An unprecedented (6,8)-connected self-penetrating network based on two distinct zinc clusters†

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Received (in Cambridge, UK) 28th June 2007, Accepted 24th August 2007
First published as an Advance Article on the web 19th September 2007
DOI: 10.1039/b709835a

The first (6,8)-connected self-penetrating metal–organic framework has been constructed using an asymmetric neutral ligand based on dinuclear zinc clusters, as six-connected nodes, and trinuclear zinc clusters as eight-connected nodes, representing the highest-connected binodal network topology presently known for self-penetrating systems.

Known metal–organic frameworks (MOFs) are rapidly increasing in number because of their wide potential applications as functional materials and intriguing structures.[1] The topological analysis of multitudinous networks has become a topical research area, and is not only an important tool for simplifying complicated compounds but also plays an instructive role in the rational design of certain functional materials with desirable properties.[2] The classification of structures by Wells laid the foundation for our general understanding of some natural prototypes in metallic or binary inorganic solids.[3] To date, a variety of uninodal network topologies have been realized. The majority are based on three-, four- and six-connected topologies.[1b,4] Examples of seven-, eight- and twelve-connected metal–organic coordination frameworks are extremely rare[5] due to the limited coordination numbers of metal centers and steric hindrance issues of the most commonly-used organic ligands. On the other hand, some metal–organic frameworks with mixed-connected topologies have been reported, for example: Pt_3O_4, boracite, twisted boracite, PtS, rutile, pyrite and anatase.[6] However, there is an unfavorable lack of investigation on binodal high-connected structures, such as (3,8)-, (4,8)- and (3,9)-connected frameworks.[7] The (6,8)-connected framework, compared to the above-mentioned nets, is more difficult to achieve owing to it containing two kinds of high-connected nodes. Until now, this net had not been observed in metal–organic frameworks.

Of concurrent interest has been the construction of entangled systems, as discussed in several excellent reviews.[1g,8] Of the many reported types of entanglement in polymeric architectures, the phenomenon of self-penetration (self-catenation or polyknotting) has attracted much attention. These species are single nets, having the peculiarity that the smallest topological rings are catenated by other rings belonging to the same network.[8a] Hitherto, only a limited number of self-penetrated nets have been observed in metal–organic frameworks.[9]

As shown above, it is a great challenge to achieve self-penetrating MOFs based on binodal high-connected nets in coordination chemistry. Recently, metal clusters with substituted single metal atoms have been used as nodes for high-connected metal–organic frameworks.[7b] A feasible approach to building binodal high-connected self-penetrating networks is to choose two distinct metal clusters with suitable coordination geometries and to rationally design the appropriate ligands. According to previous literature, multi-carboxylate[10] and long flexible[9b] ligands with different characters are excellent candidates for the construction of novel high-connected formworks based on the following considerations: (i) the synthesis of metal clusters is usually by the controlled hydrolysis of metal salts with the aid of carboxylate ligands,[11] because the carboxylate group may induce core aggregation and it should be feasible to link discrete clusters into an extended network *via* its bridging ability; (ii) an asymmetric ligand may induce dissymmetric building blocks by coordinating to different metal centers or metal clusters with different coordination atoms (N and O), which benefits the formation of mix-connected frameworks;[12] and (iii) long flexible ligands are selected for constructing MOFs because they benefit the formation of self-penetrating networks.[8a]

