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ARTICLE TYPE

## Two coordination polymers constructed from a multidentate carboxylic acid ligand with tertiary amine serve as acid-base catalysts for the synthesis of chloropropene carbonate from CO<sub>2</sub> under atmospheric pressure

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Two new coordination polymers, [Ni(H<sub>2</sub>O)(Hpdc)(H<sub>2</sub>O)<sub>2</sub>]·DMF (**1**) and [Co(H<sub>2</sub>O)(Hpdc)(H<sub>2</sub>O)<sub>2</sub>]·DMF (**2**) (H<sub>3</sub>pdc = 1-(4-carboxyphenyl)-2,5-dimethyl, 1H-pyrrole-3,4-dicarboxylic acid), which were designed based on a tertiary amine ligand, were synthesized and characterized using multiple spectroscopic techniques, including single-crystal X-ray diffraction. These two 1D linear chains possess the properties of both Lewis acid and organic base, which was confirmed by temperature programmed desorption of ammonia and on-line mass spectrometry (NH<sub>3</sub>-TPD-MS), and selective sorption for carbon dioxide. Due to their acid-base properties, the compounds exhibited high catalytic activity, in the absence of co-catalysts, for solvent-free synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin under atmospheric CO<sub>2</sub> pressure. The yields of chloropropene carbonate were 88% and 87% for **1** and **2**, respectively, under the optimized conditions.

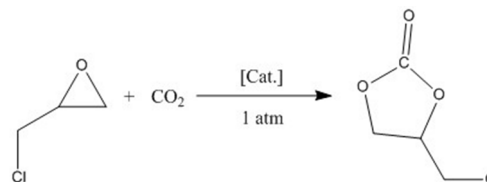
### 1. Introduction

The development of chemical fixation of carbon dioxide (CO<sub>2</sub>) has attracted much attention in recent years, due to the increasing awareness of the global warming caused by CO<sub>2</sub> accumulation in the atmosphere. Meanwhile, CO<sub>2</sub> is an attractive C1 building block in organic synthesis, given its advantages in renewability, abundance, and nontoxicity. One of the most promising methodologies in this area is the synthesis of cyclic carbonates via coupling of CO<sub>2</sub> and epoxides, which can be used as aprotic polar solvents, monomers, pharmaceutical/fine chemical intermediates, and for many biomedical applications.<sup>1</sup>

Due to the low chemical reactivity of CO<sub>2</sub>, the current commercial production of cyclic carbonates employs homogeneous quaternary ammonium or phosphonium salts as catalysts, requiring a temperature above 150°C and a pressure of above twenty bar.<sup>2</sup> Recently, some efficient metal complex catalysts, such as metallosalens and metalloprophyrins, have been developed and exhibited high activity in the reaction of CO<sub>2</sub> and epoxide coupling under the atmospheric pressure, during which process quaternary ammonium was used as a co-catalyst.<sup>3,4</sup> Mechanistic studies have revealed that the metal center plays a role in the activation of the epoxide and quaternary ammonium acts as an *in situ* source of tributylamine to activate the carbon dioxide.<sup>5</sup> However, the complicated separation of these homogenous catalysts from the reaction product has been limiting their application. Although several solid catalysts, such as metal oxides<sup>6</sup>, immobilized complexes or ionic liquids<sup>7</sup>, titanosilicates<sup>8</sup> and metal-organic frameworks (MOFs)<sup>9</sup>, have been explored for the cyclic carbonates from CO<sub>2</sub> and epoxides, the co-catalysts or

high pressure are essential for the reaction, as a result of which the cost and separation difficulty would be increased. Therefore, it is still very challenging to develop new highly efficient heterogeneous catalysts for the solventless synthesis of cyclic carbonates at atmospheric CO<sub>2</sub> pressure and mild temperature independent of co-catalysts.

During the past decade, we have delved into the design and synthesis of coordination polymers for their intriguing structural topologies as well as their heterogeneous catalytic applications.<sup>10</sup> We have noticed that some of these coordination polymers feature site-isolated Lewis acidity of the metal centers together with ligand base groups, and the highly ordered metal ions can be well separated by the organic base linkers that can avoid acid-base neutralization. These observations have suggested that these coordination polymers might be ideal self-supporting heterogeneous acid-base catalysts for the formation of cyclic carbonates independent of co-catalysts.



Scheme 1 Synthesis of cyclic carbonate using CO<sub>2</sub> and epichlorohydrin.

