# Dalton Transactions

An international journal of inorganic chemistry

### Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Zhang, D. Meng, F. Ge, J. Huang, M. Meng, L. Wang, Y. Xu, X. Liu, H. Yan, Z. Lu, H. Zheng and W. Huang, *Dalton Trans.*, 2020, DOI: 10.1039/C9DT04068D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/dalton

View Article Online

View Journal

#### ARTICLE

# Tetrazole-based porous metal-organic frameworks for selective CO<sub>2</sub> adsorption and isomerization studies

Rui Zhang,<sup>a</sup> De-Xian Meng,<sup>a</sup> Fa-Yuan Ge,<sup>b</sup> Jv-Hua Huang,<sup>a</sup> Li-Fei Wang,<sup>a</sup> Yong-Kai Xv,<sup>a</sup> Xing-Gui Liu,<sup>a</sup> Mei-Mei Meng,<sup>a</sup> Hong Yan,<sup>c</sup> Zhen-Zhong Lu,<sup>\*a</sup> He-Gen Zheng,<sup>\*b</sup> Wei Huang<sup>\*a,d</sup>

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx.

**Abstract:** Tetrazole-based molecules are of numerous bridging coordination modes affording great synthetic possibilities for the preparation of porous metal-tetrazolate architectures for many applications, such as carbon captures. We reported here three tetrazole-based MOFs: **1**,  $\{[Cu_{12}(ttz)_{8/3}Cl_5(H_2O)_{16}]^{11+}\cdot11Cl^{-}\}_n$  (H<sub>3</sub>ttz =  $N^2, N^4, N^6$ -tris(4-(1*H*-tetrazol-5-yl)phenyl)-1,3,5triazine-2,4,6-triamine), contains highly positively charged Cu<sub>12</sub> clusters and largest mesopores (32 Å) in the reported MOFs based on tri-topic tetrazole ligand. **2** and **3** are two MOF isomers built by Cu<sup>II</sup> and 2-(1H-tetrazol-5-yl)pyrimidine. **3** contains nonporous layers, while **2** contains 1D channel and showed high selectivity for adsorbing CO<sub>2</sub>, which should be attributed to the high density of free nucleophilic tetrazole N atoms on the pore surfaces. We found that the isomerization between **2** and **3** was caused by the diverse coordination mode of tetrazole-based ligand and can be controlled in the synthesis processes.

#### Introduction

Published on 14 January 2020. Downloaded by University of Connecticut on 1/14/2020 4:52:36 AM

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are a new class of porous solids consisting of metal-based nodes (single ions or clusters) bridged by organic linking groups have attracted much recent attention.<sup>1,2</sup> One of the most attractive aspects of MOFs is their porous structure showing high surface area, diverse pore size, shape and functionality, which provide MOFs excellent prospects in many applications, such as carbon capture, molecular separation and heterogeneous catalysis.<sup>3,4</sup> As for building porous MOFs for carbon dioxide capture, the choice of ligand that can form strong metal-ligand bonds to sustain porous structures and provide binding sites for interacting with gaseous CO<sub>2</sub> selectively is a key point.<sup>5,6</sup>

Nitrogen-containing heterocyclic groups-based molecules are good choices, the nucleophilic nitrogen is able to form stable metal–N bond to construct porous MOFs and also able to interact with  $CO_2$  strongly.<sup>7</sup> For example, imidazole- or pyrazole-based ligands formed many zeolitic imidazolate frameworks

<sup>b.</sup> State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China. E-mail: zhenghg@nju.edu.cn and MOFs showing stable open structures and excellent carbon capture properties.<sup>8,9</sup>

Tetrazoles are aromatic five-membered heterocycles containing four nitrogen atoms, which exhibit more bridging coordination possibilities, such as deprotonated tetrazole group can bridge two, three and up to four metal ions.<sup>10,11</sup> These numerous bridging coordination modes afford great synthetic possibilities for the design and preparation of porous metal-tetrazolate architectures, while tetrazole-based molecules are less studied although some very successful works have proven powerfulness of them in building porous MOFs for carbon capture and other applications.<sup>12,13</sup> We report herein the design and synthesis of three MOFs built by tetrazole-based ligands including MOF containing 3D mesopore and MOF containing 1D micro-channel for selective adsorption of CO<sub>2</sub>. And the effects of the coordination diversity of tetrazole-based ligands on the structure and the formation of MOF isomers are discussed.

