43, H 2.52, N 1.50, Y 27.98 %. IR (KBr, $cm^{-1}$): 3127(m), 2840(m), 1672(s), 1579(s), 1502(s), 1396 (s), 1151(m), 1098(m), 1015(m), 888(w), 821(m), 752(s), 667(w).

**$[(CH_3)_2NH_2][Tb_3(\mu_3\text{-}OH)(BDC)_3(HCOO)_3]$ (Tb-BDC).** Yield: 71 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{29}H_{24}O_{19}NTb_3$: C 29.84, H 2.07, N 1.20, Tb 40.85 %. Found: C 29.76, H 2.10, N 1.18, Tb 40.90 %.

**$[(CH_3)_2NH_2][Er_3(\mu_3\text{-}OH)(BDC)_3(HCOO)_3]$ (Er-BDC).** Yield: 76 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{29}H_{24}O_{19}NEr_3$: C 29.21, H 2.03, N 1.17, Er 42.09 %. Found: C 29.18, H 2.05, N 1.16, Er 42.12 %.

Synthesis of **$[(CH_3)_2NH_2][RE_3(\mu_3\text{-}OH)(NDC)_3(HCOO)_3]$ (RE-NDC, RE=Y, Tb, Er)**: The synthesis process of **RE-NDC** was similar to that of **RE-BDC** except that another ligand $H_2NDC$ (12.3 mg, 0.057 mmol) was used.

**$[(CH_3)_2NH_2][Y_3(\mu_3\text{-}OH)(NDC)_3(HCOO)_3]$ (Y-NDC).** Yield: 73 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{41}H_{30}O_{19}NY_3$: C 44.47, H 2.73, N 1.26, Y 24.09 %. Found: C 44.55, H 2.71, N 1.28, Y 24.16 %. IR (KBr, $cm^{-1}$): 3429(w), 3071(m), 2926(m), 2840(m), 1675(s), 1604(s), 1575(vs), 1491(m), 1411(s), 1356 (s), 1252(m), 1191(m), 1099(m), 1019(w), 928(m), 797(s), 775(s), 675(w), 641(w).

**$[(CH_3)_2NH_2][Tb_3(\mu_3\text{-}OH)(NDC)_3(HCOO)_3]$ (Tb-NDC).** Yield: 69 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{41}H_{30}O_{19}NTb_3$: C 37.38, H 2.30, N 1.06, Tb 36.19 %. Found: C 37.66, H 2.29, N 1.03, Tb 36.23%.

**$[(CH_3)_2NH_2][Er_3(\mu_3\text{-}OH)(NDC)_3(HCOO)_3]$ (Er-NDC).** Yield: 80 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{41}H_{30}O_{19}NEr_3$: C 36.68, H 2.25, N 1.04, Er 37.38 %. Found: C 36.69, H 2.23, N 1.01, Er 37.42 %.

## Crystallography

**Table S1** Crystallographic data for **Er-BDC** and **Er-NDC**.

| | **Er-BDC** | **Er-NDC** |
|---|---|---|
| Empirical formula | $C_{27}H_{16}O_{19}Er_3$ | $C_{39}H_{22}O_{19}Er_3$ |
| Formula weight | 1146.18 | 1296.36 |
| Wavelength/ Å | 1.54184 | 1.54184 |
| Crystal system | hexagonal | hexagonal |
| Space group | $P6_3/m$ | $P6_3/m$ |
| $a$/ Å | 10.2846(2) | 10.3534(3) |
| $b$/ Å | 10.2846(2) | 10.3534(3) |
| $c$/ Å | 20.0277(5) | 24.6485(7) |
| $\gamma$/ ° | 120 | 120 |
| $V$/ Å$^3$ | 1834.58(8) | 2288.16(15) |
| $Z$ | 2 | 2 |
| $Dc$/mg m$^{-3}$ | 2.053 | 1.880 |
| $\mu$/ mm$^{-1}$ | 12.903 | 10.436 |
| $F$(000) | 1064 | 1222 |
| Range for data collection/$^o$ | 4.42-73.03 | 4.93-73.23 |
| Reflections collected | 4248 | 5315 |
| Max., min. transmission | 0.165, 0.095 | 0.152, 0.110 |
| $T$/ K | 100(2) | 100(2) |
| Data/restraints/parameters | 1260/0/71 | 1546/42/105 |
| Final $R$ indices [$I > 2\sigma(I)$] | $^aR_1 = 0.0781$, | $R_1 = 0.1129$, |
| | $^bwR_2 = 0.2205$ | $wR_2 = 0.2642$ |
| $R$ indices (all data) | $R_1 = 0.0859$, | $R_1 = 0.1149$, |
| | $wR_2 = 0.2266$ | $wR_2 = 0.2653$ |

