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# Structural Design of Mn-Metal–Organic Frameworks toward Highly Efficient Solvent-Free Cycloaddition of CO<sub>2</sub>

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**AbSTRACT:** Three new manganese-based metal-organic frameworks (Mn-MOFs),  $[Mn(L)(H_2O)] \cdot 2DMA$  (1),  $[Mn_2(L)_2(H_2O)_3] \cdot 2DMA$  (2), and  $[Mn_2(L)_2(DMF)_2(H_2O)] \cdot 3DMF$  (3), have been synthesized with the ligand  $H_2L$  (*N*phenyl-*N'*-phenylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxdiimide dicarboxylic acid). The secondary building units (SBUs) of the Mn-MOFs are controlled by changing the anions of the manganese salts, and the structures are modified from two-fold interpenetrating to non-interpenetrating by adjusting the mixed solvent systems. Along with the structural modification of the Mn-MOFs, we optimized their catalytic activities for the reaction of CO<sub>2</sub> and epoxides toward cyclic carbonates. Both the activity and



reusability of the Mn-MOFs are successfully improved in the solvent-free cycloaddition of  $CO_2$  with various epoxides under the mild conditions of atmospheric pressure and 70 °C.

## 1. INTRODUCTION

Since the industrial revolution, carbon stored in the stratum such as coal, oil, and natural gas has been overutilized as fossil fuels, and the overexploitation of forests by humans has caused the  $CO_2$  content in the atmosphere to rise sharply.<sup>1</sup> On the one hand,  $CO_2$  is the main greenhouse gas, which is leading to more serious global warming. On the other hand,  $CO_2$  is safe, cheap, and renewable and the most abundant C1 resource.<sup>2</sup> Therefore, utilization of  $CO_2$  through chemical means can not only reduce its impact on the environment but also benefit the production of high value-added chemicals. So far, the chemical use of  $CO_2$  mainly includes the reduction of  $CO_2$  by H<sub>2</sub> to produce methanol,<sup>3</sup> the reaction of  $CO_2$  and  $CH_4$  to produce synthesis gas,<sup>4</sup> the reaction of  $CO_2$  with methanol to synthesize dimethyl carbonate (DMC),<sup>5</sup> and the carboxylation of  $CO_2$  and alkylene oxide to synthesize cyclic carbonate.<sup>6-11</sup>

As an important raw material, cyclic carbonate has been widely used as a polar solvent, fuel additive, polymer precursor, and electrolyte solvent in lithium batteries.<sup>12,13</sup> The traditional synthesis of cyclic carbonate usually requires toxic reagents, such as phosgene and CO,<sup>14</sup> and pollutant byproducts such as hydrogen chloride are produced. Therefore, the synthesis of cyclic carbonate by  $CO_2$  and alkylene oxide, which is easy to obtain, renewable, and environmentally friendly, has become an attractive procedure. Homogeneous catalysts, such as ionic liquids,<sup>15</sup> are generally effective for this reaction, but the

difficulty of separation is a disadvantage of homogeneous catalysts. Heterogeneous catalysts, such as binuclear molybdenum alkoxides,<sup>16</sup> clusters,<sup>17</sup> metal-salen,<sup>18</sup> metal–organic frameworks (MOFs),<sup>19</sup> and polyoxometalates (POMs),<sup>20</sup> have thus been developed. Because of the characteristics of high porosity and high specific surface area, MOFs can automatically capture  $CO_2$  and catalyze the conversion efficiently.<sup>21–26</sup> With the abundant valency and various potential active sites, manganese-based metal–organic frameworks (Mn-MOFs) have been considered as excellent catalysts for this reaction.<sup>27</sup> However, the structure–activity relationship of Mn-MOFs in such a reaction has been rarely investigated, and the conversion conditions for a large part of Mn-MOFs are not optimized.

In this work, we synthesized three new Mn-MOFs  $[Mn(L)(H_2O)]$ ·2DMA (1),  $[Mn_2(L)_2(H_2O)_3]$ ·2DMA (2), and  $[Mn_2(L)_2(DMF)_2(H_2O)]$ ·3DMF (3) with the ligand  $H_2L$  (*N*-phenyl-*N'*-phenylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetra-carboxdiimide dicarboxylic acid) subsequently (Scheme 1).

