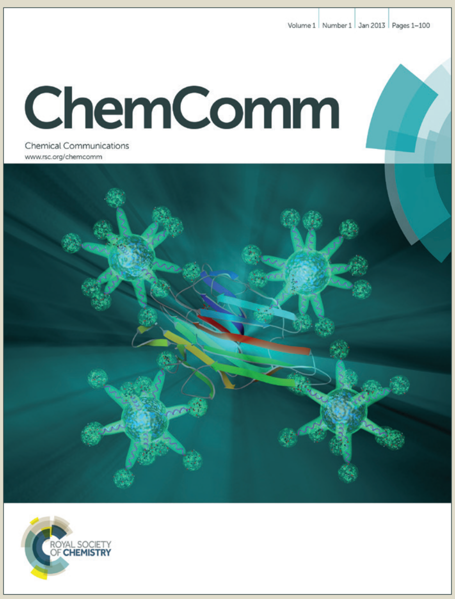

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ARTICLE TYPE

Structure-Directing Method to Semiconductive Zeolitic Cluster-Organic Frameworks with Cu_3I_4 Building Units

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Two semiconductive cluster-organic frameworks based on Cu_4I_4 and Cu_3I_4 building units were obtained by the application of different organic structure-directing agents; the latter Cu_3I_4 nodes are tetrahedrally connected through 1,4-diazabicyclo[2.2.2]octane (DABCO) linkers and Cu-I bridges, giving rise to a zeolitic framework with SOD topology.

Zeolites are a class of well known crystalline porous materials containing TO_4 (T = Si, Al, P, Ge) tetrahedral units, which are of current interest for their industrial applications in catalysis, ion exchange and gas separation.[1-4] With the development of coordination chemistry and crystal engineering, the search for new zeolitic materials has been extended from traditional pure inorganic zeolites to zeotype metal-organic frameworks (MOFs), such as zeolitic imidazolate frameworks (ZIFs),[5-8] and boron imidazolate framework (BIFs).[9-10] In the syntheses of inorganic zeolites, organic structure-directing agents (OSDAs) are widely applied and make significant influence on the structures and properties of these inorganic porous materials.[11-13] However, this OSDAs methodology has received much less attention in the field of zeotype MOFs,[14,15] whose structure design and performance modulation usually relies on the rational selection of organic ligands.[5-10]

For the construction of zeotype structures, tetrahedrally connected building units are necessary, like Si and Al in aluminosilicate zeolites,[11] Zn in ZIFs,[7] Li and B in BIFs[16]. To improve their performances in targeted applications and create multifunctional zeolitic materials, there is a high demand for new multinuclear building units which endow the materials with large pore sizes, unique catalytic attributes and possibility of introducing additional functionalities. It has been reported that chalcogenide clusters can serve as pseudotetrahedral units to form zeotype structures.[17] Metal-halide clusters, especially metal iodides, display comparable polarizabilities to chalcogenides, making them also suitable to serve as tetrahedral units of zeotype frameworks. Whilst, due to the multiple forms and structural diversities of metal iodides, it still remains a great challenge to prepare metal-iodides clusters based zeolitic materials.[18-20]

In previous study, we have successfully prepared a MTN-type zeolitic porous framework using Cu_4I_4 clusters as tetrahedral building units.[6] To continue our research on cluster-organic zeolitic materials and obtain various zeotype frameworks with fascinating properties, we decide to introduce the OSDAs method

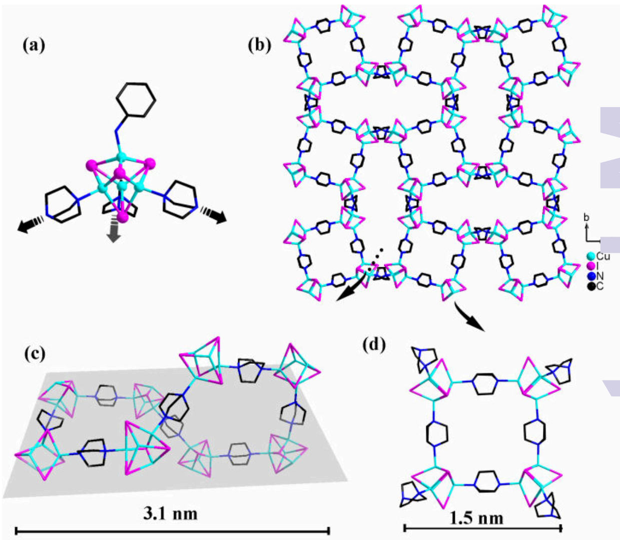

Fig. 1 (a) Coordination environment of the Cu_4I_4 cubane in **1**. (b) The top view of the 3-connected layer structure of **1**. (c-d) The wire view of the twisted 8-member ring and square wheel, respectively. The CHA ligands are omitted for clarity.

