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Supporting Information for Zn-BTC MOFs with active metal sites synthesized *via* structural-

directing approach for highly efficient carbon conversion

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Table of contents

- 1. Experimental procedures
- 2. General procedure for BIT-103 catalyzed cycloaddition of CO₂ to cyclic carbonate
- 3. Reuse experiments
- 4. Scheme S1 A plausible reaction mechanism for the catalytic cycle for carbon cycloaddition using BITs
- 5. Table S1 Synthesis of propylene carbonate from CO_2 and propylene epoxide based different catalysts
- Table S2 The conversion of propylene epoxide and selectivity of cyclic carbonate over BIT-101, BIT-102 and BIT-103
- 7. Table S3 Crystallographic data for BIT-101, BIT-102 and BIT-103
- 8. Figure S1 The plausible pathway of structural-directing synthetic approach for MOFs. (a) BIT-102.(b) BIT-103
- 9. Figure S2 The powder XRD pattern data for compound BIT-102
- 10. Figure S3 The powder XRD pattern data for compound BIT-103
- 11. Figure S4 The FT-IR spectrum data for BIT-102
- 12. Figure S5 The FT-IR spectrum data for BIT-102
- 13. Figure S6 Propylene oxide adsorption data for BIT-101
- 14. Figure S7 Propylene oxide adsorption data for BIT-102
- 15. Figure S8 Propylene oxide adsorption data for BIT-103
- 16. Figure S9 The powder XRD patterns of BIT-103 for seven catalytic cycles
- 17. Figure S10 The FT-IR spectra of BIT-103 for seven catalytic cycles
- 18. Figure S11 Recycle experiments of BIT-103 on cycloaddition of CO₂ and cyclic epoxide
- 19. The IR spectra of as-prepared BIT-103, 1, 2-propylene carbonate, BIT-103 after catalysis and the dichloromethane solution after washing the catalyst

Experimental procedures

All reagents and solvents for synthesis were purchased from commercial sources and used without further purification. The metal content of the compounds BIT-102 and BIT-103 was measured by inductively coupled plasma (ICP) on a JY-ULTIMA2 analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm⁻¹ on Nicolet 170 SXFT-IR spectrometer. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-1701 Sil capillary column. The GC mass spectra were recorded on Agilent 7890A-5975C at an ionization voltage of 1200 V. The C, H and N elemental analyses were conducted on Perkin-Elmer 240C elemental analyzer. Propylene oxide adsorption were measured on Intelligent Gravimetric Analyser IGA-100B at 298K. Powder X-ray diffraction (PXRD) patterns of the samples were analyzed with monochromatized Cu-K α (λ = 1.54178 Å) incident radiation by a Shimadzu XRD-6000 instrument operating at 40 kV voltage and 50 mA current, PXRD patterns were recorded from 4° to 50° (20) at 298 K.

Synthesis of BIT-101

Trimesic acid (0.16 g, 0.7614 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.50 g, 1.681 mmol) were successively added to 10 mL DMF/DMAC = 2:1 mixed solution in a 20 mL glass vial. The resulting solution was stirred at room temperature for a while until the solution was clear. The vial was put in an oven with the temperature raised from 30 °C to 85 °C in 180 mins, kept unchanged for 1440 mins and cooled to 30 °C in 180 mins. The obtained colourless crystals were washed by mother liquor. After 3 times, the mother liquor was poured out and chloroform was added to wash the crystals for 3 times. The resulting crystals were placed in a 100 mL glass bottle with 50 mL fresh chloroform. Bromoform was added drop-wise until the crystals were stratified. Then the crystals in the upper layer were collected and stored in mother liquor. Yield: 31%.

Synthesis of BIT-102

Trimesic acid (0.16 g, 0.7614 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.50 g, 1.681 mmol) and 5-aminoisophthalic acid (0.09 g, 0.4968 mmol) were successively added to 10 mL DMF/DMAC = 2:1 mixed solution in a 20 mL glass vial. The resulting solution was stirred at room temperature for a while until the solution was

clear. The vial was put in an oven with the temperature raised from 30 °C to 85 °C in 180 mins, kept unchanged for 1440 mins and cooled to 30 °C in 180 mins. The obtained reddish brown crystals were washed by fresh mother liquor (DMF/DMAC = 2:1). After 3 times, the mother liquor was poured out and chloroform was added to wash the crystals for 3 times. The resulting crystals and precipitation mixture were placed in a 100 ml glass bottle with 50 mL fresh chloroform. Bromoform was added drop-wise until the mixture was stratified. Then the crystals in the upper layer were collected and stored in mother liquor. Yield: 48%. Anal. calcd. (found) for $Zn_{22}(BTC)_{12}(H_2O)_{22} \cdot (16.23)DMF \cdot (13.02)DMAC \cdot (26.63)H_2O$: C, 35.03 (35.11); H, 5.58 (5.51); N, 5.42 (5.72); Zn, 20.18 (20.10). IR spectrum, v (cm⁻¹): 2928 (m), 1634 (s), 1578 (s), 1503 (s), 1447 (m), 1372 (s), 1259 (s), 1193 (s), 1099 (s), 1015 (m), 940 (m), 780 (s), 716(s) cm⁻¹.

