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### Syntheses, crystal structures and knoevenagel condensation reactions

### of three coordination polymers assembled with Lewis basic ligand

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#### ABSTRACT

Three functional coordination polymers (CPs), [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Cd<sub>3</sub>L<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O (1),  $[Ba_4L_2(H_2O)_8] \cdot H_2O$ (2)and  $[Zn(H_2L)(H_2O)_2] \cdot H_2O$ (3) (H<sub>4</sub>L 3,5-bis(3',5'-dicarboxylphenyl)-1H-1,2,4-triazole), were synthesized under solvothermal conditions. Structures of 1-3 were confirmed by crystallography and further physically characterized by elemental analysis, IR and TG 1-3 exhibit fascinating multi-dimensional framework structures. Knoevenagel condensation reactions were systematically investigated by using 1-3 as heterogeneous catalysts under solvent-free conditions. Among them,  $\mathbf{1}$  as a recyclable catalyst shows highly efficient catalytic performance in respect to 2 and 3, which may be attributed to the open Lewis base sites and Lewis acid Cd(II) sites in the open channel of 1.

*Keywords*: Coordination polymers  $\cdot$  Knoevenagel condensation  $\cdot$  Heterogeneous catalyst  $\cdot$  Crystal structure

### 1. Introduction

Coordination polymers (CPs), as crystalline solid materials, are composed of metal ions and organic ligands [1-3]. Thus far, an enormous amount of CPs materials have been assembled by using metal ions as the nodes and various multi-functional organic ligands as the linkers [4-10]. In recent years, various applications, such as ion exchange, gas storage and separation, selective adsorption of organic molecules, luminescence and catalysis, have been exploited in CPs materials [11-16]. Particularly, CPs as the heterogeneous catalysts based on their structural elements such as metal vertex, organic ligand and pore system have attracted considerable attention and significant achievements have been gained [17-20].

In this regard, chemical transformation involving C-C bond formation reactions promoted by base catalysis plays an important role in synthetic chemistry [21-24]. Particularly, C-C bond formation reactions represented by Knoevenagel condensation are extensively applied in the syntheses of pharmaceutical products, fragrances and chemical intermediates [25-27]. The conventional base catalysts are mainly focused on organic nitrogen-containing compounds and alkali metal hydroxides [28,29]. Nevertheless, in contrast to heterogeneous catalysts, those conventional base catalysts have some disadvantages in catalyst separation and recycling [30,31]. Very recently, much effort has been devoted to design and synthesis of heterogeneous base catalysts [32-39]. Nevertheless, the development of new heterogeneous catalytic materials with efficient catalytic activity still remains challenging.

In this work, four new CPs, namely,  $[(CH_3)_2NH_2]_2[Cd_3L_2(H_2O)_2]\cdot 6H_2O$  (1),  $[Ba_4L_2(H_2O)_8]\cdot H_2O$  (2), and  $[Zn(H_2L)(H_2O)_2]\cdot H_2O$  (3), have been synthesized utilizing functionalized Lewis basic ligand 3,5-bis(3',5'-dicarboxylphenyl)-1H-1,2,4-triazole (H<sub>4</sub>L). Remarkably, microporous framework 1 possesses abundant Lewis base nitrogen sites and Lewis acid Cd(II) sites in the skeleton and shows excellent heterogeneous catalytic performance for Knoevenagel condensation reactions.

### 2. Experimental

### 2.1. Synthesis

#### 2.1.1 Synthesis of $[(CH_3)_2NH_2]_2[Cd_3L_2(H_2O)_2] \cdot 6H_2O(1)$ .

A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.148 g, 0.48 mmol), H<sub>4</sub>L (0.095g, 0.24 mmol), DMF (24 mL), and distilled water (6 mL) was placed in a Teflon reactor (100 mL) and heated at 120 °C for 3 days. After cooling the mixture to room temperature, colorless crystals of **1** were isolated in a 41% yield. Anal. calcd for C<sub>40</sub>H<sub>46</sub>Cd<sub>3</sub>N<sub>8</sub>O<sub>24</sub> (*Mr* = 1360): C, 35.29; H, 3.38; N, 8.24. Found C, 35.00; H, 3.80; N, 7.98. IR data (KBr, cm<sup>-1</sup>): 3394 (s), 1608 (s), 1552 (s), 1407 (s), 1356 (s), 1310 (m), 1190 (w), 1113 (w), 1024 (w), 920 (w), 771 (m), 749 (s), 592 (m), 458 (m).