#### Experimental

#### Materials and methods

All reagents were used as received from commercial suppliers without further purification. 2-(1H-tetrazol-5-yl)pyrimidine was synthesized following reported procedures.<sup>14</sup> Analyses for C, H and N were carried out on a CE-440 elemental analyzer (EAI Company). Powder X-ray diffraction data (PXRD) were collected over the 2 $\theta$  range 4-50° on a Bruker Advance D8 diffractometer using Cu-K $\alpha_1$  radiation ( $\lambda$  = 1.54056 Å, 40 kV/40mA). CO<sub>2</sub> and N<sub>2</sub> sorption isotherms were recorded on an ASAP-2020 system under ultrahigh vacuum. The CO<sub>2</sub> and N<sub>2</sub> gases used were of ultrapure research grade (99.99%).

<sup>&</sup>lt;sup>a</sup> Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211800, China. E-mail: iamzzlu@njtech.edu.cn, iamwhuang@nwpu.edu.cn

<sup>&</sup>lt;sup>c.</sup> 23rd Middle School of Daqing city, No. 385 Jingsan street, Sartu District, 163000, Daqing city, China

<sup>&</sup>lt;sup>d</sup> Institute of Flexible Electronics (IFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, China

Electronic Supplementary Information (ESI) available: Experimental details for ligand synthesis, X-ray crystallographic files, further descriptions of the structures. CCDC 1956834-1956836. See DOI: 10.1039/x0xx00000x

#### Journal Name

#### ARTICLE

Published on 14 January 2020. Downloaded by University of Connecticut on 1/14/2020 4:52:36 AM

## Synthesis of ligand $N^2$ , $N^4$ , $N^6$ -tris(4-(1*H*-tetrazol-5-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (H<sub>3</sub>*ttz*):

Synthesis of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzonitrile: cyanuric chloride (1.84 g) and 4aminobenzonitrile (3.89 g) were added to 75 mL glacial acetic acid. The reaction mixture was stirred at reflux for 24 hours, white solid was formed and collected by vacuum filtration, washed with 300 mL hot water and vacuum dried (3.16g, yield: 74%) and used for next step without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  10.01 (s, br, 3H), 7.73 (d, *J*=7.58 Hz, 6H), 7.43(d, *J*=7.58 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  163.1, 141.6, 133.3, 117.6, 116.4, 103.5. MS: 429.33.

4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))-tribenzonitrile (1.43 g), NaN<sub>3</sub> (1.95 g), NH<sub>4</sub>Cl (1.0 g) and LiCl (0.4 g) were added to 40 mL anhydrous DMF, the reaction mixture was stirred at 130°C for 24 hours. After removing DMF by rotary evaporation, the solid obtained was added into 20 mL sodium hydroxide aqueous solution (2M) and stirred for 30 minutes, white gel-like precipitation was formed by adjusting pH to 4 with hydrochloric acid (2M), which were collected by vacuum filtration, washed with water and ethanol and vacuum dried. H<sub>3</sub>*ttz* was obtained as white solid (0.57 g, yield: 31%). <sup>1</sup>H NMR (CDCl3):  $\delta$  9.72 (s, br, 3H), 9.32 (m, 6H), 8.65 (m, 6H), 8.61 (s, br, 3H). <sup>13</sup>C NMR (CDCl3):  $\delta$  159.3, 155.1, 140.9, 127.8, 120.6, 119.9.

#### Synthesis of single crystals of 1, ${[Cu_{12}(ttz)_{8/3}Cl_5(H_2O)_{16}]^{11+1}11Cl^-}_n$

A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.096 g), H<sub>3</sub>ttz (0.056 g), DMF (10.0 mL), acetonitrile (0.5 mL) and hydrochloric acid (0.1 mL, 1.0 M) was transferred into a 23 mL Teflon lined autoclave and sealed. Reaction took place at 90°C for 3 days, and dark green octahedron-shaped crystals were formed (yield: ~80% based on ligand). The crystals of **1** was preserved in acetone, which cracked into small pieces and became amorphous when put in air for several minutes.

#### Synthesis of single crystals of 2, Cu<sub>3</sub>(pmtz)<sub>6</sub>·DMF

A mixture of  $Cu(NO_3)_2$ ' $3H_2O$  (0.241 g), *pmtz* (0.075 g), DMF (5.0 mL) and nitric acid (0.1 mL, 1.0 M) was transferred into a 23 mL Teflon lined autoclave and sealed. Reaction took place at 50°C for 1 day, and afforded dark green prism-shaped crystals, which were collected by filtration, washed with fresh DMF and then acetone (yield: 90% based on ligand). Elemental analysis (%) for **2**,  $C_{33}H_{25}Cu_3N_{38}O$ : Calcd: C, 34.16; H, 2.17; N, 45.87. Found: C, 34.02; H, 2.15; N, 45.76.

