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## COMMUNICATION

Zn-BTC MOFs with active metal sites synthesized *via* structural-directing approach for highly efficient carbon conversionXianqiang Huang,<sup>‡a,b</sup> Yifa Chen,<sup>‡a</sup> Zhengguo Lin,<sup>a</sup> Xiaoqian Ren,<sup>a</sup> Yuna Song,<sup>a</sup> Zhenzhu Xu,<sup>a</sup> Xingguo Li,<sup>c</sup> Changwen Hu<sup>\*a</sup> and Bo Wang<sup>\*a</sup>Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX  
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Three zinc-trimesic acid (Zn-BTC) MOFs, BIT-101, BIT-102 and BIT-103, have been synthesized *via* structural-directing strategy. Interestingly, BIT-102 and -103 exhibit extraordinary catalytic performance (up to Conv. 100% and Sele. 95.2%) in the cycloaddition of CO<sub>2</sub> under solvent- and halogen-free conditions without any additives or co-catalysts.

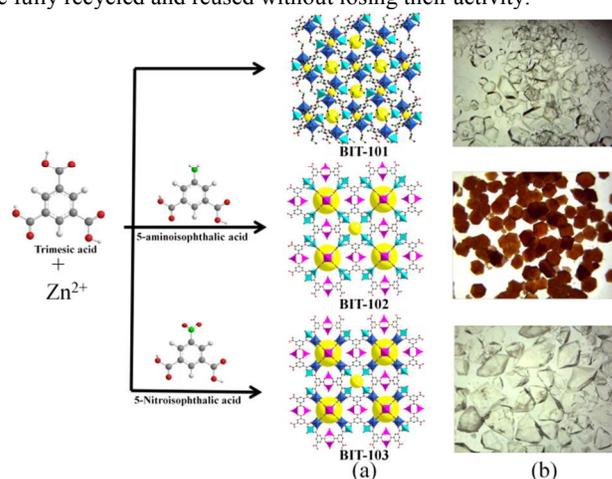
One of the most pressing issues currently facing humanity is the problem of anthropogenic CO<sub>2</sub>. The development of an efficient capture process for the CO<sub>2</sub> production stemming from the combustion of fossil fuels is a feasible solution for mitigating global warming.<sup>1</sup> But carbon sequestration and 'permanent' storage in the underground formations may cause further geological and environmental hazards.<sup>2</sup> Therefore preventing emissions altogether through carbon conservation will be ideal yet remains challenging.

Insertion of CO<sub>2</sub> into epoxides is a feasible industrial carbon conversion technology. Thus-obtained five-membered cyclic carbonates can serve as valuable monomers for polycarbonates and electrolytes in secondary batteries and chemical sources.<sup>3</sup> Although many cyclic carbonations have been developed, these reactions are carried out in the presence of halogen and harmful solvents.<sup>4</sup> Hence catalytic conversion of CO<sub>2</sub> in a solvent- and halogen-free system is highly desirable and long-sought-after.

Metal-organic frameworks (MOFs) are a class of crystalline microporous materials replete with well-defined channels and rich functionalities formed by coordination of metal clusters or ions with organic linkers.<sup>5</sup> Beyond exceptional porosity and gas uptake and storage properties, MOFs are often considered as efficient heterogeneous catalysts candidates because: 1) maximum dispersed and uniformly distributed metal ions in MOFs provide numerous potential catalytic centers; 2) highly ordered open channels with well-defined size and shape offer excellent selectivity of substrates; 3) heterogeneous nature of MOFs facilitates the recovery and reuse of the catalysts. However, many MOFs reported to date are not catalytically active due to the coordinative saturation of their metal sites. Therefore incorporating desirable active metal centers into MOFs is very important to achieve framework activity.<sup>6</sup>

Herein, we report three Zn-BTC MOFs, BIT-101, BIT-102 and BIT-103, with active metal sites prepared *via* structural-directing method by employing low-cost starting materials and facile one-pot synthesis (Figure 1). Interestingly BIT-102 and -103 exhibit extraordinary catalytic performance in the cycloaddition of CO<sub>2</sub> to cyclic carbonates under solvent- and halogen-free conditions

