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Interpenetrated Three-Dimensional Copper–Iodine Cluster-Based Framework with Enantiopure Porphyrin-like Templates

Juan Liu,^{†,‡} Fei Wang,^{*,†} Li-Yang Liu,[†] and Jian Zhang^{*,†}

[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian350002, P. R. China

[‡]University of Chinese Academy of Sciences, 100049 Beijing, P. R. China

S Supporting Information

ABSTRACT: Presented here is an interpenetrated threedimensional copper–iodine cluster-based framework with dia topology based on two different kinds of Cu_4I_4 subunits that is templated by an enantiopure porphyrinlike $Cu^{I}(5\text{-eatz})_2$ unit and shows excellent photocatalytic activity to degrade methylene blue under visible light.

Z eolites, as an important class of inorganic crystalline microporous materials containing TO_4 (T = Si, Al, P, Ge) tetrahedral units, are of current interest for their applications in the petroleum refining and fine chemical industries.¹ However, because of the inherent insulating characteristic of oxide-based zeolites, their applications in photocatalytic/electric-related processes were greatly limited. To broaden their performances in targeted applications and create multifunctional zeolitic materials, there is a high demand for new multinuclear building units.

It has been reported that chalcogenide clusters can serve as pseudotetrahedral units to form zeotype structures.² In comparison, metal halide clusters, especially copper iodides, display polarizabilities comparable to those of chalcogenides, making them also suitable to serve as tetrahedral units of zeotype frameworks. However, because of the multiple forms and structural diversities of metal iodides, it still remains a great challenge to prepare metal iodide cluster-based zeolitic materials.³

Herein we report an interpenetrated three-dimensional (3D) $copper-iodine cluster-based framework, [N-(CH_3)_4)]_2^{2+}[Cu_{14}I_{12}(5-eatz)_4]^{2-}$ [1; 5-eatz = (1R)-1-(5-tetrazolyl)ethylamine], based on two kinds of Cu₄I₄ subunits (secondary building units, SBUs), a cubane and an eightmembered ring, which exhibits 2-fold-interpenetrated dia topology and is templated by an enantiopure porphyrin-like Cu¹(5-eatz)_2 unit. Furthermore, such a 2-fold-interpenetrated copper-iodine clusters were linked by the Cu-5-eatz units, giving rise to a zeolitic framework with 4,4-connected (6⁴.8²)₂(6⁶) topology. Furthermore, this copper-iodine cluster-based framework shows excellent photocatalytic activity to degrade methylene blue (MB) under visible light because of its narrow band gap of 1.49 eV.

The orange crystal of 1 was prepared by the reaction of 5-eatz, $N(CH_3)_4Br$, CuI, and KI under hydrothermal conditions. The structure and composition of 1 were characterized by single-crystal X-ray diffraction (XRD) and elemental analysis, and its

phase purity and thermal stability were identified by powder XRD (PXRD) and thermogravimetric analysis (TGA), respectively (Supporting Information). Single-crystal XRD revealed that 1 crystallizes in tetragonal symmetry with space group $P4_2$ and contains eight copper atoms, six iodine atoms, two 5-eatz ligands, and $[N(CH_3)_4]^+$ ions (Figure S3).

The prominent structural feature of 1 is that it has an interpenetrated 3D copper-iodine cluster based on two types of Cu_4I_4 SBUs generated in situ from CuI. The first one is the common tetrahedral Cu_4I_4 cubane (Figure 1a). Each Cu_4I_4



Figure 1. (a) Cu_4I_4 cubane. (b) Cu_4I_4 eight-membered ring. (c) dia topology cage. (d) 3D copper–iodine clusters with 2-fold interpenetration. (e) dia topology of the copper(I)–iodine clusters.

cubane in 1 consists of four tetrahedrally coordinated Cu⁺ ions bonded by four μ_3 -I⁻ anions. The relatively short Cu···Cu distances ranging from 2.549 to 2.825 Å are comparable or even less than twice the van der Waals radius (1.4 Å) of Cu¹, implying strong Cu–Cu interaction. The second one is an unusual Cu₄I₄ subunit with an eight-membered ring (Figure 1b). Notably, it shows an interesting configuration: four copper and two iodine atoms are coplanar, and the other two I⁻ ions locate oppositely along the plane. The Cu···Cu distances of the eight-membered ring range from 2.879 to 3.443 Å, which are longer than that of a Cu₄I₄ cubane. It should be noted that the coexistence of two such

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different Cu_4I_4 SBUs in one compound has never been observed previously. Each Cu_4I_4 cubane serves as a tetrahedral node, which was linked by four Cu_4I_4 eight-membered rings, while each Cu_4I_4 eight-membered ring, acting as linkers, uses its two edges to connect two Cu_4I_4 cubane tetramers. Both Cu_4I_4 SBUs link each other to form 2-fold-interpenetrated 3D clusters (Figure 1d), which can be simplified into a dia net (Figure 1e).⁴ A typical dia cage substructure, including 10 Cu_4I_4 cubanes and 12 Cu_4I_4 eight-membered rings, is presented (Figure 1c).

