

$[\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_6]_n$: the firstborn of a metallosilicate–organic hybrid material family ($\text{C}_8\text{H}_4\text{O}_4 = \text{isophthalate}$)

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

State Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, Xiamen University, Xiamen 361005, China. E-mail: lsong@jingxian.xmu.edu.cn; lszheng@xmu.edu.cn

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$[\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_6]_n$ ($\text{C}_8\text{H}_4\text{O}_4 = \text{isophthalate}$), synthesized by hydrothermal reaction, possesses a diamondoid framework structure constructed from hexahedron-like $\text{Zn}_8(\text{SiO}_4)$ cores and $\text{C}_8\text{H}_4\text{O}_4$ linkers and remains stable up to 500 °C in air, representing the first member of a new class of metallosilicate–organic hybrid materials.

The Earth's crust is composed almost entirely of silicates and silica. Silicates are known for their structural stability, so they contribute to most inorganic building materials, ranging from natural rocks to artificial products. Silicates have also found applications in various fields such as heterogeneous catalysis, separation science and electronic devices.¹ Like other inorganic materials, however, they are difficult to modify or derivatize in a systematic way so as to improve their properties. The assembly of metal silicate–organic frameworks by the copolymerization of metal ions with organic linkers can combine the advantages of their structural stability and flexibility. The hybrid materials may thus create much richer structural variations and still maintain chemical thermal stability. Unfortunately, although various inorganic–organic hybrid materials have been synthesized in recent years, a material composed of both a metallosilicate and organic linkers has not been prepared. Failure to synthesize this material might be attributed to the difficulties of selecting proper metal nuclei and organic linkers. Here we report the synthesis, crystal structure and thermal stability of the first metal–organic framework constructed from silicate tetrahedra with striking stability, namely, $[\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_6]_n$ ($\text{C}_8\text{H}_4\text{O}_4 = \text{isophthalate}$) **1**. **1** is synthesized by hydrothermal reaction of zinc nitrate, isophthalic acid, sodium silicate and water.[†] X-Ray single-crystal analysis[‡] reveals that **1** is made up of a diamondoid-framework with a hexahedron-like $\text{Zn}_8(\text{SiO}_4)$ core and $\text{C}_8\text{H}_4\text{O}_4$ anion building blocks, in which the silicate anion is located in the center of the hexahedron-like core with each oxygen atom of the silicate anion bridging two zinc(II) atoms in an η^2 bridging mode, forming a distorted hexahedron with each zinc(II) atom occupying one apex of the hexahedron (Fig. 1). Each zinc(II)

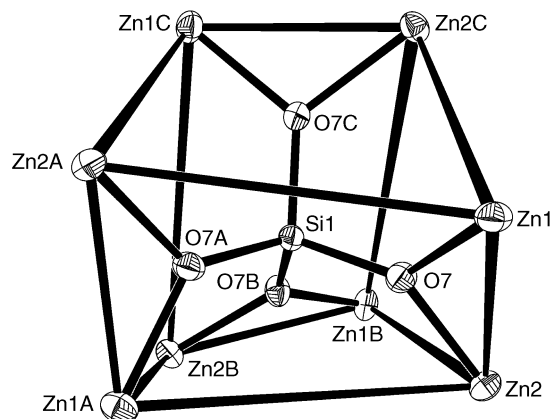


Fig. 1 Perspective view of the hexahedron-like core of $\text{Zn}_8(\text{SiO}_4)$ in **1**.

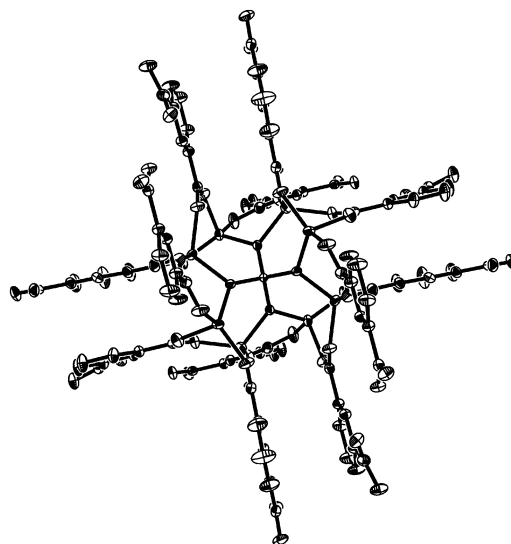


Fig. 2 Perspective view of the $\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_{12}$ cluster. All hydrogen atoms are omitted for clarity.

atom at the vertex of the core is further capped by three oxygen atoms from carboxylate groups of isophthalate in a *cis-cis* mode to form a $\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_{12}$ cluster (Fig. 2).