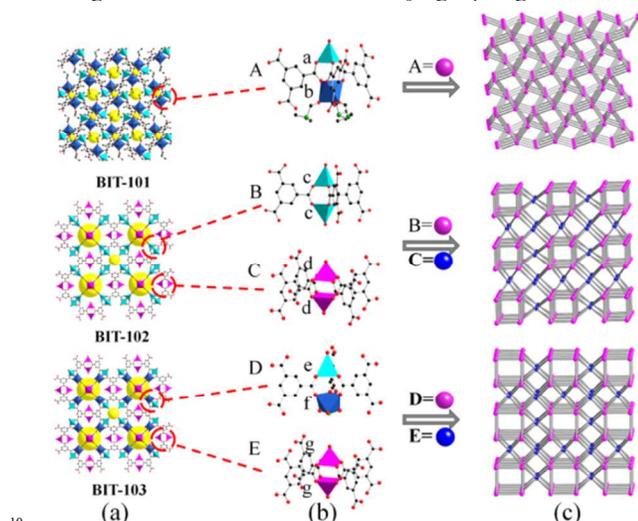
without any additional co-catalysts. Furthermore these MOFs can be fully recycled and reused without losing their activity.



**Figure 1** Synthetic pathway of BIT-101, BIT-102 and BIT-103. Colour codes: C, black; O, red; N, green; gray, H. (a) The topology structures of three Zn-BTC MOFs. (b) The micro-graphs of three Zn-BTC MOFs.

Structural-directing synthetic approach is widely used in, among others, the preparation of zeolites and molecular sieves, as well as self-assembly of nano structures. However it is not common in MOF synthesis and only a few examples are reported to date.<sup>7</sup> It has been shown that mixed-ligand MOFs with unprecedented gas selectivity can be obtained using organic linkers with the same topology and connectivity.<sup>8</sup> Furthermore many recent papers have proved that organic linkers in MOFs can be easily substituted by similar ligands with different functionalities without altering the MOF structures.<sup>9</sup> Hence we sought to use organic ligands with similar structure to our targeting backbone organic linker as the potential structure directing agents in MOF synthesis. Specifically we picked A-BDC and N-BDC (Figure 1), in which one out of three carboxylic groups as in BTC is replaced by an amino and a nitro group respectively. Based on the final results, we believe that these functional groups with weaker coordination capability to zinc ions may participate in the self-assembly process and direct the architectures and underlying topologies. At the meantime, these linkers can be gradually replaced by BTC with stronger covalent bonds to give the final 3D frameworks with higher thermodynamic stabilities (Figure S1).

Commercial available simple organic ligand, BTC, was used to synthesize three new Zn-BTC MOFs. The solvothermal reactions between BTC and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in a mixture of DMF and DMAC with the addition of none, A-BDC and N-BDC afforded colourless crystals of BIT-101, reddish brown crystals of BIT-102 and colourless crystals of BIT-103, respectively. Single X-ray diffraction (SXR) data reveal that three Zn-BTC MOFs have 3D open networks constructed from the same metal joints and organic linkers with distinct underlying topologies.



**Figure 2** The basic topology structures of BIT-101, BIT-102 and BIT-103. (a) The pore structural of three Zn-BTC MOFs. Cyan for four-coordinated Zinc, Magenta for five-coordinated Zinc, Royal blue for six-coordinated Zinc and yellow ball stands for the pore area of the structural. (b) The basic structural unit of three Zn-BTC MOFs enlarged from (a), Colour codes: C, black; O, red and green for N. (c) The net topology of three Zn-BTC MOFs.

BIT-101 crystallizes in a cubic  $P2_13$  space group as evidenced by SXR determination. In the 3D open framework of BIT-101, Zn(II) ions are coordinated by BTC linkers (Figure 2). Each asymmetric unit A of BIT-101 is comprised of one tetrahedral coordinated Zn(II) center (named **a**) and one octahedral coordinated Zn(II) center (named **b**), and the tetrahedral **a** is connected to the octahedral **b** through meta-positioned carboxyl groups of three BTC. Tetrahedral **a** and octahedral **b** are saturated by one oxygen atom from water and three oxygen atoms from three DMF molecules in the axial positions, respectively. Each asymmetric unit A is connected with five other A units to form triangle and quadrilateral pores (Figure 2). However, these two kinds of pores are too small ( $7.46 \text{ \AA}$  and  $7.46 \text{ \AA}$ ) and thus the diffusion of reactants and products will be challenging.