In this paper, we report the syntheses and crystal structures of two new coordination polymers constructed from a tertiary amine ligand H<sub>3</sub>pdc (where H<sub>3</sub>pdc = 1-(4-carboxyphenyl)-2,5-dimethyl, 1H-pyrrole-3,4-dicarboxylic acid, Fig S1), namely [Ni(H<sub>2</sub>O)(Hpdc)(H<sub>2</sub>O)<sub>2</sub>]·DMF (**1**) and

[Co(H<sub>2</sub>O)(Hpdcd)(H<sub>2</sub>O)<sub>2</sub>]DMF (**2**). As expected, the Lewis acidity of the unsaturated metal sites could be created by removal of the terminal H<sub>2</sub>O molecule in the two compounds. Plus the alkalinity of the tertiary amine of the ligand, the two coordination polymers exhibited excellent catalytic activity for solvent-free synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin in the absence of co-catalysts under atmospheric pressure (Scheme 1).

## 2. Experimental section

### 2.1 General information

All solvents were obtained commercially and used without further purification. FTIR spectra were recorded on a Nicolet-5700 spectrophotometer using KBr pellets. Elemental analyses were conducted on a Perkin-Elmer 240 elemental analyzer. Inductively coupled plasma data was collected on an ICP-AES OPTIMA 5300DV spectrophotometer. Powder X-ray diffraction (PXRD) was performed on a Siemens D5005 diffractometer with filtered Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 KV and 30 mA. Diffraction patterns were collected from 5° to 40° with a step size of 1° min<sup>-1</sup>. Thermogravimetric measurements were carried out with a TA SDTQ600 instrument. Samples were heated to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under air atmosphere (50 mL min<sup>-1</sup>). CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms under static conditions were measured with a Micromeritics ASAP 2020 system. The overall surface acidity of the samples was determined by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD, Micromeritics AutoChem 2920 instrument). A multichannel mass spectrometry (TPD-MS, THERMO star<sup>TM</sup>) was employed for on-line analysis of the released gas. Prior to ammonia sorption the sample was pretreated in He (30 mL/min) at 150 °C for 1 h. A mixture of NH<sub>3</sub> in N<sub>2</sub> (0.5 vol. %) was passed (30 mL/min) at 30 °C for 1 h. Then, the sample was flushed with He (30 mL/min) for 1 h. Desorption was carried out by raising the temperature from 30 °C to 200 °C at a linear heating rate of 10 °C/min. Desorption of ammonia was studied by monitoring the signals at m/e = 17.

### 2.2 Synthesis of H<sub>3</sub>pdcld ligand

The H<sub>3</sub>pdcld ligand was prepared according to the reported procedure with some slight modifications.<sup>11</sup> Typically, 15.2 g diacetylsuccinic ester and 8 g p-aminobenzoic acid were dissolved in 70 mL ethanol and refluxed for 10 hours. The resulting ester was saponified and acidized. To refine the crude product, it was purified by recrystallization from ethanol and water (1:1). Colorless crystals were collected in 45% yield of the theoretical amount. <sup>1</sup>H-NMR (300.4 MHz, DMSO-D<sub>6</sub>, rt,  $\delta$ /ppm): 2.16 (s, 6H, CH<sub>3</sub>), 7.5 (d, 2H, Ar-H), 8.1 (d, 2H, Ar-H), 11.0 (s, 3H, OH).

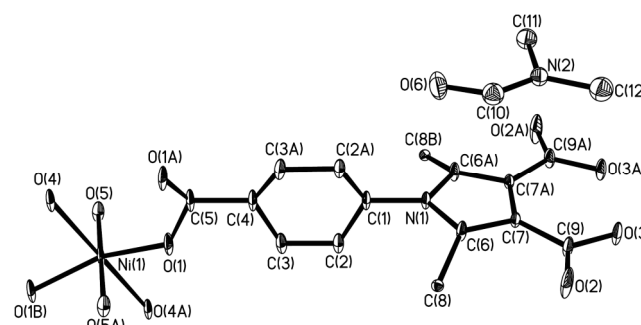
### 2.3 Synthesis of the coordination polymers

The coordination polymers were synthesized by solvothermal reaction of the respective metal nitrates [M = Ni(II) and Co(II)] (0.05 mmol), H<sub>3</sub>pdcld (0.025 mmol), triethylamine (0.06 mL), DMF (1 mL), H<sub>2</sub>O (0.5 mL), and ethanol (2.5 mL) at 75 °C for 3 days. After slowly cooling to room temperature and filtration, green blocky crystals and pink blocky crystals suitable for single-

crystal X-ray diffraction were obtained for Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, respectively. The products (in about 70% yield based on Ni or Co source) were washed with distilled water and further dried at 60 °C for 4 hours. Calcd. for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>NiO<sub>10</sub> (Fw = 487.08): C 44.39, H 4.96, N 5.75 %; found C 44.35, H 4.87, N 5.87 %. FTIR (KBr pellet, cm<sup>-1</sup>): 3410, 1671, 1610, 1540, 1412, 1277, 1175, 1091, 1024, 874, 787, 726, 518. Calcd. for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>CoO<sub>10</sub> (Fw = 487.32): C 44.36, H 4.96, N 5.75 %; found C 44.31, H 4.95, N 5.91 %. FTIR (KBr pellet, cm<sup>-1</sup>): 3423, 1671, 1607, 1540, 1408, 1274, 1175, 1088, 982, 870, 787, 723, 518.