$^aR_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $^bwR_2 = \Sigma[w(Fo_2 - Fc_2)_2]/\Sigma[w(Fo_2)_2]_{1/2}$

Crystallographic data of **Er-BDC** and **Er-NDC** were collected at 100 K with a SuperNova diffractometer equipped with Cu-K$\alpha$ radiation (λ = 1.5418 Å) and graphite monochromator using the $\omega$-scan mode. The structures were solved by direct methods and refined on $F^2$ by full-matrix least squares using SHELXTL.[1] Crystallographic data and experimental details for structural analyses are summarized in Table S1. The CCDC reference numbers 1525133 and 1525134 for **Er-BDC** and **Er-NDC**. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

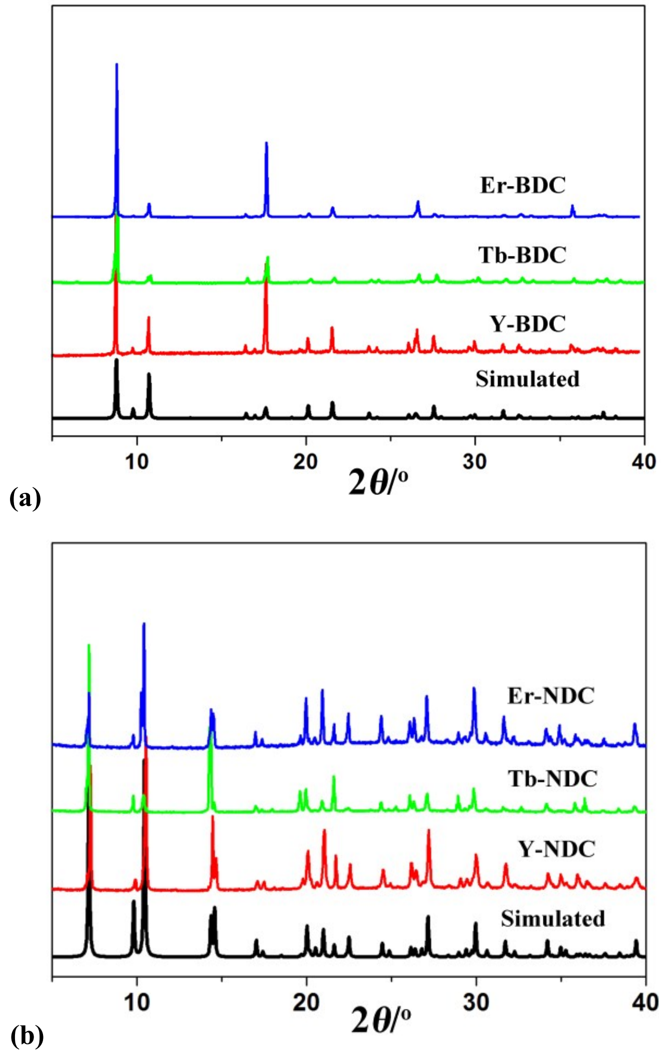


**Fig. S1.** PXRD patterns of **RE-BDC (a)** and **RE-NDC (b)**.

The empirical chemical formulas were estimated by $^1$H-NMR measurements for digested MOF crystals in DCl/$D_2O$/DMSO using a Varian-300 MHz NMR spectrometer.

