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An unprecedented organic-inorganic hybrid material with the I^3O^3 framework based on cadmium hydroxide and in situ generated 1*H*-tetrazolate-5-acetic acid

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Herein, we report a novel high-dimensional I^3O^3 organic-inorganic hybrid framework, namely $[Cd_3(OH)_2(tza)_2]_n$ (1) (H_2tza = 1*H*-tetrazolate-5-acetic acid), where a rare pure *ths* inorganic connectivity of $Cd–O_{hydroxyl}$ is observed. Meanwhile, 1 displays blue emissions and high thermal stability up to 370 °C.

Organic-inorganic hybrid materials as a very active research area have received much attention for decades due to their highly tunable structures and intriguing properties combining the advantages of both organic and inorganic materials.[1] To date, a large number of organic–inorganic hybrids with I^nO^m ($I^0O^{1–3}$, $I^1O^{0–2}$, $I^2O^{0–1}$, and I^3O^0) frameworks, where *n* and *m* refer to the dimensionalities of inorganic (I) and organic (O) connectivity, respectively, have been reported in several current reviews[2] and promising applications in gas storage, separation, magnetism, catalysis and photochemistry have also been recognized.[3] The whole dimensionality of most hybrid frameworks is between 0 and 3 ($m + n \leqslant 3$). There has been considerable interest in the possible existence of superimposed dimensionality over 3 ($m + n > 3$).[4] A striking example of I^2O^3 hybrid framework, $[Cd_3(OH)_2(TCBA)(H_2O)]$ (H_4TCBA = 3,4,5-tris(carboxymethoxy)-benzoic acid), has been recently reported.[5] Notably, the hybrid frameworks possessing extended inorganic connectivity (especially I^3O^n) are desirable for enhanced thermal, magnetic, electronic, and optical properties, as embodied by metal oxides. However, 3-D inorganic connectivity in such systems remains a significant challenge.[6] This is because of the prerequisite for it that the polyhedron around the central atom must share corners or edges with at least three adjacent polyhedra toward three separated directions. To the best of our knowledge, a few I^3O^n (only one I^3O^3, two I^3O^1, and other I^3O^0) examples have been successfully synthesized so far.[7,8] Interestingly, the only I^3O^3 example, $[Cd_7(OH)_6(tzf)_4]_n$ (H_2tzf =1*H*-tetrazolate-5-formic acid) shows a highly connected trinodal (4,8,16-*c*) topological net.

We herein report another unique high-dimensional I^3O^3 framework, namely $[Cd_3(OH)_2(tza)_2]_n$ (**1**, H_2tza = 1*H*-tetrazolate-5-acetic acid), in which a rare pure *ths* inorganic connectivity of $Cd–O_{hydroxyl}$ is observed. Notably, the $tza^{2–}$ ligand is successfully used as a structure-directing agent in organic-inorganic hybrids for the first time. Meanwhile, compound **1** exhibits blue emissions and high thermal stability up to 370 °C.

