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Porous Metal–Organic Frameworks with Chelating Multiamine Sites for Selective Adsorption and Chemical Conversion of Carbon Dioxide

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Supporting Information

ABSTRACT: A combination of carbon dioxide (CO_2) capture and chemical fixation in a one-step process is attractive for chemists and environmentalists. In this work, by incorporating chelating multiamine sites to enhance the binding affinity toward CO_2 , two novel metal–organic frameworks $(MOFs) [Zn_2(L)(2,6-NDC)_2(H_2O)] \cdot 1.5DMF \cdot 2H_2O$ (1) and $[Cd_2(L)(2,6-NDC)_2] \cdot 1.5DMF \cdot 2H_2O$ (2) $(L = N^1 - (4 - (1H - 1, 2, 4 - triazole - 1 - yl) benzyl) - N^1 - (2 - aminoethyl) ethane - 1, 2-diamine, 2, 6 - H_2NDC = 2, 6 - naphthalenedicarboxylic acid, DMF = <math>N, N$ -dimethylformamide) were achieved under solvothermal conditions. Both 1 and 2 possess high selectivity for adsorption of CO_2 over CH_4 at room temperature under atmospheric pressure. Moreover, 1 has one-dimensional tubular channels decorated with multiactive sites including NH₂ groups and coordination unsaturated Lewis acid metal sites, leading to efficient catalytic activity for chemical fixation of CO_2 by reaction with epoxides to give cyclic carbonates under mild conditions.



■ INTRODUCTION

Carbon dioxide (CO_2) , as a continuing increasing greenhouse gas, mainly originates from burning of fossil fuels and now has become one of the greatest environmental concerns.^{1,2} Development of green processes for promising CO₂ capture and fixation is a pressing task. Much effort has been made in the past few years to capture and fix CO₂ using varied porous materials such as zeolites,³ organic polymers,⁴ ionic liquids,⁵ and metal-organic frameworks (MOFs).⁶ Furthermore, it has been recognized that conversion of adsorbed CO₂ into high value-added species is very significant from both industrial and academic standpoints. However, the chemical fixation of CO₂ is difficult due to its high thermodynamic stability and kinetic inertness, even though CO2 is an inexpensive, nontoxic, and renewable C1 feedstock.⁷ Inspiringly, porous MOFs have designable architectures and facile pore functionalization, and accordingly can be used for efficient conversion of CO₂ into valuable chemicals such as urea derivatives,⁸ cyclic carbonates,⁵ and formic acid.¹⁰ Particularly, cyclic carbonates as important industrial intermediates are manufactured by highly toxic phosgene, and thus an alternative and green route is required. Cycloaddition of CO₂ with epoxides produces cyclic carbonates without other byproducts and is a green process and atom economy reaction.^{11,12} Varied homogeneous catalysts have been employed for the preparation of cyclic carbonates; however, high temperature and high pressure are needed for the reactions.¹³ As an ideal goal, efficient and reusable heterogeneous catalysts working under mild reaction conditions with high selectivity and a simple workup procedure are

desired.¹⁴ To reach the target for capture and conversion of CO_2 , MOFs should have crucial features including high stability, adsorption capacity, and selectivity for CO_2 .¹⁵ Therefore, design and construction of new MOFs with such features is an important but challenge task for capture and conversion of CO_2 .¹⁶

Following these considerations, a triazole tripodal ligand with a chelating multiamine site, namely, N^{1} -(4-(1H-1,2,4-triazole-1yl)benzyl)-N1-(2-aminoethyl)ethane-1,2-diamine (L), was used to prepare new MOFs.¹⁷ The incorporation of a chelating multiamine site and triazole group not only enriches the coordination fashion of L but also enhances the binding affinity toward CO₂. In this work, two porous MOFs $[Zn_2(L)(2,6 NDC_{2}(H_{2}O)$]·1.5DMF·2H₂O (1) and $[Cd_{2}(L)(2,6-NDC)_{2}]$ · $1.5DMF \cdot 2H_2O(2)(2,6-H_2NDC = 2,6-naphthalenedicarboxylic$ acid, DMF = N,N-dimethylformamide) were achieved. Both 1 and 2 show selectively adsorption of CO_2 over CH_4 at 273 and 298 K under atmospheric pressure. In addition, 1 possesses one-dimensional (1D) tubular channels decorated with abounding active sites: NH2-groups and unsaturated coordination metal sites generated by the removal of coordinated water molecules, leading to efficient catalytic activity for chemical fixation of CO₂ by reaction with epoxides to give cyclic carbonates under mild conditions.

