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Zhi-Wei Zhai,<sup>a,b</sup> Shuang-Hua Yang,<sup>b</sup> Ya-Ru Lv,<sup>a</sup> Chen-Xia Du,<sup>a</sup> Lin-Ke Li,<sup>\*a</sup> Shuang-Quan Zang<sup>\*a</sup>

Two amino functionalized Metal–Organic Frameworks (MOFs),  $[[Zn(Py_2TTz)(2-NH_2-BDC)] \cdot (DMF)]_n$  (1),  $\{[Cd(Py_2TTz)(2-NH_2-BDC)] \cdot (DMF) \cdot (DMF)]_n$  (2), (where Py\_2TTz = 2,5-Bis(4-pyridyl)thiazolo[5,4-d]thiazole, 2-NH\_2-BDC = 2-amino-1,4-benzenedicarboxylate, and DMF = *N*,*N*-dimethylformamide), were synthesized and characterized, using primary ligand 2-amino-1,4-benzenedicarboxylic acid (2-NH\_2-H\_2BDC) and auxiliary ligand 2,5-bis(4-pyridyl)thiazolo[5,4-d]thiazole (Py\_2TTz). They possess similar 2-fold interpenetrated three-dimensional bipillared-layer framework structures composed of the typical binuclear metal nodes, 2-NH\_2-BDC two-dimensional layers and Py\_2TTz bipillars. Notably, the thiazole nitrogen atoms and pendant -NH<sub>2</sub> groups are present in channels in the two frameworks. Given that their good chemical stabilities, high thermal stabilities, and exposed nitrogen sites, gas adsorption and catalytic experiment of the two MOFs were investigated. The results demonstrate that MOF **2** can selectively adsorb gas carbon dioxide, and moreover, the two MOFs can be employed as recyclable heterogeneous catalyst for Knoevenagel condensation reaction under solvent-free conditions.

## Introduction

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As one of the most promising crystalline materials, metal-organic frameworks (MOFs) have attracted tremendous attention because of their permanent porosities, diversities, and designabilities in the past decades,<sup>1-5</sup> which display extensive potential applications in gas adsorption/separation,<sup>6-</sup> chemical sensing,<sup>13-23</sup> opto-electronic materials,<sup>24-26</sup> pollutants adsorption/removal,<sup>27-31</sup> heterogeneous catalysis,<sup>32-</sup> <sup>35</sup> etc. Accordingly, design and synthesis of the performance superior and multifunctional MOFs have been one of the research hotspots. However, it is very difficult to obtain the targeted structure because many factors will cause the diverse structure of MOFs, such as the coordination mode of organic linker, the nature of metal ion, as well as the synthesis condition. Therefore, combining the typical secondary building units (SBUs) with customized linkers has become a common and effective strategy for the construction of the desired MOFs, which provide a versatile platform for accomplishing the targeted applications through introducing suitable functional groups.<sup>36-39</sup>

As is well known, carbon dioxide  $(CO_2)$  is one of the major greenhouse gases resulting in the dramatic environmental issues (global warming), which is able to be alleviated effectively by the CO<sub>2</sub> capture and storage.<sup>40-42</sup> Furthermore,

the natural gas purification and the flue gas separation are also important topics relating CO<sub>2</sub> selective adsorption.<sup>43-46</sup> Hence, it is imperative to develop materials with the capability of selective adsorption CO<sub>2</sub>. Fortunately, MOFs materials with nitrogenous functional groups might be one of the best candidates as selective adsorbent. It is reported that uncoordinated nitrogen atoms can offer openly accessible Lewis basic sites for CO<sub>2</sub> binding in MOFs.<sup>49-51</sup> Additionally, MOFs containing –NH<sub>2</sub> groups could generate easy-on/easy-off reversible CO<sub>2</sub> adsorption equilibrium with selectivity.<sup>52-57</sup> Moreover, the presence of uncoordinated nitrogen sites and -NH<sub>2</sub> groups might afford an opportunity to perform basecatalyzed reactions such as Knoevenagel condensation, which is one of the classic and versatile C–C bond forming reactions in synthetic chemistry.58-63 However, such functionalization is not easy to realize owing to the strong coordination abilities of nitrogen atoms. So far, only a few MOFs with nitrogenous functional groups have been obtained by direct synthesis.<sup>64-67</sup>