### 2.4 Procedure for the coupling reaction of CO<sub>2</sub> to epichlorohydrin

Epichlorohydrin (15mL, 193 mmol) and the pretreated catalyst (100 mg, 0.2 mmol) were placed in a glass reaction flask equipped with a condenser and a magnetic stirrer bar. The mixture was allowed to stir at a desired temperature under CO<sub>2</sub> atmosphere (20 mL/min with 1 atm) for the setting time. At the end of the reaction, the product mixture was filtered through a 0.45  $\mu$ m filter and then analyzed by GC to determine the yield of the corresponding carbonate. The structure of the product was further defined by GC-MS and <sup>1</sup>H nuclear magnetic resonance spectroscopy (NMR).



**Fig. 1** ORTEP view of **1** showing the atom labeling scheme (30% thermal ellipsoids). The H atoms have been omitted for clarity.

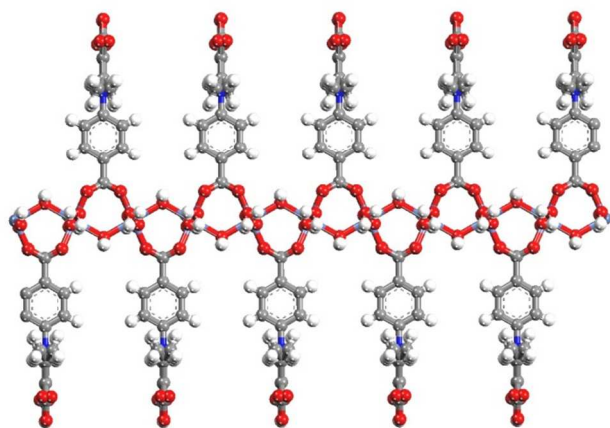
### 2.5 Determination of crystal structures

A suitable single-crystal was selected for single-crystal XRD analysis. The data were collected on a Bruker Smart CCD diffractometer [ $\lambda$  (Mo K $\alpha$ ) = 0.71073  $\text{\AA}$ ] at 20  $\pm$  2 °C. A total of 9454 reflections for compound **1** and 9884 reflections for **2** were collected, with 1339 and 1384 unique reflections respectively ( $R_{\text{int } 1} = 0.0253$ , and  $R_{\text{int } 2} = 0.0510$ ). Data processing was accomplished with the Process-Auto processing program. The structures of the two compounds were all solved by direct methods and refined by a full-matrix least-squares approach on  $F^2$  using SHELXTL 5.1 software package.<sup>12</sup> The metal atoms were first located, then the O, C and N atoms were found in the final difference Fourier maps. The hydrogen atoms of the framework were initially located from difference Fourier maps and for the final refinement were placed geometrically except for those of guest DMF molecule due to its high disorder. Finally, the nonhydrogen atoms were all refined anisotropically. The detailed crystallographic data of the two compounds are listed in Table S1.

## 3. Results and discussion

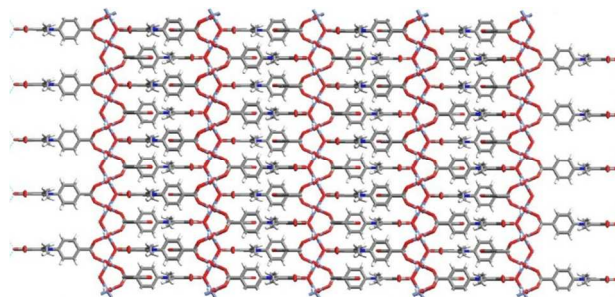
### 3.1 Crystal structure

The X-ray crystal structure analysis of **1** and **2** revealed that the two coordination polymers are isostructural. Here, we describe only the structure of compound **1** as a representative. **1** crystallizes in Orthorhombic, C<sub>2</sub>cm space group. As shown in Fig. 1, each asymmetric unit contains one crystallographically independent nickel(II) ion, one H<sub>2</sub>pdcd ligand, two coordinated water molecules and one guest DMF molecule. The nickel atom resides on the 2-fold rotation axis with a center of symmetry and adopts a distorted octahedral geometry due to the Jahn-Teller effect, which is defined by two carboxylic oxygen atoms (O(1) and O(1A)) from H<sub>2</sub>pdcd ligands, two bridging  $\mu$ -OH group (O(4) and O(4A)) and two coordinated water molecules (O(5) and O(5A)). Interestingly, the H<sub>2</sub>pdcd ligand of **1** adopts a partially deprotonated form (H<sub>2</sub>pdcd<sup>-</sup>), and possess Brønsted acid and Lewis base centers simultaneously. On one hand, a H peak of electron density is found between the O(3) atoms of the carboxylic group, revealing that the H(3) atom is scrambled/disordered by C–O/C=O functionalities to give rise a –COOH group, which is further evidenced by the presence of characteristic absorption band of the carboxylic group around 1675 cm<sup>-1</sup> (IR, Fig. S2).<sup>13,14</sup> On the other hand, the tertiary amine ligand can provide the lone-pair electron and reveals a certain Lewis base characteristic.