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EXPERIMENTAL SECTION

Preparation of $[Zn_2(L)(2,6-NDC)_2(H_2O)]\cdot 1.5DMF\cdot 2H_2O$ (1). A mixture of $Zn(ClO_4)_2\cdot 6H_2O$ (37.23 mg, 0.1 mmol), L (13.01 mg, 0.05 mmol), 2,6-H_2NDC (21.61 mg, 0.1 mmol), and NaOH (0.41 mg, 0.01 mmol) was stirred in a DMF/H₂O mixed solvent (5 mL, v/v: 4/1). Then the mixture was transferred and sealed in a Teflon reactor (20 mL) and heated at 120 °C for 3 days. Colorless crystals of 1 were isolated in 47% yield after being cooled to room temperature. Anal. Calcd for $C_{41.5}H_{48.5}N_{7.5}O_{12.5}Zn_2$: C, 50.70; H, 4.97; N 10.68%. Found: C, 50.65; H, 4.98; N, 10.65%. IR (KBr pellet, cm⁻¹): 3286 (w), 3177 (w), 1683 (w), 1662 (w), 1608 (s), 1584 (s), 1518 (m), 1498 (w), 1393 (w), 1354 (s), 1277 (w), 1199 (w), 1188 (w), 1138 (w), 1088 (w), 1007 (w), 984 (w), 955 (w), 926 (w), 886 (w), 857 (w), 792 (s), 671 (w), 643 (w), 576 (w), 480 (m).

Preparation of $[Cd_2(L)(2,6-NDC)_2]$ **·1.5DMF·2H₂O (2).** The title complex was achieved by the same procedure used for synthesis of **1**, except that Cd(ClO₄)₂·6H₂O (41.9 mg, 0.1 mmol) was utilized instead of Zn(ClO₄)₂·6H₂O. Yellow block crystals of **2** were achieved in 40% yield. Anal. Calcd for C_{41.5}H_{46.5}N_{7.5}O_{11.5}Cd₂: C, 47.06; H, 4.43; N, 9.92%. Found: C, 47.12; H, 4.38. N, 9.90%. IR (KBr pellet, cm⁻¹): 3317 (m), 3264 (m), 1674 (s), 1606 (s), 1549 (s), 1526 (w), 1493 (s), 1397 (s), 1356 (s), 1279 (m), 1225 (w), 1198 (w), 1138 (w), 1067 (w), 998 (w), 978 (w), 791 (s), 670 (m), 572 (w), 479 (m), 446 (m).

Procedures for Cycloaddition of CO₂ with Epoxides. All the reactions were performed under carbon dioxide atmosphere unless otherwise stated. The reactions with corresponding catalyst were carried out using sealed test tubes (10 mL) with magnetic stirrers. A rubber bladder containing CO₂ (0.1 MPa) was used to control the reaction tube pressure. The cycloaddition reactions were checked by thin-layer chromatography (TLC) using silica gel plates (GF254). After being cooled to room temperature, the gas in the reaction tube was released slowly. The final target products were isolated using flash chromatography (EtOAc/*n*-hexane = 1:3).