#### Synthesis of single crystals of 3, Cu(pmtz)<sub>2</sub>

A mixture of  $CuSO_4$ ·5H<sub>2</sub>O (0.250 g), *pmtz* (0.075 g) and DMF (5.0 mL) was transferred into a 23 mL Teflon lined autoclave and sealed. Reaction took place at 50°C for 1 day, and afforded dark green prism-shaped crystals, which were collected by filtration, washed with fresh DMF and then acetone (yield: 70% based on ligand). Elemental analysis (%) for **3**, C<sub>10</sub>H<sub>6</sub>CuN<sub>12</sub>: Calcd: C, 33.57; H, 1.69; N, 46.98. Found: C, 33.49; H, 1.62; N, 46.59.

#### **Results and discussion**



Figure 1. (a) Side view and (b) Top view of the Cu<sub>12</sub> cluster in **1** (Cu, light blue; C, black; H, grey; N, dark blue; O, red; Cl, green, water molecules are omitted for clarity in (b)).

**1**, {[Cu<sub>12</sub>(*ttz*)<sub>8/3</sub>Cl<sub>5</sub>(H<sub>2</sub>O)<sub>16</sub>]<sup>11+·</sup>11Cl<sup>-</sup>}<sub>n</sub>, crystalizes in cubic space group Fm-3c, and contains a [Cu<sub>12</sub>(tetrazole)<sub>8</sub>Cl<sub>5</sub>(H<sub>2</sub>O)<sub>16</sub>]<sup>11+</sup> cluster including twelve Cu<sup>II</sup> atoms, eight tetrazole groups, five chloride anions and sixteen coordinated water molecules (Figure 1a). Four Cu<sup>II</sup> atoms in the center of the Cu<sub>12</sub> clusters (Cu1, Figure 1b) are bridged by eight tetrazole groups through N atoms at 2, 3-positions, eight Cull atoms on the periphery of the Cu<sub>12</sub> clusters (Cu2, Figure 1b) are bridged by the eight tetrazole groups through N atoms at 1, 4-positions. The Cl<sup>-</sup> atom in the center of the cluster connects four 'central' Cu1 atoms in a  $\mu_4$  mode, and the rest four Cl<sup>-</sup> atoms bridge the 'periphery' Cu2 atoms in a  $\mu_2$  mode. Cu1 is in an octahedral coordination environment defined by two Cl<sup>-</sup> in the axial direction and four tetrazole N atoms in the equatorial plane (Cu1-Cl1 = 2.546(2), Cu1–Cl2 = 2.477(2), Cu1–N = 2.060(1) Å). Cu2 is five-coordinated by two tetrazole N atoms, one Cl<sup>-</sup> and two water molecules. The Cu2-Cl2 bond distance (2.592(2) Å) is comparable to those of



Figure 2. (a) 3D framework in 1 (Cu<sup>II</sup> shown as blue polyhedrons). (b) The topology of 'the' of 1 (Cu<sub>12</sub> cluster and *ttz* ligand are shown as 8- and 3-connected red balls). (c) Octahedral cage formed by six Cu<sub>12</sub> clusters and eight *ttz* ligands (the Cl<sup>-</sup> counter-anions are shown as green balls). (d) Truncated cube-shaped cage with square-shaped windows formed by packing of octahedrons.

#### Journal Name

Cu1–Cl1, while Cu2–N (2.230(2) and 2.264(2) Å) are much longer than Cu1–N.

The Cu<sub>12</sub> clusters are linked by *ttz* ligands into a highly porous 3D framework (Figure 2a). The overall topology of the framework is '**the**' following the classification from *RCSR* (reticular chemistry structure resource)<sup>15</sup> with Cu<sub>12</sub> cluster and *ttz* ligand acting as 8- and 3-connector, respectively (Figure 2b). The topology of '**the**' are often observed in MOFs based on tritopic carboxylate ligands<sup>16</sup> and much less observed in tetrazole-based MOFs.<sup>17</sup>

It is interesting to notice that six  $Cu_{12}$  clusters are linked by eight *ttz* ligands into an octahedral cage (Figure 2c), the innerspace of one cage is as large as 2727 Å<sup>3</sup> calculated by *PLATON*.<sup>18</sup> The charge of one  $Cu_{12}$  cluster is +11, so the overall 3D framework is highly positively charged and a large number of counterions are needed. There are 33 uncoordinated Clobserved in one octahedral cage (Figure 2c, the shortest Cl<sup>-...</sup>Cl<sup>-</sup> separation is 3.92 Å), which are exactly adequate to maintain the charge balance of the framework. Besides Cl<sup>-</sup> counterion, 30 acetonitrile molecules were also observed in one octahedral cage.