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## Scheme 1. Synthesis Diagrams for 1-3



The secondary building units (SBUs) of Mn-MOFs were changed from the paddle-wheel unit (1) to the dinuclear Mn node with more potential metal sites (2) via adjusting anions of manganese salts. The two-fold interpenetrating conformations of 1 and 2 were further modified into the non-interpenetrating conformation of 3 by adjusting the mixed solvent systems. Along with the structural modification, the stability, activity, and reusability of the Mn-MOFs were significantly improved in the solvent-free cycloaddition of  $CO_2$  under the mild conditions of atmospheric pressure and 70 °C. Especially, the amount of cocatalyst was significantly reduced, and the conversion of cyclohexene oxide was dramatically increased over the other known heterogeneous catalysts.

#### 2. EXPERIMENTAL SECTION

**Materials and Methods.** All the reagents were procured from a reagent company and were used directly without further purification. IR spectra were recorded on a Bruker Alpha spectrometer. Elemental analyses were carried out on an Elementar vario EL CUBE instrument. Powder X-ray diffraction (PXRD) was carried out using an Ultima IV X-ray diffractometer. Thermal analysis was carried out using a NETZSCH TG 209F3 device. Gas chromatography was carried out using a GC 7900 instrument.

**Synthesis of H<sub>2</sub>L.** The ligand H<sub>2</sub>L was synthesized by a modified procedure.<sup>28</sup> The mixture of 4-aminobenzoic acid (20 mmol, 2.74 g) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride (10 mmol, 2.48 g) was added into a 250 mL round-bottom flask and then 100 mL of acetic acid was poured into the flask and refluxed at 120 °C for 12 h. Then the mixture was removed from heat, cooled to room temperature, washed three times by distilled water, and dried in a vacuum at 100 °C. Finally, a white powder product was obtained (yield 92.8%, m.p. > 310 °C). H<sub>2</sub>L was used for next procedures without further purification. Anal. Calcd. (%) for C<sub>26</sub>H<sub>18</sub>O<sub>8</sub>N<sub>2</sub> (H<sub>2</sub>L): C 63.85, H 4.02, N 5.78; found: C 64.20, H 3.73, N 5.76.

Synthesis of  $[Mn(L)(H_2O)]$ ·2DMA (1).  $H_2L$  (0.2 mmol, 0.0972 g) and  $Mn(OAc)_2$ ·4 $H_2O$  (0.1 mmol, 0.0245 g) were dissolved in 4 mL of *N*,*N*-dimethylacetamide (DMA) and 2 mL of *n*-octanol, then sealed in a 20 mL screw-capped vial, and heated in an oven under 110 °C for 3 days. Then the mixture was washed three times by methanol and dried at room temperature. Finally, colorless block crystals were

obtained. Yield: ca. 33.78% (based on  $H_2L$ ). Anal. Calcd. (%) for  $C_{34}H_{36}MnN_4O_{11}$  (1): C 55.82, H 4.96, N 7.66; found: C 54.98, H 4.65, N 7.06; After drying in a vacuum, Anal. Calcd. (%) for  $C_{26}H_{18}MnN_2O_9$ : C 55.75, H 3.29, N 4.9; found: C 56.09, H 3.45, N 5.28.

**Synthesis of [Mn<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]·2DMA (2).** H<sub>2</sub>L (0.2 mmol, 0.0972 g) and MnCl<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol, 0.0198 g) were dissolved in 4 mL of *N*,*N*-dimethylacetamide (DMA) and 2 mL of *n*-octanol, then sealed in a 20 mL screw-capped vial, and heated in an oven under 110 °C for 3 days. Then the mixture was washed three times by methanol and dried at room temperature. Finally, colorless block crystals were obtained. Yield: ca. 31.32% (based on H<sub>2</sub>L). Anal. Calcd. (%) for C<sub>60</sub>H<sub>56</sub>Mn<sub>2</sub>N<sub>6</sub>O<sub>21</sub> (2): C 55.14, H 4.32, N 6.43; found: C 54.59, H 4.70, N 6.02; After drying in a vacuum, Anal. Calcd. (%) for C<sub>52</sub>H<sub>38</sub>Mn<sub>2</sub>N<sub>4</sub>O<sub>19</sub>: C 55.75, H 3.29, N 4.97; found: C 55.71, H 3.32, N 5.01.