RESULTS AND DISCUSSION

Crystal Structure of [Zn₂(L)(2,6-NDC)₂(H₂O)]·1.5DMF· 2H₂O (1). Crystal structural analysis revealed that 1 crystallizes in monoclinic space group $P2_1/n$ (Table 1) and the asymmetric unit of 1 contains two crystallographically independent Zn(II) atoms, one ligand L, two 2,6-NDC²⁻, and one coordinated aqua molecule. As exhibited in Figure 1a, Zn1 is six-coordinated by three chelating N atoms (N1, N2, and N3) from one L and three carboxylate O ones (O1, O2, and O3) from two different 2,6-NDC²⁻ ligands to form distorted octahedral coordination geometry, while Zn2 is surrounded by three carboxylate O atoms (O4, O6, and O8) from three 2,6-NDC²⁻ moieties and one O (O1W) from coordinated aqua molecule to give a distorted tetrahedral coordination geometry. The Zn-N bond lengths fall in the range of 2.059(4)-2.353(3) Å, and the Zn-O ones are from 1.933(3) to 2.552(3) Å (Table S1 in Supporting Information), which are well-matched to those in the reported Zn(II) complexes.¹⁸

It is notable that 2,6-NDC²⁻ in 1 presents three different coordination modes (Figure S1 in Supporting Information). 2,6-NDC²⁻ ligands with $(\mu^2 \cdot \eta^1 : \eta^1) \cdot (\mu^1 \cdot \eta^1 : \eta^0)$ and $(\mu^1 \cdot \eta^1 : \eta^0) \cdot (\mu^1 \cdot \eta^1 : \eta^0)$ coordination modes connect Zn2 atoms to generate a two-dimensional (2D) network (Figure 1b), while the one with $(\mu^1 - \eta^1 : \eta^1) \cdot (\mu^1 - \eta^1 : \eta^1)$ coordination mode links Zn1 atoms to extend the 2D network into a three-dimensional (3D) architecture with large channels of 14.38 × 30.87 Å² (Figure 1c). Subsequently, L uses its chelating N atoms to coordinate with Zn1 as terminal ligand and filled into the Zn-NDC 3D architecture to give the final 3D framework of 1 with 15.9 × 14.4 Å² 1D channels (Figure 1d,e). The PLATON was utilized to estimate the solvent molecule accessible volume since there are one coordinated and two free water, and one and a half

Table 1. Crystallographic Data and Structure Refinements for 1 and 2

compound	1	2
chemical formula	$C_{37}H_{34}N_6O_9Zn_2$	C37H32N6O8Cd2
formula weight	837.44	913.48
temperature/K	293(2)	293(2)
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\overline{1}$
a/Å	13.385(2)	10.362(2)
b/Å	13.338(2)	10.417(2)
c/Å	25.365(4)	21.282(4)
$\alpha/^{\circ}$	90	78.838(3)
$\beta/^{\circ}$	93.990(3)	84.996(3)
$\gamma/^{\circ}$	90	76.052(3)
volume/Å ³	4517.1(12)	2185.2(7)
Ζ	4	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.231	1.388
μ/mm^{-1}	1.114	1.024
F(000)	1720	912
reflections collected	28573	12303
unique reflections	10357	7641
parameters	525	478
restraints	31	0
GOF	1.054	1.067
R_1	$R_1 = 0.0583$	$R_1 = 0.0419$
$wR_2 \left[I > 2\sigma \left(I\right)\right]^{a,b}$	$wR_2 = 0.1627$	$wR_2 = 0.1222$
R_1	$R_1 = 0.1025$	$R_1 = 0.0526$
wR_2 (all data)	$wR_2 = 0.1853$	$wR_2 = 0.1393$
${}^{a}R_{1} = \sum F_{0} - F_{c} / \sum F_{0} $	$b_{wR_2} = \sum w(F_0 ^2 -$	$ F_{c} ^{2}) /\sum w(F_{0})^{2} ^{1/2}$
where $w = 1/[\sigma^2(F_0^2) + (a)]$	$(P)^{2} + bP]. P = (F_{0}^{2} + bP)$	$2F_{\rm c}^{2})/3.$

noncoordinated DMF molecules per formula of 1. After these solvent molecules were removed, the void volume is approximately 1248.8 Å³ per 4517.2 Å³ unit cell, and the void ratio is found to be 27.6%.

