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Luminescent MTN-Type Cluster−Organic Framework with 2.6 nm Cages

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Supporting Information

ABSTRACT: From a basic tetrahedral Cu_4I_4 cluster, a new **MTN**-type cluster−organic framework (**COZ-1**) containing giant 6^45^{12} and 5^{12} cages was successfully constructed. The 6^45^{12} cage has an inner diameter of 2.6 nm and a large pore volume of 9.2 nm^3; these tetrahedral Cu_4I_4 clusters with bulky size offer new opportunities for not only the formation of 4-connected zeotype structures but also the integration of porosity and photoluminescent properties from both the cluster and the framework.

Inorganic zeolites and metal−organic frameworks (MOFs) are two families of functional porous materials that are fascinating because of their established large-scale industrial applications and enormous potential in emerging energy- and environment-related applications.[1−4] Of particular interest is combining the structural features and functionality of both zeolites and MOFs, as this would allow the creation of a special class of zeolitic MOFs with unusual zeotype topologies and high surface areas.[5] The most common method of constructing zeolite frameworks makes use of individual tetrahedrally coordinated atoms, as demonstrated in the original aluminosilicate zeolites (Si and Al) and in the recently developed zeolitic imidazolate frameworks (Zn in ZIFs) and boron imidazolate frameworks (Li and B in BIFs).[6,7] Some indium-based MOFs are also known.[8] The potential limitations of such methods include the usually small pore size and the small number of atoms capable of tetrahedral coordination geometry.

The development of composite tetrahedral clusters is highly desirable because of the potential diversity in such clusters, their large pore sizes, and the possibility of introducing additional functionality through the construction of clusters.[9] With this method, even elements that usually do not exhibit tetrahedral geometry can be incorporated into the frameworks, thereby creating rich opportunities for structural design and property engineering.

It has recently been demonstrated that chalcogenide clusters can function as pseudotetrahedral units in the formation of zeolite-type structures, which allows the possibility of integrating semiconductivity with porosity.[10] However, despite the great diversity of metal halides, few zeolite-type structures based on halide clusters are known. Iodides are particularly interesting because of some similarities between iodides and chalcogenides, for example, in terms of their comparable polarizabilities and their tendencies to generate semiconducting and electro-optical properties and fast ion conductivity.[11] Our recent studies, together with those of others, have shown that metal iodide clusters can exist in multiple forms, and the competing crystallization processes of various cluster species in metal iodides make it highly challenging to form zeolite-type frameworks.[12] The preferential formation of tetrahedral iodide clusters and methods for inducing their crystallization into zeolite-type structures are the focus of our studies with metal halides.

We have now developed a synthetic procedure that demonstrates the feasibility of creating zeolite-type frameworks using copper iodide clusters as pseudotetrahedral units. We report here an extraordinary photoluminescent cluster−organic framework based on tetrahedral Cu_4I_4 clusters, namely, $[Cu_4I_4(dabco)_2]_n$ (**COZ-1**; dabco = 1,4-diazabicyclo[2.2.2]-octane; **COZ** denotes *c*luster−*o*rganic framework with *z*eotype structure), which features an **MTN**-type zeolitic porous framework with giant 6^45^{12} and 5^{12} cages. Remarkably, the 6^45^{12} cages in **COZ-1** have an inner diameter of 2.6 nm and a large pore volume of 9.2 nm^3.

Yellow crystals of **COZ-1** were synthesized solvothermally by mixing CuI, dabco, triethylamine, and hypoxanthine in *N*,*N*-dimethylformamide (DMF)/ethanol solvent at 100 °C for 15 days.[13] Single-crystal X-ray diffraction (XRD) revealed that **COZ-1** features a 4-connected porous neutral framework containing tetrahedral Cu_4I_4 clusters linked by the linear dabco ligands.[14] The structure contains giant cages, and the guest molecules in the pores are all structurally disordered. The contribution of the disordered solvent molecules was subtracted from the reflection data by the SQUEEZE method as implemented in PLATON.[15] As a basic tetrahedral building unit, each Cu_4I_4 cluster in **COZ-1** is generated in situ from CuI and consists of four tetrahedrally coordinated Cu^+ ions bonded by four μ_3-I^- anions (Figure 1a). The average Cu···Cu distance in this cluster is ∼2.68 Å.

