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3d-4f Heterometal-Organic Frameworks for Efficient Capture and Conversion of CO_2

*Wan-Zhen Qiao, Hang Xu, Peng Cheng, Bin Zhao**

Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry (MOE), and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

ABSTRACT: Two novel three-dimensional 3d-4f heterometallic-organic frameworks $\{[TbZn(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot 5H_2O\cdot 0.5DMA\}_n$ **(1)** and $\{[TbCo(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot 8H_2O\cdot 0.5DMA\}_n$ **(2)** have been synthesized and structurally characterized. They are isostructural and exhibit irregular one-dimensional channels with large potential pore volume. Importantly, both of them demonstrate excellent catalytic activity for the chemical fixation of CO_2 into cyclic carbonates under mild conditions. Moreover, the catalytic recycling of compound **1** as a representative example was explored, it can be easily separated and reused for at least four times without significant reduction in catalytic ability.

INTRODUCTION

Carbon dioxide (CO_2), as the major greenhouse gas, has been considered to cause great environmental concerns, such as ocean acidity, melting of glaciers.[1,2] The CO_2 emission mainly originates from burning of fossil fuels and accumulates in the atmosphere at an alarming pace.[3] It is imperative to explore CO_2 capture and sequestration (CCS) technologies to decrease CO_2 from emission sources.[4-6] Up to date, extensive efforts have been made to obtain new materials for advanced CCS technologies.[7-9] Additionally, as a renewable carbon feedstock, CO_2 can be utilized to transform into high value chemicals.[10-16] Particularly, the cyclic carbonates formed by the coupling of CO_2 with epoxides have attracted significant attention owing to its 100% atom economic nature.[17,18] Besides, cyclic carbonates possess potential extensive application as electrolytes in the lithium-ion batteries, precursors for polymeric materials, intermediates of fine chemicals, organic solvents and so on.[19-21] Impressively, various catalytic systems have been developed for CO_2 fixation into cyclic carbonates, including homogeneous catalysts and heterogeneous catalysts, such as ionic liquids,[22,23] alkali metal salts,[24] metal oxides,[25] and functional polymers.[26,27] Thus, it is more favorable to develop materials which can efficiently capture CO_2 and simultaneously catalyze CO_2 conversion.

Emerging as a new class of functional materials, metal organic frameworks (MOFs),[28-33] which feature tailorable structures, exceptional properties,[34-41] have been proposed to be promising materials to meet the dual challenge of CO_2 capture and conversion for the following reasons: (a) the porous MOFs can significantly absorb CO_2,[42-45](b) the well ordered porous structures can enrich substrates and facilitate the accessibility of substrates to active sites, (c) the metal ions can serve as Lewis acid sites to efficiently activate epoxide,[46-49] (d) stable MOFs, as heterogeneous catalysts, remain excellent catalytic performance after being successively reused. Thus, it is of vital importance to develop MOF-based catalysts for efficient CO_2 capture and conversion.[50-53]

In this contribution, two 3d-4f heterometallic MOFs $\{[TbZn(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot5H_2O\cdot0.5DMA\}_n$ (**1**) and $\{[TbCo(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot8H_2O\cdot0.5DMA\}_n$ **(2)** were obtained based on 5,5′-dicarboxylate-2,2′-dipyridine (H_2BPDC) and structurally characterized. They are isostructural and exhibit one-dimensional open channels with large potential pore volume. Furthermore, both of them exhibit excellent catalytic performance for CO_2 conversion into cyclic carbonates in the absence of solvent under mild conditions and compound **1** can be used as a recoverable heterogeneous catalyst with high activity.

EXPERIMENT SECTION

Synthesis of $\{[TbZn(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot 5H_2O\cdot 0.5DMA\}_n$ (1)

A mixture of $Tb(ClO_4)_3\cdot 6H_2O$ (28.5 mg, 0.05 mmol), H_2BPDC (24.4 mg, 0.1 mmol), $ZnCl_2$ (6.8 mg, 0.05 mmol), H_2O (1 mL) and DMA (4 mL) were added into a 8 mL glass vial. The glass vessel was heated at 80 °C for three days under autogenous pressure and then cooled to room temperature at 2 °C/h under ambient conditions. The colorless block crystals were obtained and washed with DMA. Yield: 50%, based on $Tb(ClO_4)_3\cdot 6H_2O$. Elemental analysis (%) Calcd for compound **1** **(**$TbZnC_{26}H_{34.5}N_{4.5}O_{17.5}Cl$): C 32.86, H 3.63, N 6.64. Found: C 32.89, H 3.69, N 6.68.