into this area and investigate the influence of different OSDAs on the composition, geometry and coordination of tetrahedral iodide clusters. Herein we report two cluster-organic frameworks, $[(Cu_4I_4)_2(DABCO)_3(CHA)_2]$ (**1**) and $[(Cu_3I_4)(DABCO)]_2[Cu(DACH)_2]$ (**2**), where CHA = cyclohexylamine and DACH = 1,2-diaminocyclohexane are used as structure-directing agents. The changes of OSDAs result in great diversity of coordination environments of cuprous halide clusters and topological differences among the obtained frameworks. Compound **1** features a layered *fes* network based on 3-connected Cu_4I_4 clusters, while complex **2** exhibits 3D zeotype framework with SOD topology constructed from 4-connected Cu_3I_4 clusters. Moreover, optical absorption studies reveal that these two complexes are semiconductive materials with optical band gaps of 5.01 eV and 3.63 eV, respectively.

The two compounds were solvothermally synthesized‡ and structurally characterized by single-crystal X-ray diffraction. Complex **1** contains cubane type Cu_4I_4 clusters with four vacancies wholly occupied by N atoms. Thereinto, one N atom comes from CHA, and the other three ones belong to DABCO ligands (Fig. 1a). Although the coordination of CHA with Cu has early been reported, the graft of CHA to copper halide clusters has not been observed according to the Cambridge Structural Database (CSD, Version 5.35, March 2015 update). As CHA is a unidentate terminal ligand, the connectivity of the Cu_4I_4 cluster is reduced from four to three. Thus the coordination geometry of the Cu_4I_4 cluster is changed from tetrahedral to tripodal. Each Cu_4I_4 cluster is connected to three neighbouring ones through three linear DABCO linkers, forming a two-dimensional (2D) double-decker network with a thickness of 3.6 nm (Fig. 1b, S5). And this layer structure is prevented from forming a higher order dimensional framework by the terminal CHA ligands that hang beside the two sides of the layer.

A prominent structural feature of **1** is the presence of two types of rings on the basis of Cu_4I_4 clusters. The larger twisted 8-ring window consists of eight Cu_4I_4 clusters and eight DABCO ligands (Fig. 1c), while the smaller 4-ring window contains four Cu_4I_4 clusters and four DABCO ligands (Fig. 1d). All 4-ring windows are parallel to the *ab* plane. The diameter of the twisted 8-ring and 4-ring is approximately 3.1 nm and 1.5 nm, respectively. Every 4-ring is encircled by four twisted 8-rings, whereas every twisted 8-ring is surrounded by four neighboring perpendicular ones and four 4-rings (Fig. S6). From the viewpoint of topology, the layer network of **1** can be described as a 3-connected *fes* topology considering the Cu_4I_4 clusters as nodes and the linear DABCO ligands as linkers (Fig. S7). It is worth noting that the adjacent layers in **1** are aligned in the -ABAB- sequence along the *c* axis, and the staggered arrangement of the layers creates two types of channels (diameter 4.4 Å and 8.4 Å) along the *c* axis (Fig. S8).

To further explore the role of the OSDAs, we replace the CHA by DACH and keep other experimental parameters unchanged. To our surprise, complex **2** crystallizes in different space groups from complex **1**. The detailed structure analyses suggest that complex **2** features a 3D zeotype structure built from vertex-missing-cubane like Cu_3I_4 clusters, which are connected to four adjacent ones through two DABCO ligands and two Cu-I bridges. As is known, Cu_4I_4 cluster can serve as a tetrahedral node *via* four Cu ions to generate 4-connected MTN,[6] dia,[20] bbf,[21] 6^6,[22] and 6^54 topologies.[18] Here in structure **2**, Cu_3I_4 clusters are firstly applied as 4-connected nodes. Moreover, the Cu-I bridges between adjacent Cu_3I_4 subunits give rise to a pure inorganic chain along the *c* axis direction. Compared to the formerly reported cuprous iodide chain stabilized by double Cu-I bridges,[23] the Cu_3I_4 clusters herein are linked end to end through single Cu-I bridge (Fig. S9). The propagation of these cuprous iodide chains by the DABCO ligands along the *a* and *b* directions forms the 3D framework structure of **2** with hexagonal channels (Fig. 2b, S10). These channels are further blocked by the $[Cu(DACH)_2]^{2+}$ cations, which reside in the rhomboid 6-membered circuits *via* weak interactions (Cu···I, 3.3 Å) and balance the negative charges of the framework (Fig. S11). Thus, the total potential solvent-accessible volume ratio is only 25.4% according to the PLATON program.