#### 2.1.2 Synthesis of $[Ba_4L_2(H_2O)_8] \cdot H_2O(2)$

The preparation of **2** was similar to that of **1** except that  $BaCl_2 \cdot 2H_2O$  was used instead of  $Cd(NO_3)_2 \cdot 4H_2O$ . Compound **2** was obtained as colorless crystals in a 51% yield. Anal. calcd for  $C_{40}H_{32}Ba_4N_6O_{25}$  (*Mr* = 1498): C, 28.86; H, 2.15; N, 5.61. Found C, 28.80; H, 2.05; N, 5.66. IR data (KBr, cm<sup>-1</sup>): 3209 (m), 1624 (m), 1550 (s), 1404 (s), 1370 (s), 1311 (m), 1189 (m), 1105 (m), 1026 (w), 920 (w), 869 (w), 818 (w), 790 (m), 754 (m), 723(m), 592 (w), 516 (w), 452(w).

### 2.1.3 Synthesis of $[Zn(H_2L)(H_2O)_2] \cdot H_2O(3)$

A mixture of  $Zn(NO_3)_2 \cdot 6H_2O(0.143 \text{ g}, 0.48 \text{ mmol})$ ,  $H_4L$  (0.095g, 0.24 mmol), ethanol (24 mL), and distilled water (24 mL) was placed in a Teflon reactor (100 mL) and heated at 120 °C for 3 days. Compound **3** was obtained as colorless crystals in a 64% yield. Anal. calcd for  $C_{18}H_{15}ZnN_3O_{11}$  (*Mr* = 514): C, 42.03; H, 2.92; N, 8.17. Found C, 42.20; H, 2.90; N, 8.33. IR data (KBr, cm<sup>-1</sup>): 3648 (w), 3541 (w), 3191 (m), 2520 (w), 1665 (s), 1622 (s), 1660 (s), 1546 (m), 1512 (w), 1448 (m), 1417 (m), 1364 (s), 1322 (m), 1289 (s), 1197 (m), 1110 (m), 1020 (m), 919(m), 783 (m), 704 (m) 636 (w), 542 (w), 438(w).

#### 2.2 Knoevenagel condensation reactions

In a typical procedure, aldehyde (1 mmol), malononitrile (2 mmol), and as-synthesized catalyst (0.5 mol%) were stirred in a round-bottom flask at 60 °C for 1

h. The yields were analyzed by GC and <sup>1</sup>H NMR spectra.

### 3. Results and discussion

#### 3.1. Description of the structures

### 3.1.1 Crystal structure of $[(CH_3)_2NH_2]_2[Cd_3L_2(H_2O)_2]\cdot 6H_2O(1)$

Single-crystal X-ray diffraction revealed that 1 crystallizes in the space group C2/c. The asymmetric unit of 1 consists of three Cd(II) ions, two  $L^{4-}$  anions, two  $[(CH_3)_2NH_2]^+$  cations, two coordinated water molecules and six free water molecules. The  $[(CH_3)_2NH_2]^+$  from the decomposed DMF as a positive charge balanced the framework [40-42]. As illustrated in Fig. 1a, Cd1 and Cd3 exhibit analogous pentagonal bipyramid coordination geometries. Both Cd1 and Cd3 are encircled by four L<sup>4-</sup> anions and one water molecule, while Cd2 is coordinated by five carboxylate oxygen atoms of distinct L<sup>4-</sup> anions. Three Cd(II) ions, Cd2, Cd3 and symmetry-related Cd1<sup>#2</sup>, are connected by carboxylate oxygen atoms of nine L<sup>4-</sup> anions to generate a trinuclear secondary building unit (SBU) with the Cd1...Cd2 separation of 4.153Å and Cd2…Cd3 distance of 4.345Å. The Cd–O–Cd bond angles range from 114.7° to 115.8°, and the Cd–O bond lengths vary from 2.575 Å to 2.191 Å (Fig. 1b, Table S1). As shown in Fig. 1c, one L<sup>4-</sup> anion links six Cd(II) ions and another L<sup>4-</sup> links seven Cd(II) ions through carboxylate groups of four isophthalate moieties, yielding a 3D microporous framework (Fig. 1d). The free solvent-accessible volume calculated from PLATON is 39.2% of the unit cell [43].