As shown in Figure 2d, truncated cube-shaped cage with square-shaped windows is formed by the packing of octahedrons, the separation between octahedrons is as large as 32 Å and the square-shaped windows is  $13.6 \times 13.6$  Å taking *van der waals* radii into consideration (Figure S1). Therefore, 3D interconnected mesopores are formed, which corresponds to 70 % of the total crystal volume (the inner space of the octahedral cages was uncounted). The pore size of **1** is the largest in the reported MOFs based on tri-topic tetrazole ligand.<sup>17</sup> We expected that the large Cu<sub>12</sub> cluster would afford



Figure 3. (a) Coordination environment of Cu<sup>II</sup> in **2**. (b) 2D layer of Cu<sub>3</sub>(*pmtz*)<sub>3</sub> triangles, Cu<sub>6</sub>(*pmtz*)<sub>6</sub> hexagons and 1D channels. (c) The  $\pi$ ··· $\pi$  interactions between pyrimidine rings of adjacent layers (the pyrimidine and tetrazole groups of different layers are shown in different color). (d) A perspective view showing the positions of free tetrazole N atoms on the inner-pore surfaces. (C/H, grey; N, blue; O, red; Cu, purple)



Figure 4. (a) Coordination environment of Cu<sup>II</sup> in **3**. (b) 2D layer of distorted  $Cu_4(pmtz)_4$  tetragons in **3**.

high stability to the overall framework since more metal-ligand bonds are formed, which might combine metal clusters and ligands tighter. While powder X-ray diffraction (PXRD) result showed that the porous framework of **1** collapsed when solvent guests removed, which probably because the *ttz* ligand is not rigid enough to support such a highly porous and positively charged structure, similar cases were observed in other MOFs with large pores.<sup>19</sup>

**2**,  $Cu_3(pmtz)_6$ ·DMF, was obtained by solvothermal reaction of  $Cu(NO_3)_2$  with a much smaller tetrazole-based ligand 2-(1Htetrazol-5-yl)pyrimidine (*pmtz*). **2** crystalizes in space group *P*-1. The *pmtz* ligand is in a chelating and bridging mode (Figure 3a), and the Cu<sup>II</sup> atom is in an octahedral coordination environment defined by four chelating N atoms in the equatorial plane and two N atoms in the axial direction. Cu–N bonds in the equatorial plane (1.958 ~ 2.091 Å) are much shorter than those in the axial direction (2.394 ~ 2.422 Å) due to the Jahn-Teller effect.

2D layers containing  $Cu_3(pmtz)_3$  triangles and  $Cu_6(pmtz)_6$  hexagons are formed in **2** (Figure 3b). The  $Cu_6(pmtz)_6$  hexagon is large enough for incorporating a DMF molecule, while the  $Cu_3(pmtz)_3$  triangle is too small to incorporate any guests (Figure 3b, c). The 2D layers are packed parallelly forming a hexangular channel, all of the pyrimidine rings are involved in forming  $\pi \cdots \pi$  interactions between adjacent layers with c.g., pyrimidine ".c.g., pyrimidine distances of 3.809(2) and 3.839(2) Å (Figure 3c). Although the individual  $\pi \cdots \pi$  interaction is not strong as indicated by the relatively long c.g...c.g. separations, the synergy effect of many  $\pi \cdots \pi$  interactions between adjacent layers make the porous structure very stable as proved by PXRD and gas adsorption tests.

**3**,  $Cu(pmtz)_2$ , an isomer of **2**, crystalizes in space group  $P 2_1/c$ . It is interesting to notice that **3** also contains layers of  $Cu_4(pmtz)_4$  tetragons, while the tetragon is too distorted to incorporate any guest molecules (Figure 4). The coordination mode of *pmtz* ligand and the coordination environment of Cu<sup>II</sup> atom are both similar to those in **2** (Figure 4a), and the Cu–N bond distances in the equatorial plane (1.985 ~ 2.055(1) Å) are also comparable to those in **2**, while the Cu–N bond distances in axial direction (2.518 Å(1)) are much longer than those in **2**.

In order to study the isomerization between **2** and **3**, we summarized all the reported MOFs based on *pmtz* and transition metals (Table S3).<sup>20-24</sup>  $M(pmtz)_2$  (**M** = Zn<sup>II</sup>, Co<sup>II</sup>, Fe<sup>II</sup> or Ni<sup>II</sup>, we named them as **4R** hereafter, R is for reported) represent a serial of isostructural MOFs, in which the

Published on 14 January 2020. Downloaded by University of Connecticut on 1/14/2020 4:52:36 AM

**Manus** 

alton Iransactions Accepted

#### **Journal Name**

#### ARTICLE

coordination mode of *pmtz* ligands and coordination environment of metal centers are both quite similar to those in **2** and **3**. **4R** contains 2D layers of  $M_4(pmtz)_4$  tetragons, but the adjacent *pmtz* molecules in the tetragons are orthogonal to each other (Figure S4). The **M**–N bond lengths in the equatorial plane and axial direction are in a very narrow range (such as Zn– N bonds are in the range of 2.114 ~ 2.169 Å for  $Zn(pmtz)_2$ , Table S4), in a sharp contrast to the highly elongated octahedral coordination environment of Cu<sup>II</sup> in **2** or **3**.