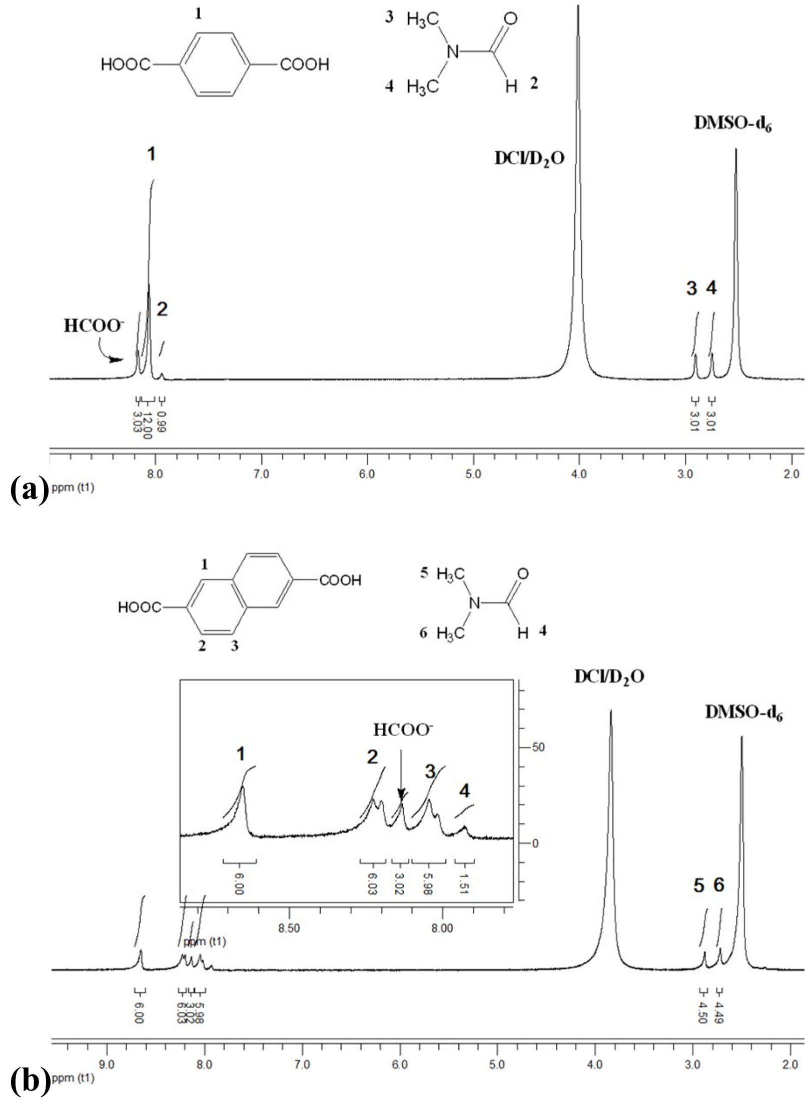


**Fig. S2**. $^1$H-NMR spectra for **Er-BDC (a)** and **Er-NDC (b)** after digesting in DCl/$D_2O$/DMSO-$d_6$ solution. **(a)** The integration value of 12 at peaks 1 is attributed to 12 aromatic protons of three $H_2$BDC. Comparing to the integration of 3 BDC and 3 HCOO- (3.03H) were also observed. From the molar ratio, the empirical formula of **Er-BDC** is **$[(CH_3)_2NH_2][Er_3(\mu_3\text{-}OH)(BDC)_3(HCOO)_3]$**. **(b)** The integration value of 18.01 at peaks 1 to 3 is attributed to 18 aromatic protons of three $H_2$NDC. Comparing to the integration of 3 BDC and 3 HCOO$^-$ (3.02H) were also observed. From the molar ratio, the empirical formula of **Er-NDC** is **$[(CH_3)_2NH_2][Er_3(\mu_3\text{-}OH)(NDC)_3(HCOO)_3]$**. Combined with the TGA and elemental analyses results of **Er-BDC** and **Er-NDC** (Fig. S8), the DMF molecules are the residue on the surface of MOFs.

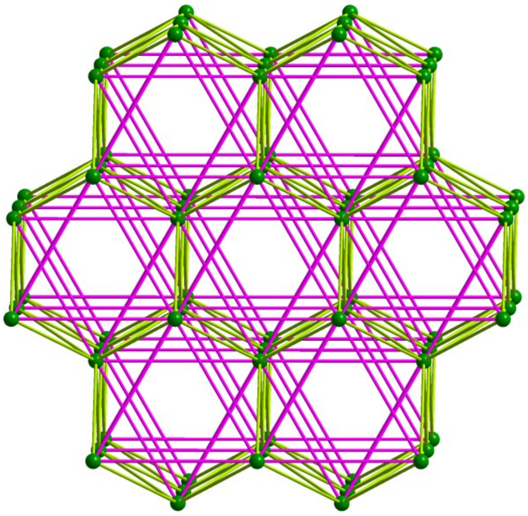


**Fig. S3.** The 12-connected network of hcp topology (the green nodes represent the [$RE_3(\mu_3$-$OH)(COO)_6$] nodes, the pink lines represent the $HCOO^-$ and the lime lines represent dicarboxylates).