Crystal Structure of [Cd₂(L)(2,6-NDC)₂]·1.5DMF·2H₂O (2). When $Cd(ClO_4)_2 \cdot 6H_2O$ was used instead of $Zn(ClO_4)_2 \cdot 6H_2O$ $6H_2O$ without a change of other reaction conditions, 2 with a different structure was isolated. The results of structural analysis show that 2 crystallizes in the triclinic space group $P\overline{1}$ rather than monoclinic $P2_1/n$ in 1 (Table 1). As shown in Figure 2a, the asymmetric unit of 2 has two crystallographically independent Cd(II) atoms. Cd1 is surrounded by N₃O₃ coordination donor set, comprised of three multiamine N atoms (N1, N2, and N3) from L and three carboxylate O ones (O1, O2, and O3A) from two distinct 2,6-NDC²⁻, while Cd2 is seven-coordinated by six O atoms (O3, O4, O5, O6, O7, and O8) from three carboxylate groups of three 2,6-NDC²⁻ and one triazole N (N6) from L to form distorted pentagonal bipyramidal coordination geometry. The Cd-N and Cd-O bond lengths are in the ranges of 2.251(5)-2.461(4) Å and 2.317(5)-2.499(4) Å, respectively (Table S1 in Supporting Information), which are close to the Cd-N and Cd-O bond distances appearing in the previously reported Cd(II) frameworks.¹⁹

In 2, 2,6-NDC²⁻ ligands act as bridging linker with $(\mu^1 - \eta^1:\eta^1) - (\mu^1 - \eta^1:\eta^1)$ and $(\mu^2 - \eta^2:\eta^1) - (\mu^2 - \eta^1:\eta^2)$ coordination modes (Figure S2 in Supporting Information) to link Cd(II) to give a 3D Cd-NDC framework with channels possessing a diameter of 10.42 Å (Figure 2b). In addition, L acts as bridging ligand to join two Cd(II) and fills into the channel of the Cd-NDC framework to generate the final 3D net of 2 (Figure 2c,d). The

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Figure 1. (a) Coordination environment of Zn(II) in 1 with ellipsoids drawn at the 30% probability level. Hydrogen atoms and noncoordinated solvent molecules are omitted for clarity. (b) Zn2-NDC 2D network in 1. (c) 3D Zn-NDC architecture in 1. (d) Part of the 3D framework of 1. (e) Space-filling view of the 3D structure of 1.

calculated void volume after the solvent molecules are removed is 584.6 $Å^3$ per unit cell with a void volume ratio of 26.8%.

PXRD and Thermal Stability. The phase purity of the bulky 1 and 2 was confirmed by powder X-ray diffraction (PXRD) measurements, and the results are provided in Figure S3 in the Supporting Information. The good consistency of the PXRD patterns between the as-synthesized bulky sample and the corresponding simulated one confirms the purity of 1 and 2. Thermogravimetric analysis (TGA) was involved in the evaluation of the thermal stability of the frameworks. As shown in Figure S4 in Supporting Information, 1 displays a 16.41% weight loss from 30 to 220 °C, corresponding to the release of the solvent including free and coordinated water and DMF molecules (calcd 16.63%), and the framework starts to decompose from about 300 °C. MOF 2 loses its weight of 13.53% between 30-300 °C originated from the removal of the noncoordinated solvent molecules (calcd 13.75%), followed by the decomposition of the framework.

Dyes Adsorption. On the basis of the fact that there are large void volumes (27.6% for 1; 26.8% for 2) in 1 and 2, dye molecular adsorption in solution can be expected. Before adsorption measurements, the solvent molecules in 1 or 2 were exchanged by acetone for 48 h, then desolvation was performed at 130 °C for 10 h, and the corresponding desolvated samples 1' and 2' were obtained. The exclusion of solvent molecules and the maintaining of the framework were confirmed by TG and PXRD data (Figures S3 and S4 in Supporting Information). Dye molecules such as methyl orange (MO),

methylene blue (MB), and rhodamine B (RhB) (Figure S5 in Supporting Information) were employed to examine the adsorption abilities of 1 and 2.