Most interestingly, if the Cu_3I_4 clusters are assigned as 4-connected nodes, the framework of **2** can be simplified into a zeotype SOD topology (Fig. 2c). The dimensions of the edges of the 4-connected node are about 6.8 Å and 10.1 Å, which are much longer than those of TO_4 in zeolites (2.4 Å) (Fig. S12). The T-O-T angles in standard tetrahedral configuration are about 140°,

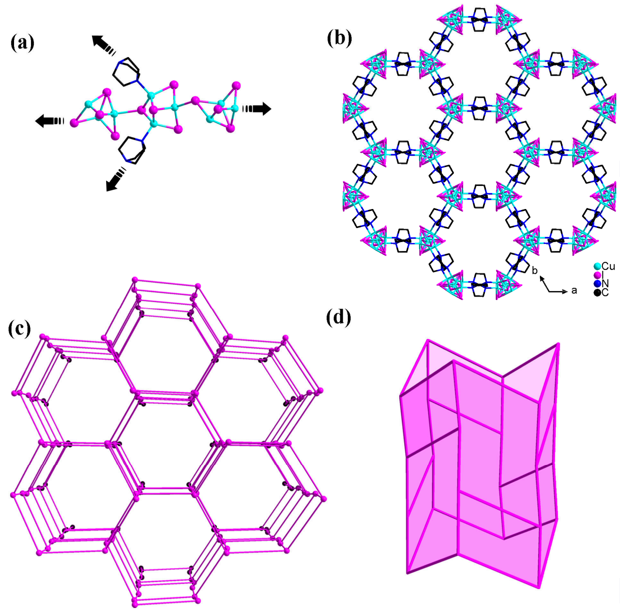

Fig. 2 (a) Coordination environment of the Cu_3I_4 cluster in **2**. (b) The top view of the 3D zeotype framework of **2**. (c) The perspective view of the SOD topology. (d) The distorted SOD cage.

while the counterparts here are 57.7°, 63.8°, 116.2° and 116.9°. Resulted from the irregular edges and angles of the nodes, the SOD cages in **2** are largely distorted (Fig. 2d). In a typical SOD cage of zeotype MOFs, there are 24 nodes and 36 linkers, most of which are organic ligands. However, half of the linkers in **2** are inorganic bridges. Additionally, the rhomboid 4-membered, 6-membered and chair-like 6-membered circuits here are unusual configurations in comparison to the typical SOD cages (Fig. S13).

From the synthesis and structural analysis of compound **1** and **2**, we can conclude that structure-directing agents make significant influence on the formation of cuprous iodide clusters based frameworks. The unidentate CHA molecules in complex **1** act as terminal tailors to reduce the connectivity of Cu_4I_4 nodes to three and thus prevent the layer from extending to high dimensional structure. Whilst the bidentate DACH molecules in complex **2** act as chelating ligands of isolated Cu^{2+} ions and only function as charge balancing guests, making the Cu_3I_4 clusters in **2** remain tetrahedrally connected building units to give rise to SOD-type framework. These results illustrate that the OSDAs method could be an efficient method for the construction of cluster based zeolitic MOFs.

The optical absorption spectra of compounds **1** and **2** were measured by a solid state ultraviolet-visible (UV-vis) diffuse reflection method at room temperature (Fig. 3). According to the Kubelka-Munk function, $(F(R) = (1-R)^2/2R)$,[24] the optical band gaps are 5.01 eV and 3.63 eV for **1** and **2**, respectively (Fig. S14). This result is consistent with the color of their crystals, with white for **1** and red for **2**. Generally, the band gap of the materials decrease with the increase of the framework density.[25] Similar behavior has been observed here. The layered network of complex **1** is less dense than the zeotype framework of compound **2**. Consequently, the former one exhibits a larger band gap. Moreover, by comparing the UV absorption spectra of compound **1** and pure DABCO ligands, it is reasonable to assign the peak