BIT-102 crystallizes in a cubic  $P\bar{m}3m$  space group and is composed of dimeric zinc tricarboxylate units B and tetracarboxylate units C (Figure 2), with a short Zn-Zn internuclear distance of  $3.52(2) \text{ \AA}$  and  $3.00(2) \text{ \AA}$ , respectively. The dimeric zinc tricarboxylate unit B contains two tetrahedral Zn(II) center (named **c**), and each tetrahedral **c** is connected to another **c** by three BTC in the equatorial position through carboxylate oxygen atoms whereas the axial positions are occupied by one oxygen atom from water. Similarly the dimeric zinc tetracarboxylate unit C is composed of two pyramidal Zn(II) center (named **d**) and each pyramidal **d** is connected to another **d** by four BTC in the equatorial position through carboxylate oxygen atoms while the axial positions are capped by one oxygen

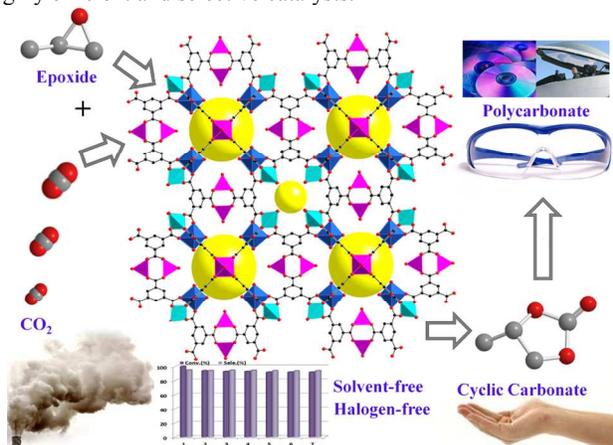
atom from water. One dimeric zinc tetracarboxylate unit C is connected with eight dimeric zinc tricarboxylate units B, and each eight dimeric zinc tricarboxylate B are connected by one vertical tetracarboxylate unit C to form the big cage. This cage with a diameter of  $13.60 \text{ \AA}$  has relatively big strip opening gates ( $7.45 \text{ \AA} \times 9.61 \text{ \AA}$ ) and every four big cages form a small cage with square opening gates ( $6.06 \text{ \AA} \times 6.06 \text{ \AA}$ ) in the middle constituted by four tricarboxylate units B. The structure of BIT-103 is isoreticular to that of BIT-102. It is composed of dimeric zinc tricarboxylate unit D and tetracarboxylate unit E. The structure of unit E resembles that of unit C in BIT-102. While as for B in BIT-102, the coordination water of the tetrahedron **c** is replaced by a nitrate ion to give a rare octahedral Zn(II) center **f** and thus the whole building unit is denoted as unit D (Figure 2).

Given the weak interaction of these solvent molecules that are coordinated to Zn centers, many evenly distributed and well-spaced active metal centers are now available in these Zn-BTC MOFs for catalysis. It is noteworthy that the pore size and accessibility of BIT-101 ( $7.46 \text{ \AA}$ ), as proved by SXR and the adsorption of propylene oxide (Figures S6-8), largely limit its activity. In comparison, BIT-102 and BIT-103 show a pore diameter and propylene oxide uptake of  $9.61 \text{ \AA}$ ,  $0.72 \text{ wt\%}$  and  $9.47 \text{ \AA}$ ,  $0.64 \text{ wt\%}$  at  $298 \text{ K}$ , respectively. Based on these findings, we picked BIT-102 and BIT-103 to further investigate the catalytic activity of cycloaddition of  $\text{CO}_2$  to cyclic carbonate under solvent- and halogen-free conditions.

To investigate the effectiveness of the Zn-BTC MOFs in catalytic carbon conversion by cycloaddition of  $\text{CO}_2$  to propylene epoxide, the reactions were performed under the same conditions using BIT-101, BIT-102, BIT-103,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{Zn}(\text{NO}_3)_2$  along with BTC and N-BDC. The yield and TON of catalyst in each reaction are summarized and illustrated in Table S1. As shown in Table S1, the yield of product catalyzed by  $\text{Zn}(\text{NO}_3)_2$  with and without organic ligands present in the reaction media, was  $3.9\%$  and  $2.5\%$  (Entries 4-5, Table S1), respectively. Since BIT-101, BIT-102 and BIT-103 encompass numerous potential catalytic centers, the conversion of propylene carbonate was dramatically increased. Because the size of the pores and the coordination environments of zinc atoms in these MOFs are very different, the catalytic yields vary from  $84.7\%$  to  $95.2\%$ . Specifically, without any further optimization, the yield of propylene carbonate using BIT-103 reaches  $95.2\%$  (Entry 15, Table S1, Figure 3), no other co-catalysts, such as quaternary ammonium salt, or additives are used. And indeed, yield and TON of BIT-103 outperform many effective homogeneous and heterogeneous catalysts reported to date, i.e. MOF-5,<sup>10</sup>  $\text{Zn}_4(\text{OCOCF}_3)_6\text{O}$ ,<sup>11</sup> (Entries 6-7, Table S1) etc. Although the TON is lower than that of homogeneous catalysts (Entry 3, Table S1), it also indicates that BIT-103 is indeed very promising as a new heterogeneous catalyst for cycloaddition reaction by virtue of 1) satisfactory yields and high selectivity, 2) environmental friendly carbon conversion process--no solvents, co-catalysts or any other additives needed, and 3) reusability and ease of continuous production.

