

An Unprecedented 3D Self-catenated Four-coordinated Dense Net of Silver-Organic Framework

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The rational design and synthesis of novel coordination polymers (CPs) or metal-organic frameworks (MOFs) is of great interest in modern inorganic chemistry not only for their potential applications as functional materials in fields such as gas storage, luminescence, catalysis, ion exchange, and so on, but also for their intriguing variety of topologies.¹ In particular, topology focuses on the network connectivity generated *via* the reduction of periodic nets into node-and-linker/vertex-and-edge representations, which helps greatly the understanding of structural complexity, variety and entanglements of the coordination architectures.^{2,3} It is no doubt that the discovery of artificial MOFs with predicted subnet topologies is of great significance in understanding supernet-subnet relations based on the knowledge of the chemical properties of the components (metals and ligands). Therefore, tiny variation of nodes may generate huge differences on topologies since the network topology is reflected by the symmetry of nodes and nature of edges.^{2g}

From both zeolite chemistry and crystal engineering points of view, the nets built from 4-coordinated (4-c) centers capture much attention both for their inherent interest (all zeolites are 4-c nets) and from a theoretical point of view: many 4-c nets have been deduced and summarized firstly by Wells^{2a} followed by several comprehensive discussions.⁴ O’Keeffe collected some “dense and rare” 4-c nets in 1991,⁵ among which there is the first example of self-catenated 4-c net observed in a high-pressure polymorph of silica, coesite (**coe**) which appears to be unique among nets found in nature in that it contains 8-rings that are linked as in a chain. In 2000, the only example so far of coordination polymer with **coe** net was isolated.⁶ O’Keeffe⁵ also derived a new uninodal net by merging together pairs of vertices of the **coe** net, which still maintains the self-catenation property and contains the smallest 6-rings. This new net was considered “not very likely to be found as a net in a crystal structure but nevertheless clearly belongs in the relatively small inventory of uninodal four-connected nets.” Because there was one distance between two nodes that was shorter than edges.⁵ The net has a vertex symbol of 6.6.6.6.6.2.8₂ (point symbol 6⁵.8) and named **mok** in RCSR database.⁷ Recently, Gong *et al.* reported two **mok** nets built by amide derivative and

organodicarboxyl co-ligands and existing in three-fold interpenetrated array.⁸

Self-catenated framework structures are a subclass of the most fascinating topological nets in the family of entanglements. These species are single nets having the peculiarity that the smallest topological rings are catenated by the other smallest rings belonging to the same network.⁹ As has been proved, using the co-ligands of long and flexible organonitrogen and organocarboxylate ligands is capable to synthesize the self-catenated CPs/MOFs.^{8,10} In this work, we report the synthesis, topology structure and fluorescence properties of one example of Ag-MOF architecture constructed by co-ligands, namely, [Ag(bbbm)(H₂BDC)_{0.5}(BDC)_{0.5}]_n (bbb = 1,1’-(1,4-butanediyl)-bis-1*H*-benzimidazole, H₂BDC = 1,4-benzenedicarboxylic acid), featuring self-catenated 4-coordinated uninodal dense (TD₁₀ = 2953) underlying net.

Experimental Section

Materials and Characterization Methods. All the reagents and solvents for synthesis were commercially available and used directly without further purification. The ligand bbbm was synthesized according to a literature method.^{10d} Elemental analysis of C, H, N was carried out with a Perkin-Elmer 240C elemental analyzer. The IR spectrum was obtained on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the 4000-400 cm⁻¹ range. Thermal analysis was performed on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C under nitrogen atmosphere with a heating rate of 10 °C min⁻¹. Luminescence spectrum for the solid sample was determined with a Cary Eclipse fluorescence spectrophotometer. Powder X-ray diffraction measurement was performed on a Bruker Smart 1000 CCD X-ray diffractometer using Cu-K α radiation (λ = 0.1542 nm) in the 2 θ range of 5-50° with a step size of 0.02° and a scanning rate of 10° min⁻¹.