In the pursuit of performance superior multifunctional materials for CO<sub>2</sub> adsorption, catalysis as well as other applications, we have been working on design and synthesis of the MOFs with nitrogenous functional groups. Based on our previous studies,<sup>68,69</sup> we envisioned that the MOFs constructed by nitrogenous linkers 2,5-bis(4-pyridyl)thiazolo[5,4-*d*]thiazole (Py<sub>2</sub>TTz) and 2-amino-1,4-benzenedicarboxylic acid (2-NH<sub>2</sub>-H<sub>2</sub>BDC) will provide a multifunctional platform for adsorbing CO<sub>2</sub> selectively and catalyzing Knoevenagel reaction effectively. Herein, assembling Py<sub>2</sub>TTz and 2-NH<sub>2</sub>-H<sub>2</sub>BDC with d<sup>10</sup> metal ions Zn(II)/Cd(II), two MOFs, {[Zn(Py<sub>2</sub>TTz)(2-NH<sub>2</sub>-BDC)]·(DMF)}<sub>n</sub> (1), {[Cd(Py<sub>2</sub>TTz)(2-NH<sub>2</sub>-BDC)]·(DMF)·0.5(H<sub>2</sub>O)}<sub>n</sub> (2), (where Py<sub>2</sub>TTz = 2,5-Bis(4-pyridyl)thiazolo[5,4-*d*]thiazole, 2-NH<sub>2</sub>-BDC = 2-amino-1,4-benzenedicarboxylate, and DMF = *N*,*N*-dimethylformamide), have been obtained successfully. They possess similar three-

<sup>&</sup>lt;sup>o</sup> College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450001, P. R. China.

<sup>&</sup>lt;sup>b</sup> School of Environmental Engineering and Chemistry, Luoyang Institute of Science and Technology, Luoyang 471023, P. R. China.

E-mail: lilinke@zzu.edu.cn, zangsqzg@zzu.edu.cn

<sup>\*</sup>Electronic Supplementary Information (ESI) available: Crystallographic data, TGA, PXRD patterns, IR spectra, gas adsorption date for complexes 1 and 2; PXRD patterns, IR spectra, SEM for complexes 1a and 2a. CCDC numbers 1882223 and 1882224 for complexes 1 and 2. See DOI: 10.1039/x0xx00000x

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dimensional (3D) bipillared-layer framework structures composed of the typical binuclear metal nodes, 2-NH<sub>2</sub>-BDC twodimensional (2D) layers and Py<sub>2</sub>TTz bipillars. Interestingly, the numerous thiazole nitrogen atoms and pendant -NH<sub>2</sub> groups are exposed to their channels, which provide a good platform to explore CO<sub>2</sub> adsorption and base-catalyzed reactions. The experimental results demonstrate that MOF 2 can selectively adsorb CO<sub>2</sub>, and moreover, both MOFs can be employed as efficient heterogeneous catalysts for the Knoevenagel condensation reaction. Furthermore, the substituent effects for various benzaldehyde derivatives in Knoevenagel reaction were also examined systematically.

## Experimental

#### Materials and methods

All the chemicals for experiment are commercially available and used as received without further purification. 2,5-Bis(4pyridyl)thiazolo[5,4-d]thiazole (Py<sub>2</sub>TTz) and 2,5were diphenylthiazolo[5,4-d]thiazole (Ph₂TTz) prepared according to the reported procedures but modified slightly.<sup>70,71</sup> Infrared spectra (IR) (KBr pellets) were recorded on a Nexus 870 FTIR spectrometer in the range of 400-4000 cm<sup>-1</sup>. Elemental analyses (EA) were conducted with a Perkin-Elmer 240 elemental analyzer. <sup>1</sup>H NMR spectra were recorded on a Bruker DRX spectrometer (400 MHz) in CDCl<sub>3</sub>. Powder X-ray diffraction (PXRD) patterns of the samples were recorded in the  $2\vartheta = 5-50$ ° range on a Bruker D8 Advance diffractometer with Cu Kα radiation ( $\lambda$  = 1.5418 Å) at room temperature. Thermogravimetric analyses (TGA) were performed on a TA Q50 thermogravimeter from room temperature to 800 °C with a heating rate of 10 °C·min<sup>-1</sup> under Ar atmosphere. Gas sorption isotherms were measured on BEL-max physisorption analyzer after the removal of guest molecules by evacuation at 100 °C for 12 h. Scanning electron microscope (SEM) images were acquired using a Zeiss Sigma 500 emission scanning electron microscope with an accelerating voltage of 2-10 kV.