Another extraordinary feature of 1 is the presence of derivation from 4-connected dia topology to 4,4-connected topology. Besides the above-mentioned two Cu_4I_4 clusters, another interesting unit, denoted by $Cu^I(5-eatz)_2$, is also observed in 1 (Figure 2a). Such an enantiopure porphyrin-like unit is formed



Figure 2. (a) Strong hydrogen-bonding interactions between enantiopure porphyrin-like templates consisting of Cu^{I} and 5-eatz. The hydrogen atoms were omitted for clarity. (b) Whole framework of **1**. (c) 2-fold-interpenetrated dia nets of the 3D copper-iodine clusters. (d) Whole topology of **1**.

by two homochiral 5-eatz ligands chelating one Cu^I. There are strong hydrogen-bonding interactions between them. Moreover, $Cu^{I}(5-eatz)_{2}$ only located between two $Cu_{4}I_{4}$ eight-memberedring SBUs, which linked the 2-fold-interpenetrated 3D clusters (Figure 2c) into one and further stabilized the framework (Figure 2d). The attendance of the $Cu^{1}(5-eatz)_{2}$ unit also brings a new node, the planar four-connected (Cu_4I_4 eight-membered ring) node, for the whole framework topology. The whole framework of 1 can be topologically represented as a 4,4-connected net with a point symbol of $(6^4.8^2)_2(6^6)$. Interestingly, the introduction of the planar 4-connected node generates an unusual cage structure, including six Cu₄I₄ cubanes, 12 Cu₄I₄ eight-membered rings, and eight $Cu^{I}(5-eatz)_{2}$ units (Figure 3c) with the symbol of 6⁸, which has never been observed in both zeolite and zeolitic imidazolate frameworks before.⁵ The $[N(CH_3)_4]^+$ cations just fill in the center of the cage.

It should be noted that only a few examples of 3D copper(I) halide clusters have been reported before.⁶ Among them, just two compounds are based on copper–iodine clusters.^{6a,b} The compound reported here is the first one with 3D copper–iodine clusters based on two different copper–iodine clusters. The main



Figure 3. (a) dia cages interpenetrating each other. (b) $Cu^{I}(5\text{-eatz})_{2}$ units linking adjacent dia cages to form another kind of small cage. (c) Magnification of the cage and relative tile. (d) 6^{8} topology with the $[N(CH_{3})_{4}]^{+}$ ion located in the center of it. There are no obvious interactions between the $[N(CH_{3})_{4}]^{+}$ ion and the framework.

reason may be that the in situ captured enantiopure porphyrinlike $Cu^{I}(5-eatz)_{2}$ units act as effective templates. In the synthesis of inorganic zeolites as well as metal halide clusters, organic amines are widely applied as structure-directing agents (SDAs). However, metal–organic templates such as the SDAs reported here have never been observed before.

The band gap of 1 was investigated by a UV–vis diffusereflectance measurement method at room temperature (Figure 4a). According to the equation $\alpha h \nu^2 = K (h \nu - E_g)^{1/2}$ (where α is



Figure 4. (a and b) Solid-state UV-vis reflectance spectra of crystal 1. (c) Temporal UV-vis absorption spectral changes of MB aqueous solutions with photodegradation catalyzed by 1 in the presence of a H_2O_2 additive. (d) Photodegradation rates of 1 (red), H_2O_2 (black), and 1 in the presence of a H_2O_2 additive (blue).

the absorption coefficient, $h\nu$ is the discrete photo energy, *K* is a constant, and $E_{\rm g}$ is the band-gap energy), the extrapolated values (the straight lines to the *x* axis) of $h\nu$ at $\alpha = 0$ give absorption edge energies corresponding to $E_{\rm g} = 1.49$ eV for **1**. It has an absorption response to visible light due to its narrow-band-gap size.⁷ This result is also consistent with the color of their crystals, with yellow for **1** (Figure 4a).

The photocatalytic activities of **1** were evaluated for MB photodegradation under visible-light illumination. The characteristic absorption of MB at about 665 nm was selected for monitoring the adsorption and photocatalytic degradation process. The photocatalytic activity of **1** was gradually enhanced with time increasing from 0 to 25 min, which demonstrated that **1** has a much higher activity (Figure 4). After 25 min, MB in the solution almost disappeared when using **1** as the photocatalyst. Moreover, **1** is stable under repeated application with a nearly constant photocatalytic degradation rate (Figures S4b and S6). These results show that **1** is an excellent photocatalyst under visible light.