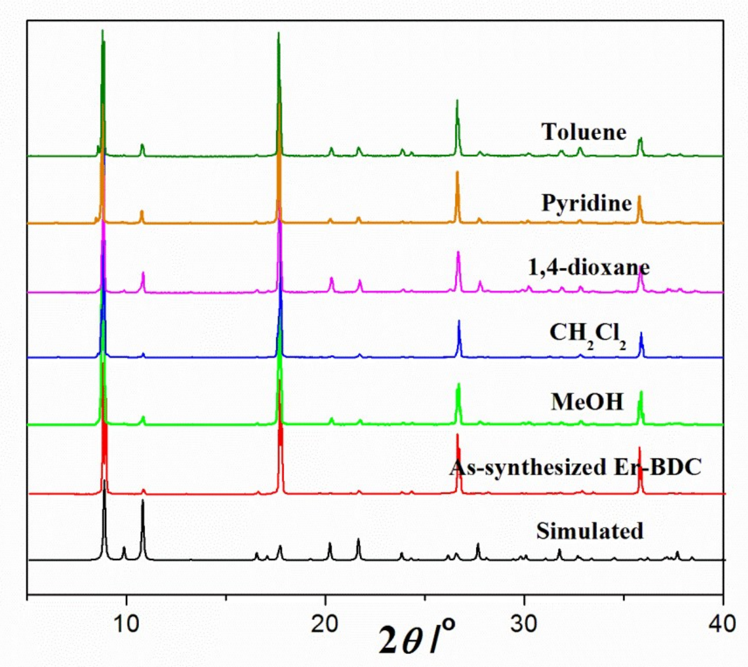
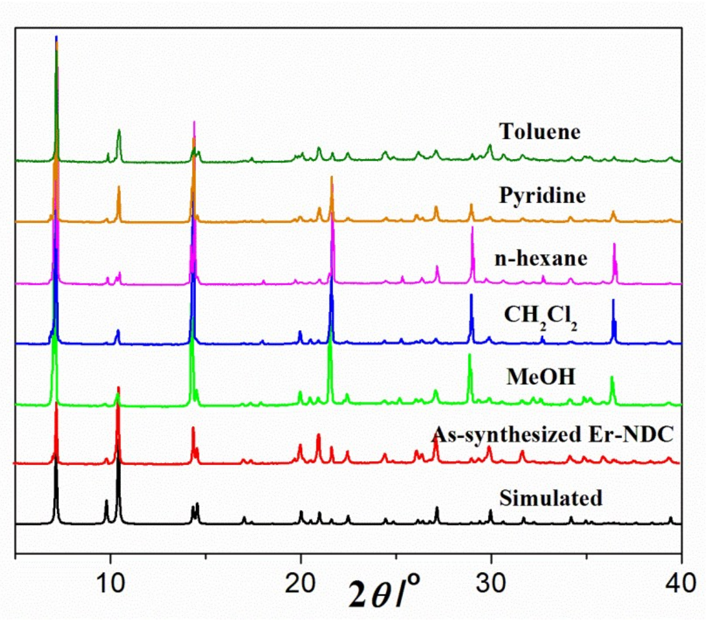


