An Exceptionally Stable Metal−Organic Framework Constructed from the $Zn_8(SiO_4)$ Core

S. Y. Yang, L. S. Long,* Y. B. Jiang,
R. B. Huang, and L. S. Zheng†

State Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, Xiamen University, Xiamen 361005, China

Received April 8, 2002
Revised Manuscript Received June 24, 2002

Metal silicate, the most common inorganic material, has been widely used in heterogeneous catalysis, separation science, ion exchange, and electronic devices.[1−5] Although chemically and thermally stable, these materials allow rather limited variation of chemical formulation and functionality[6,7] that hinders their application.[8,9] Recent advances in synthesizing metal−organic frameworks offer great potential for chemical and structural diversity[10−19] through the design of the secondary building unit (SBU) and the selection of organic linkers.[20−23] An example of the work is the successful use of SBU in the formation of the metal−organic framework of $[Zn_4O(O_2C-C_6H_4-CO_2)]_n$ [8] that, by borrowing the metal carboxylate chemistry, extends the three-dimensional network and is stable when fully desolvated and heated to 300 °C. In comparison with metal silicate materials, however, the thermal stability of these materials still remains to be improved significantly. In our effort to seek higher thermal stability of coordination polymers, we have successfully used zinc(II) silicate and isophthalate to assemble a $[Zn_8(SiO_4)(C_8H_4O_4)_6]_n$ coordination polymer[22] based on the synthetic strategy of the geometry matching between silicate anion and zinc ion; i.e., the zinc(II) ion in tetrahedral geometry can match well the silicate anion. The thermal property measurement shows that this coordination polymer possesses higher thermal and structural stability (500 °C), because of the highest negative charge of the silicate ion often leading to the combination of more metal ions at a network vertex, so that more organic linkers can be joined through coordination bonds.[21] Obviously, the benefit of hybridization between metal silicate and organic ligand is a combination of the higher thermal stability of metal silicate with chemical and structural diversity of metal−organic frameworks. As a systematic investigation on the assembly rule of metallosilicate coordination polymers, in this paper, we report herein the synthesis, crystal structure, and properties of a metal−organic framework $[Zn_8(SiO_4)(C_8H_4O_4)_6]_n$ (**1**; $C_8H_4O_4$ = terephthalate dianion).

The synthesis[24] is achieved by hydrothermal reaction of zinc nitrate, terephthalic acid, and sodium silicate in water at about pH 7. Single-crystal analysis[25] reveals that **1** is made up of an infinite interpenetrating three-dimensional framework with a $Zn_8(SiO_4)$ core as a building unit, in which the silicate anion, located in the center of the unit with each oxygen atom of the silicate anion bridging two zinc(II) atoms in a η^2 bridging mode, forms a distorted cubane-like core, with each zinc(II) atom occupying one apex of the hexahedron (Figure 1a). To the best of our knowledge, the $Zn_8(SiO_4)$ core has the highest positive charge and the largest number of metal ions among those reported in the inorganic−organic coordination polymers.

Two zinc(II) atoms at each edge of the core are further capped by a carboxylate group of terephthalate in cis−cis mode to form a 6-connected $Zn_8(SiO_4)(C_8H_4O_4)_{12}$ cluster (Figure 1b). Each zinc(II) atom is four-coordinated by three oxygen atoms from three μ-carboxylates of terephthalate and one oxygen atom from the silicate anion to furnish a tetrahedral geometry. The bond lengths of $Zn-O_{carboxylate}$ are in the range of 1.903(4)−1.938(3) Å, compared to that found in $[Zn_4O(O_2CPH)_6]$ (ave 1.939 Å).[26] The bond lengths of $Zn-O_{silicate}$ range

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* To whom correspondence should be addressed. E-mail: lslong@jingxian.xmu.edu.cn.
† E-mail: lszheng@xmu.edu.cn.

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(24) Terephthalic acid [p-$C_6H_4(COOH)_2$; 0.33 g, 2.0 mmol], $Na_2SiO_3\cdot 9H_2O$ (0.06 g, 0.2 mmol), and NaOH (0.16 g, 4 mmol) were dissolved in 35 mL of water, and 1 mol/L HNO_3 was added drop by drop to pH ~ 7. Then to the above solution was added $Zn(NO_3)_2\cdot 6H_2O$ (0.59 g, 2.0 mmol). Finally 10 mL of ethylene glycol was added. The suspension was heated to 180 °C at the rate of 2.5 °C/h, and the resulting solution was kept at 180 °C for 100 h and then cooled to room temperature at the rate of 5 °C/h. This gave colorless cuboid crystals of the compound (0.09 g, yield 28% based on $Na_2SiO_3\cdot 9H_2O$). Elem anal. Calcd for $C_{48}H_{24}O_{28}SiZn_8$: C, 36.04; H, 1.51. Found: C, 36.06; H, 1.54. FT-IR (KBr pellet): 2926(w), 1635(w), 1597(s), 1506, 1439, 1399(vs), 1319(w), 1290(w), 1161(w), 1107(w), 1019, 950, 881(w), 824, 739, 617, 562 cm^{-1}. TGA performed on a polycrystalline sample under a flow of air showed no weight loss below ca. 500 °C. Further heating of the sample from 500 to 800 °C results in the decomposition of the material with a weight loss of 55.34%.