**Fig. 1.** (a) Coordination environments of the Cd(II) ions in **1**. (b) View of the trinuclear Cd(II) unit connected by the carboxylate groups from nine  $L^{4-}$  anions. (c) Coordination modes of **1**. (d) View of the 3D microporous framework of **1**.

### 3.1.2 Crystal structure of $[Ba_4L_2(H_2O)_8] \cdot H_2O(2)$

2 crystallizes in the space group *P*-1. The asymmetric unit of 2 is composed of four Ba(II) ions, two L<sup>4</sup>, eight coordinated water molecules and one free water molecule. As illustrated in Fig. 2a, both Ba1 and Ba2 are seven-coordinated. Ba1 is encircled by four carboxylate oxygen atoms and three water molecules, while Ba2 is surrounded by six carboxylate oxygen atoms and one water molecule. Ba3 is eight-coordinated by six carboxylate oxygen atoms of four different L<sup>4-</sup> anions and three coordinated water molecules. Ba4 is nine-coordinated by eight carboxylate oxygen atoms. The Ba–O bond lengths range from 3.275 Å to 2.659 Å, and the O–Ba–O bond angles vary from 149.0° to 43.2° (Table S2). As shown in Fig. 2b, the L<sup>4-</sup> anion bridges nine Ba(II) ions in two different ways to yield a 3D framework (Fig. 2c).





Fig. 2. (a) Coordination environments of the Ba(II) in 2. (b) Coordination modes of 2.(c) View of the 3D framework of 2.

### 3.1.3 Crystal structure of $[Zn(H_2L)(H_2O)_2] \cdot H_2O(3)$

**3** crystalline in the space group *C2/c*. In **3**, each Zn(II) ion is in an octahedral coordination style, surrounded by four carboxylate oxygen atoms from two H<sub>2</sub>L<sup>2-</sup> anions and two water oxygen atoms (Fig. 3a). The Zn–O bond lengths vary from 1.998 Å to 2.125 Å, and the O–Zn–O bond angles range from 85.9° to 140.7° (Table S3). As shown in Fig. 3b, each H<sub>2</sub>L<sup>2-</sup> anion bridges three Zn(II) cations with four isophthalate arms to yield a layer. Remarkably, there exists  $\pi$ - $\pi$  stackings among the benzene rings of the H<sub>2</sub>L<sup>2-</sup> anions between neighboring layers (inter-plane and inter-center lengths of 3.33 and 3.52 Å, respectively), leading to a 3D supramolecular architecture (Figs. 3c and 3d).





**Fig. 3.** (a) Coordination environment of the Zn(II) ion in **3**. (b) Coordination modes of **3.** (c) View of the layer of **3**. (d) View of the 3D supramolecular architecture by  $\pi$ - $\pi$  stackings.

#### 3.2 Knoevenagel condensation reaction

Catalytic activities of 1-3 were investigated in Knoevenagel condensation reaction of benzaldehyde (BA) with malononitrile [44]. Typically, the catalytic reactions were carried out at 60 °C with 0.5 mol% of catalyst loading (with respect to the amount of benzaldedyde). The yields of benzylidene malononitrile (BM) were confirmed by <sup>1</sup>H NMR studies and gas chromatography (GC) (Fig. S1 and S2) [37]. When 2 and 3 were used as catalysts for Knoevenagel condensation reactions, only conversion yields of 5% and 7.2% were achieved, respectively, after 1 hour. Meanwhile, a lower conversion yield of 11.2% was acquired with the H<sub>4</sub>L as heterogeneous catalyst. In contrast to 2 and 3, 1 exhibits much higher catalytic activity as the heterogeneous catalyst with high selectivity more than 99% and turnover frequency (TOF) of 200  $h^{-1}$  (Table 1). Notably, no catalysis was observed in the absence of catalysts 1-3 and  $H_4L$ , demonstrating that 1-3 and  $H_4L$  indeed exhibit the catalytic activities towards the Knoevenagel condensation reaction. Furthermore, PXRD demonstrates that the framework of 1-3 retained after treatments (Fig. S3). In contrast 2 and 3, the large pore of 1 facilitates the mass transfer of guest molecules, leading to excellent catalytic performance for Knoevenagel condensation reaction [19,38].