From structure point of view, pmtz ligands in 2, 3, and 4R are all in the chelating and bridging coordination mode, the chelated metal atom (M<sub>c</sub>, Scheme 1) is in the same plane of pmtz molecule, but the bridged metal atom (M<sub>b</sub>, Scheme 1) can be in the plane or out of the plane of pmtz. In 4R, pmtz ligands are all in the in-plane mode, so that a 2D layer containing regular Cu<sub>4</sub>(pmtz)<sub>4</sub> tetragons is formed with pmtz molecules orthogonally arranged (Figure S5); In **3**, *pmtz* ligands are all in the out-of-plane mode leading to a layer containing highly distorted  $Cu_4(pmtz)_4$  tetragons; In **2**, there are 1/3 pmtz ligands in the in-plane and 2/3 pmtz ligands in the out-of-plane mode, which should account for the formation of a more complicated layer containing a combination of  $Cu_3(pmtz)_3$  and  $Cu_6(pmtz)_6$ grids. More importantly, the Cull showing highly distorted octahedral environment (elongated Cu-N bonds in the axial direction) meet the request of the out-of-plane coordination of pmtz in 2 and 3.

We found that the isomerization between **2** and **3** can be controlled in the synthesis processes, and phase-pure samples of both **2** and **3** can be obtained directly. A good majority of MOF isomers were obtained as a mixture of phases, and phasepure samples were obtained by further separations, such as separation based on density differences. Phase-pure samples of both **2** and **3** were obtained directly by using different Cu<sup>II</sup> salts as starting materials (see experiment section), and the phase purity were confirmed by PXRD results (Figure 5a).

The pore size of the 1D channels in **2** is 4.5 Å in diameter (taking *van der waals* radii into consideration), which is ideal for  $CO_2$  adsorption selectivity.<sup>25,26</sup> And there are full of free nucleophilic tetrazole nitrogen atoms on the inner-pore surfaces (Figure 3d), which might be strong binding sites for  $CO_2$ 



Scheme 1. (a) The in-plane and (b) out-of-plane mode of *pmtz* ligand ( $M_b$  and  $M_c$  denote bridged and chelated metal atoms by *pmtz* ligand, respectively).



molecules. So that **2** should be a very good candidate for carbon capture.

TG result of **2** showed a weight loss of 4 wt% below 80°C corresponding to the loss of weakly bonded solvent molecules, and a weight loss of 10 wt% starting at 200°C corresponding to the loss of adsorbed DMF guests, and a sharp weight loss of 62 wt% at 310°C should be ascribed to the loss of *pmtz* and collapse of the porous structure (Figure 5b).

As suggested by TG result, we 'activated' as-synthesized sample of 2 by removing the adsorbed solvents at 240°C under vacuum, and take the solvent-free sample for gas adsorption tests. The CO<sub>2</sub> uptake capacity are 18.3 and 12.9 cm<sup>3</sup>·g<sup>-1</sup> at 273 and 293K and 1.0 bar, in a sharp contrast to the uptake capacity for N<sub>2</sub>, which is 0.7 cm<sup>3·</sup>g<sup>-1</sup> at 273K and 1.0 bar (Figure 6a). The IAST selectivity for equal-molar mixture of CO<sub>2</sub> and N<sub>2</sub> is ~110 in favor of CO<sub>2</sub> at low pressure, and decreases to 80 as pressure increases (Figure 6b). The low-coverage isosteric heat of adsorption for CO<sub>2</sub> is 31 kJ<sup>-</sup>mol<sup>-1</sup>, which is comparable to that for the benchmark MOF HKUST-1 (29 kJ mol-1, and most MOFs show isosteric heat of adsorption for CO<sub>2</sub> below 29 kJ<sup>-mol<sup>-1</sup></sup>),<sup>27,28</sup> and lower than that for Mg<sub>2</sub>(dobdc) containing very high density of open metal sites (40 kJ·mol<sup>-1</sup>)<sup>26</sup> and those for alkanolamines functionalized MOFs (50~100 kJ·mol<sup>-1</sup>, but the mechanism of CO<sub>2</sub> adsorption in these MOFs fall into the chemisorptive



Figure 6. (a) Isotherms of  $CO_2$  and  $N_2$  for 2. (b)  $CO_2/N_2$  IAST selectivity for 2 (calculated for equimolar mixtures at 273 K and 0~1 bar), inset: variation of isosteric heat of adsorption for  $CO_2$ .