Synthesis of $\{[TbCo(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot 8H_2O\cdot 0.5DMA\}_n$ (2)

A mixture of $Tb(ClO_4)_3\cdot 6H_2O$ (28.5 mg, 0.05 mmol), H_2BPDC(24.4 mg, 0.1 mmol), $CoCl_2\cdot 6H_2O$ (11.9 mg, 0.05 mmol), H_2O (1 mL) and DMA (4 mL) were added to a 8 mL glass vial. The glass vessel was heated at 80 °C for three days under autogenous pressure and then cooled to room temperature at 2 °C/h under ambient conditions. The colorless block crystals were obtained and washed with DMA. Yield: 50%, based on $Tb(ClO_4)_3\cdot 6H_2O$. Elemental analysis (%) Calcd for compound **2** **(**$TbCoC_{26}H_{40.5}N_{4.5}O_{20.5}Cl$): C 31.31, H 4.06, N 6.32. Found: C 31.36, H 4.10, N 6.34.

Catalytic Performance Evaluation

In each individual reaction, 2 mmol epoxide substrate and 20 mg compound **1** catalyst (1 mol % based on Tb metal center) together with 32 mg tetrabutylammonium bromide (TBAB, 5 mol %) were added into a 10 mL reaction tube. The tube was purged with CO_2 at 1 atm under solvent free environment and then was stirred (600 rpm) for 12h to complete the reaction. After the catalytic reaction, the catalyst was separated by centrifugation and the product yields were determined by ^{1}H NMR. To explore the recyclability, the catalyst was isolated from the reaction solution, washed with CH_2Cl_2 for three times, dried at ambient temperature, and then reused in the next run of the reaction.

RESULTS AND DISCUSSION

Structure

The X-ray single-crystal diffraction analysis reveals that **1** and **2** are isostructural. They both crystallize in the monoclinic system with space group C2/c. Thus compound **1** as a representative example is selected to describe the crystal structures in details. The asymmetric unit in **1** consists of one Tb^{3+} ion, one Zn^{2+}ion, one μ_2-H_2O molecule and two $BPDC^{2-}$ anions. Eight-coordinated Tb^{3+} has an triangular dodecahedron geometry, which is achieved by four carboxylic oxygen atoms, two water molecules and two μ_2-H_2O molecules (Figure 1). The framework is composed of two distinct building blocks $[Tb_2(\mu_2\text{-}H_2O)_2(COO)_8(H_2O)_4]$ (abbr. as $[Tb_2]$ unit) and $[Zn(BPDC)_2(H_2O)Cl]$ (abbr. as $[Zn(BPDC)_2]$ unit) (Figure S2). Two Tb^{3+} ions are bridged into a binuclear $[Tb_2]$ unit by two μ_2- H_2O molecules. Four nitrogen atoms from two $BPDC^{2-}$ ions, one water molecule and one chloride ion complete the six-coordinated environment of Zn^{2+} anions (Figure 1a), forming a $[Zn(BPDC)_2(H_2O)Cl]$ motif, which connects the $[Tb_2]$ unit into a 3D neutral framework (Figure 1b). The framework possesses one-dimensional irregular channels along *c* direction with a diameter of about 6 Å (Figure 1b). Additionally, the potential pore volume of **1** is as high as 46%, calculated by the PLATON program.

In order to simplify the complicated framework, each [Tb_2] unit is considered as an 8-connected node which links with eight [$Zn(BPDC)_2$] units and each [$Zn(BPDC)_2$] unit is regarded as a 4-connected node which bridges four [Tb_2] units. Thus the framework can be simplified into a (4,8)-connected topological structure with topology symbol of ***flu***[54] (Figure 1c, Figure S2). Thermogravimetric (TGA) analysis and elemental microanalyses (EA) indicate that five water molecules and half of one N,N-dimethyl acetamide (DMA) molecule are in the asymmetric unit.