As-synthesized, hydrothermal reaction of $CdCl_2·2.5H_2O$, $NCCH_2COOH$ (cyanoacetic acid), NaN_3 and NaOH afforded **1**.[9] The $tza^{2–}$ ligand was produced through *in situ* [2 + 3] cycloaddition of nitrile and azide, which was from *in situ* hydrolysis of ester group in our previously reported $tza^{2–}$-based complexes.[10] The result of single-crystal *X*-ray diffraction analysis indicates that **1** crystallizes in an acentric F*dd*2 space group.[‡] The asymmetric unit of **1** contains one and a half crystallographically independent Cd(II) atoms, one $tza^{2–}$ ligand and one μ_3-$OH^–$ anion (Fig. 1). Notably, there is no coordinated aqua or lattice water molecule found in **1**, although it was synthesized in a water solution. The Cd1 atom adopts a distorted N_2O_4 (N4, N4F, O1L, O1G, O3 and O3F) octahedral geometry, while the Cd2 center has a distorted N_2O_5 (N3J, N1H, O2H, O1G, O2K, O3 and O3I) pentagonal bipyramidal geometry. Both Cd(II) centers are surrounded by four symmetrically related $tza^{2–}$ ligands and two μ_3-$OH^–$ anions. The Cd2–O2K distance of 2.734(2) Å is much longer than other Cd–O (2.247(2)–2.498(2) Å) and Cd–N (2.313(3), 2.358(3) and 2.362(3) Å) distances, indicating the weak interaction between Cd2 and O2K atom. Each μ_3-$OH^–$ anion links two Cd2 and one Cd1 centers. The $tza^{2–}$ ligand bonds to six Cd(II) centers through three N atoms and two O atoms, exhibiting an unusual μ_6-κN1,O2:κN3:κN4:κO1:κO1:κO2 mode (Fig. 1). Interestingly, it is similar to that of $tzf^{2–}$ in the reported hybrid $[Cd_7(OH)_6(tzf)_4]_n$, μ_6-κN1:κN3:κN4:κO1:κO2 without the *N*,*O*-chelated mode, which readily forms extended inorganic conne-

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† Electronic Supplementary Information (ESI) available: Crystallographic data in CIF, selected bond lengths for **1** and TGA, PXRD results. CCDC reference number 1410588. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

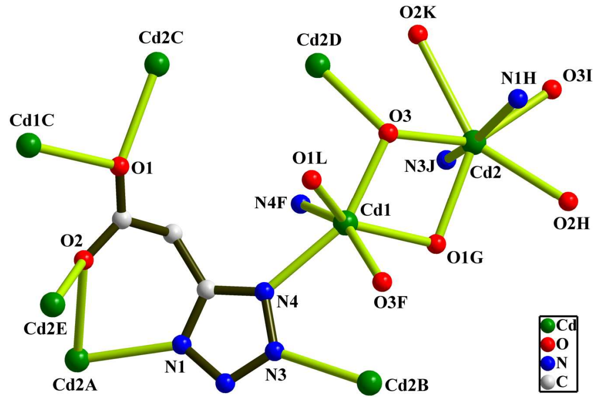

Fig. 1 The coordination environments around the Cd(II) centers and tza^{2-} ligand in **1**. Symmetry codes: (A) –x, 1 – y, –1+z; (B) –0.25 – x, 0.25 + y, –0.25 + z; (C) 0.5 + x, y, –0.5 + z; (D) 0.25 – x, 0.75 – y, –0.25 + z; (E) 0.25 – x, 0.25 + y, –0.75 + z; (F) –x, 1 – y, z; (G) –0.5 + x, y, 0.5 + z; (H) –x, 1 – y, 1 + z; (I) –0.25 + x, 0.75 – y, 0.25 + z; (J) –0.25 – x, –0.25 + y, 0.25 + z; (K) 0.25 – x, –0.25 + y, 0.75 + z; (L) 0.5 – x, 1 – y, 0.5 + z.

