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A rare I^2O^3 hybrid organic-inorganic material with high-connection and quadruple-stranded helices

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A novel organic-inorganic hybrid material with 2D inorganic and 3D organic connectivity has been assembled with one Cd−O$_{\mathbf{hydroxyl}}$ helix and two kinds of quadruple-stranded Cd−ligand helices, which also shows a highly-connected binodal (5,14-c) topological net.

The research field of organic−inorganic hybrid materials, in which both organic and inorganic frameworks co-exist, has achieved tremendous advancements over the past decade. According to the classification made by Cheetham, Rao and Feller, the vast number of organic−inorganic hybrid frameworks all contain two parts: metal-organic and metal-inorganic networks.[1] The dimensionality of organic frameworks was defined with 'metal to organic ligand to metal' (M−L−M) connectivity and the dimensionality of inorganic frameworks by M−X−M (X = O, N, Cl, S) connectivity. Therefore, the structural dimensionality of a hybrid framework can be represented with a simple notion of I^nO^m, where I^n (n = 0−3) is the dimensionality of inorganic structure (M−X−M) and O^m (m = 0−3) as organic ligand-based dimensionality (M−L−M). To date, a variety of organic−inorganic hybrid with I^0O^{0-3}, I^1O^{0-3}, I^2O^{0-2}, and I^3O^{0-1} hybrid frameworks have been constructed.[2] However, it is very rear to see any organic−inorganic frameworks with both inorganic and organic structure simultaneously to be 2-D or more.[2g,3] To the best of our knowledge, no hybrid organic−inorganic framework with I^2O^3 dimensionality has been reported so far.

Recently, the construction of helical coordination polymers also has attracted a lot of attention because of the frequent appearance of helix structures in proteins, collagens, quartz and single-walled carbon nanotubes.[4] Commonly, much effort has been devoted to the preparation of helical coordination polymers with metals in the backbone by using specifically designed bridging ligands such as flexible and angular ditopic ligands, rigid and hinge-like ditopic ligands, and some rigid pyridine- or carboxylate-based ligands.[2j,5] Nevertheless, the incorporation of helix structures certainly increases the complexity of the frameworks. The topology approach is an effective method to reduce these complicated structures to simple node-and-linker nets for the analysis.[6] Herein we report an organic−inorganic hybrid material of $[Cd_3(OH)_2(TCBA)(H_2O)]$ (**1**) (H_4TCBA = 3,4,5-tris(carboxymethoxy)benzoic acid) with one Cd−O$_{hydroxyl}$ helix and two kinds of quadruple-stranded Cd−TCBA helices, which also exhibits an unprecedented I^2O^3 hybrid framework and a highly-connected binodal (5,14-c) topological net.

Hydrothermal reaction of H_4TCBA with $CdCl_2\cdot 2.5H_2O$ and NaOH in distilled water at 110 °C for 72 h led to the formation of colorless block crystals of **1**. The result of single X-ray structure analysis‡ reveals that **1** crystallizes in the monoclinic space group $P2_1/c$. The structure of **1** contains three crystallographically independent Cd(II) ions (Fig. 1a). Cd1 is six-coordinated by two hydroxyl oxygen, three carboxylate oxygen atoms and one water molecule. Cd2 bonds to eight oxygen atoms: one hydroxyl oxygen, two ether oxygen and five carboxylate oxygen atoms. Cd3 is only coordinated to three hydroxyl oxygen and two carboxylate oxygen atoms. In **1**, each $TCBA^{4-}$ ligand bonds to seven Cd(II) ions through eight carboxylate oxygen and two ether oxygen atoms (Fig. 1a). It is worth noting that two types of μ_3-OH bridges are observed. One bridge (O12) connects to one Cd1, one Cd2 and one Cd3 atom. Another bridge (O13) links one Cd1 and two Cd3 atoms (Fig. 1a).

An unique I^2O^3 framework is formed via an inorganic network and an organic network interconnected with each other at Cd(II) ions (Fig. 1b). The inorganic connectivity goes through those two types of μ_3-OH groups linking three crystallographically independent Cd(II) ions to form a 2D M−O−M inorganic network (Fig. 1c). And $TCBA^{4-}$ ligands link three crystallographically independent Cd(II) ions to form a 3D M−L−M organic framework (Fig. 1d). Clearly, **1** is a well defined I^2O^3 hybrid framework. To our knowledge, this is the first I^2O^3 framework reported.