**Fig. 2** Ball and stick view of the chain in **1** running parallel to the [100] direction.

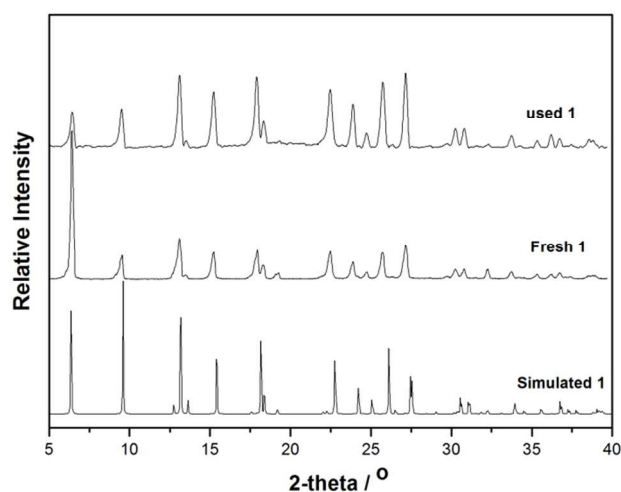
The nickel ions are bridged by *trans*-OH and *syn, syn*-carboxylic groups of H<sub>2</sub>pdcd<sup>-</sup> to form an infinite linear chain (Fig. 2). The chain of Ni atoms is exactly linear along the *c*-axis and Ni...Ni separations are 3.672 Å. The partially deprotonated H<sub>2</sub>pdcd<sup>-</sup> groups decorate the chain and protrude upwards and downwards along the *b*-axis. It should be noted that the chain of **1** is overall similar to that of {Ni(Htmopa)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}<sub>n</sub> (Htmopa = 2,3,6,7-tetramethoxyphenanthrene-9-carboxylic acid) reported recently,<sup>15</sup> except that (i) the carboxylate ligands are Htmopa instead of H<sub>2</sub>pdcd<sup>-</sup>, and (ii) there are no solvent molecules instead of guest DMF molecules in **1**. However, no hydrogen-bonding interaction is found between the chains and guest DMF molecules in **1**. The intermolecular hydrogen bonds, O(4)–H(4)•••O(2) (*x*+1/2, *y*-1/2, *z*) and O(5)–H(5)•••O(3) (*x*+1/2, *y*-1/2, *z*) with the distance d(D•••A) being 2.681 and 2.898 Å, connected the parallel chains into a 3D supramolecular structure, as depicted in Fig. 3.



**Fig. 3** Packing diagram of compound **1** showing hydrogen-bonded interactions into 3D supramolecular framework. The hydrogen bonds are depicted by the blue dotted lines.

### 3.2 XRPD and thermal analyses

The phase purities of compounds **1** and **2** were confirmed by powder X-ray diffraction (XRPD) measurements (Fig. 4 for **1** and Fig. S3 for **2**). It is obvious that the peak positions in the experimental patterns were both in good agreement with the corresponding simulated patterns generated by the X-ray single crystal data, indicating the phase purities of the two coordination polymers. The different reflection intensities between the simulated and experimental patterns might be attributed to a certain degree of preferred orientation of the crystals in the powder samples during data collection.<sup>16</sup>



**Fig. 4** XRD patterns of simulated compound **1** from single-crystal X-ray data, the sample of fresh compound **1**, and used **1** after three cycles.

The thermal properties of **1** and **2** were examined by thermogravimetric analysis under air atmosphere with a heating rate of 10 °C / min from room temperature to 800 °C. As depicted in Fig. S4, the two compounds showed similar curves and the compositions remained stable up to 150 °C. On further heating, the release of DMF and terminal water molecules occurred between 150 °C and 220 °C with a weight loss of 22.0% for **1** (calcd: 22.4%) and 22.5% for **2** (calcd: 22.4%), respectively. Then the two coordination polymers began to decompose and ended at above 410 °C. The weight loss was attributed to the organic ligand. The remaining residual weight (15.88 % for **1** and 16.4 % for **2**) indicated that the final products were the metal oxides, NiO and Co<sub>3</sub>O<sub>4</sub> (calcd 15.14 % for **1** and 16.54 % for **2**),

as confirmed by powder X-ray diffraction.

### 3.3 The properties of acid-base sites

As described by the crystal structure analyses, the partially deprotonated H<sub>3</sub>pdcd ligand of **1** and **2** possessed –COOH group of Brønsted acid and the tertiary amine center of Lewis base. After dehydration, the compounds could further create the Lewis acidity of the unsaturated metal sites. We also demonstrated the acid-base properties of the compound using various characterization approaches.