Synthesis of  $[Mn_2(L)_2(DMF)_2(H_2O)]$ ·3DMF (3).  $H_2L$  (0.3 mmol, 0.1458 g) and  $MnCl_2$ ·4 $H_2O$  (0.2 mmol, 0.0396 g) were dissolved in 2 mL of acetonitrile and 4 mL of *N*,*N*-dimethylformamide (DMF), then added into a 20 mL screw-capped vial, and heated in an oven under 110 °C for 3 days. Then the mixture was washed three times by methanol and dried at room temperature. Finally, colorless block crystals were obtained. Yield: ca. 35.76% (based on  $H_2L$ ). Anal. Calcd. (%) for  $C_{67}H_{69}Mn_2N_9O_{22}$  (3): C 55.04, H 4.72, N 8.62. found: C 54.91, H 4.68, N 8.16. After drying in a vacuum, Anal. Calcd. (%) for  $C_{58}H_{48}Mn_2N_6O_{19}$ : C 56.04, H 3.87, N 6.76; found: C 55.03, H 3.94, N 5.97.

Crystallographic Data Collection and Refinement. The data collections of 1 and 3 were performed on a SuperNova, single source at offset/far, Eos diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) with a CCD detector. The data of MOF 2 were collected on a XtaLAB Synergy diffractometer using Cu-Klpharadiation ( $\lambda = 1.54184$  Å) with an Hypix6000HE detector. The obtained diffraction data were reduced by the program suite CrysAlispro (Rigaku Oxford Diffraction, CrysAlisPro Software system, Rigaku Corporation, Oxford, UK, 2019). The structure determination was operated in the OLEX2 graphical user interface. The structures were solved using the SHELXT program using Intrinsic Phasing and refined using the SHELXL refinement package with Least Squares minimization.<sup>29-31</sup> All the thermal parameters of non-hydrogen atoms were refined anisotropically. The H atoms of H<sub>2</sub>O were generated from different maps and refined with isotropic temperature factors. The H atoms of ligands were located geometrically. The unresolved

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# Table 1. Crystal Data and Structure Refinements for 1-3

compound	1	2	3
formula	C <sub>34</sub> H <sub>36</sub> MnN <sub>4</sub> O <sub>11</sub>	$C_{60}H_{56}Mn_2N_6O_{21}$	C67H69Mn2N9O22
formula weight	731.6	1306.99	1462.18
temp, K	298.10(10)	100.00(10)	131.0(7)
crystal system	orthorhombic	monoclinic	triclinic
space group	Ibam	Pc	$P\overline{1}$
a (Å)	11.7452(9)	21.6275(4)	11.5426(6)
b (Å)	20.0711(14)	24.3471(4)	21.3222(13)
c (Å)	36.576(2)	39.6245(7)	21.4823(9)
$\alpha$ (deg)	90	90	73.160(5)
$\beta$ (deg)	90	98.228(2)	85.511(4)
γ (deg)	90	90	80.155(5)
V (Å <sup>3</sup> )	8622.3(11)	20650.2(6)	4983.5(5)
Z	8	8	2
$D_{\rm c} ({\rm g/cm^3})$	0.859	0.729	0.877
$\mu \ (\mathrm{mm}^{-1})$	0.340	2.339	0.304
R <sub>int</sub>	0.1062	0.0511	0.1044
reflections collected	11930	137759	43530
independent reflections	4985	61655	22441
F(000)	2280.0	4640.0	1360.0
GOF on F <sup>2</sup>	0.885	1.028	0.846
$R_1, wR_2 [I > 2\sigma(I)]$	0.0951, 0.2183	0.0648, 0.1790	0.0788,0.1365
$R_1$ , $wR_2$ [all data]	0.2044, 0.2865	0.0839, 0.1996	0.1835,0.1824
max/min e <sup>-</sup> density (e Å <sup>-3</sup> )	0.48/-0.59	0.65/-0.74	0.39/-0.35



Figure 1. (a) Dinuclear SBUs of 1, 2, and 3; (b) the 2D lattice structures along the *a*-axis of 1, 2, and 3; and (c) the packing diagrams of 1, 2, and 3.