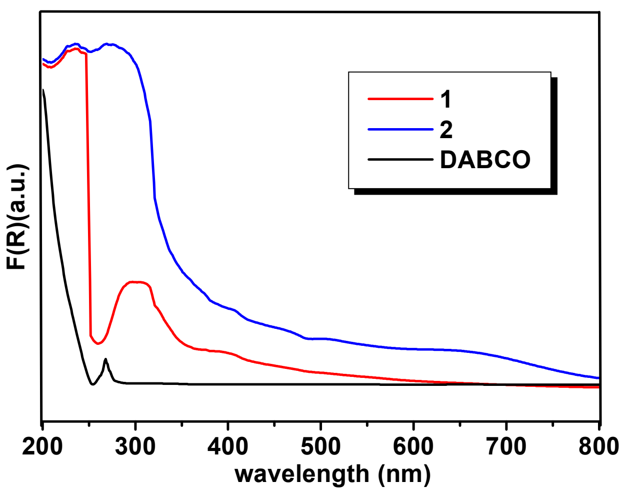

Fig. 3 Plots of UV-*vis* absorption spectra of **1**, **2** and DABCO ligands.

between 200 and 250 nm to the absorption of DABCO ligands, and the increase of the intensity might be due to the coordination interactions. Whilst the absorption above 280 nm should be attributed to the presence of Cu_4I_4 clusters in **1**. Furthermore, because of the inorganic cuprous iodide chains, the corresponding Cu_3I_4 absorption of complex **2** becomes much stronger than that in **1**. Therefore, **2** displays almost a single broad peak that covers the absorption areas of both **1** and DABCO ligands. These results indicate that increasing the dimensions of inorganic compositions in cluster-organic frameworks could significantly strengthen their long wavelength absorption.

The photoluminescence properties of the two complexes have been studied, which are similar to other previously reported cuprous halide cluster complexes (Fig. S4).[6,20] In view of the UV cut off edge and the non-centrosymmetric space group *I*422, the second-order nonlinear optical (NLO) measurement of compound **1** was carried out. The result shows it has SHG intensity of 0.2 versus that of technologically useful potassium dihydrogen phosphate (KDP).

In summary, two cluster-organic frameworks exhibit different semiconductive properties are obtained by means of OSDAs. The coordination positions of bulky larger Cu_4I_4 clusters in **1** can partly be occupied by unidentate OSDA, reducing the connectivity to three and forming a layered *fes* network. Bidentate OSDA does not participate the coordination of smaller Cu_3I_4 clusters and gives rise to a 4-connected zeotype framework **2** with SOD topology. Moreover, **2** shows smaller band gap than **1** due to the presence of cuprous iodide chains in this zeolitic structure. Our results demonstrate that the OSDAs approach has great potential for the construction of zeotype frameworks and also enrich the building units family of zeolitic materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-Ray structure data in CIF files for compounds **1** and **2**; Materials and physica measurements; IR spectra; TGA curves; PXRD patterns; luminescent dat CCDC 1041633 and 1041634.

‡ Synthesis of $[(Cu_4I_4)_2(DABCO)_3(CHA)_2]$ (**1**): A mixture of DABC (0.097 g), CuI (0.306 g), cyclohexylamine (CHA) (0.101 g) was added to a mixed solvent of DMF (3 ml), and EtOH (2 ml). After stirring for half an hour, the mixture was sealed in a 20 ml vial an transferred into an preheated oven at 100 °C for 3 days. When cooled to room temperature, white crystals of complex **1** wer obtained (Yield: 30%). Synthesis of $[(Cu_3I_4)(DABCO)]_2[Cu(DACH)_2]$ (**2**): red crystals of complex **2** was obtained by the similar procedure of complex **1** except for using DACH instead of CHA (Yield: 31%).

§ Crystal data for **1**: $C_{30}H_{58}Cu_8I_8N_8$, *Mr* = 2054.36, tetragonal, I422, a = 18.5097(3) Å, c = 36.1113(15) Å, V = 12372.1(6) Å^3, Z = 8, D_c = 2.206 cm^{-3}, μ = 6.713 mm^{-1}, F (000) = 7600, GOF = 1.067. Of total 14340 reflections collected, 5431 are unique (R_{int} = 0.0317). R_1/wR_2 = 0.0390/0.1064 for 4446 reflections and 210 parameters (I>2σ(I)).Crysta data for **2**: $C_{24}H_{44}Cu_7I_8N_8$, *Mr* = 1904.65, trigonal, $R\bar{3}$, a = 25.9051(15) Å, c = 20.4603(16) Å, V = 11890.9(13) Å^3, Z = 9, D_c = 2.394 g cm^{-3}, μ = 7.460 mm^{-1}, F (000) = 7839, GOF = 1.016. Of total 6874 reflection collected, 4616 are unique (R_{int} = 0.0479). R_1/wR_2 = 0.0631, 0.1478 fo 2936 reflections and 214 parameters (I>2σ(I)).

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