Another interesting feature in **1** is its helix chains. There is a M−O(hydroxyl) helical chain in the inorganic layer (Fig. 1c), the repeat unit is Cd1−O13−Cd3−O12−Cd1−O13−Cd3−O12, and the pitch of it running along the *b* axis is the same as the *b*-axis unit. Up to now, only a few M−O helix chains have been reported,[7a,b,c] and M−O(hydroxyl) helical chains are extremely rarely reported.[7d] Furthermore, the structure-directing ligand, $TCBA^{4-}$ with branching out four carboxylate groups facilitate the formation of multi-stranded helix chains. In **1** TCBA^{4-} ligands link Cd^{2+} ions to form two kinds of quadruple-stranded helix chains, which are named as Ha and Hb respectively, both with two right-handed and two left-handed helices (Fig. 1d). The repeating units of Ha and Hb are −Cd3−O5−Cd2−O10−C13−C12−O9−C6−C5−C4−O3−C8−C9−O5−Cd2−O10−Cd1−O1−C1−C2−C7−C6−C5−O6−C10−C11−O7− and −Cd1−O10−Cd2−O6−C5−C4−O3−C8−C9−O5−Cd2−O11−C13−O10−Cd2−O8−C11−O7−Cd3−O5−Cd2−O9−C6−C7−C2−C1−O1− respectively, and the pitches of them (23.68 Å) running along the *a*-axis are twice the length of *a* axis unit (11.84 Å).

From a network topological point of view to the framework of **1**, a subunit, [Cd$_6$(OH)$_4$]$^{8+}$ of the network has been formed by a centrosymmetric hexameric Cd cluster consisting of two Cd1, two Cd2 and two Cd3 ions connected via four hydroxyl oxygen atoms (Fig. 1c). Therefore, each TCBA^{4-} ligand, linking five [Cd$_6$(OH)$_4$]$^{8+}$ clusters, can be regarded as a five-connection node (Fig. 2a). At the same time, each [Cd$_6$(OH)$_4$]$^{8+}$ cluster, surrounded by four [Cd$_6$(OH)$_4$]$^{8+}$ and ten TCBA^{4-} ligands, should be viewed as a fourteen-connection node (Fig. 2b). Consequently, after introducing TCBA^{4-} ligands into the inorganic skeleton, the topological net of **1** is changed from 4-connected pure inorganic net to a rare 2-nodal (5,14)-connected net, with the Schläfli symbol of $\{3^{12}\cdot4^{34}\cdot5^{30}\cdot6^{14}\cdot7\}\{3^{3}\cdot4^{6}\cdot5\}_2$ (Fig. 2c), in which the ratio of [Cd$_6$(OH)$_4$]$^{8+}$ and TCBA^{4-} anions is 1:2. Topology analysis for existing networks reveals that small number of nodes and edges, such as 3-C srs, 4-C dia and 6-C pcu nets are the most common nets with high frequency. Bi-nodal such as (3,8)-, (3,9)-, (3,12)-, (4,8)- and (4,10)-c are occasionally documented,[8] however, among the reported nets based on polynuclear metal clusters, the ones with this kind of high connections have not been observed so far.