**Fig. S4.** PXRD patterns of **Er-BDC** soaking in various organic solvents for 48h.



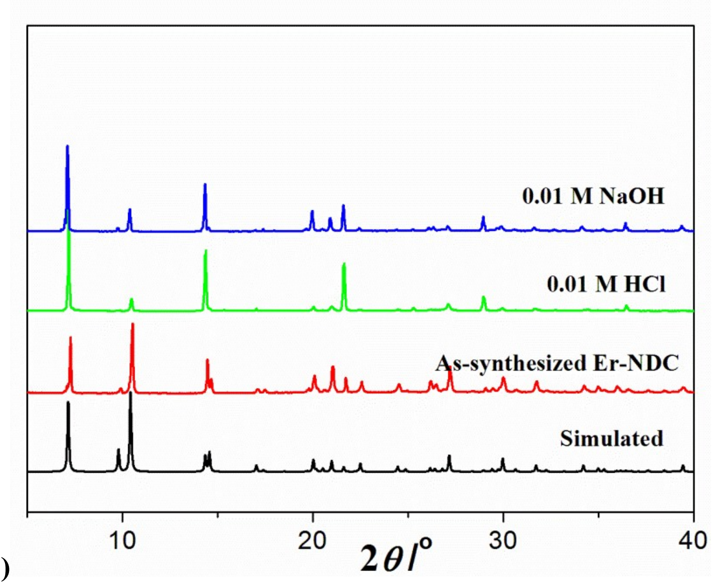


**Fig. S5.** PXRD patterns of **Er-NDC** soaking in various organic solvents **(a)**, 0.01M HCl and 0.01M NaOH **(b)**.

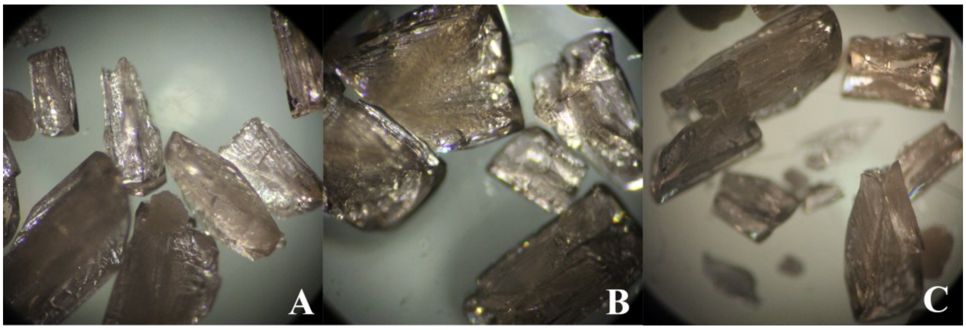
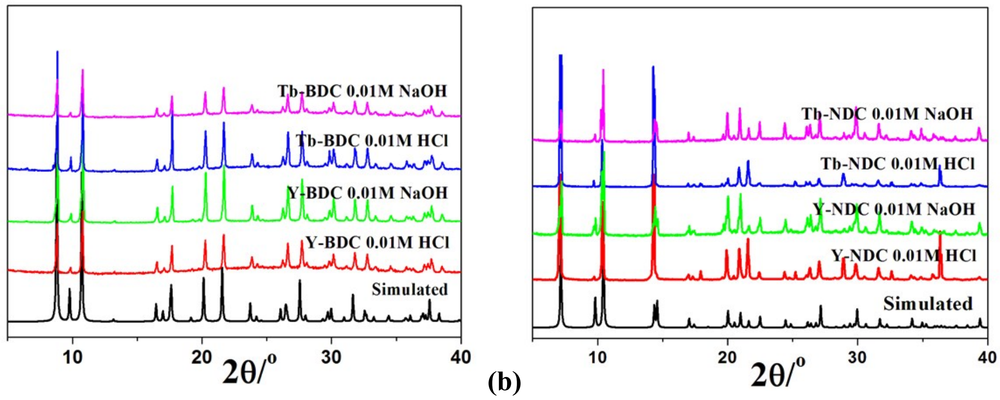
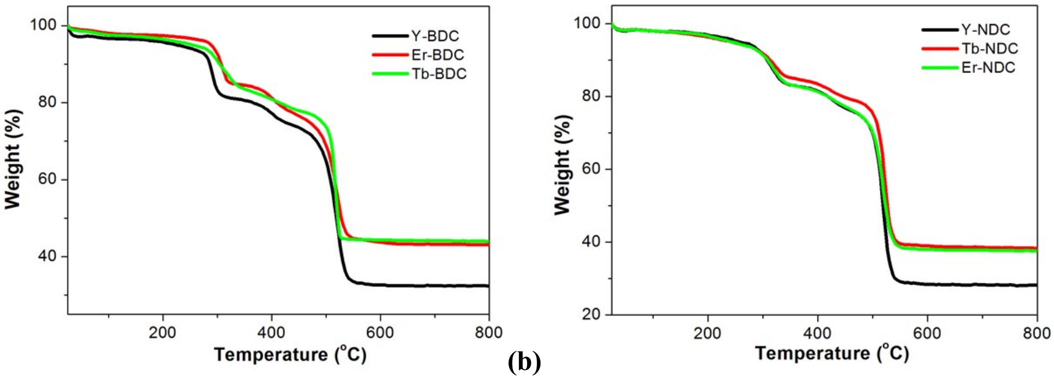


**Fig. S6.** Pictures of **Er-NDC** under optical microscope. As-synthesized (A), after treatment with 0.01 M HCl (B) and 0.01 M NaOH (C).



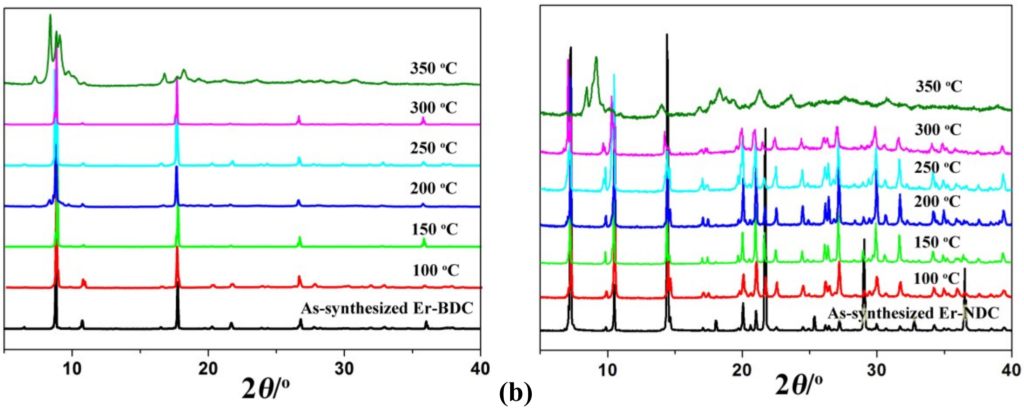
(a) (b)

**Fig. S7.** PXRD patterns of **Y/Tb-BDC (a)** and **Y/Tb-NDC (b)** soaking in 0.01M HCl and 0.01M NaOH.



(a) (b)

**Fig. S8.** TG curves of **RE-BDC (a)** and **RE-NDC (b)**.



(a) (b)

**Fig. S9.** Thermal stability tests for **Er-BDC (a)** and **Er-NDC (b)** monitored by variable temperature PXRD analysis. The variable temperature PXRD studies were heated at a constant rate of 5 °C min$^{-1}$ from room temperature to 350 °C in air, and the samples stay at each temperature for 5 min, respectively.