The three-dimensional structure of **1** can be viewed as an 8-connected net in two stages: 1), $\text{Zn}_8(\text{SiO}_4)$ core links four adjacent $\text{Zn}_8(\text{SiO}_4)$ cores with four one-isophthalate bridges, forming an infinite two-dimensional $\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_6$ sheet parallel to the *ab* plane (Fig. 3); 2), the $\text{Zn}_8(\text{SiO}_4)$ core in the sheet is further connected in tetrahedral geometry with four adjacent $\text{Zn}_8(\text{SiO}_4)$ cores by four two-isophthalate bridges, in which two $\text{Zn}_8(\text{SiO}_4)$ cores from the upper sheet and two from

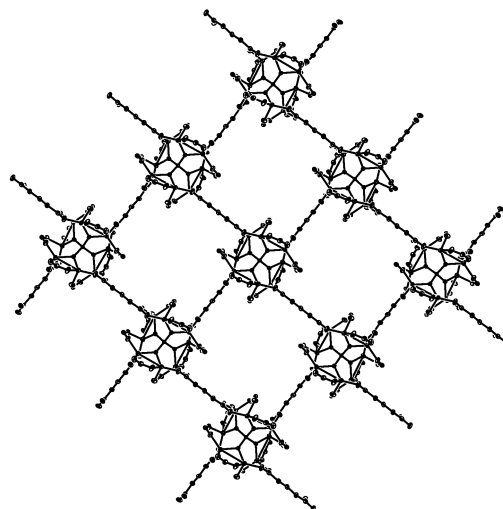


Fig. 3 Perspective view of the two-dimensional sheet of **1**. All hydrogen atoms are omitted for clarity.

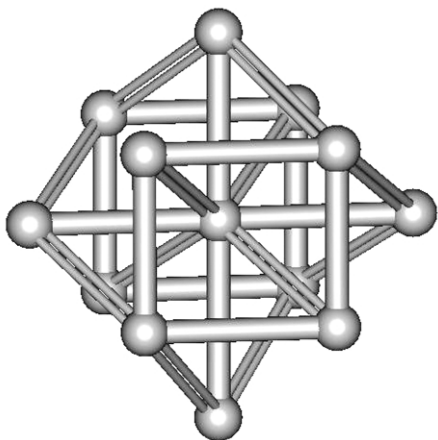


Fig. 4 Framework topology of **1**, in which the balls stand for Zn_8SiO_4 cores, the single bars for one-isophthalate bridges and the double bars for two-isophthalate bridges.

the lower sheet along the *c*-axis generate a diamondoid three-dimensional framework (Fig. 4). The lattice water molecules are located in the channels of the three-dimensional framework, forming relatively weak hydrogen bonds with the carboxylate oxygen atoms.

In the structure, the silicate tetrahedron is slightly distorted with O–Si–O bond angles deviating from 109.5° to $107.72(14)$ – $113.0(3)^\circ$, but all the four Si–O bond lengths are still equivalent to $1.623(4)$ Å, typical in silicate compounds. The central zinc(II) atoms also adopt distorted tetrahedral geometries with O–Zn–O bond angles ranging from $100.2(2)$ to $122.1(2)^\circ$. The bond lengths of Zn–O(carboxylate) range from $1.906(5)$ to $1.966(4)$ Å, while the bond lengths of Zn–O(silicate) are $1.946(4)$ Å and $1.948(4)$ Å, compared to the bond lengths of Zn–O previously reported in ZnO_4 (1.889 – 2.110 Å).² The Zn···Zn distances are $3.0676(11)$ Å and 3.325 Å respectively, indicating that the metal···metal distances are primarily governed by the nature and mode of coordination of the bridging groups.³

The most striking feature in the structure is the directional guidance provided by the silicate anions in the supramolecular assembly. Firstly, due to steric hindrance, the silicate anions direct the zinc(II) atoms to adopt tetrahedral geometries. Secondly, the coordination geometries of the zinc(II) atoms further influence the linking directions of the isophthalate ligands. As a result, not only are the zinc(II) atoms in tetrahedral geometries, but also the isophthalate anions bridging the cores are arranged in tetrahedral directions.