Synthesis of BIT-103

Trimesic acid (0.16 g, 0.7614 mmol), Zn(NO₃)₂·6H₂O (0.50 g, 1.681 mmol) and 5-nitroisophthalic acid (0.01 g, 0.0474 mmol) were successively added to 10mL DMF/DMAC = 2:1 mixed solution in a 20 mL glass vial. The mixture was stirred at room temperature for 10 mins. The resulting solution was stirred at room temperature for a while until the solution was clear. The vial was put in an oven with the temperature raised from 30 °C to 85 °C in 180 mins, kept unchanged for 1440 mins and cooled to 30 °C in 180 mins. The obtained colourless single crystals were washed by fresh mother liquor (DMF/DMAC = 2:1). After 3 times, the mother liquor was poured out and chloroform was added to wash the crystals for 3 times. The resulting crystals and precipitation mixture were placed in a 100 mL glass bottle with 50 mL fresh chloroform. Bromoform was added drop-wise until the mixture was stratified. Then the crystals in the upper layer were collected and stored in mother liquor. Yield: 25%. Anal. calcd. (found) for $Zn_{22}(BTC)_{12}(H_2O)_{14}(NO_3)_8$ ·(8.02)DMF·(23.16)DMAC·(4.74)H₂O: C, 36.24 (36.05); H, 5.02 (4.98); N, 7.16 (7.36); Zn, 19.32 (19.43). IR spectrum, v (cm⁻¹): 2937 (m), 1625 (s), 1578 (s), 1501 (s), 1435 (m), 1382 (s), 1257 (s), 1191 (s), 1102 (s), 1021 (m), 764 (s), 719 (s) cm⁻¹.

X-ray Crystallography

Single-crystal X-ray diffraction data for BIT-101, BIT-102 and BIT-103 were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 77 K. All absorption corrections were applied using multi-scan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F² using the SHELXTL 97 crystallographic software package.^{1, 2} The hydrogen atoms of the organic ligands were refined as rigid groups. Crystallographic data for BIT-101, BIT-102 and BIT-103 are summarized in Table S3. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries 963915 for BIT-101 and 963916 for BIT-103.

General procedure for BIT-103 catalyzed cycloaddition of CO₂ to cyclic carbonate

In a 50 mL stainless-steel autoclave with a magnetic stirring bar in the absence of solvent and cocatalyst under CO₂ pressure, catalyst (3.76 µmol) and epoxides (20 mmol) were added. The system was carried out at 3 MPa CO₂. The reaction was conducted with magnetic stirring for the appropriate time upon heating at 160 °C. After the reaction was completed, the resulting mixture was analyzed by GC-MS and GC.

Reuse experiments

The reuse experiments were carried out for the cycloaddition of CO_2 and cyclic epoxide. The reaction was carried out under the conditions in Table 1. After the reaction was completed (100% conversion of cyclic epoxide was determined by GC). The catalyst was retrieved by filtration, washed and soaked with CH_2Cl_2 (ca. 3 * 10 mL), and air-dried prior to being used for the reuse experiment. The IR spectrum of the retrieved catalyst was identical to that of the fresh catalyst (Figure S10). In addition, the retrieved catalyst could be reuse for the cycloaddition of CO_2 and cyclic epoxide without an appreciable loss of its high catalytic performance. When the cycloaddition of CO_2 and cyclic epoxide was carried out with the retrieved catalyst under the conditions in Table 1, 94% conversion of cyclic epoxide was obtained as determined by GC. The experiment of the third run was prepared in the same way as that for the second run, and finally the 93% conversion of cyclic epoxide was also determined by GC. BIT-103 is easily recovered by centrifugation and washing with CH_2Cl_2 (ca. 3 * 10 mL), and subsequently used in the successive runs for seven cycles. The experiment of the seventh run was done in the same way as that for the second run, and finally the 92% conversion of cyclic epoxide was also determined by GC. The IR spectrum and XRD of the recovered catalyst **BIT-103** was identical to that of the freshly prepared **BIT-103** (Figures S9 and S10).

