

## Gyroidal metal–organic frameworks by solvothermal subcomponent self-assembly†

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**Solvothermal subcomponent self-assembly has been employed as a convenient and advanced route to prepare metal–organic frameworks (MOFs). A new gyroidal MOF with gie topology was successfully synthesized and characterized; gas adsorption properties were also investigated.**

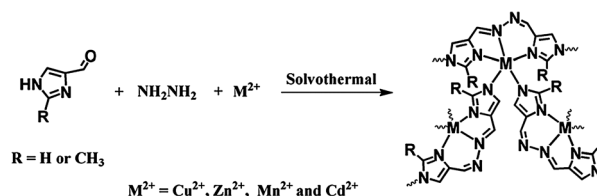
Metal–organic frameworks (MOFs) have attracted increasing attention in the past decade for their fascinating structures, porous properties and potential applications in many areas (*e.g.* gas storage,<sup>1,2</sup> separation,<sup>3</sup> sensing,<sup>4</sup> *etc.*). A straightforward strategy for the design and synthesis of MOFs is using elaborately prepared multitopic organic molecules as linkers to bind metal ions. In recent years, *in situ* ligand formation reactions (conventionally, conducted under solvothermal conditions) as a non-conventional method have been also exploited,<sup>5–7</sup> *e.g.* hydrolysis of carboxylate esters, organic nitriles and aldehydes into the corresponding carboxylates, cycloaddition of organic nitriles with azide and ammonia, and transformation of inorganic to organic sulfur. One-pot synthesis has become a convenient approach in constructing MOF materials, albeit such reactions are irreversible and the in-depth understanding of the mechanism for some reactions is complex.

*Subcomponent self-assembly* involving the formation of coordination and covalent bonds spontaneously has been developed as a feasible and green route to yield coordination compounds by multi-component assembly in one step.<sup>8</sup> Many beautiful and sophisticated molecular assemblies including macrocycles,<sup>9,10</sup> pentafoil knot,<sup>10</sup> Borromen rings,<sup>11</sup> helicates,<sup>12</sup> and cages<sup>13,14</sup> have been fabricated successfully in conventional reactions, however, coordination polymers (or MOFs) are rarely reported to be constructed by this strategy, probably due to their poor solubility in common solvents and difficulty in growing single crystals.

In this work, we introduce solvothermal reactions to subcomponent self-assembly technology in the preparation of MOF materials. Noting its dynamic properties, good coordination ability and simple reactions with high yields, the condensation between amino and carbonyl groups was employed to synthesize Cd(2-BmIm) (denoted as STU-5, 2-BmIm = 1,2-bis((2-methyl-1*H*-imidazol-4-yl)methylene)hydrazine). In this reaction, imine bonds are dynamically assembled and the resulting ligand 2-methyl-4-formylimidazole, as an aldehyde source is reacted directly with hydrazine and metal ions under solvothermal conditions to afford the MOF (Scheme 1, Fig. 1). The structure of STU-5 features a novel **gie** net and gyroid surface, an analogous topology as observed in our recently reported compounds STU-1, -2 and -3, obtained from the reactions of the pre-synthesized ligand 1,2-bis((5*H*-imidazol-4-yl)methylene)hydrazine and metal ions, respectively.<sup>15</sup>

For comparison, the reactions of 4-formylimidazole and hydrazine with the respective metal salts (Zn<sup>2+</sup>, Mn<sup>2+</sup> and Cu<sup>2+</sup>) under solvothermal conditions (DMF–ethanol as solvent, heating at 100, 120 or 140 °C for 3 days) yielded good quality single crystals of STU-1, -2, -3 (for details see Experimental Section in ESI†). X-ray diffraction analysis and FT-IR spectra (Table S1, Fig. S1 and S2†) verified that the step-wise synthesized gyroidal MOFs can be also obtained as bulky pure products by solvothermal subcomponent self-assembly.

STU-5 crystallizes in a space group *Ia3d*, the same as that of STU-1. However, the unit-cell parameters of STU-5 are significantly expanded from STU-1 (*a* = 37.8124(1) Å, *V* = 54063.3(2) Å<sup>3</sup> for STU-5; *a* = 34.6471(2) Å, *V* = 41591.1(4) Å<sup>3</sup> for STU-1, *V*<sub>STU-5</sub>/*V*<sub>STU-1</sub> = 1.30).