Synthesis of [Ag(bbbm)(H₂BDC)_{0.5}(BDC)_{0.5}]_n. A mixture of silver acetate (33 mg, 0.2 mmol), H₂BDC (33 mg, 0.2 mmol), bbbm (58 mg, 0.2 mmol) and H₂O (16 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 140 °C for 3 days under autogenous pressure. After the mixture

was cooled to room temperature at a rate of $5\text{ }^{\circ}\text{C h}^{-1}$, colorless block crystals of the complex were obtained with yield 51% (based on Ag). Anal. Calcd. for $\text{C}_{26}\text{H}_{23}\text{AgN}_4\text{O}_4$ (563.35): C, 55.43; H, 4.11; N, 9.95%. Found: C, 55.72; H, 3.96; N, 10.15%. IR (KBr, cm^{-1}): 3083w, 2925w, 1701s, 1635s, 1508s, 1450m, 1403w, 1376m, 1297m, 1264w, 1226s, 1010m, 913w, 739s, 501m.

Crystallography. Intensity data for the complex were collected at 293 K on a Bruker Smart 1000 CCD diffractometer with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). Data reductions and absorption corrections were carried out by the SAINT and SADABS software packages.^{S1} The structure was solved by direct methods and refined by full-matrix least squares based on F^2 using Sheldrick's SHELXTL program package.^{S2} The positions of some of the heavier atoms, including the silver atom, were located from the E -maps and other non-hydrogen atoms were found in a series of alternating difference Fourier maps and least-square refinements. The hydrogen atoms of organic ligands were generated geometrically and were riding on their parent atoms. CCDC-917949 contains the supplementary crystallographic data. The crystallographic data for the complex are summarized in Table S1†, and the selected bond lengths and angles are listed in Table S2† († means the supporting information file.).

Results and Discussion

The crystals of the complex conform to the monoclinic space group $P2_1/c$ and each asymmetric unit contains one Ag(I) ion, one bbbm ligand, a half of H_2BDC and a half of BDC dianion. As illustrated in Figure 1(a), the Ag(I) ion has a distorted tetrahedral geometry with two nitrogen atoms from two different bbbm ligands ($\text{Ag1-N1} = 2.182(2)\text{ \AA}$, $\text{Ag1-N3\#1} = 2.178(2)\text{ \AA}$, symmetry codes: $\#1 = x, 3/2-y, z-1/2$) and two oxygen atoms from one H_2BDC and one BDC dianion ($\text{Ag1-O3} = 2.546(2)\text{ \AA}$, $\text{Ag1-O1} = 2.567(2)\text{ \AA}$). The μ_2 -bridging bbbm and carboxylic ligands coordinate to adjacent Ag(I) atoms to generate $-\text{Ag}-\text{bbbm}-\text{Ag}-$ wave-like chain, $-\text{Ag}-\text{BDC}-\text{Ag}-\text{H}_2\text{BDC}-\text{Ag}-$ zigzag chain, respectively. The $\text{Ag}\cdots\text{Ag}$ distance bridged by bbbm is 13.319 \AA ; the coordinated silver atoms $\text{Ag}\cdots\text{Ag}$ separations are 9.756 \AA (for BDC dianion ligand) and 12.396 \AA (for H_2BDC ligand). Further, these 1D infinite chains along different directions are interconnected into a 3D network. Each Ag atom connects with four adjacent Ag atoms through the linking of two bbbm and two carboxylic ligands, which can be simplified as a 4-connected node. The bbbm and carboxylic ligands both coordinate with two Ag atoms, only considering as linkers. Topological analysis using TOPOS software¹¹ identifies the resulting 3D network as a new type topology (TOPOS calculations†), which is self-catenated with 6-rings catenation and has the same point symbol ($6^5.8$) with **mok**, but different vertex symbol, $6.6.6.6.6_2.10_{12}$, *i.e.* contains 10-rings instead of 8-rings in **mok** (vertex symbol $6.6.6.6.6_2.8_2$). We have deposited this net to TOPOS TTD collection¹² under the named **cg4**. Like **mok**, it is self-