Figure 2. (a) The coordination environment of 1, 2, and 3; (b) the coordination modes of  $H_2L$  in 1, 2, and 3. Green: Mn; red: O; blue: N; gray: C. Hydrogen atoms are omitted for clarity.

electron densities were removed by PLATON/SQUEEZE.<sup>32</sup> The detailed data of the three crystals are recorded in Table 1.

Catalytic Cycloaddition of CO<sub>2</sub> with Epoxides toward the Production of Cyclic Carbonates. Before the reaction, 1-3 were activated by solvent exchange with CH<sub>2</sub>Cl<sub>2</sub> for 24 h and heated in a vacuum for 12 h under 100 °C. In a typical CO<sub>2</sub> coupling reaction with epoxides, a mixture of catalyst (0.03 mmol based on  $Mn^{2+}$ ) and tetrabutylammonium bromide (TBAB, 0.1 mmol) was added into a 25 mL Schlenk flask and activated under vacuum for several hours. A CO<sub>2</sub>-containing balloon was introduced into the Schlenk flask, and then styrene oxide (0.5 mL, 5 mmol) was added into the Schlenk flask through a syringe. Then, the mixture was stirred at the selected temperature for 48 h. After the reaction was cooled down to room temperature, the product was extracted with ethyl acetate and washed with water to remove TBAB. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and subjected to gas chromatography to calculate the yield. The products were analyzed and identified by gas chromatography (GC, Techcomp GC7900, TM-5 capillary column, 30 m  $\times$  0.32 mm) with a flame ionization detector (FID) and nitrogen as the carrier gas.

### 3. RESULTS AND DISCUSSION

Crystal structure of [Mn(L)(H<sub>2</sub>O)]·2DMA (1). The synthesis routes of 1-3 are shown in Scheme 1. 1 was synthesized by the reaction of  $Mn(OAc)_2$  with the ligand in a mixed solvent system of DMA and n-octanol. 1 crystallizes in Ibam, which is an orthorhombic space group, with a sqltopology structure. In the asymmetric unit, there are two Mn<sup>2+</sup>, one L<sup>2-</sup>, and one water molecules. The Mn<sup>2+</sup> ion is fivecoordinated by one H<sub>2</sub>O molecule and four carboxylic O atoms separately from ligands  $(\kappa^1 - \kappa^1) - (\kappa^1 - \kappa^1) - \mu_4 - L^{2-}$  (Figure 2b). 1 showed an uncommon Mn paddle-wheel building unit with the two ends of the Mn centers coordinated by two H<sub>2</sub>O molecules to form the penta-coordinated mode (Figure 1a).<sup>33</sup> Each SBU is coordinated with four curved ligands to build a 2D layer with rhombic lattices (Figure 1b). Because of the curved ligands, every two 2D layers interlace with each other to form a 2-fold interpenetrating conformation (Figure 1c). The distances of Mn-O range from 2.040(12) Å to 2.446(16) Å, and the angles of O-Mn-O are in the scope of 55.0(5)- $178.1(7)^{\circ}$ . The PXRD pattern shows that the peak positions of the obtained crystalline samples of 1 match well with the

Table 2. Temperature Gradient Experiments of the Solventfree CO<sub>2</sub> Cycloaddition Catalyzed by 1-3



entry <sup>a</sup>	catalyst	temp (°C)	time (h)	yield (%) <sup>c</sup>
1	1	50	48	58
2	2	50	48	65
3	3	50	48	65
4	1	60	48	83
5	2	60	48	93
6	3	60	48	91
7	1	70	24	55
8	2	70	24	77
9	3	70	24	76
10	1	70	48	98
11	2	70	48	>99
12	3	70	48	>99
13	none	70	48	50
14 <sup>b</sup>	2	70	48	21
15 <sup>b</sup>	3	70	48	19

<sup>*a*</sup>Reaction conditions: Styrene oxide (0.5 mL, 5 mmol); catalyst (0.03 mmol based on  $Mn^{2+}$ ); TBAB (0.1 mmol); CO<sub>2</sub>: 1 atm. <sup>*b*</sup>Without TBAB. <sup>*c*</sup>The products were analyzed and identified by gas chromatography.