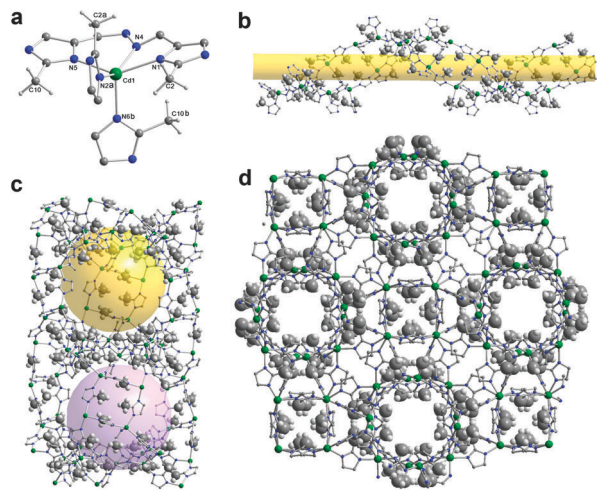


**Scheme 1** Solvothermal subcomponent self-assembly of 4-formylimidazole, hydrazine and metal ions.

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† Electronic supplementary information (ESI) available: Syntheses and characterizations of STU-1, 2, 3, 5 and Cu(BImED)NO<sub>3</sub>, crystallographic (CIF) data for STU-5 and Cu(BImED)NO<sub>3</sub>. CCDC 922411 and 922412. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc39287b



**Fig. 1** (a) The coordination geometry of  $\text{Cd}^{2+}$  of STU-5. (b) A representative right-handed helical ribbon. (c) Hydrophobic void in STU-5 (large yellow and purple balls showing opposite handedness space voids separated by the gyroid surface). (d) Overview of the 3D framework of STU-5 along the  $a$ -axis. The methyl groups are highlighted with large grey balls. Symmetry operations: (a)  $-z + 1/4$ ,  $-y + 7/4$ ,  $x - 1/4$ ; (b)  $y - 1/2$ ,  $-z + 1$ ,  $x$ .

The asymmetric unit of STU-5 contains one  $\text{Cd}^{2+}$  ions and one 2-BmIm, which suggested the successful formation of the ligand during solvothermal subcomponent assembly. The IR spectrum shows a strong absorption at around  $1622\text{ cm}^{-1}$  (Fig. S3†), confirming the existence of imine bonds formed by the reaction between 2-methyl-4-formylimidazole and hydrazine. The  $\text{Cd}^{2+}$  ion adopts a distorted square-pyramidal coordination geometry (Fig. 1a), being coordinated by five nitrogen atoms from 2-BmIm ligands, similar to that of  $\text{Zn}^{2+}$  in STU-1. However, the Cd–N bond distances (2.208(5)–2.425(10) Å) are obviously longer than those of Zn–N bonds (2.009(3)–2.342(9) Å) in STU-1. The longer Cd–N bond distances probably result in the larger unit-cell volume in STU-5. Another obvious difference between STU-5 and STU-1 is that each  $\text{Cd}^{2+}$  ion is surrounded by four methyl groups of the imidazole ring in STU-5 (Fig. 1a). The distances between  $\text{Cd}^{2+}$  ion and methyl groups are quite short, ranging from 3.441(6) to 3.802(3) Å (Cd1···C2 and Cd1···C10, respectively). Methyl groups should provide a hydrophobic environment for  $\text{Cd}^{2+}$  centres, and thus trigger unique properties for STU-5 compared with STU-1, in which there is no methyl groups around the  $\text{Zn}^{2+}$  centre.

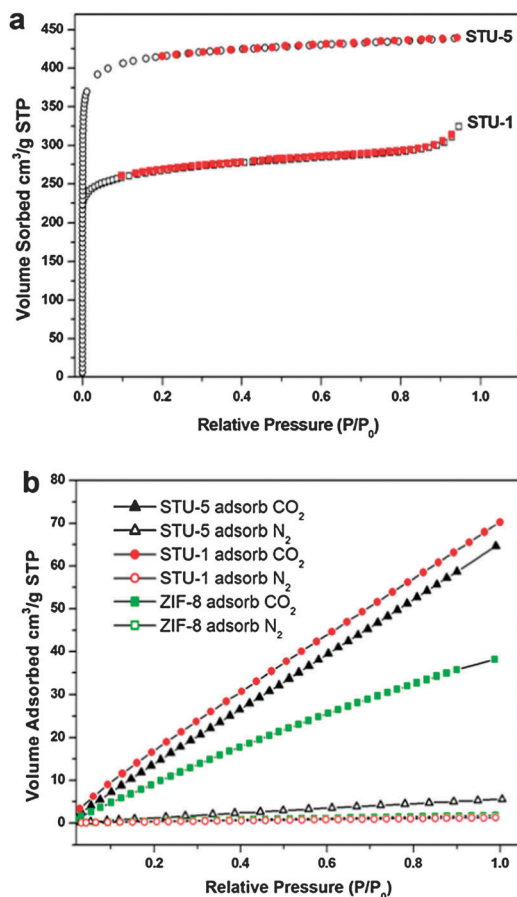
Similar to BIm in STU-1, each 2-BmIm ligand binds three  $\text{Cd}^{2+}$  ions, and a three-dimensional extended framework of STU-5 is constructed (Fig. 1b–d). The  $\text{Cd}^{2+}$  atoms can be regarded as tetrahedral connection nodes, while the hydrazones have no contribution to the linkage for the extended framework (Fig. 1a). The envisaged tetrahedral  $\text{Cd}^{2+}$  nodes are highly distorted (ranging from  $95.89(15)$  to  $142.71(18)^\circ$ ) like that of  $\text{Zn}^{2+}$  in STU-1, and linked by imidazole groups, giving rise to a labyrinthine zeolitic imidazolate framework with a rare **gie** topology and gyroidal surface (Fig. S4†). Of note, due to the longer Cd–N bonds, the size of 12-ring windows formed by intersecting of three same handedness helical ribbons (Fig. 1b) in STU-5 is obviously larger ( $ca. 29.49(3) \times 17.08(4)$  Å) than that of STU-1 ( $27.30(8) \times 15.41(2)$  Å) (Fig. S5†). At the same time, the