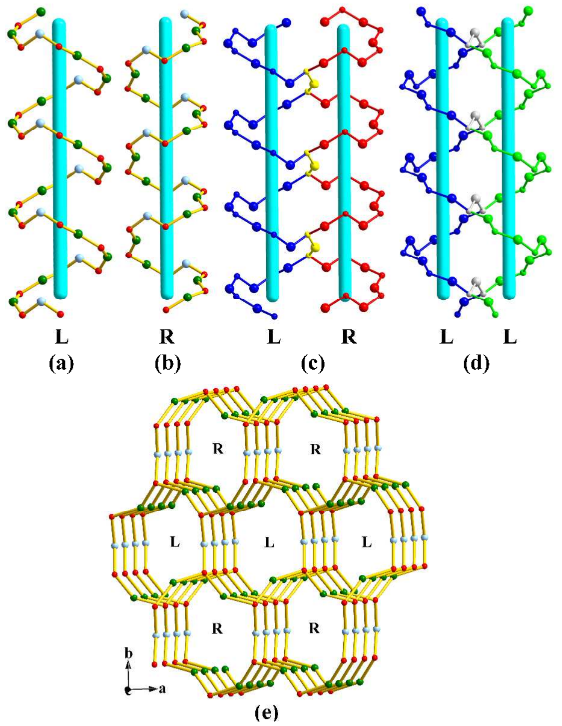

Fig. 2 (a, b) View of a left- and a right-handed $\{CdO\}_n$ helical chain. Green: Cd2, pale blue: Cd1, red: μ_3-OH^-. (c, d) View of a left-handed helix (blue) that shares edge with a right-handed (red) and a left-handed helix (bright green). The shared edges {O3–Cd2–O3} and {O3–Cd1–O3} are shown in yellow and gray, respectively. (e) View of the 3-D inorganic framework of cadmium hydroxide from the *c*-axis. Green: Cd2, pale blue: Cd1, red: μ_3-OH^-.

ctivity. However, both μ_6-bridging modes of tetrazolate-5-carboxylate have not been found in reported MOFs,[11] where these ligands tend to link metal centers in lower μ-bridging modes (μ_1–μ_5). It implies that the connecting modes of ligands can be important in the construction and structural types of hybrids.

The outstanding structural feature of **1** is the presence of a rare pure 3-D inorganic framework of cadmium hydroxide when μ_6-tza^{2-} ligands are omitted (Fig. 2). Viewed down the *c*-axis, the intricate inorganic network can be described as the close-packed arrangement of left- and right-handed $\{CdO\}_n$ helical chains (Fig. 2a,b). The helix is formed in the sequence of {-Cd2-O3-Cd2-O3-Cd1-O3-} and the helical pitch is 7.7275(17) Å. Each left-handed helix is surrounded by four right-handed and two left-handed ones (and vice versa) by sharing its segment of {O3-Cd2-O3} and {O3-Cd1-O3} respectively (Fig. 2c,d), leading to the formation of 3-D inorganic network (Fig. 2e). Better insight of this complicated 3D inorganic net can be achieved by topology analysis. Each Cd(II) atom is linked by two μ_3-OH^- anions, and each μ_3-OH^- anion links three Cd(II) atoms, generating a 3-connected *ths* ($ThSi_2$) net (Fig. S1). Note that it differs from the *dia* (diamond) inorganic subnet in the reported hybrid $[Cd_7(OH)_6(tzf)_4]_n$,[7] although both are fully linked by μ_3-OH^- anions. Note, too, that the other reported 3-D M-O-M inorganic connection (within organic-inorganic hybrids) are all linked by oxygen atoms of carboxylates.[6,8]

Another interesting feature of **1** is the 3-D organic network interlinked by the tza^{2-} ligands and Cd(II) centers, when the inorganic μ_3-OH^- bridges are omitted (Fig. 3). Both Cd1 and Cd2 atoms are linked by four tza^{2-} ligands, and each tza^{2-} ligand links six Cd(II) atoms (four Cd2 and two Cd1), corresponding to a new trinodal (4,4,6-*c*)-connected topology with the Schläfli symbol of $\{4^2{\cdot}6^4\}_2\{4^4{\cdot}6^2\}\{4^4{\cdot}6^9{\cdot}8^2\}_2$ (Fig. S2). Taking into account inorganic skeleton, the whole dimensionality of **1** can be described as I^3O^3 (Fig. 4). Accordingly, the final hybrid framework of **1** is changed to a simplified (3,6,6,6-*c*)-connected net with three-connected μ_3-OH^- and six-connected Cd1, Cd2 and tza^{2-} ligands as depicted in Fig. S3. Interestingly, the simplified net sustains the integrity of inorganic connectivity and close-packed arrangement of $\{CdO\}_n$ helical chains, along with the appearance of μ_6-tza^{2-} ligands, which connect Cd(II) atoms in the helical chains and fit very well with respect to the helix axis (Fig. S3b,c). Thus, the μ_6-tza^{2-} ligands in **1** can also be considered as decorative linkages to strengthen the existing 3-D inorganic framework.