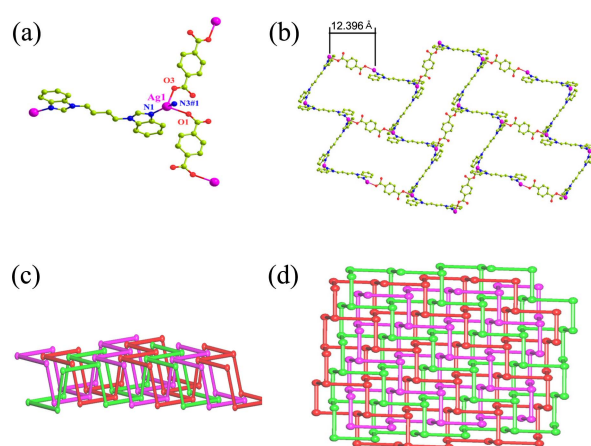


Figure 1. View of: (a) the coordination environment of Ag(I) center in the complex; (b) the **hcb** subnet with sides of 13.319 and 12.396 Å; (c) the 3-fold interpenetrated **hcb** array; (d) the 3-fold interpenetrated **hcb** array along (100).

catenated, but even stronger. To show this, let us use the method of describing self-catenated net as an interpenetrating array by breaking some edges. Gong *et al.* applied this method to represent **mok** as an array of two interweaved honeycomb (**hcb**) layers.⁸

In the complex, two types of interpenetrating **hcb** layers can be obtained by breaking one of two rather weak Ag–O bonds, respectively. If we ignore the Ag–O bonds of 2.567 \AA , *viz.*, the Ag–Ag bonds of 9.756 \AA are disconnected in the underlying net that results in a set of interpenetrated **hcb** subnets. In each **hcb** subnet, adjacent $-\text{Ag}-\text{bbbm}-\text{Ag}-$ wave-like chains are bridged by H_2BDC *via* Ag–O bonds of 2.546 \AA (Fig. 1(b)). The basic 6-membered cycles of the **hcb** subnet are formed by six Ag, four bbbm and two H_2BDC with the sides of 13.319 and 12.396 Å. Three kinds of the **hcb** subnets interpenetrate each other by sharing the same average plane to accomplish a 3-fold interpenetrated **hcb** array (Fig. 1(c)-(d)). Similarly, a 5-fold interpenetrated **hcb** array can also be obtained by breaking Ag–O bonds of 2.546 \AA , or, equivalently, by cutting the Ag–Ag edges of 12.396 \AA

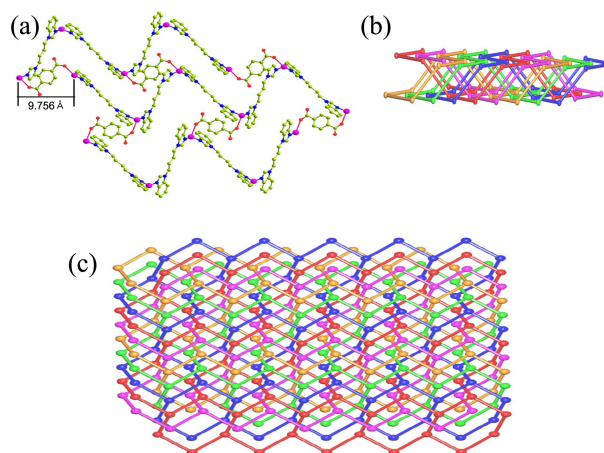


Figure 2. View of: (a) the **hcb** subnet with sides of 13.319 and 9.756 Å; (b) the 5-fold interpenetrated **hcb** array; (c) the 5-fold interpenetrated **hcb** array along (100).