A prominent structural feature in **COZ-1** is the presence of two types of giant cages built from these tetrahedral Cu_4I_4 clusters. The larger ones are 6^45^{12} cages containing 28 Cu_4I_4 clusters as nodes and 42 dabco ligands as linkers (Figure 1d,e). From the van der Waals surfaces, the inner diameter of these ball-like cages is ∼2.6 nm, and their calculated pore volume is

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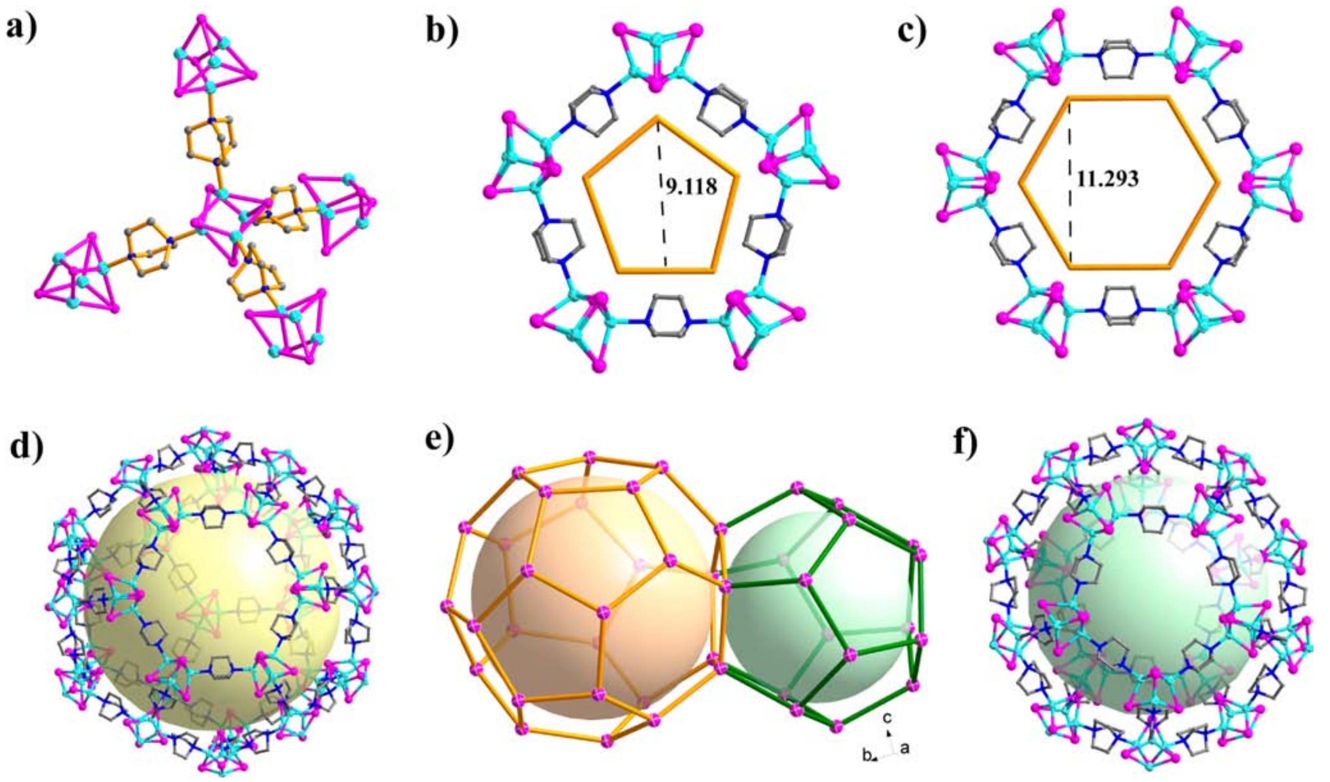

Figure 1. (a) Tetrahedral Cu_4I_4 clusters in **COZ-1**. (b) Pentagonal and (c) hexagonal windows. (d) 6^45^{12} cage with an inner diameter of 2.6 nm. (e) Topological representation of the 6^45^{12} and 5^{12} cages. (f) 5^{12} cages with an inner diameter of 2.0 nm. Colors: (a−d, f) Cu, aqua; I, pink; N, blue; C, gray; (e) Cu_4I_4 clusters, pink ellipsoids; 6^45^{12} cage, orange sticks; 5^{12} cage, green sticks.