#### Synthesis of $\{[Zn(Py_2TTz)(2-NH_2-BDC)] \cdot (DMF)\}_n$ (1)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (10 mg, 0.034 mmol), Py<sub>2</sub>TTz (6 mg, 0.020 mmol) and 2-NH<sub>2</sub>-H<sub>2</sub>BDC (6 mg, 0.033 mmol) were added to the mixed solvent (2.5 mL, DMF/H<sub>2</sub>O = 4/1) and sonicated for 30 minutes. Subsequently, the reaction mixture was transferred to a PTFElined stainless-steel vessel, which was placed in the oven and was kept at 100 °C for 48 h. After cooling to ambient temperature, needle-shaped yellow crystals were obtained. Crystals were filtered, washed with DMF, and dried in air (10.8 mg, 87% yield based on Py<sub>2</sub>TTz ligand). Elemental analysis (%) calcd for  $C_{25}H_{20}N_6O_5S_2Zn$ : C 48.90, H 3.28, N 13.69, S 10.44; found: C 48.49, H 3.19, N 13.46, S 10.14. Main infrared spectral data (KBr, cm<sup>-1</sup>): 3544 (s), 3455 (s), 3417 (s), 3357 (s), 3056 (w), 3031 (w), 2921 (w), 2850 (w), 1668 (m), 1616 (s), 1575 (s), 1444 (m), 1421 (m), 1382 (s), 1322 (m), 1259 (m), 1213 (m), 1145 (m),1030 (s), 1091 (m), 1064 (m), 1029 (m), 825 (m), 769 (m), 705 (m), 665 (m), 620 (s), 582 (m), 509 (s), 478 (m), 406 (m). (IR spectrum is shown in Figure S1).

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## Synthesis of {[Cd(Py2TTz)(2-NH2-BDC)]·(DMF)·0.5(H2O)

According to the aforementioned procedure except that  $Zn(NO_3)_2 \cdot 6H_2O$  was replaced by  $Cd(NO_3)_2 \cdot 4H_2O$  (10 mg, 0.032) mmol), the block-shaped light yellow crystals of 2 were obtained. Crystals were filtered, washed with DMF, and dried in air (8.8 mg, 66% yield based on Py2TTz ligand). Elemental analysis (%) calcd for C<sub>25</sub>H<sub>21</sub>N<sub>6</sub>O<sub>5.5</sub>S<sub>2</sub>Cd: C 44.82, H 3.16, N 12.54, S 9.57; found: C 44.86, H 2.94, N 12.45, S 9.45. Main infrared spectral data (KBr, cm<sup>-1</sup>): 3452 (s), 3409 (s), 3361 (s), 3297 (s), 3054 (w), 3031 (w), 2921 (w), 2852 (w), 1670 (m), 1602 (s), 1560 (s), 1506 (m), 1444 (m), 1417 (s), 1371 (s), 1323 (m), 1245 (m), 1215 (m), 1143 (s), 1091 (m), 1064 (m), 1027 (s), 1012 (m), 823 (s), 775 (m), 702 (s), 665 (m), 617 (s), 584 (m), 505 (s). (IR spectrum is shown in Figure S2).

#### X-ray Crystallography

Single-crystal X-ray diffraction data of 1 and 2 were collected on a Rigaku XtaLAB Pro diffractometer with Cu-K $\alpha$  radiation ( $\lambda$  = 1.54178 Å) at 150 K. Crystallographic data reduction were performed using the program CrysAlisPro.72 The structures were solved with direct methods (SHELX),<sup>73</sup> and refined by fullmatrix least squares on F<sup>2</sup> using OLEX2,<sup>74</sup> which utilizes the SHELXL-2013 module.<sup>75</sup> The hydrogen atoms were placed geometrically. All non-hydrogen atoms were refined anisotropically. In 2, the guest DMF molecules and water molecules are too disordered to be modeled properly. So the diffuse electron densities resulting from these solvent molecules are removed by using the SQUEEZE routine of PLATON program to produce solvent-free diffraction intensities of 2.76 The guest molecules were quantified through the elemental analyses and thermogravimetric analyses. So the final molecular formulae for 1 and 2 were determined. The relevant crystallographic data are summarized in Table S1. Selected bond lengths and angles are summarized in Table S2. CCDC numbers of 1 and 2 are 1882223 and 1882224, respectively.

#### Catalytic Experiment

Before used as catalysts, 1 and 2 were activated by following procedure. 1 and 2 were soaked in methanol for 3 days and the used methanol was replaced 4 times every day. Then, the samples were collected and dried at 80 °C for 10 h under vacuum, obtaining activated samples **1a** and **2a**. The activated samples (1a and 2a) were employed to catalyze Knoevenagel condensation reactions with benzaldehyde derivatives and malononitrile. In typical procedure, benzaldedyde (1 mmol), malononitrile (2 mmol) and catalyst (1a or 2a) (0.02 mmol) were added into 10 mL round-bottomed flask and stirred at 60 °C under solvent-free condition. The process of reaction was monitored by thin layer chromatography (TLC). After the reaction finished completely, the yield of desired product was determined by <sup>1</sup>H NMR spectroscopy. The Knoevenagel reactions involving other benzaldehyde derivatives and malononitrile were also proceeded according to the aforementioned procedure.