A plausible reaction mechanism for the catalytic cycle for carbon cycloaddition using BITs

We also studied the catalytic mechanism reported in other similar reactions ^{3, 4} and further consulted with our previous carbon dioxide cycloaddition results confirmed by DFT calculations.⁵ Herein we proposed a possible catalytic cycle for carbon cycloaddition using BITs. In Scheme S1: first, dissociation of nitrate anions of BIT-103 (named **A**) occurs (this dissociation proceeds more readily at higher temperatures) and yields the species **B**;⁶ then, the Zn active sites of **B** can activate the epoxide, and consequently the epoxide molecule coordinates with the Zn center to form species **C**;⁷ CO₂ attacks the βcarbon atom of the epoxide to generate the oxy anion of species **D**;⁸ and the cyclocarbonate is then formed through ring-closure, caused by an intramolecular nucleophilic attack;⁹ finally, the product dissociates from the Zn center, which subsequently combines with nitrate anions again to form **A**.



GM=Guest Molecule

Scheme S1 The plausible reaction pathway of cycloaddition of propylene epoxide. (GM = Guest Molecule).

Table S1 Synthesis of propylene carbonate from CO₂ and propylene epoxide based different catalysts^[a]



	Ent ry	Catalyst	Co- Catalyst	Solvent	Yield(%)	TON ^{[i}]	Recycle Yield(%	Ref
Homogeneous system	1.	NA	-	-	-	-	-	
	2.	TBAB	-	-	99	99	-	10
	3.	Al catalyst ^[b]	PPN-Br	-	36	72000	-	11
	4.	$Zn(NO_3)_2 \cdot 6H_2O$	-	-	3.9	13.3	-	present work
	5.	$\frac{Zn(NO_3)_2 \cdot 6H_2O + BTC +}{N \cdot BDC^{[c]}}$	-	-	2.5	8.5	-	present work
Heterogonous system	6.	MOF-5	n- Bu ₄ NBr	-	97.6	68.8	96; 96	12
	7.	Zn ₄ (OCOCF ₃) ₆ O	Bu ₄ NI	-	83	83	79; 77	13
	8.	$ZIF-8^{[d]}$	-	-	43.7	18.1	22.7; -	14
	9.	ZIF-8-f ^[e]	-	-	73.1	32.3	30.6; -	14
	10.	Mg-MOF-74 ^[f]	-	chlorobenzene	95.0	28.5	95; 95	15
	11.	Co-CMP 100	TBAB	-	98.1	201	98.1; 96	16
	12.	UIO-66-NH ₂ ^[g]	-	chlorobenzene	96	48.9	95; 95	17
	13.	BIT-101	-	-	84.7	174.9	-	present work
	14.	BIT-102	-	-	89.4	216.2	-	present work
	15.	BIT-103 ^[h]	-	-	95.2	230.2	88.5; 88.2	present work

[a] Reaction conditions: cyclic epoxide (20 mmol), catalyst (3.76 μ mol), CO₂ (3 MPa), 160 °C, 24h; [b] Reaction conditions: 1,2-epoxyhexane (10.0 mmol), Al complex 1 (0.0005 mol%), PPN-Br (0.05 mol%), Initial TON during the first 2 h. [c] Zn(NO₃)₂·6H₂O (0.0805 mmol), BTC (0.0805 mmol), N-BDC (0.0805 mmol); [d] Catalytic performance of ZIF-8 and Functionalized ZIF-8 in the cycloaddition of CO₂ to epichlorohydrin Reaction; [e] ZIF-8-f stands for functionalized ZIF-8; [f] Catalytic performance of Mg-MOF-74 in the cycloaddition of CO₂ and styrene oxide reaction; [g] Catalytic performance of UIO-66-NH₂ in the cycloaddition of CO₂ and styrene oxide reaction; [h] Sele. = 95.2%; [i] TON = moles of aimed product / moles of active metal sites.

Table S2 The conversion of propylene epoxide and selectivity of cyclic carbonate over BIT-101, BIT-102 and BIT-103^[a]



[a] Reaction conditions: cyclic epoxide (20 mmol), catalyst (3.76 µmol), CO₂ (3 MPa), 160 °C, 24h.