#### 4 | J. Name., 2012, 00, 1-3

This journal is © The Royal Society of Chemistry 20xx

Published on 14 January 2020. Downloaded by University of Connecticut on 1/14/2020 4:52:36 AM

#### Journal Name

regime and more energy is needed to release adsorbed  $CO_2$ ).<sup>29</sup> The magnitude of the isosteric heat of adsorption indicates the affinity of the pore surface toward  $CO_2$ , which in turn plays a crucial role in determining the adsorptive selectivity and the energy required to release the  $CO_2$  molecules during regeneration.<sup>30</sup> This high magnitude of isosteric heat of adsorption of  $CO_2$  in **2** is probably attributed to the high density of free nucleophilic tetrazole nitrogen atoms on the pore surfaces, which makes **2** interact with  $CO_2$  strongly.<sup>31</sup>

#### Conclusions

We have synthesized three tetrazole-based MOFs. 1 contains highly positively charged Cu12 clusters and the largest 3D mesopores (32 Å) in the reported MOFs based on tri-topic tetrazole ligand. 2 and 3 are a pair of isomers originated from the versatile coordination mode of a tetrazole-based ligand. We managed to control the isomerization between 2 and 3 and make phase-pure samples for both 2 and 3 directly. More interestingly, 2 represents the most porous MOFs based on pmtz ligand, and showed high selectivity for adsorbing CO<sub>2</sub> with low-coverage isosteric heat of adsorption up to 31 kJ<sup>-mol-1</sup>, which should be attributed to the very high density of free nucleophilic tetrazole nitrogen atoms on the pore surfaces. Further work on studying isomerization effect of MOFs and building stable porous frameworks with tetrazole or other nitrogen-containing heterocyclic groups-based molecules is ongoing.

#### **Conflicts of interest**

The authors declare no competing financial interests.

#### Acknowledgements

We thank China Postdoctoral Science Foundation (2018M640478), Nanjing Tech University, National Natural Science Foundation of China (No. 21771101), Fundamental Studies of Perovskite Solar Cells (2015CB932200) and Primary Research & Development Plan of Jiangsu Province (BE2016770) for funding.

#### Notes and references

- Recent reviews: M. Y. Masoomi, A. Morsali, A. Dhakshinamoorthy and H. Garcia, *Angew. Chem. Int. Ed.*, 2019, **58**, 2; G. Yilmaz, S. B. Peh, D. Zhao and G.-W. Ho, *Adv. Sci.*, 2019, **6**, 1901129; N. Hosono and S. Kitagawa, *Acc. Chem. Res.*, 2018, **51**, 2437.
- 2 J. A. Zárate, E. Sánchez-González, D. R. Williams, E. González-Zamora, V. Martis, A. Martínez, J. Balmaseda, G. Maurin and I. A. Ibarra, J. Mater. Chem. A, 2019, 7, 15580; J.-F. Lyu, X. Zhang, K. I. Otake, X.-J. Wang, P. Li, Z.-Y. Li, Z.-J. Chen, Y.-Y. Zhang, M. C. Wasson, Y. Yang, P. Bai, X.-H. Guo, T. Islamoglu and O. K. Farha, Chem. Sci., 2019, 10, 1186; K. Shen, L. Zhang, X. D. Chen, L.-M. Liu, D.-L. Zhang, Y. Han, J.-Y. Chen, J.-L. Long, R. Luque, Y.-W. Li and B.-L. Chen, Science, 2018, 359, 206; C. Avci, I. Imaz, A. Carné-Sánchez, J. A. Pariente, N. Tasios, J. Pérez-Carvajal, M. I. Alonso, A. Blanco, M. Dijkstra, C. López and D. Maspoch, Nat. Chem., 2018, 10, 78.