The desolvated sample 1' or 2' (10 mg) was suspended in aqueous solution of MO, MB, or RhB (10 mg L^{-1} , 20 mL) at 25 °C under dark conditions, and UV-vis absorption spectroscopy was used to monitor the dye adsorption. As a result, 1' exhibits better adsorption ability than 2' for MO compared with MB and RhB. MO was effectively removed after 20 h from aqueous solution in 1' which was supported by the color change from yellow to nearly colorless, and UV-vis spectra at different time intervals indicated that the concentration of MO in aqueous solution changed from the initial 20 mg g^{-1} to 2 mg g^{-1} (Figure 3a,b). Although the color variation of MO solution in 2' was less obvious, it was still producing a good adsorption amount (11.2 mg g^{-1}) for MO (Table S2 in Supporting Information). For the MB and RhB solutions, as shown in Figure 3c-f, the UV spectra of 1' and 2' indicated almost no uptake and color variation for the blue MB solution (adsorption amount is 1 mg g^{-1} for 1'; 3 mg g^{-1} for 2') and rose RhB solution (adsorption amount is 1.2 mg g^{-1} for 1'; 1.5 mg g^{-1} for 2') (Tables S3 and S4 in Supporting Information). The differences in adsorption properties of these three dye molecules might result from the size fitting between the channels of the framework and the dye molecules. The better adsorption ability of 1' over 2' toward MO could be attributed to the appropriate pore size of 1'. In addition to the molecular size, electrostatic interactions between the frame-



Figure 2. (a) Crystal structure of 2 with ellipsoids drawn at the 30% probability level. For clarity, hydrogen atoms, free DMF and water molecules are omitted. (b) 3D Cd-NDC architecture in 2. (c) 3D framework of 2. (d) Space-filling view of the 3D structure of 2.

works and dye molecules may also contribute to selectively adsorption of dye molecules. The electrostatic interactions between the triazole group of L in 1' and the anionic dye MO might be helpful for adsorption, while in the case of MB, much less adsorption was observed probably due to the cationic charge of MB.²⁰

To further understand the intrinsic of dye adsorption, kinetic studies were carried out. Typically, MO was employed as a representative dye to examine the adsorption characteristics of 1' and 2', and the results are given in Figures S6 and S7 in Supporting Information. The adsorption kinetic studies were performed at 25 °C under neutral conditions. Figures S8 and S9 in Supporting Information show the adsorption kinetics curves for 1' and 2' as a function of time. 1' shows better uptake than 2' to MO and is best fitted by a pseudo-first-order model rather than a pseudo-second-order, while the adsorption of MO by 2' is closely in accord with a pseudo-second-order kinetic process based on the good R^2 value (Table 2).²¹

Gas Adsorption. The porosity of the frameworks further inspired us to investigate their gas uptake capacities. The sorption performances of the activated samples $\mathbf{1}'$ and $\mathbf{2}'$ for N₂ at 77 K, CO₂ at 195, 273, and 298 K, and CH₄ at 273 and 298 K, are discussed below.

As shown in Figure 4a,c, the amounts of CO_2 uptake for 1' and 2' are 41.95 and 60.66 cm³ g⁻¹ at the 195 K under 1 bar and exhibited typical type-I gas uptake isotherms. The

hysteresis loop in the CO₂ sorption profiles and incomplete desorption imply strong adsorbate–adsorbent interactions.²² It is noteworthy that 1' exhibited type-I N₂ sorption isotherms at 77 K with a value of 20.54 cm³ g⁻¹, but almost no N₂ adsorption was observed for 2' at 77 K. The Brunauer– Emmett–Teller (BET) surface area of 1' calculated from the N₂ sorption data is 79 m² g⁻¹ with a pore volume of 0.03 cm³ g⁻¹. According to Horvath–Kawazoe (HK) model, the pore size distribution curve based on N₂ adsorption isotherm at 77 K shows the main size range of 12.4 Å (Figure S10 in Supporting Information), agreeing with that of the crystal structure.