Following the success of propylene epoxide cycloaddition and evaluating the scope and limitations of the current procedure, cycloaddition reactions with an array of epoxy compounds were examined using BIT-103. A series of epoxide substrates were examined for the synthesis of corresponding cyclic carbonates (Table 1). Cyclic carbonates with alkyl side chain groups, aryl side chain groups were successfully synthesized from

corresponding epoxides in high conversion (96.6-100%) and selectivity (90.8-98.6%). The di-substituted epoxide, gave lower activity toward the production of the corresponding cyclic carbonates, which is presumably due to the effect of the high steric hindrance and slow diffusion of these substrates inside the pores of BIT-103. These preliminary results exhibit that Zn-BTC MOFs can facilitate the cycloaddition of epoxides and serve as highly efficient and selective catalysts.

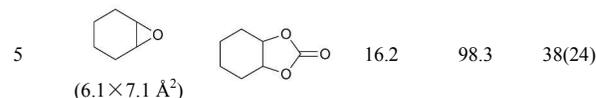


**Figure 3** Catalytic performance of BIT-103 in the cycloaddition of CO<sub>2</sub> and propylene epoxide reaction under solvent- and halogen-free conditions without any additives or co-catalysts. Inset shows that the catalytic cycles of BIT-103 in the cycloaddition of CO<sub>2</sub> and propylene epoxide reaction.

Furthermore, recyclability is an important and essential feature of any catalyst to be considered for use in industrial applications. Thus we sought to explore the influence of catalyst recycles on the catalytic properties of BIT-103. In the recycle experiments, the catalyst was separated by centrifugation, and washed using CH<sub>2</sub>Cl<sub>2</sub>. The IR spectra and PXRD patterns of the recovered BIT-103 were identical to those of the freshly prepared BIT-103 (Figures S9-10). In addition, the recovered BIT-103 can be reused in repetitive reactions without any appreciable loss of its high catalytic performance [Conv. of propylene epoxide: 100% (First run), 94% (Second run), 93 % (Third run), 92 % (Seventh run)] (Figure S11).

**Table 1** Results of cycloaddition of epoxides catalyzed by BIT-103<sup>a</sup>

Entry	Epoxides	Products	Conv.(%)	Sele.(%) <sup>c</sup>	TON <sup>d,e</sup>
1	 (5.5×6.7 Å <sup>2</sup> ) <sup>b</sup>		100	95.2	230(24)
2	 (5.6×7.8 Å <sup>2</sup> )		100	90.8	219(8)
3	 (6.7×9.6 Å <sup>2</sup> )		96.6	97.8	236(24)
4	 (6.7×11.7 Å <sup>2</sup> )		100	98.6	238(24)



[a] Reaction conditions: epoxides (20 mmol), BIT-103 (3.76 μmol), CO<sub>2</sub> (3 MPa), 160 °C. [b] Numbers in the brackets represent the size of epoxides, which refers to CPK Van der Waals Radii measured by Chem3D. [c] Selectivity to cyclic carbonate. [d] TON = moles of aimed product molecular / moles of active metal sites. [e] Numbers in the brackets represent the reaction time. [f] The result of conversion of CO<sub>2</sub> and propylene without BIT-103.

In summary, we developed a facile yet powerful one-pot method and successfully synthesized three new Zn-BTC MOFs, BIT-101, BIT-102 and BIT-103, by employing BTC analogues as the structural-directing agents. These MOFs with highly active metal centers show distinct structures and different coordination environments. Importantly BIT-102 and BIT-103 exhibit exceptional catalytic activity, up to Conv. 100% and Sele. 95.2%, in the cycloaddition of CO<sub>2</sub> to cyclic carbonates under solvent- and halogen-free conditions without any additional co-catalysts. These novel catalysts are heterogeneous and can be fully recovered and reused without losing the catalytic activity. This offers a starting point to gain insight into the formation of catalytic active new open framework materials and shed light on developing strategies aimed at ameliorating increasing atmospheric carbon dioxide levels.

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## Notes and references

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