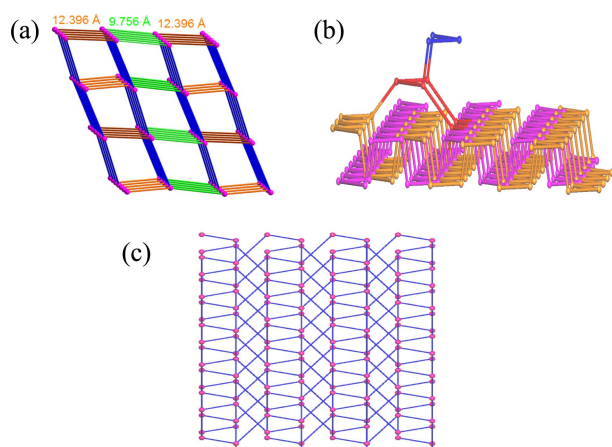


Figure 3. View of: (a) the **cgh4** net along (010), with blue bonds of 13.319 Å, orange bonds of 12.396 Å and green bonds of 9.756 Å; (b) the 6-ring from 3-fold (5-fold) array cross-link neighboring three **hcb** subnets of 5-fold (3-fold) subunit; (c) the **cgh4** net along (001) with ABAB stacking sequence of 3-fold **hcb** and 5-fold **hcb** arrays.

in the underlying net. In this case, adjacent $-\text{Ag}-\text{bbm}-\text{Ag}-$ wave-like chains are bridged by BDC dianions *via* $\text{Ag}-\text{O}$ bonds of 2.567 Å to give a wavy **hcb** subnet (Fig. 2(a)). The basic 6-membered cycles of the **hcb** subnet have the same components and configurations as the 3-fold **hcb** array (Fig. 2(b)-(c)). Furthermore, each 6-ring from 5-fold (3-fold) **hcb** subunit links two interpenetrated **hcb** nets of neighboring 3-fold (5-fold) **hcb** subunit on one side and another one on the other side (Fig. 3(a)-(b)). Thus, as viewed along (001), 3-fold **hcb** and 5-fold **hcb** subunits are interconnected alternately with an ABAB stacking sequence to generate an overall 3D single **cgh4** underlying net (Fig. 3(c)).

To find other nets that are topologically related with **cgh4**, we applied the method of shell graph, *i.e.* a graph obtained by successive growth of n coordination shells around a given node.¹³ The larger shell graphs are topologically equal for two nets to be compared, the more similar are the two nets.

We have considered shell graphs of **cgh4** with all 4-coordinated RCSR nets and found five nets to be similar to **cgh4** up to $n=3$: **cds**, **dmp**, **mok**, **nfc**, **zst**, out of which only **mok** and **zst** are self-catenated. All the five nets have point symbol $6^5.8$, moreover, **zst** has the same vertex symbol as

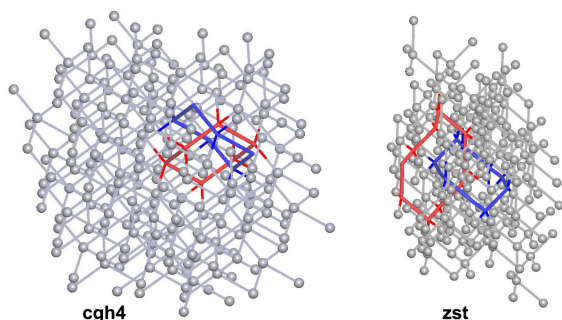


Figure 4. Two topologically equivalent 245-atom fragments of **cgh4** and **zst**. Catenated 6-rings (**cgh4**) or 10-rings (**zst**) are shown by different colors.

cgh4 and topologically equal shell graphs up to $n=5$ (Fig. 4). Thus, **zst** and **cgh4** are quite similar (the equal shell graphs contain 245 metal atoms each), although in **zst** the self-catenation occurs between 10-rings, not 6-rings as in **cgh4** or **mok**. As a result, **zst** cannot be decomposed into **hcb** interpenetrated array. According to RCSR, **zst** was recently revealed by Zheng *et al.*¹³ in $\text{Li}(\text{benzimidazolate})(4,4'\text{-bpy})$ (ALIGOS), however, the authors did not mention the self-catenation. Thus **zst** and **cgh4** is a rare example of nets that are topologically equal in so large region; we do not know other such examples for self-catenated nets. Strong self-catenation provides high topological density of **cgh4** ($\text{TD}_{10} = 2953$); it is the highest density compared to the five similar $6^5.8$ nets and other dense nets described by O'Keeffe.⁶ Up to now, only one 4-coordinated net (**tcb**) with higher density ($\text{TD}_{10} = 3113$) was found in MOFs;¹⁴ it is also self-catenated.

