

## Three-dimensional metal–organic framework with (3,4)-connected net, synthesized from an ionic liquid medium†

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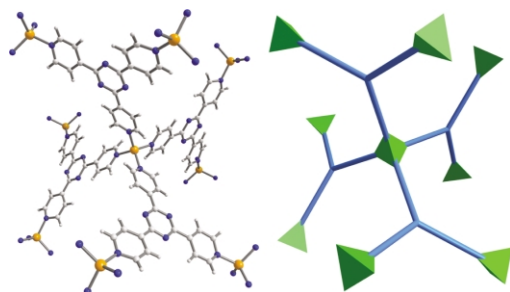
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**A new 3D metal–organic framework with a (3,4)-connected network topology is synthesized from an ionic liquid medium; its highly symmetrical structure comprises doubly interpenetrating nets with the cubic- $C_3N_4$  topology.**

Metal–organic frameworks<sup>1</sup> or coordination polymers have been extensively studied in recent years due to their potential applications, particularly in ion exchange,<sup>2</sup> separation,<sup>3</sup> catalysis,<sup>4</sup> gas storage,<sup>5</sup> magnetism,<sup>6</sup> and nonlinear optical applications.<sup>7</sup> Solvothermal syntheses, chemical reactions carried out in a closed system under an elevated temperature and pressure, have been widely employed in preparation of metal–organic frameworks using water or organic solvents as a reaction medium.<sup>8</sup> Recently, ionic liquids<sup>9</sup> have received much attention as green reaction media for chemical syntheses because of their high thermal stability and practically zero vapor pressure.<sup>10,11</sup> With their poor coordination ability ionic liquids may also be excellent and safe media for the synthesis of metal–organic frameworks. To the best of our knowledge, however, there is only one example of a 1D coordination polymer, built from  $Cu^+$  centers and linear 1,3-bis(4-pyridyl)propane ligands, synthesized in ionic liquid.<sup>12</sup> Herein, we report the synthesis from an ionic liquid solvent, and the structure of the first three-dimensional (3D) metal–organic framework with an unprecedented, 2-fold interpenetrating (3,4)-connected net.

Heating a mixture of  $Cu(NO_3)_2 \cdot 3H_2O$  and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) in ionic liquid butylmethyl-imidazolium tetrafluoroborate [bmim]( $BF_4$ )<sup>13</sup> at 170 °C in a sealed glass tube for 2 days produced deep violet crystals of  $[Cu_3(tpt)_4](BF_4)_3 \cdot (tpt)_{2/3} \cdot 5H_2O$  (**1**) which has been characterized by single crystal and X-ray powder diffraction, IR spectroscopy, TGA and elemental analysis. § Our attempts to obtain **1** from solvothermal reactions in common solvents other than the ionic liquid failed. The X-ray structure of **1** revealed a doubly interpenetrated, cationic 3D framework composed of  $Cu^+$  ions, which was apparently generated during the reaction, and tpt ligands (Fig. 1 and 2). The  $Cu^+$  ions are



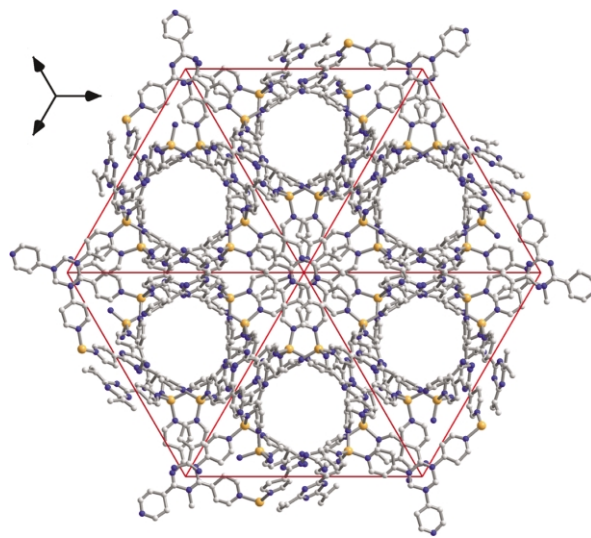
**Fig. 1** A fragment of the framework structure in **1** (left) and its simplified presentation (right): Cu—orange, N—blue, C—grey, H—white. In the simplified model  $Cu^+$  ions are shown as green tetrahedra and tpt ligands as blue wire.