The acidities of the catalysts measured by the NH<sub>3</sub>-TPD-MS are shown in Fig. 5. In comparison with the blank samples of **1** and **2** without adsorbing NH<sub>3</sub> originally, the compound samples that adsorbed NH<sub>3</sub> exhibited one NH<sub>3</sub> desorption plateau slope and one strong peak within the range of 60–140 °C and 180–220 °C, respectively, by which it can be inferred that acid sites existed on the framework of **1** and **2**. According to the literature, these types of adsorbed ammonia species could be assigned to the NH<sub>3</sub> being weakly adsorbed on the Lewis acid site or the NH<sub>4</sub><sup>+</sup> on the Brønsted acid site, and the NH<sub>3</sub> strongly adsorbed on and/or interacting with the Lewis acid, respectively.<sup>17</sup> Although guest DMF molecules released from the coordination polymers were also detected by MS within the range from 180 and 220 °C, which might interfere with the NH<sub>3</sub> signal, the signals of the NH<sub>3</sub> desorption of **1** or **2** were much stronger than those of the blank samples, further demonstrating the presence of strong Lewis acid in **1** and **2**. The nature of the acid sites was characterized by FT-IR spectroscopy of adsorbed pyridine for compound **1**, as shown in Fig. S5. The results revealed that compound **1** evacuated at 373 K after pyridine adsorption exhibited IR bands at about 1449 and 1606 cm<sup>-1</sup>, which were attributed to the Lewis acid sites.<sup>18</sup> The band at 1542 cm<sup>-1</sup> assigned to weak Brønsted acid sites and the band at 1488 cm<sup>-1</sup> attributed to pyridine chemisorbed on either the Lewis or the Brønsted acid sites were observed. Therefore, it can be seen that both Lewis acid and the weak Brønsted acid were found on the surfaces of the compound **1**, which was consistent with the data obtained in NH<sub>3</sub>-TPD-MS result.

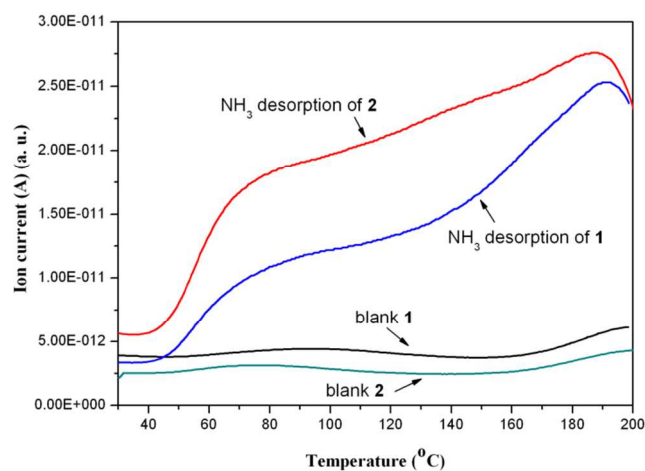


Fig. 5 NH<sub>3</sub>-TPD-MS profiles of **1** and **2** each of which consists of a blank sample without adsorbing NH<sub>3</sub> and a test sample with adsorbing NH<sub>3</sub> initially.

Fig. 6 displays the N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms for

compounds **1** and **2**. It is not surprising that there was no N<sub>2</sub> adsorption for the two compounds, even in 77 K, given the fact that the structures of both were 1D chains without porosity. However, they both exhibited the capability of selective sorption for carbon dioxide at 273 K. This gas selective behaviour can be explained by the affinity of the tertiary amine ligand to CO<sub>2</sub> via the formation of carbamate species,<sup>19</sup> implicating the alkaline property of the two compounds.

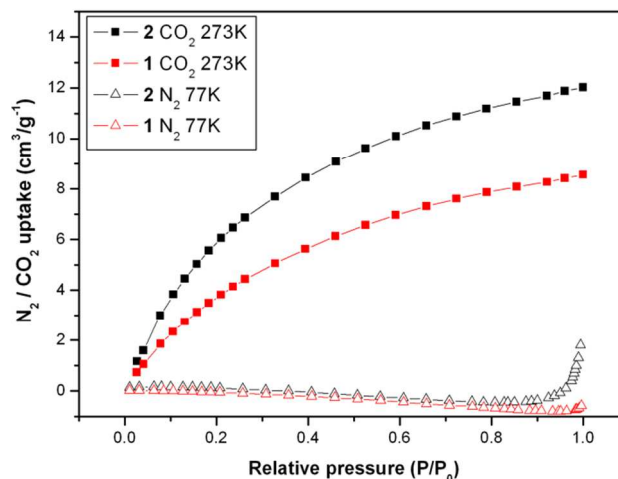


Fig. 6 Comparison of the adsorption isotherms of CO<sub>2</sub> at 273 K and N<sub>2</sub> at 77 K on **1** and **2**.