IR Spectrum and XRPD Pattern. In the IR spectrum of the complex, The characteristic bands at 1508, 1226 and 1010 cm^{-1} can be assigned to the $\nu_{\text{C}=\text{C}}$, $\nu_{\text{C}=\text{N}}$ stretching vibration of benzimidazole ring of **bbm** ligand. A broad band at 3083 cm^{-1} may be assigned to the stretching vibrations (ν_{OH}) of H_2BDC ; the band for protonated carboxylate groups of H_2BDC was observed at 1701 cm^{-1} ; the strong bands at 1635 cm^{-1} , 1376 cm^{-1} can be assigned to the ν_{COO} asymmetrical and symmetrical stretching vibration, *viz.* the $\Delta\nu[\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})]$ value is 269 cm^{-1} , which indicates that the coordinated carboxyl groups of carboxylic ligand adopting monodentate mode.^{15,16} The X-ray powder diffraction (XRPD) patterns of the complex are shown in Figure S1†. These patterns are consistent with those of simulated based on the structure models derived from single-crystal X-ray diffraction data. It can be well considered that the bulk synthesized materials and the crystals used for diffraction are homogeneous.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed to explore the thermal stability of the complex (see Figure S2†). The complex was thermal stable up to $248\text{ }^\circ\text{C}$. The weight loss is 78.6% between 249 to $419\text{ }^\circ\text{C}$, corresponding to the decomposition of all ligands (calcd. 79.4%). The remaining weight of 21.4% was assumed to the for-

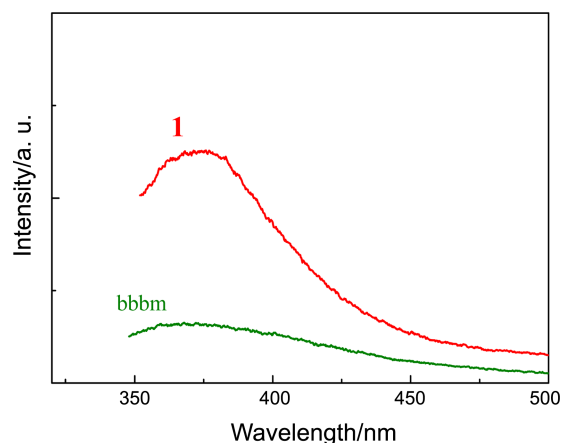


Figure 5. The emission spectra of the complex and the free **bbm** ligand.

mation of Ag₂O (20.6%).

Photoluminescence Property. The photoluminescence property of the complex was studied in the solid state at room temperature. As shown in Figure 5, the free bbbm ligand displays luminescence with emission maximum at 368 nm upon excitation at 350 nm, which can probably be assigned to the $\pi \rightarrow \pi^*$ transitions. The luminescence peak at about 376 nm is found in the emission spectrum when excite at 338 nm for the complex. 1,4-benzenedicarboxylic acid shows very weak $n \rightarrow \pi^*$ transitions and contribute a little to the photoluminescence of the complex at room temperature.¹⁷ The emission of the complex is similar to that of the free bbbm ligand, which is probably due to the intraligand $\pi^* \rightarrow \pi$ charge transitions of bbbm ligand.

In summary, we have synthesized and topologically characterized a silver(I) metal-organic framework with novel (6⁵.8) **cgh4** underlying net. This MOF gives a beautiful example of strongly self-catenated topologically dense framework that can be related to other self-catenated net (**mok**) by the procedure of decomposing initial self-catenated net into array of interpenetrating isolated subnets.

Supplementary Material. CCDC number: 917949 for the complex. The data can be obtained free of charge via https://services.ccdc.cam.ac.uk/structure_deposit (or from the Cambridge Cryst allographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033(44); or deposit@ccdc.cam.ac.uk).

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