Taking these points into account, we designed and synthesized 1-((4′-((pyridin-3-yloxy)methyl)biphenyl-4-yl)methyl)pyridinium-3-olate (**L**) as an asymmetric neutral bridging ligand, and selected 1,4-benzenedicarboxylic acid (H_2bdc) as a multi-carboxylic bridging ligand. Fortunately, compound $[Zn_{2.5}\mathbf{L}(bdc)_{2.5}]\cdot H_2O$ (**1**) was isolated by hydrothermal methods.‡ The product is very stable in air, and the framework only begins to decompose when heated to more than 346 °C (Fig. S1†). To the best of our knowledge, it represents the first example of a (6,8)-connected self-penetrating network based on two distinct zinc clusters as nodes. Single crystal X-ray analysis§ revealed that compound **1** is constructed from three kinds of Zn^{II} cations, three kinds of bdc anions and one **L** ligand (Fig. S2†). Atom Zn1 is five-coordinated and exhibits a twisted trigonal bipyramidal geometry $[ZnNO_4]$, which is surrounded by four carboxylic oxygen atoms (Zn1–O 1.983(4)–2.096(7) Å) and one nitrogen atom (Zn1–N 2.016(6) Å) from the **L** ligand. Meanwhile, Zn2 shows a tetrahedral geometry $[ZnO_4]$, which is completed by three carboxylic oxygen atoms and one oxygen atom (Zn2–O 1.942(3)–1.976(3) Å) from a hydroxyl group of the **L** ligand. Zn3 lies at an inversion center, is coordinated by four carboxylic oxygen atoms and two oxygen atoms (Zn3–O 2.035(3)–2.159(3) Å) from two hydroxyl groups of different **L** ligands, and shows a distorted octahedral geometry $[ZnO_6]$. All the bond distances and angles are within normal range.[9a,b,13] The **L** ligand exhibits an *anti*-bridging coordination mode that

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† Electronic supplementary information (ESI) available: Details of the synthesis, additional figures, TGA and luminescent spectra. See DOI: 10.1039/b709835a

coordinates to one Zn1 atom with one N atom and bridges two Zn atoms (Zn2 and Zn3) with one O atom. It is interesting to note that the three types of bdc anions (bdc1, bdc2 and bdc3) show different coordination modes (Scheme S1†).

Two carboxylic groups from the bdc1 ligand bridges two equivalent Zn1 trigonal bipyramids to generate a twisted octahedral subunit $[Zn_2(CO_2)_4N_2]$ (Fig. S3a†) with a Zn1···Zn1 distance of 4.427(5) Å, which further extends to a 2D (4,4) square-grid with a rhombic window. The dimensions of the net are 11.313 × 11.313 Å, corresponding to the distance between adjacent centers of dinuclear zinc subunits at their corner (Fig. 1(a)). Meanwhile, the Zn3 octahedron, at a crystallographic inversion center, connects two crystallographically-equivalent Zn2 tetrahedra in a vertex-sharing mode to form a $[Zn_3(CO_2)_6O_2]$ dodecahedral cluster by six carboxylic groups from four bdc2 and two bdc3 ligands, and two oxygen atoms from distinct **L** ligands with a non-bonding Zn2···Zn3 distance of 3.264(3) Å (Fig. S3b†). Each $[Zn_3(CO_2)_6O_2]$ cluster is further linked by four bdc2 and two bdc3 ligands to form a 3D framework (Fig. S4a†), showing a distorted α-Po (pcu) net with dimensions of 16.984 × 11.313 × 11.313 Å (Fig. 1(b)). It is interesting that each bdc3 ligand, coordinating to two $[Zn_3(CO_2)_6O_2]$ clusters, penetrates the 2D sheet formed by the $[Zn_2(CO_2)_4N_2]$ clusters and bdc1 ligands along the a-axis, forming a 2D/3D interpenetrating composition (Fig. S4b†).[14] The 2D (4,4) and 3D (pcu) nets are connected by asymmetric **L** ligands coordinating to di- and trinuclear zinc clusters. Therefore, each dinuclear zinc cluster, as a six-connected node (Fig. S5†), lies at the center of a distorted cube formed by eight trinuclear zinc clusters as eight-connected nodes (Fig. S6†). One body diagonal of a distorted cube therefore passes through the dinuclear zinc cluster (Fig. 2(a)). The overall structure of **1** is a 3D (6,8)-connected self-penetrating framework (Fig. 2(b)). The Schläfli symbol for **1** is $(4^{12}\cdot5.6^2)(4^{20}\cdot5^2\cdot6^6)$ (Fig. S7†).