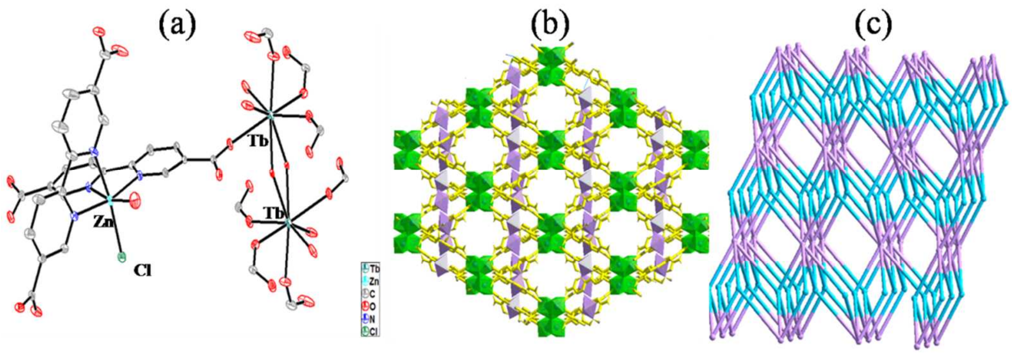


Figure 1. (a) the coordinated environments of Tb^{3+}, Zn^{2+} and $BPDC^{2-}$ ligand in compound **1**. (b) 3D framework of **1** along *c* direction. (c) Simplified ***flu*** topology of **1**.

Powder X-ray diffraction Analyses (PXRD) and Thermogravimetric Analysis (TGA)

PXRD analyses were carried out at ambient conditions. The PXRD patterns of as-synthesized samples are in conformity with the simulated ones from the single-crystal data suggesting the high phase purity of the sample (Figure S3). As shown in the Figure S4, TGA curve of compound **1** exhibits two steps of weight loss. The first weight loss of 20.3% between 36 °C and 190 °C corresponds to the loss of five free water molecules, half of one free DMA molecule and three coordinated water molecules (calcd: 19.9%). Subsequently, TGA curve mainly stays in a plateau, indicating the high thermal stability of the framework **1**. Then, the second weight loss above 350 °C stems from the decomposition of 3D framework. As to compound **2**, TGA curve also exhibits two steps of weight loss. The first weight loss of 24.4% between 46 °C and 220 °C corresponds to the loss of eight free water molecules, half of one free DMA molecule and three coordinated water molecules (calcd: 24.2%). Subsequently, TGA curve mainly stays in a plateau, indicating the high thermal stability of the framework **2**. Then, the second weight loss above 350 °C stems from the decomposition of 3D framework.

Gas Adsorption

Inspired by its large void volume, the gas adsorption property of **1** as a representative example was studied. Before the measurement, about 100 mg crystals of compound **1** was immersed in CH_2Cl_2 for six days during which the supernatant was exchanged once every eight hours. Then the crystals were outgassed under dynamic vacuum at 25 °C for 12 hours to afford **1a.** At 298 K, the CO_2 adsorption property was studied in a relative pressure ranging from 10^{-3} to 1 atm. As shown in Figure S5, the adsorption measurement shows linear increase with a maximum adsorption CO_2 capacity of 25 cm^3/g at point $P/P_0 = 1.0$, which is relatively low compared to other MOFs materials.[58] It is interesting that the desorption isotherm of **1a** does not retrace the adsorption one, showing a large hysteresis and an abrupt drop at point $P/P_0 = 0.1$. It is very difficult to desorb all of the included CO_2, possibly suggesting the strong chemisorption interaction occurs between CO_2 and the framework **1a**.[45,55.]