~9.2 nm^3. To the best of our knowledge, such large cages are unknown in MOFs except for ZIF-100, MIL-100, and MIL-101.[5,6f] Each 6^45^{12} cage has four hexagonal windows and 12 pentagonal windows. In **COZ-1**, those hexagonal and pentagonal windows formed from Cu_4I_4 clusters have very large free apertures of 11.293 and 9.118 Å, respectively (Figure 1b,c), and thus should be accessible to many big molecules. The smaller cages in **COZ-1** are 5^{12} cages that contain 20 Cu_4I_4 clusters and 30 dabco ligands and have an inner diameter of 2.0 nm and a pore volume of 4.2 nm^3 (Figure 1e,f). It is interesting that the two giant 6^45^{12} and 5^{12} cages are adjacent to each other, sharing pentagonal windows (Figure 1e).

Worthy of mention is the further assembly of these giant 6^45^{12} and 5^{12} cages in **COZ-1**. Each 6^45^{12} cage shares faces with 12 5^{12} cages and four 6^45^{12} cages, while each 5^{12} cage shares faces with six 6^45^{12} cages and six 5^{12} cages. In this way, these giant 6^45^{12} and 5^{12} cages with a 2:1 ratio in **COZ-1** give rise to a three-dimensional (3D) neutral framework with the **MTN** topology (Figure 2).[16] In comparison with MIL-100, MIL-101, and a Cd−hexamine compound that possess the same **MTN** topology,[5,17] **COZ-1** constructed from these tetrahedral Cu_4I_4 clusters is quite special. Moreover, the inclusion of Cu_4I_4 clusters into this zeotype structure makes **COZ-1** a potentially photoluminescent material.

The solvent-accessible volume of **COZ-1** was estimated by PLATON to be ~75% of the total crystal volume (241 941 Å^3). Thermogravimetric analysis (TGA) of **COZ-1** revealed that almost all of the guest molecules in the pores were removed below 150 °C (Figure S1 in the Supporting Information). Crystalline **COZ-1** is stable in air, DMF, and ethanol but not in water and methanol. An activated sample was prepared by exchange of the solvent in the as-synthesized **COZ-1** with ethanol followed by evacuation at room temperature. This activated sample retained a crystalline phase in air for ~1 h and then changed into an amorphous phase. Powder XRD (PXRD) investigation of the activated sample indicated significant peak broadening and shifting relative to the as-synthesized sample (Figure S2).

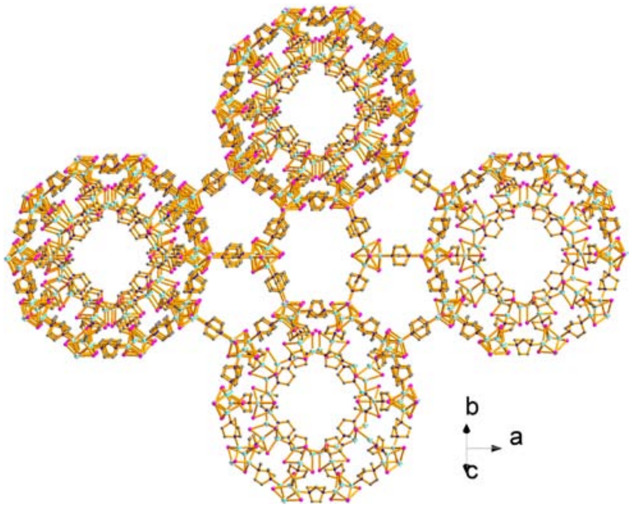

Figure 2. 3D framework of **COZ-1**.

The permanent porosity of **COZ-1** was confirmed by reversible N_2 sorption measurements at 77 K, which showed type-I adsorption isotherm behavior (Figure 3). The Langmuir and Brunauer−Emmett−Teller (BET) surface areas for **COZ-1** were 728 and 514 m^2/g, respectively. The single-point-adsorption total pore volume at P = 0.98 bar from the N_2