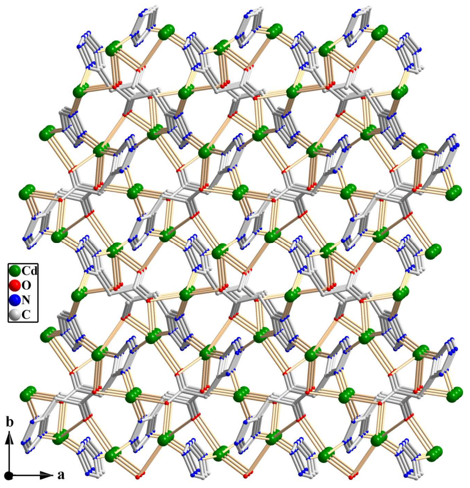

Fig. 3 View of the 3-D organic connectivity interlinked by tza^{2-} ligands and the Cd(II) centers.

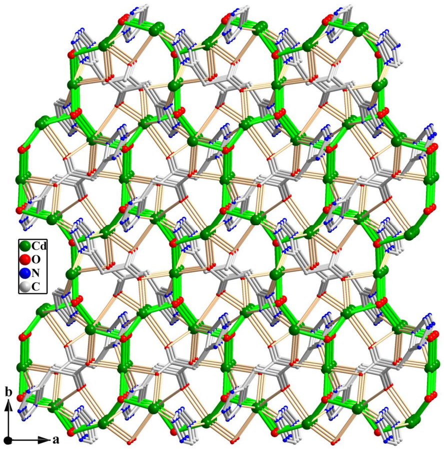

Fig. 4 The final I^3O^3 structure of **1** containing 3D inorganic and 3D organic connectivity.

Interestingly, **1** represents the second I^3O^3 hybrid framework. Clearly, both of the I^3O^3 hybrids $[Cd_7(OH)_6(tzf)_4]_n$ and $[Cd_3(OH)_2(tza)_2]_n$ **(1)** are constructed by tetrazolate-5-carboxylate ligands (tzf^{2-} and tza^{2-}), Cd(II) centers and μ_3-OH^- anions. However, their network topologies are quite different: (3,6,6,6-*c*)-connected net based on *ths* inorganic subnet for **1**, while (4,8,16-*c*)-connected net based on *dia* inorganic subnet for the former. The different structures may be attributed to the flexible nature of $tzf^{2-}$and tza^{2-} ligands, diverse coordination environments of Cd(II) centers, as well as distinct space groups (*I*-4 for $[Cd_7(OH)_6(tzf)_4]_n$ and F*dd*2 for **1**). The results imply that the flexible tetrazolate-5-carboxylate ligands can provide excellent structure-directing agent for organic–inorganic hybrids with 3D inorganic connectivity.

Hybrid **1** is insoluble in water and common solvents. The experimental X-ray powder diffraction (XRPD) pattern of **1** at room temperature agrees well with the simulated one based on the single-crystal X-ray data (Fig. S4), indicating that **1** is in a pure phase. The thermal stability of **1** was checked by thermogravimetric analysis (TGA), which revealed a temperature range (high up to 370 °C) of stability with no observable weight loss (Fig. S5).

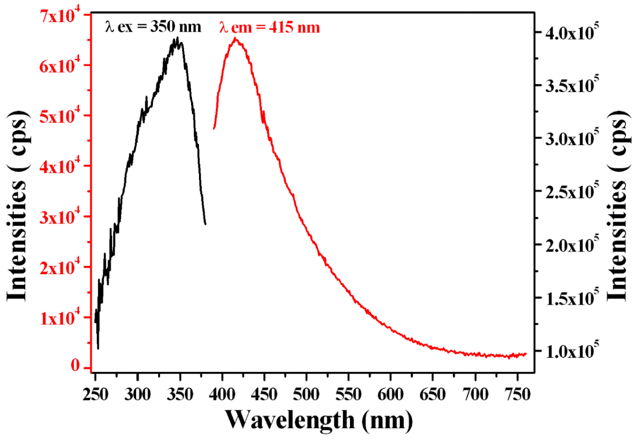

Fig. 5 The excitation and emission spectra in the solid state for **1**.