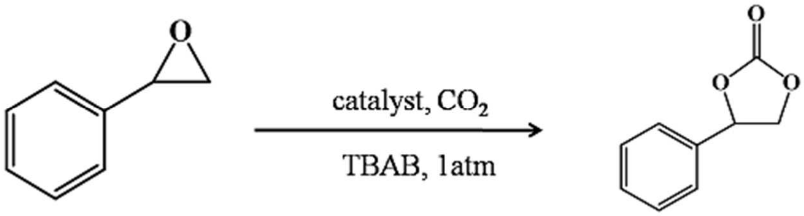
Catalytic Properties

The moderate CO_2 uptake properties of compound **1** motivated us to investigate its heterogeneous catalytic ability for cycloaddition of CO_2 with epoxides to generate cyclic carbonates. The styrene oxide was chosen as the model substrate to explore the optimized reaction condition. During our investigations of various reports, we chose relatively mild conditions in the presence of 2.5 mol % TBAB to study the catalytic ability of compound **1**, the results were summarized in Table 1. It can be seen that the yield gradually increased when the temperature was increased, but the yield was only 77% at 70 °C (Table 1, entries 1-3). In order to avoid much energy consume from higher temperature, the TBAB amount was increased to 5 mol % (Table 1, entries 4-6). The results revealed that the optimized condition should be 20 mg compound **1** and 5 mol % TBAB at 70 °C (Table 1, entry 6). Under the optimized conditions, the conversion reached over 99%. Comparably, the yield was less than 1% when TBAB was absent in the system and the yield was only 57% when compound **1** was absent in the system under the employed reaction conditions. (Table 1, entries 7 and 8). Thus, both compound **1** and TBAB performed indispensable roles in the reaction. It is proposed that metal ions serve as Lewis acid sites to efficiently activate epoxide and TBAB is employed as a cocatalyst in the experiment in the previous reports.[50,51] The synergistic effect of compound **1** and TBAB is the main reason of high catalytic activity of the catalyst system under mild conditions.

Generally, Lewis acid sites are widely considered to be responsible for CO_2 conversion with epoxides. The oxyphilic and highly Lewis acidic nature make rare metals potentially good catalysts for the activation of epoxides and the subsequent coupling with CO_2.[56,57] Furthermore, one isostructural MOF (compound **2**) was synthesized and investigated on its catalytic ability in the catalytic system.

As shown in Table 2, compound **2** was investigated on its catalytic ability in the catalytic system. In the presence of 2.5 mol % TBAB, the yield was only 77% at 70 °C (Table 2, entry 1). In order to avoid much energy consume from higher temperature, the TBAB amount was increased to 5 mol % (Table 2, entries 2-5). The results revealed that the optimized condition should be 20 mg compound **2** and 5 mol % TBAB at 80 °C (Table 2, entry 5). Under the optimized conditions, the conversion reached over 99%. Comparably, the yield was less than 1% when TBAB was absent in the system and the yield was only 69% when compound **2** was absent in the system under the employed reaction conditions. (Table 2, entries 6 and 7). In comparison, the optimized temperature for compound **1** was 70 °C. These results demonstrated that Zn and Co metal centers also activated the epoxides. Thus the excellent catalytic performance can be ascribed to significant synergistic effects between the Tb centers and transition metal (Zn, Co) centers.

Table 1. Cycloaddition reaction of CO_2 and Styrene Oxide under various conditions[a].



Entry	Catalyst **1** (mg)	TBAB (mol %)	T (°C)	Yield (%)[b]
1	20	2.5	50	57
2	20	2.5	60	72
3	20	2.5	70	77
4	20	5	50	78
5	20	5	60	85
6	20	5	70	>99
7	20	0	70	0
8	0	5	70	57

[a] Reaction conditions: styrene oxide (240.3 mg, 2.0 mmol), solvent free, 20 mg catalyst **1** loading (based on Tb metal center, 1 mol %), CO_2 (0.1 MPa), 12h

[b] Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table 2. Cycloaddition reaction of CO_2 and Styrene Oxide under various conditions[a] with compound **2**.