simulated data, confirming the crystalline structure of the obtained samples (Figure S4, Supporting Information). As shown in the XPS patterns (Figure S7, Supporting Information), the Mn  $2p_{3/2}$  peak of 1 is around 641.4 eV with a satellite feature of ca. 646 eV, indicating the +2 valence of the manganese element. The TGA measurement was carried in N<sub>2</sub> atmosphere from 25 to 800 °C (Figure S10, Supporting Information). From 25 to 350 °C, a weight loss of 24.0% was observed, corresponding to the loss of solvent molecules in the lattice and the coordinated H<sub>2</sub>O molecules. When increasing



Figure 3. Recycling experiments for catalysts 1, 2, and 3.





<sup>*a*</sup>Reaction conditions: epoxides (5 mmol); catalyst (0.03 mmol calculated according to the amount of  $Mn^{2+}$ ); TBAB (0.1 mmol); 70 °C and 1 atm CO<sub>2</sub>. Isolated product obtained by column chromatography separation.

to 400  $^{\circ}$ C, the structure began to decompose, illustrating the thermal stability of 1.

**Crystal Structure of [Mn<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]·2DMA (2).** Nevertheless, since each Mn<sup>2+</sup> center in 1 coordinated only one solvent molecule, the potential active sites of 1 were relatively limited. It is known that the structure of MOFs is affected by various synthetic factors including temperature, solvent, metal, and anion.<sup>34–37</sup> Accordingly, we synthesized 2 with MnCl<sub>2</sub> instead of Mn(OAc)<sub>2</sub> as the Mn<sup>2+</sup> resource for the synthesis of 1. 2 crystallizes in *Pc*, which is a monoclinic space group, with a *sql*-topology structure. There are two crystallographically independent six-coordinated Mn<sup>2+</sup> ions, two ligands, and three H<sub>2</sub>O molecules in the asymmetric unit (Figure 1a). One Mn<sup>2+</sup> ion of the Mn ions in the SBU is coordinated with six carboxylic O atoms from two ( $\kappa^1$ - $\kappa^2$ )- $\mu_3$ -L<sup>2-</sup>and two ( $\kappa^1$ -

 $\kappa^{1}$ )-( $\kappa^{1}$ - $\kappa^{2}$ - $\mu_{2}$ )- $\mu_{4}$ -L<sup>2-</sup>. Another Mn<sup>2+</sup> ion coordinates with three O atoms from three carboxylic O from one  $(\kappa^1 - \kappa^1) - (\kappa^2) - \mu_3 - L^{2-1}$ and two  $(\kappa^1 - \kappa^1) - (\kappa^1 - \kappa^2 - \mu_2) - \mu_4 - L^2$ , and three other O atoms from H<sub>2</sub>O molecules (Figure 2). Each SBU is coordinated by four ligands to build a 2D layer with guadrate lattices (Figure 1b), and every two 2D layers interlace each other to form a 2fold interpenetrating conformation as well (Figure 1c). The distances of Mn–O range from 1.943(6) Å to 2.635(9) Å, and the angles of O-Mn-O are in the scope of 59.1(2)- $177.0(2)^{\circ}$ . As shown in Figure S5, Supporting Information, the PXRD pattern of obtained 2 is in good agreement with the simulated data, confirming the crystalline structure of the obtained samples. The Mn  $2p_{3/2}$  peak of 2 in XPS patterns (Figure S8, Supporting Information) is around 641.4 eV with a satellite feature of ca. 646 eV indicating the +2 valence of the manganese element. As shown in the TGA measurement (Figure S11, Supporting Information), a weight loss of 18.6% was observed from 25 to 375 °C, corresponding to the loss of solvent molecules in the lattice and the coordinated H<sub>2</sub>O molecules. The structure of 2 began to decompose after further heating after 400 °C, also demonstrating the thermal stability of **2**. Probably due to the more ionic nature of the  $Mn^{2+}$  cation in MnCl<sub>2</sub> than that in Mn(OAc)<sub>2</sub>, the formed dinuclear Mn nodes in 2 suffered less steric hindrance and more potential active sites than the Mn ions in the paddle-wheel unit of 1, which might be advantageous to improve the catalytic activity.