**Table 1.** Knoevenagel condensation reactions of malononitrile with benzaldehyde catalyzed by 1-3 and  $H_4L$ .

Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), catalyst (0.5 mol% of the substrate), 1 hour, 60 °C.

To check the heterogeneity of **1** in the Knoevenagel condensation reaction, a filtration experiment was tested. After half an hour of the catalytic reaction, the catalyst was removed. Further, the reaction mixture was stirred for additional 30 minutes, but no additional BM products were achieved (Fig. 4). The results demonstrate that the catalytic reaction is indeed heterogeneous and no catalysts were dissolved into the filtrate. Moreover, recycled Knoevenagel reaction was performed with catalyst **1** under the same condition. The experiment result shows that catalyst **1** still exhibits good catalytic activity after three runs, demonstrating the excellent reusability of **1** in the Knoevenagel condensation reaction. Meanwhile, the PXRD patterns confirmed that the framework was retained after three runs (Fig. S3a).



**Fig. 4.** Conversion of the benzaldehyde in the Knoevenagel condensation reactions catalyzed by **1** (pink) and by the filtrate of **1** after 30 min of the catalytic reaction (black).

In the following catalytic reactions, a series of benzaldehyde derivatives with different functional groups were selected as substrates. As shown in Table 2, the Knoevenagel condensation reactions of malononitrile with 4-cyanobenzaldehyde (entry 3) and 4-nitrobenzaldehyde (entry 4) were completely converted to products after 1 hour at 60 °C. The high catalytic performance can be explained by the electron withdrawing substituents, which facilitate nucleophilic attack in the Knoevenagel condensation [27,45]. The synergistic effect by the inductive effect and the conjugation effect make the electron-withdrawing property of the halogenobenzaldehyde in the order of -Cl > -Br > -F. Thus, the conversion of the halogenobenzaldehyde decreases in the same order (entries 2 and 6). In contrast, the electron-rich benzaldehyde derivatives, such 4-methylbenzaldehyde, as 4-ethylbenzaldehyde and 4-methoxybenzaldehyde, gave the products with much lower yields (entries 5, 7 and 8).

 Table 2. Knoevenagel condensation reaction of malononitrile with benzaldehyde

 derivatives catalyzed by 1.



Reaction conditions: benzaldehyde derivatives (1 mmol), malononitrile (2 mmol), catalyst (0.5 mol% of the substrate), 1 hour, 60 °C.

## 4. Conclusion

We have synthesized three functional coordination polymers with exposed Lewis basic sites. The Knoevenagel condensation reactions were investigated using 1-3 as heterogeneous catalysts under solvent-free conditions. Remarkably, porous 1 shows much higher conversion and selectivity in Knoevenagel condensation reaction because of its exposed Lewis basic sites and Lewis acid Cd(II) sites in the open

channels. Moreover, catalyst **1** can be easily separated and reused three times without obvious loss of the catalytic activity. The high catalytic activity under mild reaction conditions makes **1** a promising material for Knoevenagel condensation reaction as heterogeneous catalyst.