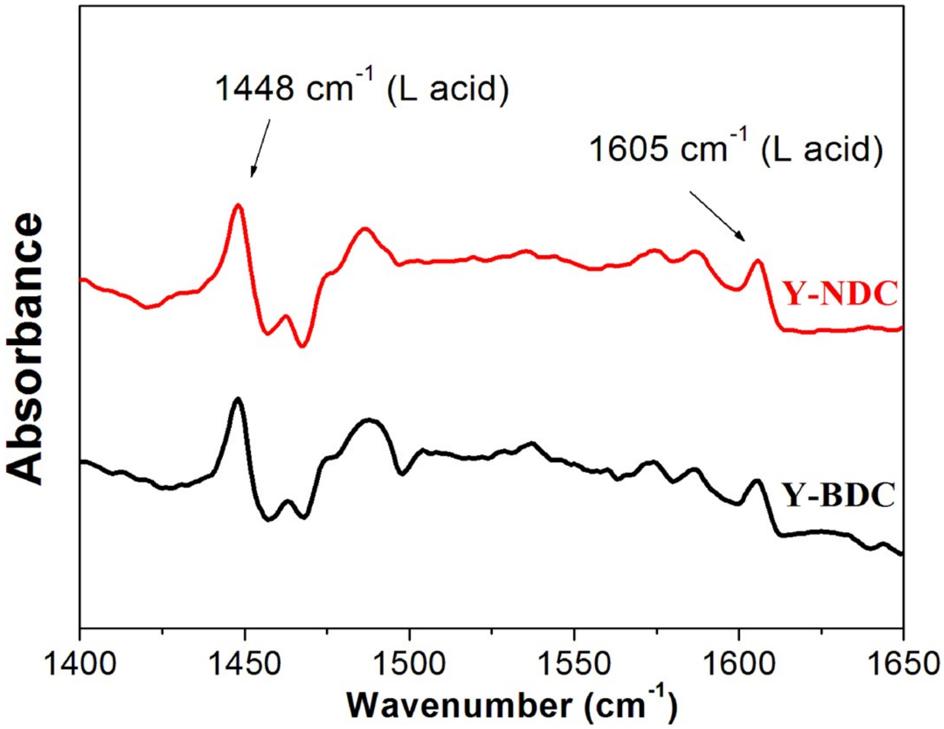


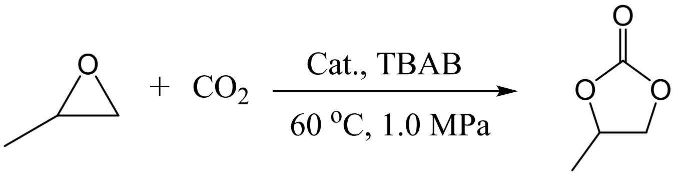
**Fig. S10.** Py-IR spectra of **Y-BDC** and **Y-NDC**. The peaks indicate the presence of accessible Lewis (L) acid sites in the samples.

## Catalytic atudies

*General procedure for the cycloaddition of $CO_2$ and epoxides*

Before the reactions, the catalysts were activated at 423 K for 12 h under vacuum to remove the residual solvent molecules on surface of MOFs. The corresponding epoxide (28.6 mmol), TBAB (0.3mmol), and catalyst (0.05mmol) were introduced into a stainless steel autoclave (20 mL). Then $CO_2$ was added until the internal pressure in the system reached 1.0 MPa at 25 °C and the resulting reaction mixture was stirred at 60 °C. After 12h, the reactor was cooled down to room temperature. The catalysts were separated by filtration, and the samples of the reaction mixture were analyzed by GC to determine the conversions.