As we know, the separation of CO_2 from CH_4 in the precombustion process for natural gas is essential because of the pipeline corrosion caused by acidic CO_2 .²³ Therefore, the CO_2 and CH_4 adsorption isotherms at the 273 and 298 K under 1 bar were tested. As shown in Figure 4b,d, the maximal sorption values of 1' at ambient pressure for pure CO_2 and CH_4 are 21.34 and 8.61 cm³ g⁻¹ at 273 K; 11.17 and 0.08 cm³ g⁻¹ at 298 K, respectively. For 2', the corresponding values at ambient pressure for pure CO_2 and CH_4 are 13.83 and 2.06 cm³ g⁻¹ at 273 K; 9.30 and 0.04 cm³ g⁻¹ at 298 K, respectively. Apparently, the results imply that 1' and 2' can selectively adsorb CO_2 over CH_4 at 273 and 298 K.

In the interest of evaluating the separation abilities of 1' and 2' for CO_2 at different temperature, the CO_2/CH_4 selectivity for CO_2-CH_4 mixtures at a general feed composition of landfill



Figure 3. Adsorption capability of 1' and 2' toward MO (a) and (b), MB (c) and (d), and RhB (e) and (f) in an aqueous solution.

Table 2. Characteristic Parameters of the Adsorption of MO for 1' and 2' $\,$

	model	Parameters	1′	2′
adsorption kinetic	pseudo-first-order	$q_{e^{j}Exp} (mg g^{-1})$	19.5	11.2
		$q_{e'Cal} (mg g^{-1})$	19.1	11.3
		$k_1 ({ m h}^{-1})$	0.1116	0.086
		R^2	0.9799	0.9207
	pseudo-second- order	$q_{e^{j} \text{Exp}} \text{ (mg g}^{-1}\text{)}$	19.8	11.4
		$q_{e'Cal} (mg g^{-1})$	19.1	11.3
		$k_2 (g mg^{-1} h^{-1})$	0.0114	0.0213
		R^2	0.9272	0.9528

gas (CO₂/CH₄ = 50:50) and natural gas (CO₂/CH₄ = 10:90 and 5:95) was analyzed using the ideal adsorbed solution theory (IAST) model (Figures S11 and S12 in Supporting Information).²⁴ As shown in Figure 5a–d, the CO₂/CH₄ selectivities of 1' at 100 kPa are 3.4, 2.5, and 3.4 at 273 K; 6.1, 2.5, and 2.5 at 298 K for the mixtures with 50, 10, and 5% CO₂ components, respectively, while 2' at 100 kPa displays

high CO_2/CH_4 selectivities of 32.6, 40.1, and 42.5 at 273 K, 28.6, 33.8, and 35.7 at 298 K for the mixtures with 50, 10, and 5% CO₂ components, respectively. The values of 2' lie in the upper region of the reported MOFs (Table S5 in Supporting Information), which are comparable to those of $[Zn(mtz)_2]$, UTSA-49, and $[Co_2(tzpa)(OH)(H_2O)_2]$ but surpass the values reported in major MOFs under similar conditions.²⁵

The significant selectivity of **1**' and **2**' for CO_2 over CH_4 and N_2 is attributed to the existence of multiple CO_2 -philic sites in channels such as amino groups and the open metal sites, which form specific interactions with CO_2 due to the larger quadrupole moment and higher polarizability value of CO_2 relative to that of CH_4 and N_2 . To determine the binding affinity, the adsorption enthalpies (Q_{st}) for CO_2 were calculated by the virial model using the data of CO_2 isotherms at 273 and 298 K (Figures S13 and S14 in Supporting Information). The values given in Table 3 were estimated from the CO_2 uptake at the lowest measured loading. For **1**' and **2**', the initial Q_{st} values of adsorption enthalpies were determined as 23.3 and 28.1 kJ mol⁻¹, which are reasonable values compared with the previously reported MOFs under the same conditions (Table



Figure 4. Adsorption isotherms of N_2 at 77 K, CO₂ at 195, 273, and 298 K and CH₄ at 273 and 298 K for 1' (a) and (b), 2' (c) and (d) (filled shape, adsorption; open shape, desorption).