cavities encompassed by the 12-ring are also expanded, with a void volume of  $30014.1\text{ \AA}^3$  in one unit cell (55.5%, *cf.* 51.2% for STU-1, as measured by the PLATON program). Another notable feature in STU-5 is that the right- and left-handed voids are divided by a hydrophobic gyroid surface (Fig. 1c) decorated with methyl groups on the inner wall of the void.

Chemical and thermal stabilities are principal consideration for industrial application of MOFs. Many MOFs are thermally stable, but hydrolytically unstable, notably MOF-5,<sup>16</sup> while a number of MOFs have high chemical and thermal stability, *e.g.* Cr-Mil-101,<sup>17</sup> UiO-66<sup>18</sup> and ZIF-8.<sup>19,20</sup> TGA data reveal that STU-5 is stable to about  $420\text{ }^\circ\text{C}$  under  $\text{N}_2$  atmosphere (Fig. S6†). Variable-temperature powder X-ray diffraction studies further document that STU-5 is highly stable, with loss of crystallinity of STU-5 occurring at *ca.*  $550\text{ }^\circ\text{C}$  (Fig. S7†). To investigate the chemical stability of STU-5, crystal samples were suspended in boiling water or methanol for 24 h. PXRD measurements show that both solid samples sustain full crystalline and local structure after the treatment, which demonstrated that STU-5 is chemically stable in water and methanol (Fig. S8†). For comparison, the PXRD profile of crystal samples of STU-1 treated with boiling water for 24 h, did not match with those of the original sample and the simulated pattern (Fig. S9†), suggesting that STU-1 is not as stable in water as STU-5. The high hydrolytic stability of STU-5 is probably due to the methyl groups around  $\text{Cd}^{2+}$  in the pores as discussed above. Creating a hydrophobic environment, methyl groups repel water and thus prevent the hydrolysis on  $\text{Cd}^{2+}$  centres.<sup>19</sup> Therefore, the introduction of hydrophobic groups (*e.g.* methyl groups) inside a framework can probably enhance the hydrolytic stability of a MOF.

The permanent porosity of evacuated STU-5 is unequivocally attested by gas adsorption analysis. As shown in Fig. 2a, STU-5 shows a type I nitrogen adsorption isotherm as a microporous material. The apparent Langmuir and Brunauer–Emmett–Teller (BET) surface areas ( $S_{\text{Langmuir}}$  and  $S_{\text{BET}}$ ) are  $1858$  and  $1258\text{ m}^2\text{ g}^{-1}$ , respectively, which were obtained by using the data points on the adsorption branch in the range of  $P/P_0 = 0.06$ – $0.3$ . By using a single data point at relative pressure 0.1, a micropore volume of  $0.628\text{ cm}^3\text{ g}^{-1}$  is obtained. The surface area of STU-5 is significantly larger than that of STU-1 ( $S_{\text{Langmuir}} = 1225\text{ m}^2\text{ g}^{-1}$ ,  $S_{\text{BET}} = 775\text{ m}^2\text{ g}^{-1}$ ), which is close to that of reported ZIF-8<sup>19</sup> ( $S_{\text{Langmuir}} = 1810\text{ m}^2\text{ g}^{-1}$ ) and BIF-9-Li<sup>21</sup> ( $S_{\text{Langmuir}} = 1810\text{ m}^2\text{ g}^{-1}$ ). The expanded surface area for STU-5 probably benefits from the elongation of Cd–N bonds, which provide a larger void volume. This result is accordance with the reported ZIFs based on  $\text{Cd}^{2+}$  centres.<sup>22</sup>