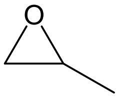
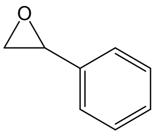
**Table S2.** Cycloaddition of $CO_2$ and propylene oxide (PO) catalyzed by various catalysts.



| Entry | Catalyst | Cat. (mmol) | Conversion (%) |
|---|---|---|---|
| 1 | Y-BDC, TBAB | 0.04 | 79 |
| 2 | Y-BDC, TBAB | 0.05 | 95 |
| 3 | Y-BDC, TBAB | 0.055 | 96 |
| 4 | Y-BDC | 0.05 | 21.6 |
| 5 | Y-NDC | 0.05 | 19.2 |

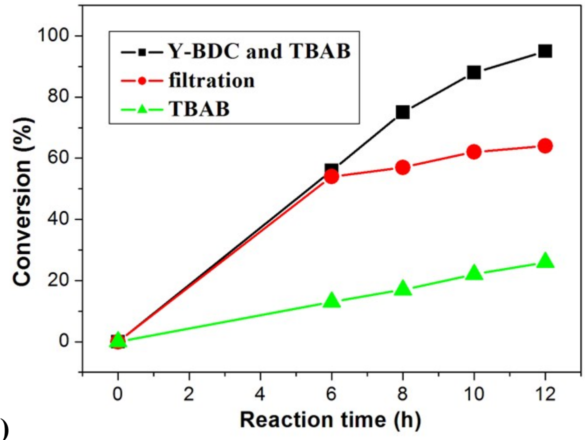
Reaction conditions: PO (28.6 mmol), TBAB (0.3 mmol) under $CO_2$ (1.0 MPa), 60 °C and 12 hours. The conversions were determined by GC.

**Table S3.** Comparison of cycloaddition of $CO_2$ and epoxides to cyclic carbonates catalyzed by various catalysts.

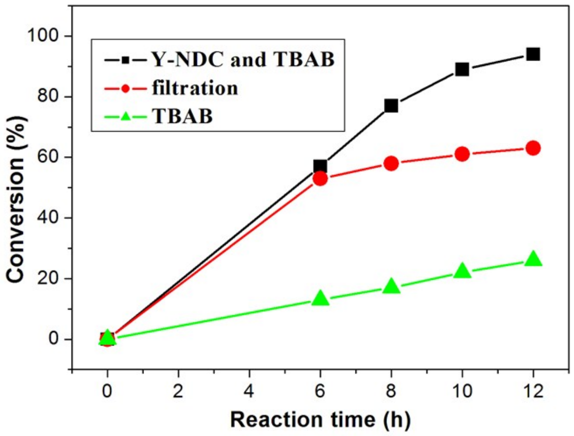
| Entry | Catalyst | Epoxide | T (°C) | $P_{CO2}$ (MPa) | t (h) | Conversion (%) | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | **Y-BDC** |  | 60 | 1 | 12 | 95 | present work |
| 2 | **Y-NDC** |  | 60 | 1 | 12 | 94 | present work |
| 3 | Gea-MOF-1 |  | 120 | 2.0 | 6 | 88 | [2] |
| 4 | PCN-224(Co) |  | 100 | 2.0 | 4 | 42 | [3] |
| 5 | ZIF-90 |  | 120 | 1.2 | 8 | 88 | [4] |
| 6 | Ni(salphen)-MOF |  | 80 | 2 | 4 | 80 | [5] |
| 7 | **Y-BDC** (0.17 mol%) |  | 60 | 1 | 12 | 72 | present work |
| 8 | **Y-NDC** (0.17 mol%) |  | 60 | 1 | 12 | 70 | present work |
| 9 | 1·Gd (2.5 mol%) |  | 60 | 0.1 | 12 | 70 | [6] |
| 10 | Ni−TCPE1 |  | 100 | 1 | 12 | 99 | [7] |
| 11 | Ni−TCPE2 |  | 100 | 1 | 12 | 86.2 | [7] |
| 12 | MIL-68(In)-$NH_2$ |  | 150 | 0.8 | 8 | 71 | [8] |

*Leaching tests*

Leaching tests and ICP analyses of the reaction mixtures filtrate were performed to verify the heterogeneous nature of the catalysts. The mixture of catalyst (0.05 mmol), PO (28.6 mmol), TBAB (0.3 mmol) and 1.0 MPa $CO_2$ was stirred at 60 °C. After 6h, the catalysts were isolated from the mixture *via* filtration, then the remaining filtrate reacted with $CO_2$ (1.0 MPa) continually at 60 °C. As shown in Fig. S11, comparing with the reactions without removal of catalysts, the reaction rates of the leaching texts decrease dramatically after removal of catalysts, implying the loss of the main active species. The very slow transformation of the PO probably is owing to the TBAB, which can also slow catalyze this reaction alone. To further exclude the possibility of the homogeneous catalysis due to the leached Y, ICP was used to analyze the metal content of the reaction solutions. Only trace amount of Y (0.2-0.3 ppm) presenting in the remaining reaction filtrate could origin from the residual catalyst particles in the solutions even after filtration, which didn't exhibit obvious catalytic activity to the reactions.