Figure 5. CO_2/CH_4 selectivity for CO_2/CH_4 binary mixtures with $CO_2/CH_4 = 50/50$ (a), $CO_2/CH_4 = 10/90$ (b), and $CO_2/CH_4 = 5/95$ (c) CO_2 , respectively. (d) Comparison of selectivity sorption at 100 kPa.

S6 in Supporting Information).²⁶ The higher Q_{st} values indicate the stronger interactions between the adsorbed gas molecules and the frameworks. Adsorption enthalpies decrease with increasing loading, implying that there are preferentially binding sites in the frameworks.²⁷

Catalytic Cycloaddition of CO₂ with Epoxides. MOFs as heterogeneous catalysts for chemical fixation of CO₂ to cyclic carbonates have been demonstrated but under high pressure (>2 MPa).²⁸ TG and PXRD curves of desolvated sample 1' showed that the coordinated aqua molecules were completely

Table 3. CO_2 and CH_4 Uptakes of 1' and 2' and Heat of Adsorption Values of CO_2

	CO ₂ uptak	$e^{a}/cm^{3} g^{-1}$		CH_4 uptake ^{<i>a</i>} /cm ³ g ⁻¹		
	273 K	298 K	$Q_{\rm st}~({\rm kJ}~{\rm mol}^{-1})$	273 K	298 K	
1′	21.34	11.17	23.3	8.61	0.08	
2'	13.83	9.30	28.1	2.06	0.04	
^a At 0.1	MPa.					

removed, and the framework maintained well (Figures S3 and S4 in Supporting Information). The high CO_2 uptake and the exposed sites of Zn(II) in the framework of 1' encourage us to examine its activity as heterogeneous catalyst for the cyclo-addition reactions of CO_2 with epoxides.

The reactions were performed with epoxide (10 mmol), CO_{2} , and NBu_4Br (1.20 mol %) as cocatalyst at 80 °C and atmospheric pressure (0.1 MPa), while the loading of the catalyst is 0.04 mol % based on the Zn2 ions. Remarkably, 1' exhibits high efficiency for the CO_2 cycloaddition especially with small-sized epoxides (Table 4, entries 1–3); for example, the conversion of 1,2-epoxybutane (1a) to 1,2-butylene carbonate (2a) finished within 2 h. The turnover number (TON) and turnover frequency (TOF) values are 2400 and 1200 h⁻¹, respectively, which are larger than the ones reported

Table 4. Catalyzed Coupling of CO₂ with Epoxides^a

previously (Table S7 in Supporting Information).²⁹ Small decreases in the conversion were observed when the methyl was substituted by electron-withdrawing substituents (1b and 1c), and the TON and TOF values are 2300 and 1150 h^{-1} for 2b and 2225 and 1113 h^{-1} for 2c, respectively. It is noteworthy that these TON and TOF values are also larger than the ones for the previously reported MOF catalysts (Table S8 in Supporting Information).³⁰

Considering the large pore width (12.4 Å) calculated by the HK method based on the N_2 sorption data of 1'. Therefore, to confirm the selective accommodation and activation of reactants by 1', epoxides with large size were used to identify the selectivity of 1', and the catalytic reactions were performed under the optimized conditions (Table 4, entries 4-7). Substrate tert-butyl glycidyl ether (1d) gave the corresponding product (2d) in good yield (91%) with TON and TOF of 2275 and 1517 h^{-1} , respectively. Glycidyl phenyl ether (1e) almost completely converted into the corresponding product (2e) within 1 h with the corresponding TOF value of 2450 h^{-1} per Zn2 cluster. Notably, the conversion of 1e to 2e gives the highest TOF value within the reported MOF catalysts (Table S9 in Supporting Information).^{30,31} The width of the substrate, substituted by naphthalene (1f), was further increased, and the corresponding product 2f could also be detected with the corresponding TOF value of 510 h⁻¹. However, further increase