#### Recyclable Experiment

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To evaluate the recycling ability catalysts, the recycling experiments of samples (**1a** and **2a**) as catalyst for the Knoevenagel condensation reaction were investigated. After the Knoevenagel condensation reaction finished, chloroform was charged into the reaction mixture and then the catalyst (**1a** or **2a**) was recollected by centrifugation. Subsequently, the recollected catalyst was washed by chloroform three times, dried under vacuum at 80 °C for 10 h, and then reused for the next round catalytic experiment. The yield of desired product was determined by <sup>1</sup>H NMR spectroscopy so as to evaluate the performance of the recycled catalyst.

#### **Results and discussion**

#### Synthetic Conditions

Synthetic conditions of **1** and **2** were investigated systematically. The results indicate that temperature, solvent, and the ratio of mixed ligands, all have important influences on the target product. Firstly, the temperature plays a crucial role. At 100 °C, 1 and 2 have been obtained with good quality. However, no obvious crystals have been gained whether at lower temperature or at higher temperature. Secondly, the solvent also affects the quality and the yield of the crystals. In the mixture solvent DMF/H<sub>2</sub>O (2 mL / 0.5 mL), 1 and 2 have been obtained with good quality and high yield. However, in the mixture solvent DMF/ethanol (2 mL / 0.5 mL), the purity and yields of target products are very poor; even no target products have been obtained in pure DMF, ethanol, H<sub>2</sub>O, respectively. Last but not least, the ratio of mixture ligands also plays an important role. When the molar ratio of ligand 2-NH<sub>2</sub>-H<sub>2</sub>BDC to ligand Py<sub>2</sub>TTz is in the range of 1.5–1.9, the purity and yields of target products are very good. Above 1.9 or below 1.5, the purity and yields of target products will all be reduced. Therefore, the optimum synthetic conditions of 1 and 2 is, the molar ratio of ligand 2-NH<sub>2</sub>-H<sub>2</sub>BDC to ligand Py<sub>2</sub>TTz in the range of 1.5-1.9, mixture solvents DMF/H<sub>2</sub>O (2 mL / 0.5 mL), at 100 °C for 48 h.

#### **Structure Description**

The single-crystal X-ray diffraction analyses illustrate that 1 and 2 are isostructural, which possess similar nodes and connection modes. However, they crystallize in the different crystal systems and space groups, which illustrates that the final structures of MOFs can be influenced by the nature of metal ions. In view of their structural similarities, only the crystal structure of  ${\bf 1}$  is described in detail for the sake of simplicity. The single-crystal data reveal that 1 is a 3D bipillared-layer framework composed of the binuclear Zn(II) nodes, 2-NH<sub>2</sub>- $BDC^{2-}$  ligands and  $Py_2TTz$  coligands. It crystallizes in the orthorhombic crystal system with Pccn space group, and the asymmetric unit consists of one Zn(II) ion, one 2-NH<sub>2</sub>-BDC<sup>2-</sup> ligand, one Py<sub>2</sub>TTz ligand, and two halves of free DMF molecules. The Zn(II) center is coordinated by four oxygen atoms from three 2-NH<sub>2</sub>-BDC<sup>2-</sup> ligands and two nitrogen atoms from two Py<sub>2</sub>TTz ligands to form a distorted octahedron geometry  $(ZnO_4N_2)$  (Figure 1a). The Zn–O bond lengths are in the range of 2.0003(14) Å – 2.3179(16) Å and the Zn–N bond lengths are in

the range of 2.1512(17) Å – 2.1893(18) Å. The  $O_{\nabla}Zn_{\Delta}Q_{\alpha}$  angles are in the range of 59.46(6)° - 151.72(6)°, the N-26-0Tangles are in the range of 87.88(6)° - 92.37(6)°, and the N-Zn-N angle is 179.70(7)° (Table S2). The deprotonated 2-NH<sub>2</sub>-BDC<sup>2-</sup> acts as  $\mu_3$ -bridging ligand, in which the two carboxylate groups adopt two different coordination modes: one adopting  $\mu_2$ - $\eta^1$ : $\eta^1$ bismonodentate bridging mode while the other one adopting  $\mu_1\text{-}\eta^1\text{:}\eta^1\text{-}$ bidentate chelating mode. The two crystallographically equivalent Zn(II) ions are bridged by two carboxylate groups to form a binuclear secondary building unit (SBU)  $Zn_2(\mu$ -OCO)<sub>2</sub>, which is further connected by 2-NH<sub>2</sub>-BDC<sup>2-</sup> ligands along the ac plane to provide a 2D sheet of {Zn<sub>2</sub>(2-NH<sub>2</sub>- $BDC)_2_n$  (Figure 1b). Further, the adjacent 2D sheets are pillared by Py<sub>2</sub>TTz ligands to construct a 3D bipillared-layer framework (Figure 1c). Because of large voids, the two single 3D networks are further intertangled each other to yield a 2-fold interpenetrated networks. However, it still exhibits significant channels along a or c axis (Figure 1d-e). There are two types of channels: pore A decorated with the pendant -NH<sub>2</sub> groups and pore B with no  $-NH_2$  groups along c axis (Figure 1e). All the channels are decorated by thiazole nitrogen atoms along a or c axis (Figure 1d-e). Additionally, these channels are occupied by