10.1021/cm025572s CCC: $22.00

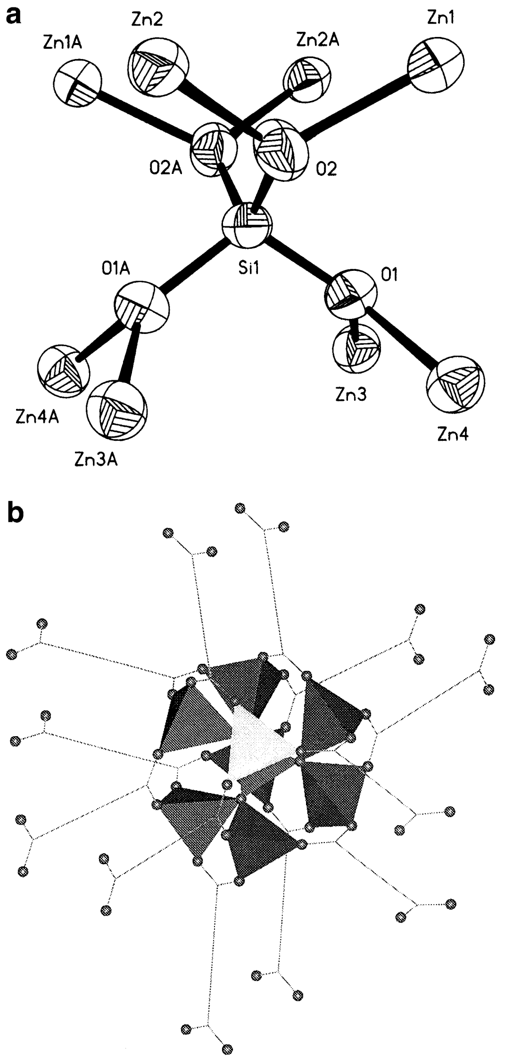

Figure 1. (a) Perspective of the distorted cuboid core of $Zn_8(SiO_4)$ in **1**. (b) The 6-connected $Zn_8(SiO_4)(C_8H_4O_4)_{12}$ cluster in **1**. Benzene rings are simplified as straight lines.

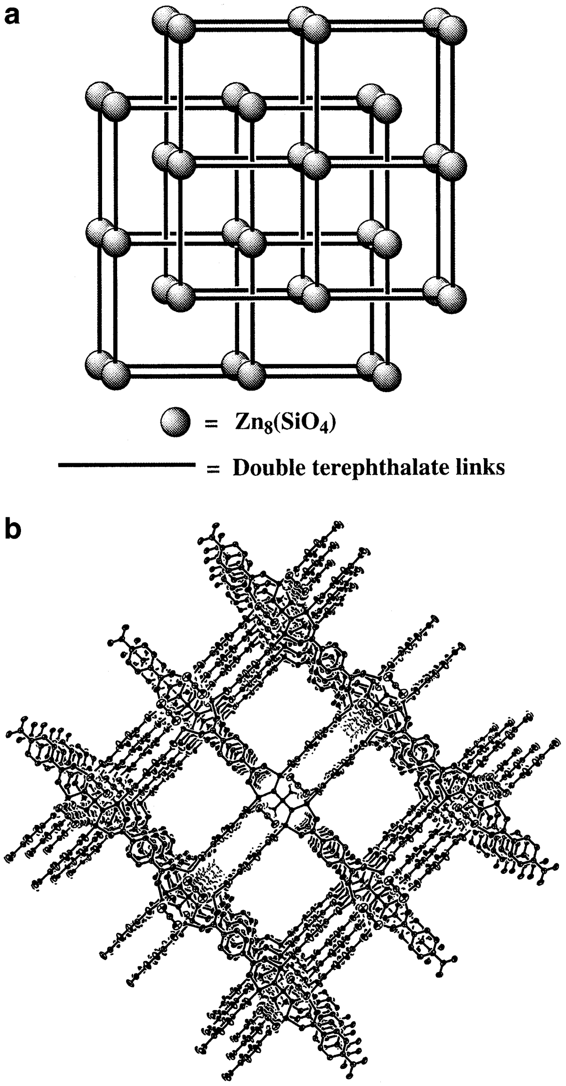

Figure 2. (a) Interpenetrating networks of **1**. (b) ORTEP (ellipsoids at 50% probability; hydrogen atoms are omitted for clarity) view of one set of the networks in **1** along the *b* axis.

from 1.936(3) to 1.946(3) Å, slightly longer than the bond lengths of $Zn-O_{carboxylate}$. The bond angles of $O_{carboxylate}-Zn-O_{carboxylate}$, $O_{carboxylate}-Zn-O_{silicate}$, and O−Si−O in the silicate anion are in the ranges of 103.63(2)−111.00(16)°, 103.31(14)−122.65(15)°, and 107.73(14)−111.8(2)°, respectively, indicating that the silicate anion matches well the ZnO_4 geometry.