- 3 Recent reviews: J.-D. Xiao and H.-L. Jiang, Acc. Chem. Res., 2019, 52 356; M. Zhong, L.-J. Kong, N. Li, Y.-Y. Liu, J. Zby: and X-31 By Confide Chem. Rev., 2019, 388, 172; H. Wang and J. Li, Acc. Chem. Res., 2019, 52, 1968.
- R. Adam, M. Mon, R. Greco, L. H. G. Kalinke, A. Vidal-Moya, A. Fernandez, R. E. P. Winpenny, A. Doménech-Carbó, A. Leyva-Pérez, D. Armentano, E. Pardo, and J. Ferrando-Soria, *J. Am. Chem. Soc.*, 2019, 141(26), 10350; X. Zhang , Z.-Y. Huang , M. Ferrandon, D.-L. Yang, L. Robison, P. Li, T.-C. Wang, M. Delferro and O. K. Farha, *Nat Catal*, 2018, 1, 356; T. Liu, P. Li, N. Yao, G.-Z. Cheng, S.-L. Chen, W. Luo and Y.-D. Yin, *Angew. Chem. Int. Ed.*, 2019, 58, 4679; M. Gharib, L. Esrafili, A. Morsali and P. Retailleau, *Dalton Trans.*, 2019, 48, 8803; L. Li, R.-B. Lin, R. Krishna, H. Li, S. Xiang, H. Wu, J. Li, W. Zhou and B. Chen, *Science*, 2018, 362, 443; A. Pulido, L. J. Chen, T. Kaczorowski, D. Holden, M. A. Little, S.-Y. Chong, B. J. Slater, D. P. McMahon, B. Bonillo, C. J. Stackhouse, A. Stephenson, C. M. Kane, R. Clowes, T. Hasell, A. I. Cooper and G. M. Day, *Nature*, 2017, 543, 657.
- 5 Recent reviews: M.-L. Ding, R.-W. Flaig, H.-L. Jiang and O. M. Yaghi, *Chem. Soc. Rev.*, 2019, **48**, 2783; R. Li, W. Zhang and K. Zhou, *Adv. Mater.*, 2018, **30**, 1705512; H.-G. Zhang, J.-Z. Li, Q. Tan, L.-L. Lu, Z.-B. Wang and G. Wu, *Chem. Eur. J.*, 2018, **24**, 18137.
- 6 F. Guo, S.-Z. Yang, Y. Liu, P. Wang, J.-E. Huang and W.-Y. Sun, ACS Catal., 2019, 9, 8464; B. An, Z. Li, Y. Song, J.-Z. Zhang, L.-Z. Zeng, C. Wang and W.-B. Lin, Nat. Catal., 2019, 2, 709; Y.-P. Wei, Y. Liu, F. Guo, X.-Y. Dao and W.-Y. Sun, Dalton Trans., 2019, 48, 8221.
- M. J. Lashaki, S. Khiavi and A. Sayari, *Chem. Soc. Rev.*, 2019, **48**, 3320;
  A. V. Desaia, S. Sharma, S. Let and S. K. Ghos, *Coordin. Chem. Rev.*, 2019, **395**, 146; S. Roland, J. M. Suarez and M. Sollogoub, *Chem. Eur. J.*, 2018, **24**, 12464.
- S. Yan, D. Zhu, Z.-Y. Zhang, H. Li, G.-J. Chen and B. Liu, *Appl. Energy*, 2019, **248**, 104; A. Gogia and S. K. Mandal, *Dalton Trans.*, 2019, **48**, 2388.
- B. Ugale, S. Kumar, T. J. Dhilip Kumar and C. M. Nagaraja, *Inorg. Chem.*, 2019, 58, 3925; Y. Rachuri, J. F. Kurisingal, R. K. Chitumalla, S. Vuppala, Y.-J. Gu, J. Jang, Y.-S. Choe, E. Suresh and D. W. Park, *Inorg. Chem.*, 2019, 58, 11389.
- X. Zhang, J. Sun, G.-F. Wei, Z.-P. Liu, H.-M. Yang, K.-M. Wang and H.-H. Fei, *Angew. Chem. Int. Ed.*, 2019, **58**, 2844; X. Zhang, Y.-L. Jiang and H.-H. Fei, *Chem. Commun.*, 2019, **55**, 11928.
- H. Benaissa, M. Wolff, K. Robeyns, G. Knör, K. V. Hecke, N. Campagnol, J. Fransaer and Y. Garcia, *Cryst. Growth Des.*, 2019, **19**, 5292; Y. Sun, F. Wang and J. Zhang, *Inorg. Chem.*, 2019, **58**, 4076.
- Y. Ye, Z. Zhang, L. Chen, S. Chen, Q. Lin, F. Wei, Z. Zhang and S. Xiang, *Inorg. Chem.*, 2019, **58**, 7754; N. Li, Z. Chang, H. Huang, R. Feng, W.-W. He, M. Zhang, D. G. Madden, M. J. Zaworotko and X.-H. Bu, *Small*, 2019, **15**, 1900426; B. Liu, H.-F. Zhou, L. Hou and Y.-Y. Wang, *Dalton Trans.*, 2018, **47**, 5298; A. Tăbăcaru, C. Pettinari and S. Galli, *Coordin. Chem. Rev.*, 2018, **372**, 1.
- Y.-X. Ye, H. Zhang, L.-J. Chen, S.-M. Chen, Q.-J. Lin, F.-F. Wei, Z.-J. Zhang and S.-C. Xiang, *Inorg. Chem.*, 2019, **58**, 7754; L.-Q. Ji, J. Yang, Z.-Y. Zhang, Y. Qian, Z. Su, M. Han and H.-K. Liu, *Cryst. Growth Des.*, 2019, **19**, 2991; H. A. Hamzah, T. S. Crickmore, D. Rixson and A. D. Burrows, *Dalton Trans.*, 2018, **47**, 14491.
- 14 A.-M. Xie, M.-P. Cao, Y.-Y. Liu, L.-D. Feng, X.-Y. Hu and W. Dong, *Eur. J. Org. Chem.*, 2014, 436.
- 15 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, Acc. Chem. Res., 2008, 41, 1782.
- Y. Kim, T. Yang, G. Yun, M. B. Ghasemian, J. Koo, E. Lee, S. J. Cho and K. Kim, *Angew. Chem. Int. Ed.*, 2015, **54**, 13273; T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, A. J. Jacobson and O. Š. Miljanić, *Angew. Chem. Int. Ed.*, 2015, **54**, 13902; S.-T. Zheng, T. Wu, C. S. Chou, A. Fuhr, P.-Y. Feng and X.-H. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 4517.
- 17 B.-X. Dong, S.-Y. Zhang, W.-L. Liu, Y.-C. Wu, J. Ge, L. Song and Y.-L. Teng, *Chem. Commun.*, 2015, **51**, 5691; C. K. Brozek, A. F. Cozzolino, S. J. Teat, Y.-S. Chen and M. Dinca, *Chem. Mater.*, 2015, **25**, 2998.
- 18 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.