† Electronic supplementary information (ESI) available: IR, XRD, TGA, details of data collection and structure refinements, as well as additional figures related to the framework. See <http://www.rsc.org/suppdata/cc/b4/b403001j/>

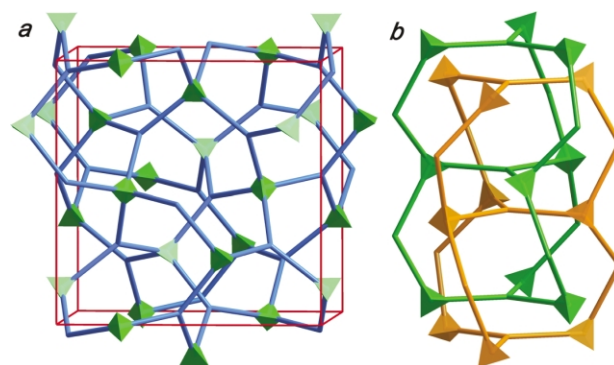
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tetrahedrally coordinated by four tpt ligands and each tpt ligand connects three  $Cu^+$  ions related by crystallographic three-fold symmetry of the cubic space group  $Ia\bar{3}d$ . Fig. 2 shows the doubly interpenetrated network of **1** along one of the three-fold axes. The large channels with a diameter of  $\sim 5$  Å are filled with non-coordinating free tpt,  $H_2O$  and disordered  $BF_4^-$  anions whose presence was unambiguously supported by FT-IR spectroscopy.

Despite the simplicity of the building blocks and the high crystallographic symmetry, the overall structure of the 3D network in **1** is quite complicated. In a simplified view, it is composed of alternating tetrahedral four-connecting ( $Cu^+$ ) and triangular three-connecting (tpt) nodes (Fig. 1). The two types of nodes are linked to each other to form an extended framework (Fig. 3a) where the shortest ring comprises eight nodes (four  $Cu^+$  ions and four tpt ligands). According to Wells,<sup>14,15</sup> such networks with 3- and 4-connecting nodes belong to the (3,4)-net family, particularly to



**Fig. 2** A view of the doubly interpenetrated network in **1** along the three-fold axis (one unit cell). Hydrogen atoms, guest tpt, water and  $BF_4^-$  ions are not shown.



**Fig. 3** (a) View of a single network in **1**.  $Cu^+$  centers are shown as tetrahedra and tpt ligands as wires. (b) View of two interpenetrating nets (green and orange) in **1**.

the net (8,3/4) where 3 and 4 indicate the connectivity of the nodes and 8 is the number of these nodes in the shortest ring. Two independent nets, related by a crystallographic inversion symmetry, interpenetrate each other. The interpenetration occurs in such a way that the tpt ligands of the two nets interact each other with short  $\pi$ - $\pi$  contacts along a 3-fold axis (Fig. 3b).

For a given combination of alternating tetrahedral and triangular nodes Wells found and described two structural types: hexagonal  $\beta$ - $\text{Si}_3\text{N}_4$  and cubic boracite, and we discovered that the substructure of Si and Cu(1) atoms in  $\text{Cu}_{15}\text{Si}_4$  also belongs to the same net family.<sup>16</sup> Among these three structure types, the boracite topology has been observed in the metal-organic framework prepared by a diffusion reaction of  $\text{Cu}^+$  and tpt ligand in acetonitrile solvent.<sup>17</sup> To the best of our knowledge, however, the network topology of **1** is unprecedented in metal-organic frameworks,<sup>18</sup> and the single net of **1** can be described as a metal-organic analogue of the above-mentioned  $\text{Cu}_{15}\text{Si}_4$ . Among the known (3,4)-connected nets in coordination polymers,<sup>19</sup> the most symmetrical and important examples<sup>20</sup> are the above mentioned boracite,  $\text{Pt}_3\text{O}_4$ <sup>5d</sup> and the twisted boracite.<sup>21</sup> Therefore, the structure of **1** provides another valuable prototype of (3,4)-connected nets which may be important for the design of metal-organic frameworks since three- and four-connected centers are readily available in coordination chemistry. It is interesting to note that the network for the single net of **1** has been theoretically predicted<sup>22</sup> for the cubic phase of carbon nitride  $\text{C}_3\text{N}_4$  which, according to the calculations, may possess higher hardness than diamond, and like diamond itself, this phase should be thermodynamically stable only at high pressures and temperatures.