The most striking feature in **1** is the 6 connection of the distorted cuboid SBU, which, joined by 12 terephthalates, gives a three-dimensional structure bearing two identical interpenetrating networks (Figure 2). To explore how the SBU influences the interpenetrating network, we also calculate the *n* value, a function of diameter of spherical SBU *d* and length of linker *l* ($d = 8.82$ Å and $l = 5.78$ Å) in **1**. The *n* value near 2 indicates that **1** has only two interpenetrating networks and consists well with the *d* ln *v* plot that relates to *n*, *d*, and *l* in the cubic system reported by Yaghi and co-workers.[27] Despite **1** being the interpenetrated network, the synthesis of the open framework of metallosilicate-containing compounds is expected if reaction conditions are optimized.

Thermogravimetric analysis (TGA) shows that **1** has exceptional thermal stability. The material has no weight loss before 520 °C in nitrogen, indicating that **1** is stable as high as 520 °C, which is significantly higher than that of the diamondoid three-dimensional framework of bis{4-[2-(4-pyridyl)ethenyl]benzoato}zinc (430 °C).[28] Especially, **1** even exhibits high chemical stability

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(25) Crystal dimensions 0.36 × 0.32 × 0.29 mm, monoclinic, space group *C*(2)/c, $a = 19.640(4)$ Å, $b = 14.064(3)$ Å, $c = 19.561(4)$ Å, $\beta = 90.30(3)°$, $V = 5403.0(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.967$ g cm^{-3}, and μ(Mo Kα) = 3.603 mm^{-1}. Of the 5465 reflections measured ($1.78 \leq \theta \leq 25.97°$), 5305 symmetry independent reflections were used to solve the structure. Based on all of these data and 370 refined parameters, $R_1 = 0.0376$, $wR_2 = 0.0897$, and the goodness of fit on F^2 is 0.986. The maximum and minimum peaks correspond to 0.520 and −0.393 e Å^{-3}, respectively. Crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-174992. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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(27) Reineke, T. M.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *122*, 4843. Assume that the icosohedron approximates a sphere with *d* being the longest C···C distance (8.82 Å) in the SBU and *l* the distance between the carboxylate C atoms (5.78 Å) within a terephthalate linker.

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in air. Further TGA in air shows that the material has no weight loss below 500 °C. The strongly endothermic peak appears at 570 °C, which is even higher than two highly thermally robust metal coordination polymers in a nitrogen atmosphere.[29] Such a chemical stability has never been reported in inorganic–organic hybrid materials. The higher stability of **1** is mainly a result of the combination of more metal ions at a network vertex joined by more organic linkers through coordination bonds.[20–22]

In solid state, **1** exhibits strong fluorescence and weak phosphorescence. The fluorescence emission occurs at 386 nm upon photoexcitation at 315 nm, which may be assigned as ligand-to-metal charge transfer.[28,30–32] Except that the fluorescence intensity of **1** is much stronger than that of the ligand, the emission wavelength of fluorescence in **1** is very similar to that of the ligand (386 nm), indicating that the stronger fluorescence of **1** is mainly attributed to the coordination of the zinc(II) atom enhancing rigidity of the terephthalato group.[28,30–32] **1** also emits green phosphorescence at 506 nm upon photoexcitation at 338 nm with a lifetime of 6.78 ms, which could be a reflection of the rigid three-dimensional structure of the polymer.[33–36] Because **1** is highly thermally stable and insoluble in common polar and nonpolar solvents, it can be a good candidate for diode devices.

The synthesis of the hybrid material assembled from metal silicate and organic ligand has provided a new metal–organic framework with exceptional thermal and chemical stability and promising photoelectronic properties. It was clear that the structure of **1** is much different from that of $[Zn_8(SiO_4)(C_8H_4O_4)_6]_n$ ($C_8H_4O_4$ = isophthalate), indicating that a different topology of the coordination polymer is obtained when different ligands are applied. Given the extremely rich structures of silicate ions and various combinations of metal ions and ligands, a large field of new and exciting materials with unique structures and properties is promising.

Acknowledgment. This work was supported by the NNSF of China (Nos. 2989021 and 20023001) and NSF of Fujian Province, P. R. China (E0110001).

Supporting Information Available: X-ray crystallographic file in CIF format (CCDC-174992; in zip-compressed format because of the existence of large files) and thermogravimetric analysis and photoluminescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

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