**Figure 1.** (a) Coordination environment of Zn(II) in 1; hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry codes: #1 1 - *x*, - *y*, 1 - *z*; #2 1 - *x*, 1 - *y*, 1 - *z*; #3 0.5 - *x*, *y*, 0.5 + *z*; #4 0.5 + *x*, - *y*, 0.5 - *z*; #5 *x*, - 1 + *y*, *z*. Two  $-NH_2$  groups in 2- $NH_2$ - $BDC^{2-}$  is due to its positional disorder. (b) 2D sheet of the { $Zn_2(2-NH_2-BDC)_2$ }. (c) 3D bipillared-layer framework of **1**. (d) View of 2-fold interpenetrated 3D framework of **1** along *a* axis; blue represent  $-NH_2$  group. (e) View of 2-fold interpenetrated 3D framework of **1** along *c* axis; blue represent  $-NH_2$  group.

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the guest molecules DMF, which can be confirmed by the elemental analyses as well as the TG analyses. The calculated solvent-accessible volume by PLATON program is approximately 25.2% after removal of guest DMF molecules.

Similarly, **2** is also a 3D bipillared-layer framework structure. However, it crystallizes in the monoclinic crystal system with  $P2_1/n$  space group. The coordination environment of Cd(II), 2D sheet of the {Cd<sub>2</sub>(2-NH<sub>2</sub>-BDC)<sub>2</sub>}, 3D bipillared-layer framework, and 2-fold interpenetrated 3D framework are shown in Figure 2a-e. The Cd-O bond lengths are in the range of 2.242(2) Å -2.409(2) Å and the Cd-N bond lengths are in the range of 2.321(3) Å – 2.340(3) Å. The O–Cd–O angles are in the range of 54.93(8)° - 149.18(8)°, the N-Cd-O angles are in the range of 84.31(9)° - 100.73(10)°, and the N-Cd-N angle is 170.09(11)° (Table S2). The channels of 2 are also occupied by guest DMF molecules and water molecules. Its void volume is approximately 28.2% of the total crystal volume after removing the guest molecules by PLATON calculations. All the channels are decorated by thiazole nitrogen atoms along a or c axis,

Figure 2. (a) Coordination environment of Cd(II) in 2; hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry codes: #1. 2 - x, 1 - y, 2 - z; #2. 1/2 + x, 3/2 *y*, - 1/2 + *z*; #3. 1 + *x*, + *y*, 1 + *z*; #4. 3/2 - *x*, - 1/2 + *y*, 5/2 - *z*; #5. 1 - x, 1 - y, 1 - z. Two  $-NH_2$  groups in 2- $NH_2$ -BDC<sup>2-</sup> is due to its positional disorder. (b) 2D sheet of the  $\{Cd_2(2-NH_2-BDC)_2\}_n$ . (c) 3D bipillared-layer framework of 2. (d) View of 2-fold interpenetrated 3D framework of 2 along a axis; blue represent amino group. (e) View of 2-fold interpenetrated 3D framework of **2** along *b* axis; blue represent amino group.

whereas only the channels are decorated with pendante-NH2 DOI: 10.1039/C9DT00391F groups along *b* axis (Figure 2d–e).

Interestingly, the pendant -NH<sub>2</sub> groups are distributed in all the channels in **2** along *b* axis, whereas the pendant  $-NH_2$ groups are only distributed in the half of the channels in 1 along c axis. Additionally, from construction perspective, the major difference of the two MOFs is the 2D sheet, in which the interior angles of the rhombus-shaped grids are 83.542(0)° in 1 and 68.402(0)° in 2, respectively (Figure S3). Meanwhile, the bond lengths of Zn–O and Zn–N in 1 are shorter than the bond lengths of Cd–O and Cd–N in 2 whereas the N–Zn–N bond angle is bigger than the N-Cd-N bond angle (Table S2). This might be the reason why they crystallize in the different crystal systems with different space groups.