According to a new approach to the analysis of high-connected frameworks proposed by Hill *et al.*,[15] namely the visualization of structures as combinations of interconnected 2D subnet tectons, the familiar six-connected net (bcu, sometimes called the CsCl net, Fig. 3(a)[1j,5e,16]) can be thus described such that the (4,4) nets (I) (orange) are cross-linked by zigzag chains (green), and the zigzag chain in the inter-layer region bridges across the diagonal of a single window in the (4,4) net. In comparison to a bcu net, compound **1** contains eight- and six-connected nodes. The net formed by all eight-connected nodes in **1** exhibits the same skeleton, which includes the similar (4,4) net (I) and zigzag chain (dark green sticks in Fig. 3(b)). Different to the bcu net, an additional series of (4,4) nets (II) are formed by six-connected nodes, which are at the midpoint of the diagonals, and all the angles between these diagonals and the nets (I), formed by eight-connected nodes, are approximately 40°. Based on the above connection mode, the other kind of diagonal, with an angle of approximately 77° (corresponding angle formed by the line of the diagonal and the plane (I)), penetrates net (II). As a result, catenations of two types of four-membered shortest-circuits, formed by six- and eight-connected nodes, respectively, are observed in the 3D net (black and light green rings in Fig. 3(b)). The resulting array is therefore a (6,8)-connected self-penetrating network. Offering further insight into the nature of this intricate architecture, it can also be considered as a distorted bcu net that is inserted by another kind of (4,4) net (II) along the crystallographic bc plane.

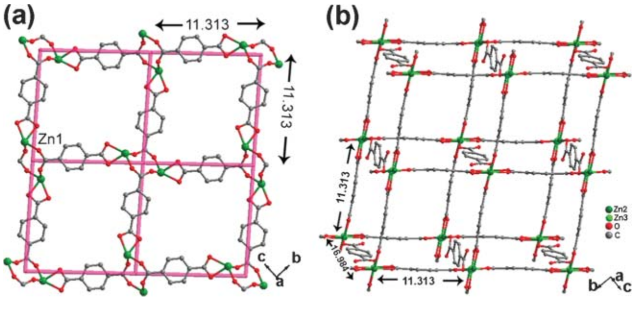

Fig. 1 Ball-and-stick representations of (a) one (4,4) layer formed by Zn1 and bdc1 ligand, and (b) pcu nets by Zn2, Zn3, bdc2 and bdc3 ligands.

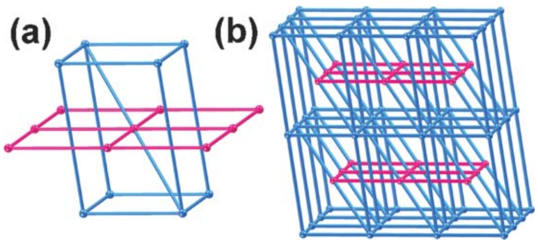

Fig. 2 (a) Schematic view of the geometrical relationship between the six-connected nodes and the net formed of eight-connected nodes. (b) Schematic representation of the (6,8)-connected self-penetrating framework of $(4^{12}\cdot5\cdot6^2)(4^{20}\cdot5^2\cdot6^6)$ topology (pink and blue spheres represent the six- and eight-connected nodes, respectively).

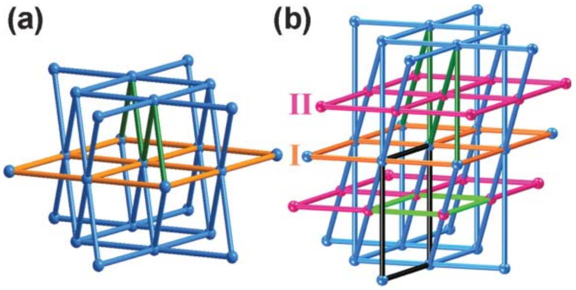

Fig. 3 Schematic representations of the topologies observed in (a) the bcu network and (b) the (6,8)-connected self-penetrating framework in **1**.