## Appendix A. Supplementary data

CCDC 1572038, 1572039 and 1572041 contains the supplementary crystallographic data for **1-3**. These data can be obtained free charge via of http://www.ccdc.cam.ac.uk/conts/retrieving.html, from the Cambridge or Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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### References

- [1] H.-C. Zhou, S. Kitagawa, Chem. Soc. Rev. 43 (2014) 5415.
- [2] Y. He, B. Li, M. O'Keeffe, B. Chen, Chem. Soc. Rev. 43 (2014), 5618.
- [3] S. Kitagawa, R. Kitaura, S.-i. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334.
- [4] Y. Yang, J. Yang, P. Du, Y.-Y. Liu, J.-F. Ma, CrystEngComm 16 (2014) 1136.
- [5] J. Li, J. Yang, Y.-Y. Liu, J.-F. Ma, Chem. Eur. J. 21 (2015) 4413.
- [6] M. Shi, J. Yang, Y.-Y. Liu, J.-F. Ma, Dyes and Pigments 129 (2016) 109.
- [7] D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe, O. M. Yaghi, Chem. Soc. Rev. 38 (2009) 1257.
- [8] F. A. Almeida Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tomé, J. A. S. Cavaleiro, J. Rocha, Chem. Soc. Rev. 41 (2012) 1088.
- [9] H. Wang, C. Huang, Y. Han, Z. Shao, H. Hou, Y. Fan, Dalton Trans. 45 (2016)

7776.

- [10]J.-J. Hou, X.-Q. Li, P. Gao, H.-Q. Sun, X.-M. Zhang, Cryst. Growth Des. 17 (2017) 3724.
- [11] J.-R. Li, J. Sculley, H.-C. Zhou, Chem. Rev. 112 (2012) 869.
- [12]L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Chem. Rev. 117 (2017) 8129.
- [13]Y. Cui, Y. Yue, G. Qian, B. Chen, Chem. Rev. 112 (2012) 1126.
- [14] L.-L. Shi, Y.-Q. Zhang, S.-S. Han, Z. Yang, L.-M. Zhu, B.-L. Li, H.-Y. Li, Polyhedron, 133 (2017) 82.
- [15] Y.-Y. Yang, L.-X. Zhou, Y.-Q. Zheng, H.-L. Zhu, Polyhedron 134 (2017) 345.
- [16] Y.-B. Zhou, Y.-Q. Wang, L.-C. Ning, Z.-C. Ding, W.-L. Wang, C.-K. Ding, R.-H. Li, J.-J. Chen, X. Lu, Y.-J. Ding, Z.-P. Zhan, J. Am. Chem. Soc. 139 (2017) 3966.
- [17]M. Ghorbanloo, V. Safarifard, A. Morsali, New J. Chem. 41 (2017) 3957.
- [18] S. Y. Hao, S. X. Hou, J. Zhu, G. H. Cui, Polyhedron 134 (2017) 88.
- [19] J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L.-B. Sun, P. B. Balbuena, H.-C. Zhou, Chem. Commun. 48 (2012) 9995.
- [20] L. Garzón-Tovar, S. Rodríguez-Hermida, I. Imaz, D. Maspoch, J. Am. Chem. Soc. 139 (2017) 897.
- [21]F. Chen, T. Wang, N. Jiao, Chem. Rev. 114 (2014) 8613.
- [22]D. R. Pye, N. P. Mankad, Chem. Sci. 8 (2017) 1705.
- [23]L. Xu, C.-g. Li, K. Zhang, P. Wu, ACS Catalysis 4 (2014) 2959.
- [24] Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, Angew. Chem. 120 (2008) 4212.
- [25]B. List, Angew. Chem. Int. Ed. 2010, 49, 1730.
- [26] N. Kan-nari, S. Okamura, S.-i. Fujita, J.-i. Ozaki, M. Arai, Adv. Synth. Catal. 352 (2010) 1476.
- [27] Y. Wang, L. Wang, C. Liu, R. Wang, ChemCatChem 7 (2015) 1559.
- [28]M. B. Ansari, H. Jin, M. N. Parvin, S.-E. Park, Catal. Today 185 (2012) 211.
- [29] S.-I. Fujita, B. M. Bhanage, D. Aoki, Y. Ochiai, N. Iwasa, M. Arai, Applied Catalysis A: General 313 (2006) 151.
- [30] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, Chem. Soc. Rev. 43 (2014)

6011.