#### **Determination of Guest Molecules**

On the basis of the crystal data, the molecular formulae of 1 and 2 are preliminarily defined as {[M(Py<sub>2</sub>TTz)(2-NH<sub>2</sub>-BDC)]·guest}<sub>n</sub> (M = Zn for 1, Cd for 2), which are electrically neutral. Furthermore, the occupancies of two DMF molecules in 1 should be 0.5 by elemental analyses and thermogravimetric analyses, accordingly its exact molecular formula can be defined as {[Zn(Py<sub>2</sub>TTz)(2-NH<sub>2</sub>-BDC)]·(DMF)}<sub>n</sub>. However, the solvent molecules in 2 are too disordered to be modeled properly, its exact molecular formula need be further determined by elemental analyses and thermogravimetric analyses. Comparing the found value of elemental analyses for 2 with the calculated value of elemental analyses for its primary framework, the found values of N, H element are higher than their calculated values, which imply the guest molecules including DMF molecules and H<sub>2</sub>O molecules (2 was synthesized in the mixed solvent DMF and H<sub>2</sub>O). Therefore, the molecular formula of 2 can be further modified as {[Cd(Py2TTz)(2-NH2-BDC)] $\cdot x$ (DMF) $\cdot y$ (H<sub>2</sub>O)}<sub>n</sub>. According to the found values of C, H element for 2, x and y are calculated to be 1 and 0.5, respectively. Accordingly, the molecular formula of 2 can be defined as  $\{[Cd(Py_2TTz)(2-NH_2-BDC)]\cdot(DMF)\cdot 0.5(H_2O)\}_n$ . The formulae of the two compounds agree well with their elemental analyses and thermogravimetric analyses, which indicate that the formulae for 1 and 2 are accurate.

#### **Powder X-ray Diffraction**

The purities of the synthesized bulk samples (1 and 2) were confirmed by PXRD experiment. As shown in Figures S4 and S5, experimental patterns of the two as-synthesized samples agree well with the simulated patterns from their single crystal data, which indicate that the synthesized bulk samples (1 and 2) are pure phase. Furthermore, stabilities of 1 and 2 were investigated in common solvents such as DMF, methanol, acetone, chloroform, and water. As shown in Figures S4 and S5, PXRD patterns of 1 and 2 soaked in common solvents for 48 h are consistent with their origins, which indicate that 1 and 2 are stable in common solvents. PXRD patterns of the activated samples 1a and 2a were also measured, which agree well with the experimental patterns of two as-synthesized samples, indicating that the frameworks of 1 and 2 still remain constant



after removal of guest DMF molecules and water molecules (Figures S4 and S5).

#### Thermogravimetric Analyses

To evaluate their thermal stabilities, thermogravimetric analyses of 1 and 2 were examined. As shown in Figure S6 and S7, two compounds have high thermal stabilities. MOF 1 undergoes a gradual weight loss of 11.72% until 343 °C due to the loss of DMF molecules in the crystal lattice (calculated value is 11.90%), and then shows a steep mass loss assigned to the decomposition of the framework. MOF 2 experiences a weight loss of 13.58% before 324 °C, which can be attributed to the liberation of the water and DMF molecules in the pores of the framework (calculated value is 13.37%). Then the framework starts to collapse at 350 °C. The thermogravimetric analyses of 1a and 2a were also examined. As shown in Figure S6 and S7, the frameworks of 1a and 2a have no obvious weight loss before 335 °C and 337 °C respectively, which indicate that the frameworks of 1a and 2a still remain even if the gust molecules are removed.

#### **Gas Adsorption**

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The structural rigidity and the big channels motivated us to investigate the gas adsorptive performances of the two MOFs. Before measurement, they were activated by methanol exchanging 3 days and then degasing at 100 °C for 12 h to remove the guest molecules. As shown in Figure S8, the two MOFs have almost no uptake for N<sub>2</sub> at 77 K. In consideration of the thiazole nitrogen and pendant -NH<sub>2</sub> group functionalized pores in both MOFs, we investigated their adsorption performances for CO<sub>2</sub>. As shown in Figure 3, MOF 2 show type I adsorption curves for CO<sub>2</sub> at 195 K and 273 K with maximum uptakes of 50 cm<sup>3</sup>/g and 35 cm<sup>3</sup>/g, which corresponds to approximately 9.8 wt % (1.5 molecules/formula) and 6.9 wt % (1 molecules/formula), respectively. Obviously, 2 can selectively adsorb  $CO_2$  from  $CO_2/N_2$  mixture (Figure 3b), which is a prerequisite for a CO<sub>2</sub> capture material.<sup>77,78</sup> The enthalpy of adsorption for CO<sub>2</sub> was obtained to be 19.7 kJ/mol by the Clausius-Clapeyron equation from the adsorption isotherm at 195 K and 273 K (Figure S9). This value is higher than the enthalpy of liquefaction of CO<sub>2</sub> (17 kJ/mol), indicating that the thiazole nitrogen atom and pendant -NH2 group provide a considerable improvement CO<sub>2</sub> adsorption, which is