To date, (6,8)-connected frameworks have not been observed in MOFs. O'Keeffe *et al.* have enumerated a (6,8)-connected net (ocu)[17] based on an octahedron, as a six-connected node, and a cube, as an eight-connected node (Fig. S8†). Compound **1** is clearly different to the ocu network, and is a self-penetrating framework constructed from a distorted octahedron, as a six-connected node, and a twisted dodecahedron, as an eight-connected node. Therefore, the net in **1** defines a new topology for (6,8)-connected coordination networks that is not only unobserved but also unenumerated, and represents the highest connected binodal network topology for self-penetrating systems.

The photoluminescence properties of compound **1** and free neutral ligand **L** have been studied at room temperature in Fig. S9.† It can be observed that a maximum emission wavelength occurs at 410 nm, with an additional shoulder peak at 454 nm

(λ_{ex} = 300 nm) for **1**. The maximum emission wavelength for **L** (λ_{ex} = 430 nm) appears at 513 nm. The origin of the emission for compound **1** might be attributed to a ligand-to-metal charge transfer and intraligand $\pi^* \rightarrow \pi$ transitions of the neutral ligand.[18]

In summary, we have prepared and characterized the first (6,8)-connected self-penetrating network using an asymmetric neutral ligand based on dinuclear zinc clusters, as six-connected nodes, and trinuclear zinc clusters, as eight-connected nodes. The successful isolation of this species not only provides an intriguing example of chemical topology but also confirms the significant potential of constructing new binodal high-connected frameworks from different metal clusters. Appropriate choices of asymmetric ligands with different coordinating conditions, as well as spatial linkers, should lead to the discovery of a large variety of new mixed-connected topological structures and types in the near future.

We are thankful for financial support from the Program for Changjiang Scholars and Innovative Research Team in University, the National Natural Science Foundation of China (no. 20573016), and the Science Foundation for Young Teachers of Northeast Normal University (no. 20070309).

Notes and references

‡ Synthesis of **1**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (297 mg, 1.0 mmol), H_2bdc (166 mg, 1.0 mmol), **L** (184 mg, 0.5 mmol) and water (10 mL) was heated at 150 °C for 72 h in a 23 mL Teflon reactor under autogenous pressure and then cooled to room temperature at a rate of 10 °C h^{-1}. Colorless crystals of **1** were obtained in 76.2% yield based on $Zn(NO_3)_2 \cdot 6H_2O$. Elemental analysis calc. for $C_{44}H_{32}N_2O_{13}Zn_{2.5}$ (M = 960.14): C, 55.03; H, 3.56; N, 2.92. Found: C, 55.01; H, 3.59; N, 2.91%. IR (/cm^{-1}): 3412 (s), 3173 (m), 1598 (s), 1502 (s), 1384 (s), 1321 (s), 1143 (m), 1012 (w), 823 (s) and 750 (m).

§ Crystallographic data for **1** ($C_{44}H_{32}N_2O_{13}Zn_{2.5}$), M = 960.14, monoclinic, space group $P2_1/c$, a = 16.9840(18), b = 16.3420(19), c = 15.648(2) Å, β = 103.230(2)°, V = 4227.9(9) $Å^3$, Z = 4, μ = 1.479 mm^{-1}, D_c = 1.508 Mg m^{-3}, $F(000)$ = 1956, 10115 unique (R_{int} = 0.0421), $R1$ = 0.0654, $wR2$ = 0.1609 ($I > 2\sigma(I)$), GOF = 1.103, max. electron density = 1.236 e $Å^{-3}$, min. electron density = −1.230 e $Å^{-3}$. A total of 25411 data were measured in the range $1.75 < \theta < 28.37°$. The data were corrected for absorption by the multi-scan, giving minimum and maximum transmission factors of 0.593 and 0.755, respectively. CCDC 652044. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b709835a

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