Crystal Structure of [Mn<sub>2</sub>(L)<sub>2</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)]·3DMF (3). Considering that the 2-fold interpenetration structure of 2 may impact the entrance of components and the release of products, we successfully synthesized 3 by changing the mixed solvent system used for the preparation of 1 and 2 with DMF and acetonitrile. As shown in Figure 1a, 3 exhibits the dinuclear Mn nodes similar to 2, except that two of the three coordinated H<sub>2</sub>O molecules were replaced by DMF. 3 belongs to  $P\overline{1}$ , which is a triclinic space group, with a sql-topology structure. There are two six-coordinated Mn<sup>2+</sup>, four ligands, two DMF molecules, and one H<sub>2</sub>O molecule in the asymmetric unit. Similar to 2, one of the Mn ions in SBU is linked to six carboxylate O atoms from two  $(\kappa^1 - \kappa^1) - (\kappa^2) - \mu_3 - L^{2-}$  and two  $(\kappa^1 - \kappa^2) - \mu_3 - L^{2-}$  $-\kappa^{1}$ )- $(\kappa^{1}-\kappa^{2}-\mu_{2})-\mu_{4}-L^{2-}$ , and another Mn ion is coordinated by three carboxylic O atoms from one  $(\kappa^1 - \kappa^1) - (\kappa^2) - \mu_3 - L^{2-}$  and two  $(\kappa^1 - \kappa^1) - (\kappa^1 - \kappa^2 - \mu_2) - \mu_4 - L^{2-}$  as well as three O atoms from two DMF and one H<sub>2</sub>O molecule (Figure 2). Each SBU is coordinated by four ligands to build a 2D layer with rhombic lattices as well (Figure 1b). But unlike 2, the 2D layers of 3 are stacked up of dislocations to form a non-interpenetrating conformation (Figure 1c). The distances of Mn–O range from 2.074(3) Å to 2.359(3) Å, and the angles of O-Mn-O are in the scope of  $57.75(10) - 176.26(14)^{\circ}$ . The phase purity of obtained 3 was also confirmed by PXRD (Figure S6, Supporting Information), and the Mn  $2p_{3/2}$  peak of 3 the XPS data is also around 641.4 eV with a satellite feature of ca. 646 eV indicating the +2 valence of manganese element (Figure S9, Supporting Information). The TGA measurement in  $N_2$  atmosphere shows the thermal stability of 3 as well (Figure S12, Supporting Information). From 25 to 310 °C, a weight loss of 25.7% was observed, corresponding to the loss of solvent molecules in the lattice and the coordinated DMF and  $H_2O$  molecules. The structure began to decompose after further heating after 400 °C.

Catalytic Cycloaddition of CO<sub>2</sub> with Styrene Oxide toward Cyclic Carbonate. The catalytic properties of 1-3 for epoxide carboxylation by CO<sub>2</sub> were surveyed with styrene



Figure 4. Proposed mechanism of the cycloaddition of  $CO_2$  to epoxides with 1 (a) and 2/3 (b) as catalysts.

oxide as the model under atmospheric pressure and solvent-free conditions.

1 was chosen at first to investigate the optimized conditions (entries 1, 4, 7, and 10 in Table 2). As the temperature increases, the yields of the desired products also increased and reached the highest 98% yield at 70 °C after 48 h. Under the same conditions, the activities of 2 and 3 were tested to explore the influence of structure on the catalytic couplings of  $CO_2$ . At either 50 or 60 °C, 2 and 3 exhibited significantly higher activities than 1 according to the obtained product yield, which should be attributed to the less steric hindrance and more potential active sites of 2 and 3. At 70 °C, almost all of the styrene oxide was converted into cyclic carbonate by catalysts 2 and 3.

To explore the reusability of these Mn-MOFs catalysts, we collected the residual catalysts and surveyed the catalytic  $CO_2$  conversion with the regenerated catalysts. As shown in Figure 3, the activity of 1 showed a ca. 35% decrease after five cycles, while the regenerated 2 and 3 still retained the product yields >92%, indicating the successful structural adjustment of the Mn-MOFs for achieving the optimized activity. PXRD patterns of the regenerated catalysts confirmed the better stability of 2 and 3 than that of 1 during the cycloaddition reactions, as shown in Figures S4–S6, Supporting Information, which is consistent with the relatively poor recycled catalytic performance of 1.