### 3.3 Catalytic performances

The formation of cyclic carbonates is believed to be catalyzed by base sites for activating CO<sub>2</sub> and accelerated by Lewis acid sites for activating epoxide.<sup>20</sup> Moreover, CO<sub>2</sub> adsorption and activation are the rate-determining step in this cycloaddition reaction due to very high thermodynamic stability. A number of complexes for CO<sub>2</sub> activated via N containing molecules have been synthesized and tested for this type of reaction.<sup>21</sup> Recently, by utilizing the weak Lewis acidity of the metal-connecting points or basicity of organic base linkers, a few MOFs have been examined as heterogeneous catalysts for CO<sub>2</sub> fixation in the presence of a co-catalyst or under high pressure conditions.<sup>22</sup> In view of their features of acidity and organic base, the two 1D chain coordination polymers have prompted us to explore their utilization as heterogeneous catalysts for the cyclic carbonates from CO<sub>2</sub> and epichlorohydrin under atmospheric pressure without any solvent and co-catalyst.

**Table 1** Cycloaddition of CO<sub>2</sub> to epichlorohydrin catalyzed by different catalysts under atmospheric pressure<sup>a</sup>

Entry	Catalyst	Yield <sup>b</sup> (%)	Selectivity (%)	TOF <sup>c</sup> (h <sup>-1</sup> )
1	none	0.7	NA	NA
2	H <sub>3</sub> pdc	14	54	2.1
3	Ni(NO <sub>3</sub> ) <sub>2</sub> +H <sub>3</sub> pdc	5	55	0.7
4	<b>1</b>	88	91	13
5	<b>1</b> <sup>d</sup>	71	90	10.6
6	<b>1</b> (2nd)	62	89	9.3
7	<b>1</b> (3rd)	53	88	8
8	<b>2</b>	87	92	12.5
9	Rh6G+Et <sub>3</sub> N <sup>e</sup>	93	95	4.08

<sup>a</sup>Typical reaction conditions: epichlorohydrin (193 mmol, 15 mL), catalyst (100 mg), CO<sub>2</sub> pressure (1 atm), reaction temperature (100 °C), reaction time (72 h).

<sup>b</sup>Yields were determined by GC.

<sup>c</sup>Moles of converted epoxide per mole of catalyst per hour.

<sup>d</sup>activated under vacuum at 150 °C for 8 h.

<sup>e</sup>Cited by literature [25], epichlorohydrin (16 mmol), Rh6G (1 mol%), Et<sub>3</sub>N (1 mol%), 90 °C, 24 h, 1 atm CO<sub>2</sub>.

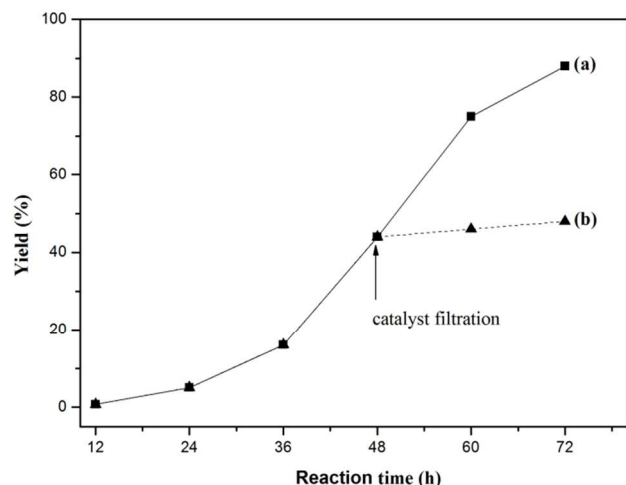
The activity of various catalysts was tested at 100 °C and under atmospheric pressure using the reaction of epichlorohydrin and CO<sub>2</sub> to produce chloropropene carbonate, and the results are summarized in Table 1. Controlled experiments under our reaction conditions confirmed that the reaction did not proceed to a significant extent in the absence of any catalyst. When the tertiary amine H<sub>3</sub>pdc ligand was used alone as a catalyst, the yield of chloropropene carbonate was 14%, illustrating that the tertiary amine moiety of H<sub>3</sub>pdc was catalytic for the reaction at the same performance as quaternary ammonium. As expected, the yield of chloropropene carbonate was remarkably increased to 88% and 87% for **1** and **2**, respectively. It is worth noting that employing the corresponding amount of Ni(NO<sub>3</sub>)<sub>2</sub> together with the free H<sub>3</sub>pdc as catalysts only generated 5% yield with lower selectivity under the similar reaction condition, indicating the existence of a synergistic catalysis effect between the metal center and the N basic moieties in the framework of the coordination polymers. Interestingly, the sample of **1** activated under vacuum at 150 °C for 8 h to remove the terminal H<sub>2</sub>O molecule exhibited lower activity (71% yield) than that of the sample without any pre-treatment. It might be explained by that the guest DMF and the presence of water dissociated from the coordination polymers could accelerate the formation of cyclic carbonates.<sup>23</sup> The coordination of the H atom of the OH group in the water with the O atom of epichlorohydrin through a hydrogen bond resulted in the activation of epichlorohydrin.<sup>24</sup> In addition, we compared the catalytic performances of **1** and **2** with other efficient Rhodamine based catalyst, which operate under atmospheric CO<sub>2</sub> pressure in the presence of a co-catalyst.<sup>25</sup> Although Rh6G exhibited greater yield and selectivity, the turn over frequencies (TOF) value (4.08 h<sup>-1</sup>) was lower than that of the as-synthesized compounds (13.0 h<sup>-1</sup> for **1** and 12.5 h<sup>-1</sup> for **2**),