$\text{CO}_2$  adsorption isotherms of STU-5 show volumetric uptake of  $64.6\text{ cm}^3\text{ g}^{-1}$  ( $2.9\text{ mmol g}^{-1}$ ) at  $273\text{ K}$  and  $1\text{ bar}$  (Fig. 2b). The  $\text{CO}_2$  uptake is slightly lower than that of STU-1 ( $70.2\text{ cm}^3\text{ g}^{-1}$ ), which may be due to its five coordinated open  $\text{Cd}^{2+}$  centres surrounded by methyl groups (Fig. 1a) increasing the difficulty for  $\text{CO}_2$  molecules to interact with  $\text{Cd}^{2+}$  centres. However, the  $\text{CO}_2$  adsorption capacity of STU-5 surpasses the values for ZIF-8 ( $38.2\text{ cm}^3\text{ g}^{-1}$ , Fig. 2b), BIF-9-Li ( $35.6\text{ cm}^3\text{ g}^{-1}$ ),<sup>22</sup> and CdIF-1 ( $30\text{ cm}^3\text{ g}^{-1}$ ,  $S_{\text{Langmuir}} = 2420\text{ m}^2\text{ g}^{-1}$ ), CdIF-4 ( $21\text{ cm}^3\text{ g}^{-1}$ ,  $S_{\text{Langmuir}} = 2420\text{ m}^2\text{ g}^{-1}$ ) and CdIF-9 ( $48\text{ cm}^3\text{ g}^{-1}$ ,  $S_{\text{Langmuir}} = 3010\text{ m}^2\text{ g}^{-1}$ ).<sup>22</sup> The higher  $\text{CO}_2$  adsorption amount for STU-5



**Fig. 2** Gas adsorption isotherms: (a) N<sub>2</sub> adsorption at 77 K of STU-1 and STU-5; open and filled symbols represent adsorption and desorption, respectively. (b) CO<sub>2</sub> and N<sub>2</sub> adsorption at 273 K of STU-1, -5 and ZIF-8. (The gas adsorption analysis data of STU-1 were obtained from step-wise synthesized sample,<sup>15</sup> while those of ZIF-8 were remeasured.<sup>19</sup>)

and STU-1 can be attributed to the additional hydrazone bridges and five open coordinated metal ions that can interact with CO<sub>2</sub> molecules. The enhancement of CO<sub>2</sub> capture by open nitrogen sites was also observed in recent reports.<sup>23,24</sup> The N<sub>2</sub> adsorption isotherms at 273 K and 1 bar for STU-1, -5 and ZIF-8 show volumetric uptakes of 1.2, 5.5 and 1.75 cm<sup>3</sup> g<sup>-1</sup>, respectively (Fig. 2b). The lower N<sub>2</sub> adsorption amounts for STU-1, -5 and ZIF-8 show that they adsorb CO<sub>2</sub> over N<sub>2</sub> with high selectivity.

We also used ethylenediamine instead of hydrazine to react with 4-formylimidazole and metal ions (e.g. Cu<sup>2+</sup>) under solvothermal conditions. A polymeric chain Cu(BImED)NO<sub>3</sub> (BImED = bis-((1*H*-imidazol-4-yl)methylene)ethane-1,2-diamine) was obtained and structurally characterized (Fig. S10–S12<sup>†</sup>). In the structure (Fig. S8<sup>†</sup>) of Cu(BImED)NO<sub>3</sub>, Cu<sup>2+</sup> centres are five-coordinated, and the imidazole group is partially deprotonated (the excess positive charges of Cu<sup>2+</sup> are balanced by NO<sub>3</sub><sup>-</sup> anions). Although the fabrication of a gyroid structure was not achieved, the successful formation of the ligand in Cu(BImED)NO<sub>3</sub> further demonstrated that solvothermal subcomponent self-assembly is suitable for the construction of polymeric coordination compounds.

In summary, gyroidal MOFs with *gie* topology have been synthesized by solvothermal subcomponent self-assembly technology. The resulting MOF STU-5 has an obviously larger unit cell, a higher surface area compared with its analogue STU-1. It is hydrolytically and thermally stable, and shows good adsorption ability for CO<sub>2</sub> over N<sub>2</sub> at 273 K. The introduction of methyl groups around metal centres was observed to increase the hydrolytic stability of the MOF. The successful synthesis of the compounds documented that the solvothermal subcomponent self-assembly is a convenient and advanced route to prepare polymeric coordination compounds. We anticipate that further interesting and unprecedented polymeric compounds will be produced with this green approach.

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