Compounds	BIT-101	BIT-102 ^[a]	BIT-103
Formula	$C_{36}H_{48}N_6O_{17}Zn_4$	$C_{108}H_{96}O_{118}Zn_{22}$	$C_{108}H_{36}N_8O_{94}Zn_{22}$
$M_{ m r}$	1098.36	4623.66	4388.03
Crystal system	Cubic	Cubic	Cubic
Space group	$P2_{1}3$	Pm3m	Pm3m
Temperature	296(2) K	296(2) K	150(2) K
<i>a</i> (Å)	14.2941(8)	20.5120(3)	20.4666 (8)
<i>b</i> (Å)	14.2941(8)	20.5120(3)	20.4666 (8)
<i>c</i> (Å)	14.2941(8)	20.5120(3)	20.4666 (8)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
$V(\text{\AA}^3)$	2920.6(3)	8630.3(2)	8573.1(6)
Ζ	2	1	1
$D_{\text{calc.}}(\text{g cm}^{-3})$	1.249	0.890	0.850
<i>F</i> (000)	1124	2252	2151
$R_1[I>2\sigma(I)]$	0.0881	0.0832	0.0844
$wR_2[I>2\sigma(I)]$	0.2344	0.2576	0.2651
R_1 (all data)	0.0951	0.0854	0.1003
$wR_2(all data)$	0.2523	0.2612	0.2818
GOOF	1.170	1.165	1.114
CCDC	963915	838771	963916

Table S3	Crystallogra	aphic data fo	or BIT-101,	BIT-102	and BIT-103.
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[a] BIT-102 was ever reported as compound **3** synthesized by different methods.¹⁸

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Figure S1 The plausible pathway of structural-directing synthetic approach for MOFs. (a) BIT-102. (b) BIT-103.



Figure S2 The simulated (black) and experimental (red) powder XRD pattern of compound BIT-102. Simulation based on the single crystal X-ray diffraction data.



Figure S3 The simulated (black) and experimental (red) powder XRD pattern of BIT-103. Simulation based on the single crystal X-ray diffraction data



Figure S4 The FT-IR spectrum of BIT-102

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Figure S5 The FT-IR spectrum of BIT-103



Figure S6 Propylene oxide adsorption of BIT-101 at 298K. The max adsorption mass for BIT-101 is 0.44%, T = 298K



Figure S7 Propylene oxide adsorption of BIT-102 at 298K. The max adsorption mass for BIT-102 is 0.72%, T = 298K



Figure S8 Propylene oxide adsorption of BIT-103 at 298K. The max adsorption mass for BIT-103 is 0.64%, T = 298K

The propylene oxide uptakes of BITs are quite different and one possible explanation is, as suggested by the referee, the distinct zinc coordination environments in these three Zn-BTC MOFs. As illustrated in Figure 2, BIT-101, -102 and -103 include 4- and 6-; 4- and 5-; 4-, 5- and 6-coordinated zinc centers, respectively. Among them, 5- and 6-coordinated zinc atoms can serve as open-metal-sites since the solvent molecules can be easily removed without altering the whole structures. We had calculated the number of open-metal-sites both per volume and per weight as 1.37 nm^{-3} , $2.19 \times 10^{21} \text{ g}^{-1}$; 2.78 nm^{-3} , $3.12 \times 10^{21} \text{ g}^{-1}$ and 3.83 nm^{-3} , $4.39 \times 10^{21} \text{ g}^{-1}$ for BIT-101, -102 and -103, respectively.

By virtue of the higher open-metal-site concentrations, BIT-102 and -103 show stronger interaction with epoxides and therefore higher uptake.

Similarly, due to the rich active sites in BIT-102 and -103, these two MOFs exhibit better catalytic performance than BIT-101 (Supporting Information Table S2, Page S6).



Figure S9 The powder XRD patterns of BIT-103 for the seven cycles. Simulated (black), experimental (red), first run (blue), second run (cyan), third run (pink) and seventh run (orange)



Figure S10 The FT-IR spectra of BIT-103 for seven runs catalytic cycles. experimental (black), first run (red), second run (blue), third run (cyan) and seventh run (pink)



Figure S11 Recycle experiments of BIT-103 on cycloaddition of CO₂ and cyclic epoxide. Reaction conditions: cyclic epoxide (20 mmol); catalyst (3.76 µmol); 160 °C; CO₂, 3 Mpa; 24 h



Figure S12 The IR spectra of as-prepared BIT-103, 1, 2-propylene carbonate, BIT-103 after catalysis (after one washing cycle with 10 ml dichloromethane) and the dichloromethane solution after washing the catalyst (the third washing cycle). Cyan, as-prepared BIT-103; black, 1, 2-propylene carbonate; red, BIT-103 after catalysis (after one washing cycle with 10 ml dichloromethane); blue, the dichloromethane solution after washing the catalyst (the third washing cycle).

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