Figure 3. (a)  $CO_2$  adsorption isotherms at 195 K for 2. (b)  $CO_2$  adsorption isotherms at 273 K and N<sub>2</sub> adsorption isotherms at 77 K for 2. Filled and open symbols represent adsorption and desorption, respectively.

#### **Catalytic Experiment**

The structural rigidities, big channels, decorated -NH<sub>2</sub> groups, and high thermal stabilities in both MOFs offered a platform to accomplish base-catalyzed reaction. Consequently, 1 and 2 were used as heterogeneous catalysts to catalyze Knoevenagel condensation reactions between benzaldehyde derivatives and malononitrile. Before used as catalysts, 1 and 2 were activated by exchange and removal of the guest molecules in the channels. The activated samples (1a and 2a) were employed in the typical procedure: benzaldehyde derivatives (1 mmol), malononitrile (2 mmol) and catalyst (1a or 2a) (0.02 mmol) were charged into 10 mL round-bottomed flask and stirred at 60 °C under solventfree condition. The reaction progress was monitored by thin layer chromatography (TLC). The conversion rate of reaction was determined directly by <sup>1</sup>H NMR spectroscopy. Taking benzaldehyde for example, the relationship between the conversion rate and the reaction time was examined. As shown in Figure S11, the reaction conversion rate gradually increases along with prolonged reaction time and the reaction is finished completely in 6 h, indicating that 1a and 2a can be used as effective catalysts for Knoevenagel condensation reaction between benzaldehyde and malononitrile. So the reaction time was fixed at 6 h when other benzaldehyde derivatives were used in Knoevenagel reaction.

To investigate the substituent effect, several different substituted benzaldehyde derivatives were employed in the aforementioned reaction. As shown in Table 1, the nature of the substituent on the benzene ring has a significant influence on Knoevenagel condensation reaction. The electron-withdrawing group (-NO<sub>2</sub>, -CN, -Br) is beneficial to improve the yield of reaction (Yield more than 99%, Entries 4-7), whereas the electron-donating group (-CH<sub>3</sub>, -OCH<sub>3</sub>) is detrimental to the conversion rate of reaction and the electron-donating ability is inversely proportional to the yield of reaction (Yield less than 90% for -CH<sub>3</sub> and 70% for -OCH<sub>3</sub>, Entries 2 and 3). Moreover, the position of the substituent on the benzene ring has also obvious impact on Knoevenagel condensation reaction. Benzaldehyde with electron-withdrawing group (-NO<sub>2</sub>, -CN, -Br) in ortho- or para-position shows an obviously higher yield (Entries 4-7) while benzaldehyde with electron-donating group (-CH<sub>3</sub>, -OCH<sub>3</sub>) in para-position reveals a relatively lower yield (Entries 2 and 3). Meanwhile, the substituent situated at ortho-position or paraposition of the aldehyde group has more serious influence than that at meta-position. Compared with para-position, -OCH<sub>3</sub> in meta-position of the aldehyde group is beneficial for the reaction (Entry 3 and 8). The reason should be that -OCH<sub>3</sub> in meta-position of the benzene ring behaves electronwithdrawing property to the whole benzaldehyde system, consequently causing that aldehyde group in meta-position shows higher reactivity. In addition, the amount of the

substituent on the benzene has also some effect on Knoevenagel condensation reaction. The more benzaldehyde contains the electron-donating group, the lower the yield of reaction is (Entries 9 and 10).

Table 1. Knoevenagel condensation reactions of	the	different
benzaldehyde derivatives catalyzed by <b>1a</b> and <b>2a</b> .		