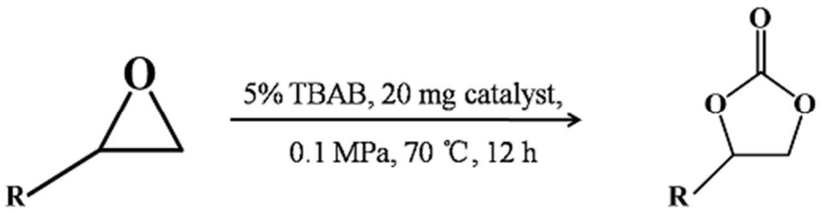
Entry	Catalyst **2** (mg)	TBAB (mol %)	T (°C)	Yield (%)[b]
1	20	2.5	70	77
2	20	5	50	27
3	20	5	60	66
4	20	5	70	90
5	20	5	80	>99
6	20	0	80	0
7	0	5	80	69

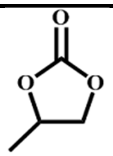
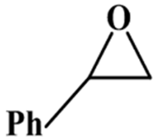
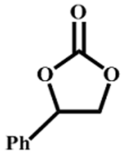
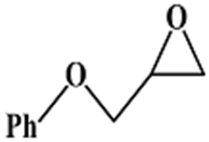
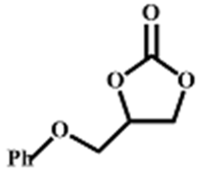
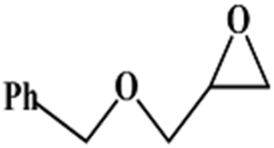
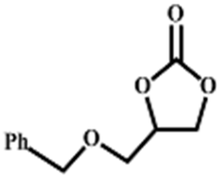
[a] Reaction conditions: styrene oxide (240.3 mg, 2.0 mmol), solvent free, 20 mg catalyst **2** loading (based on Tb metal center, 1 mol %), CO_2 (0.1 MPa), 12h.

[b] Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

In order to verify the potential generality of the catalyst system, compound **1** was selected as representative example and the scope of the reaction was further extended to other epoxides. As shown in Table 3, compound **1** revealed excellent catalytic performance toward the conversion of CO_2 with various epoxides in high yields (92−99%, Table 3). It can be inferred that compound **1** has the potential application in catalytic synthesis of cyclic carbonates from CO_2 and epoxides.

Table 3. Cycloaddition reaction of CO_2 and various epoxides with catalyst **1**[a].



Entry	Epoxides	Products	Yield (%)[b]
1			95
2			>99
3			>99
4			92

[a] Reaction conditions: epoxides (2.0 mmol), solvent free, catalyst **1** loading (based on Zn metal center, 1 mmol %), CO_2 (0.1 MPa), 70 °C, 12h, TBAB (32.4 mg, 0.1 mmol, 5 mol %).

[b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

To test its recyclability, taking the CO_2 cycloaddition with styrene epoxide as an example, catalyst **1** (as a representative example) was successively reused for four runs without any significant decrease in the catalytic efficiency (Figure 2). Additionally, the structure integrity of compound **1** after catalysis was proved by TGA analysis (Figure S6). Inductively coupled plasma (ICP) studies revealed that only trace amounts of leakage from the robust framework occurred, demonstrating its high recoverable performance (Table 4). Overall, the high efficiency and good recyclability make compound **1** appealing among heterogeneous catalysts for chemical fixation of CO_2 into cyclic carbonates.

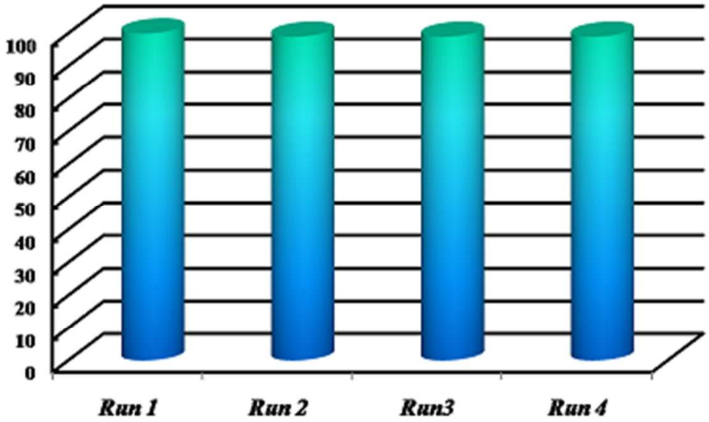


Figure 2. Recycling efficiency of compound **1** for CO_2 cycloaddition with styrene oxide.