- [31] S. Santoro, S. I. Kozhushkov, L. Ackermann, L. Vaccaro, Green Chem. 18 (2016) 3471.
- [32] E. Gianotti, U. Diaz, A. Velty, A. Corma, Eur. J. Inorg. Chem. 2012 (2016) 5175.
- [33] H. Liu, F.-G. Xi, W. Sun, N.-N. Yang, E.-Q. Gao, Inorg. Chem. 55 (2016) 5753.
- [34] S. Srivastava, M. S. Dagur, R. Gupta, Eur. J. Inorg. Chem. 2014 (2014) 4966.
- [35] S. R. Sushrutha, R. Hota, S. Natarajan, Eur. J. Inorg. Chem. 2016, 2016, 2962.
- [36] J. Xu, Y. Wang, J.-K. Shang, D. Ma, Y.-X. Li, Applied Catalysis A: General 538 (2017) 221.
- [37] W. Jiang, J. Yang, Y.-Y. Liu, S.-Y. Song, J.-F. Ma, Inorg. Chem. 56 (2017) 3036.
- [38] L. M. Aguirre-Díaz, F. Gándara, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla, M. Á. Monge, J. Am. Chem. Soc. 137 (2015) 6132.
- [39] X.-C. Yi, M.-X. Huang, Y. Qi, E.-Q. Gao, Dalton Trans. 43 (2014) 3691.
- [40] S. Dang, E. Ma, Z.-M. Sun, H. Zhang, J. Mater. Chem. 22 (2012) 16920.
- [41] B.-B. Lu, W. Jiang, J. Yang, Y.-Y. Liu, J.-F. Ma, ACS Appl. Mater. Interfaces 9 (2017) 39441.
- [42] X. Zhang, X. Li, J. Zhang, Inorg. Chem. Commun. 84 (2017) 77.
- [43] A. Spek, J. Appl. Crystallogr. 36 (2003) 7.
- [44] X. Liu, S. A, Y. Zhang, X. Luo, H. Xia, H. Li, Y. Mu, RSC Advances 4 (2014)6447.
- [45] X.-S. Wang, J. Liang, L. Li, Z.-J. Lin, P. P. Bag, S.-Y. Gao, Y.-B. Huang, R. Cao, Inorg. Chem. 55 (2016) 2641.

compound	1	2	3
formula	$C_{40}H_{46}Cd_3N_8O_{24}$	C <sub>36</sub> H <sub>32</sub> Ba <sub>4</sub> N <sub>6</sub> O <sub>25</sub>	$C_{18}H_{15}ZnN_{3}O_{11}$
Mr	1360	1498	514
crystal system	monoclinic	triclinic	monoclinic
space group	C2/c	P-1	C2/c
<i>a</i> (Å)	33.2297(12)	10.122(5)	13.526(5)
<i>b</i> (Å)	20.0890(9)	14.450(5)	17.183(5)
<i>c</i> (Å)	15.9769(5)	16.551(5)	16.667(5)
$\alpha(^{\circ})$	90	107.990(5)	90.000(5)
$\beta(^{\circ})$	100.360(3)	98.667(5)	103.208(5)
γ(°)	90	104.517(5)	90.000(5)
$V(\text{\AA}^3)$	10491.5(7)	2159.4(15)	3771(2)
Ζ	8	2	8
$D_{\text{calc}} (\text{g cm}^{-3})$	1.722	2.304	1.813
$F(0\ 0\ 0)$	5424	1428	2096
$R_{\rm int}$	0.0342	0.0559	0.0360
GOF on $F^2$	0.9340	1.0260	1.0370
$R1^a$ [I>2 $\sigma$ (I)]	0.0420	0.0688	0.0499
$wR_2^b$ (all data)	0.0987	0.1323	0.1341

 Table 3. Crystallographic data and structure refinements.

 ${}^{a}\overline{R_{1}} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|. {}^{b}wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma w(F_{o}^{2})^{2}]\}^{1/2}.$ 

### **Table of Contents**



Three coordination polymers (CPs) have been constructed with Lewis basic ligand, where the microporous framework of **1** possesses abundant Lewis base nitrogen sites and Lewis acid Cd(II) sites in the skeleton and shows excellent heterogeneous catalytic performance for Knoevenagel condensation reaction under the solvent-free conditions.