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

Shu-Lin Xiao, Guang-Hua Cui,* Vladislav A. Blatov,+† Jian-Chen Geng, and Guang-Yue Li

College of Chemical Engineering, Hebei United University, 46 West Xinhua Road, Tangshan 063009, Hebei P.R. China
*E-mail: tscghua@126.com
+Department of Chemistry, Samara State University, Ac. Pavlov St. 1, Samara 443011, Russia; Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia. E-mail: blatov@samsu.ru

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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. 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. 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.

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 followed by several comprehensive discussions. O’Keeffe collected some “dense and rare” 4-c nets in 1991, among which there is the first example of self-catenated 4-c net observed in a high-pressure polymorph of silica, coesite (coes) 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 coes net was isolated. O’Keeffe also derived a new uninodal net by merging together pairs of vertices of the coes 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. The net has a vertex symbol of 6.6.6.6.6.6;8 (point symbol 6h8) and named mok in RCSR database. Recently, Gong et al. reported two mok nets built by amide derivative and organodicarboxylic co-ligands and existing in three-fold interpenetrated array.

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 net. As has been proved, using the co-ligands of long and flexible organo-nitrogen and organocarboxylate ligands is capable to synthesis the self-catenated CPs/MOFs. 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]0 (bbbm = 1,1’-(1,4-butanediyl)-bis-1H-benzimidazole, H2BDC = 1,4-benzenedicarboxylic acid), featuring self-catenated 4-coordinated uninodal dense (TD = 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. 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-Kα radiation (λ = 0.1542 nm) in the 2θ 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]0. 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 °C h⁻¹, colorless block crystals of the complex were obtained with yield 51% (based on Ag). Anal. Calcd. for C₆₅H₅₂AgNaO₂ (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, 1101m, 913w, 739s, 501m.

**Crystalllography.** Intensity data for the complex were collected at 293 K on a Bruker Smart 1000 CCD diffractometer with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å). Data reductions and absorption corrections were carried out by the SAINT and SADABS software packages. The structure was solved by direct methods and refined by full-matrix least squares based on F² using Sheldrick’s SHELXTL program package. 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 P2₁/c and each asymmetric unit contains one Ag(I) ion, one bbbm ligand, a half of H₂BDC 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 (Ag1–N1 = 2.182(2) Å, Ag1–N3#1 = 2.178(2) Å, symmetry codes: #1 = x, 3/2−y, z−1/2) and two oxygen atoms from one H₂BDC and one BDC dianion (Ag1–O3 = 2.546(2) Å, Ag1–O1 = 2.567(2) Å). The μ₂-bridging bbbm and carboxylate ligands coordinate to adjacent Ag(I) atoms to generate −Ag−bbbm−Ag− wave-like chain, −Ag−BDC−Ag−H₂BDC−Ag− zigzag chain, respectively. The Ag−Ag distance bridged by bbbm is 13.319 Å; the coordinated silver atoms Ag−Ag separations are 9.756 Å (for BDC dianion ligand) and 12.396 Å (for H₂BDC 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 software 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°8) with mok, but different vertex symbol, 6.6.6.6.6:1012, i.e. contains 10-rings instead of 8-rings in mok (vertex symbol 6.6.6.6.6:8). We have deposited this net to TOPOS TTD collection under the named cgb4. Like mok, it is self-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.

**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).

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 Å, viz., the Ag–Ag bonds of 9.756 Å are disconnected in the underlying net that results in a set of interpenetrated hcb subnets. In each hcb subnet, adjacent −Ag−bbbm−Ag− wave-like chains are bridged by H₂BDC via Ag–O bonds of 2.546 Å (Fig. 1(b)). The basic 6-membered cycles of the hcb subnet are formed by six Ag, four bbbm and two H₂BDC 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 Å, or, equivalently, by cutting the Ag–Ag edges of 12.396 Å.

**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).
We applied the method of shell graph, by successive growth of node. Subunit links two interpenetrated components and configurations as the 3-fold overall 3D single nately with an ABAB stacking sequence to generate an other side (Fig. 3(a)-(b)). Furthermore, each 6-ring from 5-fold (3-fold) subnet (Fig. 2(b)-(c)). Thus, as viewed along (001), 3-fold subnet have the same vertex symbol as 3-coordinated nets and found five nets to be topologically equal for 6-ring system.

**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) subnet; (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 –Ag–bbbm–Ag–wave-like chains are bridged by BDC dianions via Ag–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. The larger shell graphs 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 (TD0 = 2953); it is the highest density compared to the five similar 6.8 nets and other dense nets described by O’Keeffe. Up to now, only one 4-coordinated net (tcb) with higher density (TD0 = 3113) was found in MOFs; it is also self-catenated.

**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.

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

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 ν$_{as}$ and ν$_{sym}$ stretching vibration of benzimidazole ring of bbbm ligand. A broad band at 3083 cm$^{-1}$ may be assigned to the stretching vibrations (ν$_{OH}$) of H$_2$BDC; the band for protonated carboxylate groups of H$_2$BDC was observed at 1701 cm$^{-1}$; the strong bands at 1635 cm$^{-1}$, 1376 cm$^{-1}$ can be assigned to the ν$_{as}$ and ν$_{sym}$ stretching vibration, ν$_{C=O}$, the Δν$_{as}$ and ν$_{as}$, ν$_{sym}$ value is 269 cm$^{-1}$, which indicates that the coordinated carboxyl groups of carboxylic ligand adopting monodentate mode.

**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 °C. The weight loss is 78.6% between 249 to 419 °C, corresponding to the decomposition of all ligands (calcd. 79.4%). The remaining weight of 21.4% was assumed to the for-
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.\textsuperscript{17} The emission of the complex is similar to that of the free bbbm ligand, which is probably due to the intra-ligand $\pi^* \rightarrow \pi$ charge transitions of bbbm ligand.

In summary, we have synthesized and topologically characterized a silver(I) metal-organic framework with novel (6\textsuperscript{2}8\textsuperscript{2}4\textsuperscript{-cgh4} underlying net. This MOF gives a beautiful example of strongly self-catened topologically dense framework that can be related to other self-catened net (mok) by the procedure of decomposing initial self-catened 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://structures.ccdc.cam.ac.uk/structure_deposit (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033(44); or deposit@ccdc.cam.ac.uk).

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