illustrating the high efficiency of the coordination polymers for the reaction.

In order to obtain the optimum catalytic properties, the parameters, including reaction time and temperature, were investigated carefully. Since **1** and **2** are isomorphous and obtain virtually identical yields, only the catalytic activity of **1** is described in detail. The effect of the reaction time on the chloropropene carbonate yield was investigated at 1 atm CO<sub>2</sub> pressure and 100 °C with compound **1** as a catalyst, and the result is shown in Fig. S6(a). The yield of chloropropene carbonate was increased with the increasing reaction time, and approached 88% after a reaction time of 72 h, followed by a plateau with further increase of reaction time. Taking the catalyst activity and energy consumption into account, 72 h was selected as the optimal reaction time for further investigation. Fig. S6(b) demonstrates that at 1 atm CO<sub>2</sub> pressure, if the compound **1** was used as the catalyst, the chloropropene carbonate yield was determined by temperature within the range of 80-110 °C. This result indicated that the temperature had a remarkable effect on the catalyst activity. The yield of chloropropene carbonate was quickly increased from 2.5% to 88% with increasing temperature from 80 °C to 100 °C. However, when the reaction temperature reached 110 °C, the yield of chloropropene carbonate was decreased to 70%. Most likely, the observed decrease in chloropropene carbonate yield at high temperature was due to the formation of by-products such as diols and dimers of epichlorohydrin.<sup>26</sup>

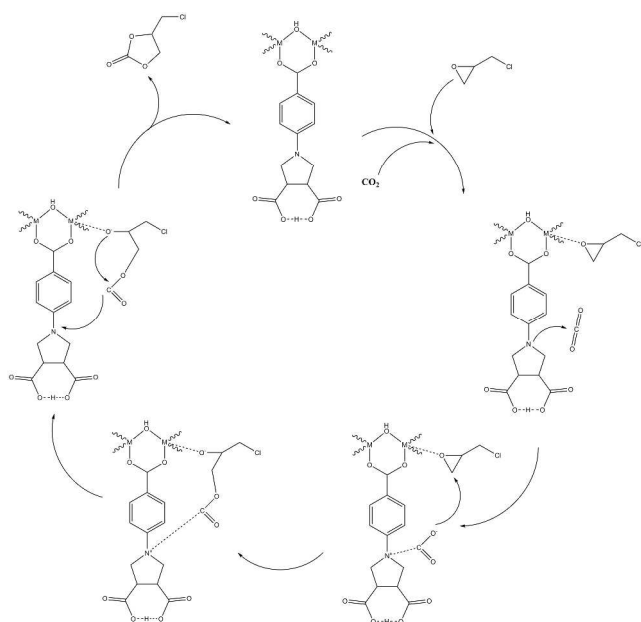
To evaluate the stability of the catalysts in such a liquid phase reaction, we investigated the recyclability of compound **1** in such reaction. In the recycle experiments, the catalyst, after use in the cycloaddition reaction, was washed with ethanol, centrifuged and air dried before reuse. As mentioned before, the yield of chloropropene carbonate was 88% in the first run after 72 h. However, the product yield was decreased to 62% and 53% in the second and third runs, respectively. The nature of the recovered **1** was studied by PXRD analysis and FT-TR spectroscopy. As shown in Fig. 4, the PXRD pattern of the recovered catalyst was as same as fresh catalyst but the peak intensity was slightly decreased. ICP analysis results of the filtered liquid showed that the concentration of Ni<sup>2+</sup> leached was about 110 ppm, indicating that the framework of **1** might have a partial degradation and consequently lose its distinctive crystalline structure, which was further evidenced by HRTEM analysis (Fig. S7). In addition, as shown in Fig. S2, the FT-IR spectra of the recovered catalyst showed a new band at around 1796 cm<sup>-1</sup>, which was ascribed to the carbonyl group in cyclic carbonate,<sup>27</sup> compared with fresh catalyst. This might suggest the blockage of the recovered catalysts by the residual cyclic carbonate poisoned the active sites. From the above discussion, the reduced activity of the recovered catalyst can be attributed, in part, to the degradation of structure of **1** and its blockage by the residual cyclic carbonate. In fact, for other solid catalysts, such as Cu<sub>3</sub>(BTC)<sub>2</sub>,<sup>28</sup> MIL-101,<sup>29</sup> and ZIF-8,<sup>30</sup> similar phenomena have also been observed for this certain reaction. In order to determine if leaching is a problem for the cycloaddition reaction, a filtering experiment was carried out at a fixed temperature (100 °C). In this case, the catalyst was filtered off after 48 h reaction and the filtrate mixture was then stirred at 100 °C for duration of up to 72 h (Fig. 7). The results showed that no significant progress was observed than in the