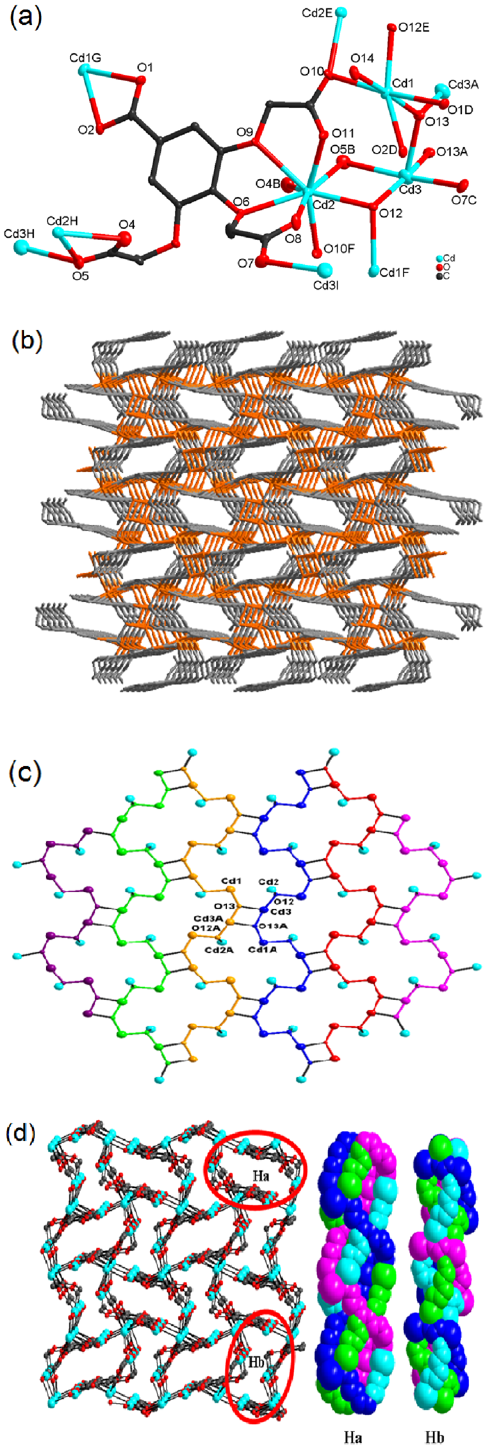

Fig. 1 (a) Coordination environment of Cd(II) ion in complex **1**, the bridging modes of TCBA^{4-} and two types of μ_3-OH bridges. (b) The structure of **1** containing 2-D inorganic (orange) and 3-D organic (gray) connectivity along *a*-axis. (c) The 2-D pure inorganic connectivity exhibiting a 4-connected layer bridged by hydroxyl oxygen atoms along *a*-axis after omitting TCBA^{4-} ligands, the hexameric Cd cluster (marked atoms), Cd−O(hydroxyl)−Cd helix chain, pink, blue and green represent right-handed helix chains, while red, orange and purple indicate left-handed helix chains. (d) The 3-D organic connectivity through the linking of TCBA^{4-} anions to three independent Cd(II) ions after omitting μ_3-OH bridges along *a*-axis, containing two kinds of quadruple-stranded helix chains (Ha and Hb) with two right handed and two left handed helices.

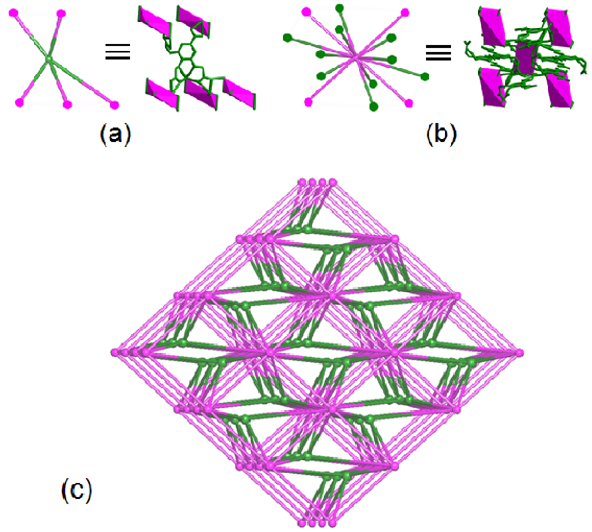

Fig. 2 Schematic representation for the nodes of TCBA^{4-} anions (a) and [Cd$_6$(OH)$_4$]$^{8+}$ cluster (b). (c) The (5,14)-connected topological net in complex **1** (green and pink represent TCBA^{4-} ligands and [Cd$_6$(OH)$_4$]$^{8+}$ clusters respectively).

The results of powder X-ray diffraction (PXRD) measurements demonstrate that the as-synthesized bulk samples of **1** is a pure single phase hybrid material (Fig. S1, ESI). The result of thermogravimetric analysis (TGA) indicates that **1** lost one coordinated water molecule and two hydroxyl groups in the temperature range of 85−150 °C, and the desolvated **1** is stable up to 350 °C (Fig. S2, ESI).

Conclusions

In conclusion, together with hydroxyl groups, structure-directing agent, 3,4,5-tris(carboxymethoxy)benzoic acid construct the first high-dimensional I^2O^3 hybrid framework, which also exhibits a highly-connected binodal (5,14-c) topological net, one Cd−$O_{hydroxyl}$ helix and two kinds of quadruple-stranded Cd−ligand helices.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallorgraphic files in CIF format for **1**, selected bond lengths and angles, and the selected hydrogen bonding lengths and angles of **1**, PXRD, TGA and crystallographic data (CCDC 999327), and details of experiments. See DOI: 10.1039/c000000x/.

‡ Crystallographic data for **1** ($C_{13}H_{12}O_{14}Cd_3$): M = 729.43, monoclinic, $P2_1/c$, a = 11.8373(10), b = 11.5492(9), c = 12.7035(10) Å, β = 95.0680(10)°, V = 1729.9(2) Å^3, Z = 4, μ = 3.735, D_C = 2.801 g·cm^{-3}, $F(000)$ = 1384, 3207 unique numbers (R_{int} = 0.0167), R_1 = 0.0228, wR_2 = 0.0881 ($I>2\sigma(I)$), *GOF* =1.089. CCDC reference number is 999327.

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TOC graphic for

A rare I^2O^3 hybrid organic-inorganic material with high-connection and quadruple-stranded helices

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A novel I^2O^3 hybrid material with one Cd-OH helix, two quadruple-stranded Cd-ligand helices and a (5,14-c) topological net was assembled.