R -CHO +  CN -CHO +  CN -CHO +  CN -CN -CN -CN -CN -CN -CN -CN -CN -CN				
Entry	Substrate	<b>1a</b> , Yield (%)	<b>2a</b> , Yield (%)	
1	СНО	99.9	99.8	
2	н <sub>3</sub> с-Сно	89	86	
3	н₃со-Сно	70	71	
4	O <sub>2</sub> N-CHO	99.7	99.9	
5	NCСНО	99.8	99.8	
6	Br—CHO	99.8	99.9	
7	СНО	99.8	99.9	
8	н <sub>з</sub> со сно	96	97	
9	H <sub>3</sub> CO-СНО	65	65	
10	H <sub>3</sub> C —СНО H <sub>3</sub> C	72	68	

To further validate the role of 2-NH<sub>2</sub>-BDC<sup>2-</sup> unit and Py<sub>2</sub>TTz unit in MOFs for catalytic experiment, the control experiments were performed with free ligand  $2-NH_2-H_2BDC$  or  $Py_2TTz$  as catalysts (Table S3). There is no product to be detected without any catalyst. With 2-NH<sub>2</sub>-H<sub>2</sub>BDC as catalyst, the conversion rate is negligible (around 1%). With  $Py_2TTz$  as catalyst, the conversion rate is relatively higher (72%), which might benefit from its partially homogeneous catalysis. With 2-NH<sub>2</sub>-H<sub>2</sub>BDC and Py<sub>2</sub>TTz as catalyst simultaneously, the conversion rate is lower than that with  $Py_2TTz$  solely, which is caused by the acidity of 2-NH<sub>2</sub>-H<sub>2</sub>BDC weakening the basicity of nitric heterocyclic moiety. Additionally, to verify the catalytic active site in Py2TTz whether lying in pyridine unit or thiazolo[5,4d]thiazole unit, the control experiment was performed with 2,5-Diphenylthiazolo[5,4-*d*]thiazole (Ph<sub>2</sub>TTz) (without pyridine unit) as catalyst (Entry 5 in Table S3). With Ph<sub>2</sub>TTz as catalyst, the conversion rate is 48%, which is lower than that with Py2TTz, indicating that both pyridine unit and thiazolo[5,4-d]thiazole unit have some catalytic active in Py<sub>2</sub>TTz. Comparing with high catalytic activities of 1a and 2a, we speculate that catalytic effect is not from the single ligand or the sum of ligands but from the synergistic effect of active  $-NH_2$  groups and this constrained in the specific structures of MOP 12 and 2a,  $-NH_2$  and this cole nitrogen can take effect synergistically and maximize their catalytic activities.

Finally, to validate the recycling and stabilities of 1a and 2a, their recyclable experiments were examined for five times (Table S4). The catalyst can be easily isolated by centrifugation and be reused in the next round catalytic experiment. The reaction conversion rate is not obviously reduced after five round catalytic experiments. Meanwhile, PXRD, IR as well as SEM were applied to characterize the catalyst before and after five round catalytic experiments. As shown in Figure S12, IR spectra of 1a and 2a are nearly unchanged before and after the catalytic reaction, indicating their good thermal and chemical stabilities. As shown in Figure S13, PXRD patterns of 1a and 2a agree well before and after the catalytic reaction, indicating that their frameworks remain unchanged. As shown in Figure S14, the morphologies of 1a and 2a remain unchanged before and after the catalytic reaction. Therefore, 1a and 2a are stable and recyclable heterogeneous catalysts for Knoevenagel condensation reaction. To the best of our knowledge, only a few MOFs have been reported as efficient catalysts for Knoevenagel condensation reaction under solvent-free condition up to now.<sup>80-82</sup>

### Conclusions

In conclusion, two amino functionalized Zn/Cd-MOFs have been successfully designed and synthesized by assembling the linkers Py<sub>2</sub>TTz and 2-NH<sub>2</sub>-H<sub>2</sub>BDC with the binuclear metal nodes. The two MOFs possess similar 2-fold interpenetrated 3D bipillaredlayer framework structures. Moreover, the numerous thiazole nitrogen atoms and pendant -NH<sub>2</sub> groups are present in the channels, coupled with the good chemical and high thermal stability, endow the two MOFs good performances for gas adsorption and catalyzing Knoevenagel condensation reaction. The gas adsorption data show that MOF 2 have a moderate CO<sub>2</sub> uptake and good CO<sub>2</sub>/N<sub>2</sub> selectivity with potential for practical separation of  $CO_2$  from  $CO_2/N_2$  mixture. Meanwhile, PXRD, IR as well as SEM of the catalyst before and after the catalytic reaction demonstrate that the two MOFs can efficiently catalyze Knoevenagel condensation reaction as stable recyclable heterogeneous catalyst under solvent-free condition. To design and synthesize the multifunctional MOFs with more superior performance, their specific active sites, intrinsic structure-active relationships, and plausible catalytic mechanism are underway.

## **Conflicts of interest**

There are no conflicts to declare.

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# **Table of Content**



Two amino functionalized Zn/Cd-MOFs can be employed to adsorb  $CO_2$  selectively and to catalyze Knoevenagel reaction under solvent-free condition.