**(a)**



**(b)**

**Fig. S11.** Catalyst leaching tests for the cycloaddition of $CO_2$ and PO catalyzed by **Y-BDC (a)** and **Y-NDC (b)**. The conversions are determined by GC.

*Catalyst Recovery*

The catalysts, **Y-BDC** and **Y-NDC**, were separated from the mixture at the end of the reaction *via* filtration. The catalysts were washed abundantly with MeOH, placed in a vial and soaked in MeOH for 4 h and subsequently dried under vacuum at room temperature, which can be used for the recycle reaction directly. The quantities of catalysts recovered after each cycle correspond to ca. 98% of the initial amounts, and were still crystalline, as confirmed by PXRD (Fig. S13).

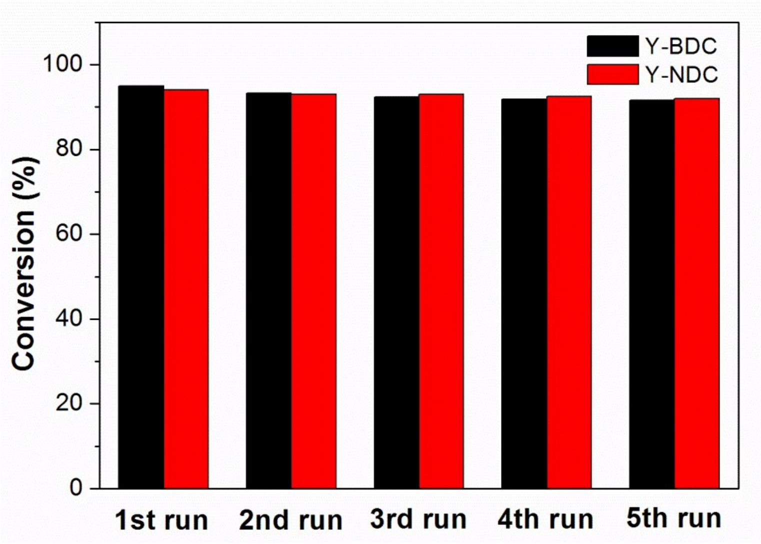


**Fig. S12.** Recycle experiments of **Y-BDC** and **Y-NDC** for the cycloaddition of $CO_2$ and PO.

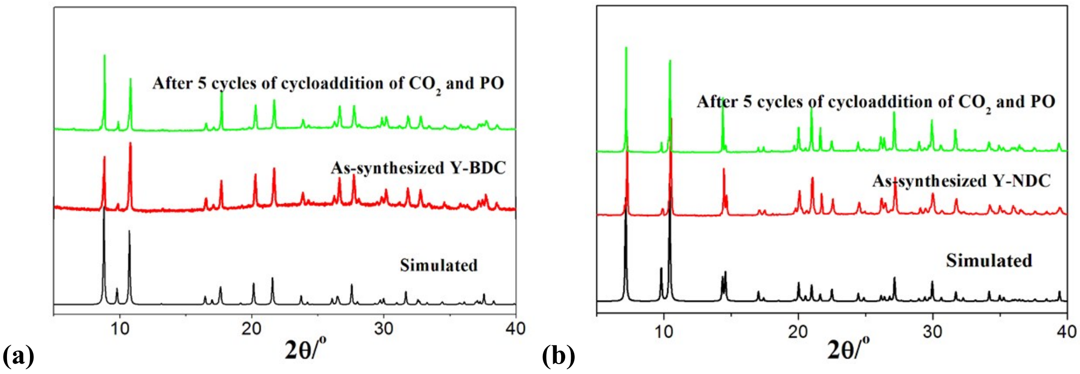


**Fig. S13.** PXRD patterns of **Y-BDC (a)** and **Y-NDC (b)** after 5 cycles of cycloaddition of $CO_2$ and PO.

Reference:

[1] SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.

[2] V. Guillerm, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil and M. Eddaoudi, *Nat. Chem.,* 2014, **6**, 673.

[3] D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 17105.

[4] J. Tharun, G. Mathai, A. C. Kathalikkattil, R. Roshan, Y. Won, S. J. Cho, J.-S. Chang and D.-W. Park, *ChemPlusChem*, 2015, **80**, 715.

[5] Y. Ren, Y. Shi, J. Chen, S. Yang, C. Qi and H. Jiang, *RSC Adv.*, 2013, **3**, 2167.

[6] J. Dong, P. Cui, P.-F. Shi, P. Cheng and B. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 15988.

[7] Z. Zhou, C. He, J. Xiu, L. Yang and C. Duan, *J. Am. Chem. Soc.*, 2015, **137**, 15066.

[8] T. Lescouet, C. Chizallet, D. Farrusseng, *ChemCatChem*, 2012, **4**, 1725.