This journal is © The Royal Society of Chemistry 20xx

**Dalton Transactions Accepted Manuscript** 

#### Journal Name

View Article Online DOI: 10.1039/C9DT04068D

- Y. Cui, B. Li, H. He, W. Zhou, B. Chen and G. Qian, *Acc. Chem. Res.*, 2016, **49**, 483; A. Dhakshinamoorthy, Z. Li and H. Garcia, *Chem. Soc. Rev.*, 2018, **47**, 8134.
- A. Rodriguez, R. Kivekas and E. Colacio, *Chem.Commun.*, 2005, 5228;
  A. Rodriguez-Dieguez, M. A. Palacios, A. Sironi and E. Colacio, *Dalton Trans.*, 2008, 2887.
- 21 J.-T. Liu and S.-D. Fan, Acta Crystallogr. E, 2007, 63, m1632.
- 22 A. Rodriguez-Dieguez, A. Salinas-Castillo, S. Galli, N. Masciocchi, J. M. Gutierrez-Zorilla, P. Vitoria and E. Colacio, *Dalton Trans.*, 2007, 1821; J.-Y. Zhang, A.-L. Cheng, Q. Yue, W.-W. Sun and E.-Q. Gao, *Chem. Commun.*, 2008, 847; J.-Y. Zhang, A.-L. Cheng, Q. Sun, Q. Yue and E.-Q. Gao, *Cryst. Growth Des.*, 2010, **10**, 2908.
- 23 X.-L. Zhang, C.-L. Zhang, Y.-E. Qiu and N. An, *Acta Crystallogr. E*, 2007, **63**, m2423.
- 24 P. Pachfule, R. Das, P. Poddar and R. Banerjee, *Cryst. Growth Des.*, 2010, **10**, 2475; A. Rodriguez-Dieguez, A. J. Mota, J. M. Seco, M. A. Palacios, A. Romerosa and E. Colacio, *Dalton Trans.*, 2009, 9578.
- 25 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.
- 26 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
- 27 S. S.-Y. Chui, S. M.-F. Lo, J. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
- 28 S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P. S. Wheatley, R. E. Morris and A. Zecchina, *Phys. Chem. Chem. Phys.*, 2007, 9, 2676.
- 29 E. B. le Bouhelec, P. Mougin, A. Barreau and R. Solimando, *Energy Fuels*, 2007, **21**, 2044.
- 30 Z.-Z. Lu, H. G. W. Godfrey, I. da Silva, Y. Cheng, M. Savage, F. Tuna, E. J. L. McInnes, S. J. Teat, K. J. Gagnon, M. D. Frogley, P. Manuel, S. Rudic, A. J. Ramirez-Cuesta, T. L. Easun, S. Yang and M. Schröder, *Nat. Commun.*, 2017, **8**, 14212.
- A. Kumar, D. G. Madden, M. Lusi, K.-J. Chen, E. A. Daniels, T. Curtin, J. J. Perry and M. J. Zaworotko, *Angew. Chem. In. Ed.*, 2015, 54, 14372;
  Y. Ye, H. Zhang, L. Chen, S. Chen, Q. Lin, F. Wei, Z. Zhang and S. Xiang, *Inorg. Chem.*, 2019, 58, 7754.

View Article Online DOI: 10.1039/C9DT04068D



Porous MOFs and isomers base on tetrazole-based molecules were synthesized for adsorbing carbon dioxide showing high selectivity.