$O \rightarrow R + CO_2 \xrightarrow{1, \text{NDU4D}} O \xrightarrow{R} R$						
	1			2		
Entry	Substrate	Product	<i>T</i> (h)	Yield (%)	TON ^[c]	TOF ^[d]
1	0 Me	0 Me	2	96 ^b	2400	1200
	1a	2a				
2	0 Br	0=	2	92 ^b	2300	1150
	1b	2b				
3	oCI	o-CI	2	89 ^b	2225	1113
	1c	2c				
)) 1 E	016	2275	1517
4	0 1d	2d	1.5	91-	2215	1517
-		0.]			
5			1	98 ^b	2450	2450
	ie	Ze				
6			4	82 ^b	2050	510
	0 If	0			2000	010
7			> 12			
			//			
	1g	2g				

41 ND. D.

0-

^{*a*}Reaction conditions: Substrates (10 mmol), NBu₄Br (0.12 mmol, 1.2 mol %), catalyst 1' (0.004 mmol, 0.04 mol %, based on Zn2). ^{*b*}Isolated yield. ^{*c*}TON = (moles of product)/(moles of catalyst). ^{*d*}TOF = TON/T.

of the substrate size, substituted by triphenylmethyl (1g), gave no desired product because of the large size (over 12.4 Å) and the large steric effect from the triphenylmethyl group. The results are in accordance with the fact that this substrateselective reaction occurs in the channels rather than the surface of 1'.

The CO₂ cycloaddition with 1,2-epoxybutane was used to examine the recyclability of the catalyst, and the results show that 1' can be reused at least 3 times without remarkable change of its catalytic activity (Figure S15 in Supporting Information). In addition, PXRD and IR (Figure S16 in Supporting Information) data confirm no structural variation of 1' after the catalytic reactions.

A possible catalytic reaction mechanism is given in Figure S17 in Supporting Information. According to the previously reported works,^{8,32} the cycloaddition reaction of epoxide with CO_2 starts from the binding of the epoxide with the open site of Zn(II) in 1', in which the Lewis acidic Zn(II) can activate epoxide toward nucleophilic substitution. In the second step, the epoxy ring is opened by attacking of Br⁻ originated from the cocatalyst NBu₄Br to the terminal C atom of the epoxide. Third, the NH₂ group in the framework of 1' is a Lewis base and activates CO_2 , which is beneficial to the interaction of the O atom of the epoxide with the C atom of CO_2 . Finally, the ring closure occurred by interaction between the negatively charged O atom from CO_2 and the positively charged C from the epoxide with release of Br⁻ and the formation of the cyclic carbonate.

CONCLUSIONS

In summary, two new Zn(II)/Cd(II)-based MOFs with multiamine sites were successfully designed and synthesized. Remarkably, 1 and 2 exhibited selective adsorption of dye (methyl orange, MO) molecule in aqueous solution and significant CO_2/CH_4 selectivity at 273 and 298 K under atmospheric pressure. In addition, the activated framework of 1 contains 1D tubular channels decorated with multiactive sites: NH₂ groups and coordination unsaturated metal sites. These structural features enhance its CO_2 adsorption capacity and heterogeneous catalytic activity for the conversion of CO_2 to cyclic carbonates. The generation of active metal centers together with functionalized channels is demonstrated to be useful for the development of materials for CO_2 capture and fixation in a one-step process.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b03099.

Tables, structure illustrations, PXRD patterns, TG figures, characterization data, and 1 H NMR and 13 C NMR spectra (PDF)

Accession Codes

CCDC 1590073–1590074 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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