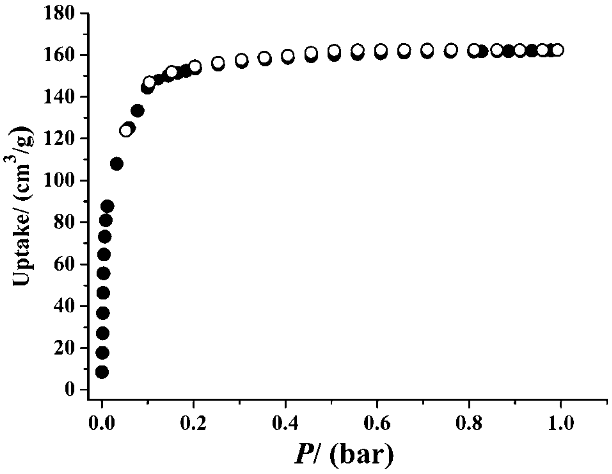

Figure 3. N_2 sorption isotherms (●, adsorption; ○, desorption) of **COZ-1**.

sorption data was 0.25 cm^3/g, which is much lower than the value of 0.84 cm^3/g estimated from the single-crystal structure. A median pore width of 1.53 nm was calculated using the Horvath–Kawazoe equation (Figure S3). The Barrett–Joyner–Halenda (BJH) adsorption average pore diameter was 2.52 nm, which is close to the calculated value.

The photoluminescent properties of the as-synthesized **COZ-1** were studied in the solid state at room temperature (Figure 4). Upon UV excitation at 350 nm, **COZ-1** displayed emission with a maximum at 588 nm. Similar to other previously reported $Cu_4I_4L_4$ (L = ligand) cluster complexes, the observed emission by **COZ-1** is due to a "cluster-centered" triplet excited state that involves both the Cu_4 and I_4 tetrahedral units and has mixed iodide-to-metal charge transfer and "metal-cluster-centered" (d^{10} Cu → d^9s^1 Cu) character.[12,18]

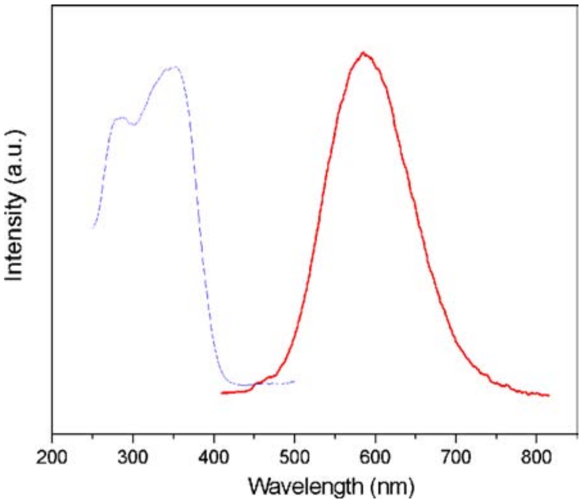

Figure 4. Emission (red line) and excitation (blue line) spectra of **COZ-1** in the solid state at room temperature.

In summary, from the assembly of tetrahedral Cu_4I_4 clusters with linear dabco ligands, a new **MTN**-type cluster–organic framework (**COZ-1**) containing giant 6^45^{12} and 5^{12} cages has been successfully synthesized. The 2.6 nm 6^45^{12} cage in **COZ-1** has large inner space and open windows. It exhibited perfect integration of porosity and photoluminescent properties from both the cluster and the framework in a porous material. The results further demonstrate that bulky tetrahedral Cu_4I_4 clusters are very good building units for the construction of functional cluster–organic frameworks with diverse zeotype topologies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TGA curve, PXRD data, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Synthesis of **COZ-1**: A mixture of CuI (0.38 g), dabco (0.056 g), hypoxanthine (0.117 g), DMF (4 mL), and ethanol (2 mL) was placed in a 15 mL vial and stirred for 10 min, and then 0.5 mL of triethylamine was added. The vial was sealed, heated at 100 °C for 15 days, and cooled to room temperature, after which yellow crystals of **COZ-1** were separated out from the powder products (25% yield).

(14) Crystal data for **COZ-1**: cubic, $a = b = c = 62.312(9)$ Å, $V = 241944(61)$ Å^3, $T = 293(2)$ K, space group $Fd\bar{3}m$, $Z = 136$, 93 020 reflections measured, 5175 independent reflections ($R_{\mathrm{int}} = 0.1089$), final $R_1 = 0.1079$ [$I > 2\sigma(I)$], final $wR(F^2) = 0.2941$ [$I > 2\sigma(I)$], goodness of fit on $F^2 = 1.094$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-97 program package.

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