It is worth noting that **1** is not only the first hybrid material constructed from a metallosilicate and organic ligands, but also a typical example of a hybrid material controlled by anion direction guiding. To the best of our knowledge, such a special framework topology has not been reported and is expected to be very rigid. In addition, **1** is also a metal-rich material owing to the highest negative charge of the silicate anion among the inorganic anions, for this reason the material is expected to have high thermal stability.

Indeed, thermogravimetric analysis (TGA) shows that the hybrid material has exceptional thermal stability. The TGA measurements show an initial weight loss at 80 – 150 °C (endothermic peak), corresponding to the mass loss of two water molecules. From 150 to 500 °C, **1** shows no weight loss, indicating that it can remain stable up to 500 °C. The TGA has also been measured in air to test its chemical stability. The results show that **1** is even stable in air below 450 °C. To the best of our knowledge, the decomposition temperature of **1** is one of the highest among those of the inorganic–organic hybrid

materials.⁴ In addition, **1** exhibits photoluminescence emission at 363.8 nm upon photoexcitation at 315.8 nm, which may be assigned as ligand-to-metal charge transfer.⁵

In summary, we have reported the synthesis, crystal structure and thermal stability of a first hybrid material assembled from a metallosilicate and organic ligands. Starting from this work, a new family of hybrid materials with novel structures and properties can be rationally designed and synthesized. Given the extremely rich structures of silicate ions and various combinations of the metal ions and the ligands, the emergence of a large field of new and exciting materials is promising. The process of synthesizing these materials is currently under way.

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Notes and references

† **1** was synthesized by the hydrothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $m\text{-C}_6\text{H}_4(\text{COOH})_2$ (isophthalic acid), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and water in the molar ratio $10:10:1:1100$. The mixture was magnetically stirred and 1 mol L^{-1} KOH added to pH ~ 6 , heated to 200 °C and kept at this temperature for 100 h after which time it was cooled down to room temperature at a rate of 5 °C per h. This gave colorless octahedral crystals of the compound (yield 50%, based on $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$). Elemental analysis (%) calcd. for $\text{C}_{48}\text{H}_{28}\text{O}_{30}\text{SiZn}_8$: C, 35.24; H, 1.73; found: C, 35.35; H, 1.68%. FT-IR (KBr pellet): $3424(\text{br})$, 3079 , $1630(\text{s})$, 1612 , $1556(\text{s})$, $1485(\text{m})$, $1459(\text{s})$, $1421(\text{s})$, $1402(\text{s})$, 1321 , 1281 , 1166 , 1104 , 1079 , $956(\text{s})$, 927 , 819 , $737(\text{s})$, $719(\text{s})$, 660 , $597(\text{m})$, $492(\text{m})$ cm^{-1} . Thermogravimetric analysis (TGA) performed on a polycrystalline sample under a flow of nitrogen showed an initial weight loss of 3.61% at 80 – 150 °C corresponding to the removal of lattice water molecules. No further weight loss steps occurred 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 39.35%.

‡ Crystal data for **1**: $\text{C}_{48}\text{H}_{28}\text{O}_{30}\text{SiZn}_8$, $M = 1635.75$, dimensions $0.50 \times 0.50 \times 0.43$ mm, tetragonal, space group $P4(2)1n$, $a = 13.7409(19)$, $c = 14.976(3)$ Å, $V = 2827.7(8)$ Å³, $Z = 2$, $\rho_{\text{calcd.}} = 1.921$ g cm^{-3} , $\mu(\text{MoK}\alpha) = 3.447$ mm^{-1} . Of the 3008 reflections measured ($1.0 \leq \theta \leq 26.0^\circ$), 2764 symmetry independent reflections were used to solve the structure. Based on all these data and 202 refined parameters, $R_1 = 0.0502$, $wR_2 = 0.1194$, and goodness-of-fit on F^2 is 1.039. CCDC reference number 167834. See <http://www.rsc.org/suppdata/cc/b1/b110557d/> for crystallographic data in CIF or other electronic format.

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