presence of catalyst that proved true heterogeneous nature of catalysis over **1**, which indicated the synergic catalysis of the acid-base sites in the framework, rather than the leaching  $\text{Ni}^{2+}$  or ligand species, plays a key role in the formation of cyclic carbonate.



**Fig. 7** Cycloaddition of  $\text{CO}_2$  to epichlorohydrin over (a) **1** and (b) filtrate solution (**1** filtered-off after 48h reaction time).

Based on the above observations and analyses, the mechanism of the current catalysis is probably similar to commonly proposed acid-base or electrophile-nucleophile synergic mechanisms.<sup>31</sup> As depicted in Scheme 2, the epichlorohydrin molecule coordinated to the unsaturated metal ions ( $\text{Ni}^{2+}$  for **1** and  $\text{Co}^{2+}$  for **2**) of the frameworks. Meanwhile, The  $\text{CO}_2$  was activated by the basic tertiary amine of the intra-/inter- ligand to form the carbamate species. Then, ring-opening of the epoxide by the attack of the carbamate species resulted in an intermediate metal ion bound alkoxide, followed by intramolecular transfer of the alkoxide onto the carbon dioxide to give a carbonate. Finally, the carbonate cyclized to form the cyclic carbonate product and regenerated the catalyst.



**Scheme 2** Possible mechanism to explain the catalytic activity of **1** or **2**.

## Conclusions

In conclusion, we have synthesized two new 1D coordination polymers bearing the tertiary amine ligand and potential Lewis acidity of the metal centers. The acid-base properties of the two compounds, further confirmed by  $\text{NH}_3$ -TPD-MS characterization and selective sorption for carbon dioxide, promoted us to explore their utilization as self-supporting heterogeneous catalysts for the cycloaddition of  $\text{CO}_2$  to epichlorohydrin under atmospheric pressure without any solvent and co-catalyst. A series of control experiments demonstrated that the as-synthesized compounds had high catalytic activities and the synergic catalysis of the acid-base sites in the frameworks played a key role in the cycloaddition reaction of  $\text{CO}_2$ . However, the product yield was decreased after several reuses of the catalysts due to the partial degradation of the structure or the poisoning of the active sites by the residual cyclic carbonate. New coordination polymer with more stability should be explored to undergo the condition of the cycloaddition reaction, and extended studies are underway.

## Acknowledgment

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## Notes and references

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† Electronic Supplementary Information (ESI) available: IR, TEM, PXRD patterns, TGA curves and single crystal X-ray crystallographic data of **1** or **2** are given in ESI. CCDC 989795 and 989794. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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## Graphical and textual abstract

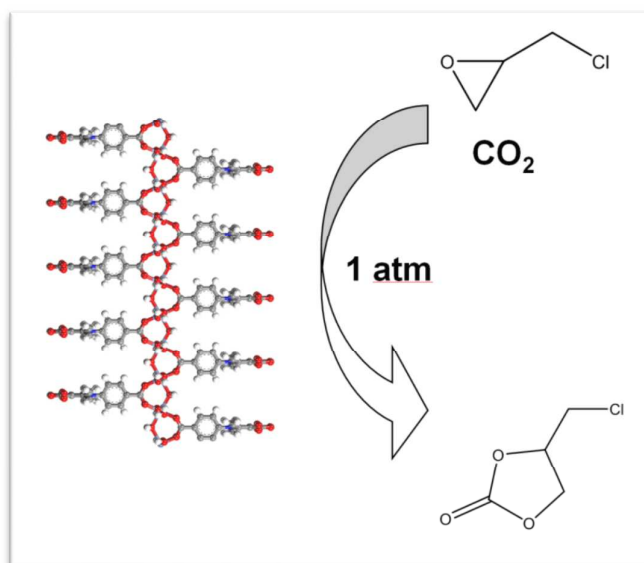
**Two coordination polymers constructed from a multidentate carboxylic acid ligand with tertiary amine serve as acid-base catalysts for the synthesis of chloropropene carbonate from CO<sub>2</sub> under atmospheric pressure**

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Two new coordination polymers have high catalytic activities and the synergic catalysis of their acid-base sites in the frameworks plays a key role in the formation of the cyclic carbonate from CO<sub>2</sub> and epoxide.