In addition, a cocatalyst, such as TBAB, is almost inevitable for the CO<sub>2</sub> cycloaddition, which is important for the ring opening of propylene oxide derivates.<sup>18</sup> However, most MOFcatalytic systems require extremely high amounts of TBAB, which leads to the increase of costs and pollution risk.<sup>25,26</sup> Benefiting from the high activity and the assistance effect of the newly synthesized Mn-MOFs, a TBAB/substrate molar ratio of only 1:50 was sufficient in the reactions. As far as we know, this is an extremely low TBAB dose among the reported MOF catalysts for the CO<sub>2</sub> cycloaddition reactions, as compared in Table S4, Supporting Information.

To show the generality of the Mn-MOF catalysts, we surveyed the substrate-scope tests of 2 and 3 as shown in Scheme 2. For the epoxides with different substituents including chloro, phenoxyl, and methylphenoxyl, both 2 and

3 exhibited outstanding catalytic activities under the solventfree soft conditions with a limited cocatalyst dose. When a substrate with a relatively bulky substituent such as naphthoxyl was used, the product yields were drastically decreased for both 2 and 3 because of the stiff nature and the difficulty to enter the MOF pore of the substrate. Notably, for the coupling of  $CO_2$  with cyclohexene oxide, the performance of 2 and 3 was quite different. The yield given by 2 was only 21%, while catalyst 3 led to a yield as high as 86%, indicating the higher activity of 3 over 2 originating from the abundant Mn active sites and the proper pore space of the non-interpenetrated structure of 3. It is worthy to mention that the cycloaddition of cyclohexene oxide by CO<sub>2</sub> is relatively difficult in comparison to other epoxides due to the steric hindrance of the tertiary carbons.<sup>17,38</sup> To achieve a high conversion rate of cyclohexene oxide, a very high reaction pressure is usually required, 39,40 while 3 shows a rare catalyst for efficiently production of hexahydrobenzo [d] [1,3] dioxol-2-one under such mild conditions.

On the basis of previous reports and the reaction results,<sup>26,41</sup> we proposed the mechanism of the cycloaddition of CO<sub>2</sub> to epoxides with 1 and 2/3 as catalyst in Figure 4. The oxygen atom in the epoxide, as a Lewis base, combines with the Lewis acidic  $Mn^{2+}$  sites to form an intermediate, which is attacked by nucleophilic Br<sup>-</sup> in TBAB on the  $\beta$ -carbon of the substrate with a ring-opening process. After insertion of CO<sub>2</sub> and elimination of Br<sup>-</sup>, the cyclic carbonate product is finally formed and released from the Mn center, and the catalyst and cocatalyst are regenerated.

#### 4. CONCLUSION

We synthesized three new Mn-MOFs with the ligand  $H_2L$  sequentially. The SBUs of Mn-MOFs are tuning from paddlewheel SBUs to the dinuclear Mn nodes with more potential active sites via the adjustment of the anions of the manganese salt. Furthermore, we successfully controlled the conformation of Mn-MOFs from 2-fold interpenetrating into non-interpenetrating by adjusting mixed solvent systems. Along with the strategy of structural modification, both activity and reusability of the Mn-MOFs are successfully improved in the solvent-free cycloaddition of CO<sub>2</sub>. Under the mild condition of

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atmospheric pressure and 70 °C, the Mn-MOFs catalyze  $CO_2$  to react with epoxides for the production of cyclic carbonate without solvent and significantly economize the consumption of cocatalyst TBAB. The efficient catalytic conversion of  $CO_2$  with various epoxides including cyclohexene oxide was achieved. Our work should contribute to the design and structural modification of Mn-MOFs catalysts as well as corresponding activity improvement and may provide new materials for  $CO_2$  management and conversion.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.1c00037.

PXRD spectra, XPS spectra, TGA spectra, and IR spectra (PDF)

#### **Accession Codes**

CCDC 2049950–2049952 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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