The solid-state photoluminescence spectra of **1** at room temperature reveal a blue emission peak at 415 nm upon excitations at 350 nm (Fig. 5). The photoluminescent mechanism is tentatively attributed to intraligand transitions mainly through the tetrazolate ring of tza^{2-} ligand.[12] The results suggest that **1** is a good blue light-emitting material candidate. On the other hand, no obvious response of second harmonic generation (SHG) for **1** is detected, although **1** crystallizes in the acentric space group F*dd*2. The relative weaker response of **1** with respect to $[Cd_7(OH)_6(tzf)_4]_n$, presumably is a result of the donor (tetrazolate group)-acceptor (carboxylate group) system separated by alkyl -CH_2- spacer for tza^{2-}.

Conclusions

In summary, utilizing structure-directing agent, 1*H*-tetrazolate-5-acetic acid, and hydroxyl groups, we have obtained an unprecedented I^3O^3 framework, $[Cd_3(OH)_2(tza)_2]_n$ **(1)**, which presents a (3,6,6,6-*c*)-connected net based on rare pure *ths* inorganic subnet of Cd–$O_{hydroxyl}$. Notably, the self-assembly of **1** not only expands the pool of inorganic building blocks, but also offers a broader vision for the construction of organic–inorganic hybrid frameworks.

Acknowledgements

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Notes and references

‡ Crystallographic data for **1** ($C_6H_6N_8O_6Cd_3$), M_r = 623.39, Orthorhombic, *Fdd*2, a = 12.808 (13) Å, b = 24.306(8) Å, c = 7.7275(17) Å, $\alpha = \beta = \gamma = 90°$, V = 2406(3) $Å^3$, Z = 8, μ = 5.309 mm^{-1}, D_c = 3.442 Mg m^{-3}, F(000) = 2320, 3715 reflections collected, 1081 unique, R_{int} = 0.0376, S = 0.958, R_1 = 0.0193, ωR_2 = 0.0304 ($I > 2\sigma(I)$). CCDC reference number is 1410588.

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9 Synthesis of **1**: A mixture of $NCCH_2COOH$ (0.026 g, 0.3 mmol), $CdCl_2·2.5H_2O$ (0.137 g, 0.6 mmol), NaN_3 (0.039 g, 0.6 mmol), and NaOH (0.020g, 0.5 mmol) in aqueous solution (5 mL) was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 140 °C for 3 days and then slowly cooled to 30 °C. Colorless block crystals suitable for X-ray analyses were obtained, washed with distilled water and dried in air. Yield: 28 mg (about 22% based on Cd) for **1**. Anal. Calcd for $C_6H_6N_8O_6Cd_3$: C, 11.56; H, 0.97; N, 17.97%. Found: C, 11.49; H, 1.01; N, 17.86%. IR (KBr pellet, cm^{-1}, Fig.S6): 3454s, 1591vs, 1550s, 1390vs, 1122m, 858w, 736m, 709m, 594w.

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Graphical Abstract

An unprecedented organic-inorganic hybrid material with the I^3O^3 framework based on cadmium hydroxide and in situ generated 1*H*-tetrazolate-5-acetic acid

Mei-Feng Wu,*[ab] Ting-Ting Shen,[a] Shuai He,[a] Ke-Qin Wu,[a] Shuai-Hua Wang,[b] Zhi-Fa Liu,[b] Fa-Kun Zheng,*[b] and Guo-Cong Guo[b]

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A novel high-dimensional I^3O^3 organic-inorganic hybrid framework was generated, based on a rare pure *ths* inorganic subnet of cadmium hydroxide and the 3-D organic network interlinked by tza^{2-} ligands and the Cd(II) centers.