In summary, we report an interpenetrated 3D copper–iodine cluster-based framework, based on two kinds of Cu₄I₄ subunits (SBUs), a cubane and an eight-membered ring. It exhibits 2-fold-interpenetrated dia topology and is templated by an enantiopure porphyrin-like Cu^I(5-eatz)₂ unit. Furthermore, this zeolitic framework exhibits outstanding photocatalytic activity under visible light.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02692.

Experimental details, TGA diagram, and PXRD (PDF) CIF file (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: wangfei04@fjirsm.ac.cn. *E-mail: zhj@fjirsm.ac.cn.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Cejka, J.; Corma, A.; Zones, S. Zeolites and Catalysis: Synthesis Reactions and Applications; Wiley: Weinheim, Germany, 2010. (b) Li, Y.; Yu, J. H. Chem. Rev. **2014**, 114, 7268–7316. (c) Schmidt, J. E.; Xie, D.; Rea, T.; Davis, M. E. Chem. Sci. **2015**, 6, 1728–1734. (d) Lin, H. Y.; Chin, C. Y.; Huang, H. L.; Huang, W. Y.; Sie, M. J.; Huang, L. H.; Lee, Y. H.; Lin, C. H.; Lii, K. H.; Bu, X.; Wang, S. L. Science **2013**, 339, 811–813. (e) Liu, T.-F.; Feng, D.; Chen, Y.-P.; Zou, L.; Bosch, M.; Yuan, S.; Wei, Z.; Fordham, S.; Wang, K.; Zhou, H.-C. J. Am. Chem. Soc. **2015**, 137, 413–419. (f) Feng, D.; Wang, K.; Su, J.; Liu, T.-F.; Park, J.; Wei, Z.; Bosch, M.; Yakovenko, A.; Zou, X.; Zhou, H.-C. Angew. Chem., Int. Ed. **2015**, 54, 149–154.

(2) (a) Sun, J.; Bonneau, C.; Cantin, A.; Corma, A.; Diaz-Cabañas, M.
J.; Moliner, M.; Zhang, D.; Li, M.; Zou, X. Nature 2009, 458, 1154–1157. (b) Zheng, N.; Bu, X.; Feng, P. Nature 2003, 426, 428–432. (c) Wu, T.; Wang, X.; Bu, X.; Zhao, X.; Wang, L.; Feng, P. Angew. Chem, Int. Ed. 2009, 48, 7204–7207. (d) Xiong, W.-W.; Athresh, E. U.; Ng, Y.
N.; Ding, J.; Wu, T.; Zhang, Q.; J. Am. Chem. Soc. 2013, 135, 1256–1259. (e) Lin, J.; Dong, Y.; Zhang, Q.; Hu, D.; Li, N.; Wang, L.; Liu, Y.; Wu, T. Angew. Chem, Int. Ed. 2015, 54, 5103–5107. (f) Lin, Q.; Bu, X.; Mao, C.; Zhao, X.; Sasan, K.; Feng, P. J. Am. Chem. Soc. 2015, 137, 6184–6187.

(3) (a) Bi, M. H.; Li, G. H.; Hua, J.; Liu, X. M.; Hu, Y. W.; Shi, Z.; Feng, S. H. CrystEngComm 2007, 9, 984–986. (b) Braga, D.; Maini, L.; Mazzeo, P. P.; Ventura, B. Chem. - Eur. J. 2010, 16, 1553–1559. (c) Kang, Y.; Wang, F.; Zhang, J.; Bu, X. J. Am. Chem. Soc. 2012, 134, 17881–17884. (d) Kang, Y.; Fang, W.; Zhang, L.; Zhang, J. Chem. Commun. 2015, 51, 8994–8997.

(4) Blatov, V. A. Struct. Chem. 2012, 23, 955-963.

(5) See the International Zeolite Association website: http://www.izastructure.org/.

(6) (a) Chan, H.; Chen, Y.; Dai, M.; Lü, C.-N.; Wang, H.-F.; Ren, Z.-G.; Huang, Z.-J.; Ni, C.-Y.; Lang, J.-P. *CrystEngComm* **2012**, *14*, 466–473. (b) Cheng, J.-K.; Chen, Y.-B.; Wu, L.; Zhang, J.; Wen, Y.-H.; Li, Z.-J.; Yao, Y.-G. *Inorg. Chem.* **2005**, *44*, 3386–3388. (c) DeBord, J. R. D.; Lu, Y.-J.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. Chem. Commun. **1997**, *15*, 1365–1366. (d) Healy, P. C.; Kildea, J. D.; White, A. H. J. Chem. Soc., Dalton Trans. **1988**, *6*, 1637–1639.

(7) Tsunekawa, S.; Fukuda, T.; Kasuya, A. J. Appl. Phys. 2000, 87, 1318–1321.