Compound	Tb^{3+} (ppm)	Zn^{2+} (ppm)
1 after catalytic recyclings (filter liquor)	0.1106	0.1901
Mass loss percent (%)	0.16	0.79

Table 4. The ICP results of compound **1** after catalytic recyclings and mass loss percent.

On the basis of some previous reports,[51] a tentative mechanism was proposed for the cycloaddition of CO_2 and epoxides into cyclic carbonates catalyzed by the strong Lewis acid based catalyst **1** (as a representative example), as illustrated in Figure 3.

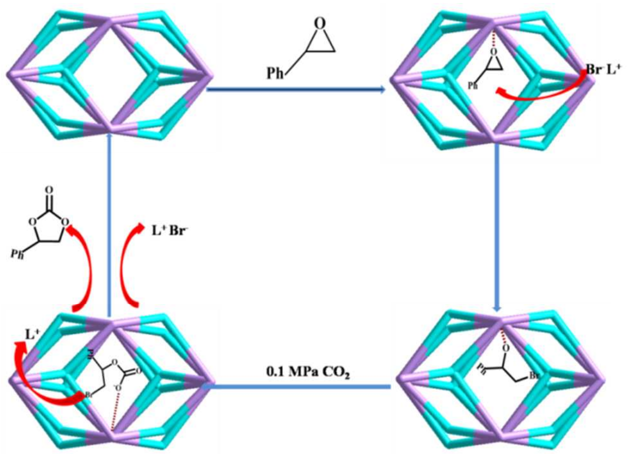


Figure 3. A representation of possible mechanism of cycloaddition of epoxide with CO_2.

First, the framework enriched CO_2 and substrates. Then the reaction was initiated by binding the epoxide with Lewis acid metal sites through the oxygen atom of epoxide to activate the epoxy ring. Thus the C-O bond of the epoxide is weakened, partly due to electron transfer from oxygen atom to metal center. Subsequently, the Br^- from TBAB attacked the less-hindered carbon atom of the coordinated epoxide to open the epoxide ring, due to its lower steric effect and higher positive charge. Then the carbon atom of CO_2 interacted with the oxygen anion of the opened epoxide ring and positively charged carbon of the epoxide interacted with one oxygen atom from CO_2, forming an alkylcarbonate anion. Finally, the corresponding cyclic carbonate was obtained through the intramolecular ring closure. It could be deduced that the synergistic effect of the Lewis acid metal sites and the moderate uptake of CO_2 promote the cycloaddition reaction, leading to high catalytic activity of compound **1** for CO_2 conversion into cyclic carbonates.

CONCLUSIONS

In summary, two microporous 3d-4f heterometallic MOFs were obtained under solvothermal condition. They are isostructural and feature large potential pore volume. Furthermore, both of them exhibit excellent performance as catalysts for chemical fixation of

CO_2 into cyclic carbonates under mild conditions. Significantly, compound **1** could be easily separated and remain its high catalytic activity after at least four runs of recyclings.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website.

PXRD, TGA and other experimental details (PDF).

Accession codes

CCDC 1520461 and 1533607 contain the supplementary crystallographic data for this paper.

These data can be obtained freely from the Cambridge Crystallographic Data Centre

via www.ccdc.cam.ac.uk/data_request/cif.

AUTHOR INFORMATION

Corresponding Author

*Email: zhaobin@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

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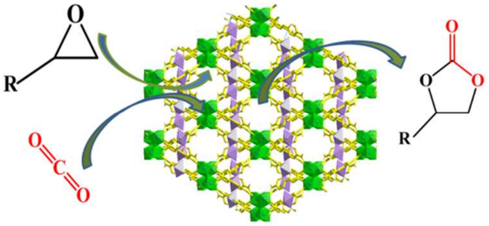
3d-4f Heterometal-Organic Frameworks for Efficient Capture and Conversion of CO_2

*Wan-Zhen Qiao, Hang Xu, Peng Cheng, Bin Zhao**



Two three-dimensional 3d-4f heterometallic MOFs demonstrate excellent catalytic ability for CO_2 conversion into cyclic carbonates with high yield, and compound **1** can be used as a recoverable heterogeneous catalyst with high activity.