The single (3,4)-connected net in **1** can be further specified by Schläfli symbol  $(8^3)(8^6)$  where the shortest rings meeting at the three and six angles of the 3- and 4-connecting vertices, respectively, are all 8-membered. The number of octagons around the three and six angles are 5, 5, 5 and 3, 3, 3, 3, 4, 4, respectively, and therefore, the single net of **1** has the vertex symbol of  $(8_5-8_5-8_5)(8_3-8_3-8_3-8_3-8_4-8_4)$ . In addition, the recently introduced tiling approach<sup>23-25</sup> may also be useful in describing the 3D net. The natural tiling of cubic- $\text{C}_3\text{N}_4$  net consists of two types of tiles (polyhedra), both having three octagonal faces (rings) and therefore could be denoted by  $[8^3]$  symbol (see ESI†). The transitivity of the natural tiling of the net is 2122, because there are two kinds of vertices, one kind of edge only, but two kinds of rings and two of tiles.

In conclusion, we synthesized a new 3D metal-organic framework with a (3,4)-connected net topology from an ionic liquid medium. This work demonstrates that ionic liquids are excellent and safe reaction media for the synthesis of metal-organic frameworks. The successful preparation of a novel network with a previously unknown 2-fold interpenetrating net having the cubic- $\text{C}_3\text{N}_4$  topology and highly symmetrical structure from readily available building motifs may provide an insight into the design and synthesis of metal-organic frameworks with desired structures and properties.

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## Notes and references

§ A mixture containing  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (20 mg, 83  $\mu\text{mol}$ ), tpt (51 mg, 163  $\mu\text{mol}$ ) and  $[\text{bmim}](\text{BF}_4)$  (1.0 ml) was heated at 170 °C for 2 days in a sealed glass tube. Dark violet, polyhedral crystals of **1** were collected by filtration, washed with acetone and benzyl alcohol to remove the ionic liquid and unreacted ligand. Orange-colored microcrystalline impurities were removed by sonicating the product in acetone for 15 seconds. Subsequent washing with diethyl ether followed by drying *in vacuo* produced **1** (48 mg,

88%). Anal. calcd. for  $\text{Cu}_3\text{C}_{90}\text{H}_{73}\text{N}_{30}\text{B}_3\text{F}_{12}\text{O}_{6.5}$ : C, 50.76; H, 3.45; N, 19.73. Found: C, 51.24; H, 3.50; N, 19.29. X-ray data for **1**:  $\text{Cu}_3\text{C}_{84}\text{H}_{66}\text{N}_{28}\text{O}_3\text{B}_3\text{F}_{12}$ ,  $M_r = 1998.70$ , cubic,  $Ia\bar{3}d$  (No. 230),  $a = 28.019(3)$  Å,  $V = 21996(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 223$  K,  $\mu(\text{Mo}-\text{K}\alpha) = 0.651$  mm<sup>-1</sup>,  $d_{\text{calc}} = 1.207$  g cm<sup>-3</sup>, 54682 reflections measured, 1814 unique ( $R_{\text{int}} = 0.060$ ), Siemens SMART CCD diffractometer ( $\lambda = 0.71073$  Å). The refinements were carried out with full-matrix least-squares on  $F^2$ ,  $R_1 = 0.0966$ ,  $wR_2 = 0.2772$  for 1486 reflections ( $I > 2\sigma(I)$ ),  $R_1 = 0.1082$ ,  $wR_2 = 0.2993$  (all data), GOF = 1.173, 160 parameters and 52 restraints. CCDC 233232. See <http://www.rsc.org/suppdata/cc/b4/b403001j/> for crystallographic data in .cif or other electronic format.

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