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COMMUNICATION

A 6-fold interpenetrated $ThSi_2$ topological metal–organic framework from a nanosized tripodal aromatic acid†

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A unique anionic 6-fold interpenetrated (10,3)-b Cd(II) framework was obtained using a novel nanosized tripodal aromatic acid ligand, in which both the Cd(II) atoms and tripodal aromatic acid ligands act as three-connected nodes. This compound displays intense and blue-shifted photoluminescence compared to that of the free H_3L ligand.

Metal–organic frameworks, that consist of inorganic connectors (metal ions or polynuclear clusters) and organic ligand linkers, have become an important class of porous materials.[1] MOFs with rigid or flexible channels have potential applications in selective molecular recognition and separation, physical gas storage, chemical absorption and photoluminescence areas.[2] It has been shown that using large organic ligands is a very successful strategy towards constructing MOFs with large pore sizes and free volumes and enhancing their gas storage and adsorption properties.[3] For example, Yaghi and his group have achieved a large series of isoreticular networks with calculated pore sizes up to 28.8 Å and fractional free volumes up to 91.1% using large organic ligands, including naphthalene-2,6-dicarboxylate, biphenyl-4,4′-dicarboxylate, pyrene-2,7-dicarboxylate or terphenyl-4,4′′-dicarboxylate.[4] More recently, Zhou and co-workers have synthesized a very large organic ligand H_6ttei and a (3,24)-connected network (PCN-610) with a high gas uptake capacity was obtained *via* a reaction between H_6ttei and copper salts.[5b] Undoubtedly, larger ligands will lead to larger voids but, occasionally, with a higher degree of interpenetration. Interpenetration has been demonstrated as a useful method for reducing the pore size and partitioning and optimizing the pore space as well as a strategy to improve the hydrothermal stability and gas uptake capacity of porous MOFs.[6] Interpenetrating networks (IPN) that consist of two or more networks of different or the same components are of great technological interest because they allow a blending of two or more otherwise incompatible properties or functions. Furthermore, synergistic effects might arise from the simultaneous operation of the two networks.[7] A variety of attractive interpenetrating frameworks have been obtained and are well discussed in the comprehensive reviews by Batten and Robson.[8] However, the discovery of novel interpenetrating networks is still a great challenge. For example, almost all the known examples of interpenetrating 3-connected 3D nets are of either the (10,3)-a type[3d,9,10] or (10,3)-b type,[11,12] along with a few other types, such as (10,3)-d and the (8,3)-c type.[13] However, to the best of our knowledge, interpenetrating nets based on (10,3)-b topology are mostly 2-fold, 3-fold, 4-fold, a few 6-fold networks, built on transition metal ions and N-donor ligands or supplementary carboxylic acid ligands[11,12] and a very rare 8-fold interpenetration structure.[11f] Thus far, there has been no reports on 6-fold interpenetrating nets with (10,3)-b topology constructed from single carboxylic acid ligands with metal ions.

Herein, we report the synthesis of a novel nanosized tricarboxylic acid ligand H_3L (H_3L = 4,4′,4′′-((benzene-1,3,5-triyltris(methylene))tris(oxy)) tribenzoic acid) and the structure and luminescent properties of a new coordination polymer $[Cd(L)(C_3H_7NO)](C_2H_8N)(H_2O)_{0.5}$ (**1**), which displays a highly porous 6-fold-interpenetrated structure with (10,3)-b topology. We chose a semi-rigid H_3L carboxylate ligand as the organic ligand based on the following considerations: (i) the carboxylate group can adopt a variety of coordination modes, for example, the chelating-bidentate and bridging-bidentate modes; (ii) owing to the presence of a $–CH_2–O–$ spacer, H_3L can be used as a flexible ligand to fabricate abundant structural motifs; (iii) the larger ligand will lead to larger voids which allow for a higher degree of interpenetration.

The H_3L ligand was synthesized *via* the condensation of a mixture of methyl 4-hydroxybenzoate, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, K_2CO_3 and 18-crown-6 in THF under a nitrogen atmosphere.[14] This ligand contains $–CH_2–O–$ linkages that can display good flexibility and may provide an abundant diversity when constructing MOFs with transition metal ions. Compound **1** was prepared by the reaction of $CdBr_2·4H_2O$ with

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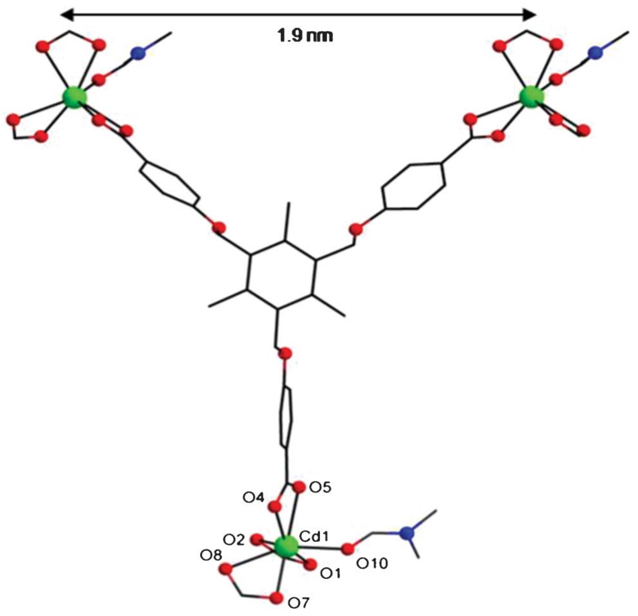

Fig. 1 The H_3L ligand connected to three Cd(II) ions in compound **1**.

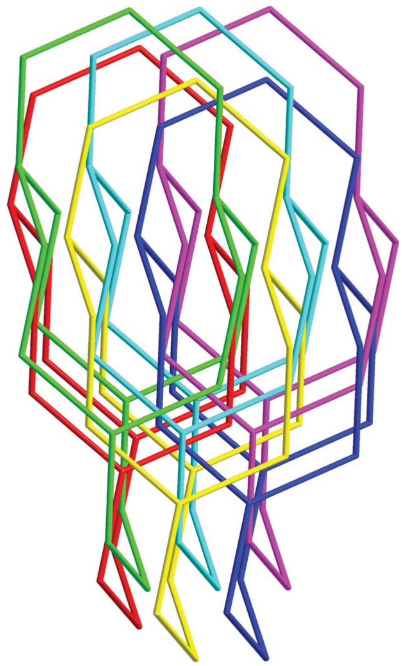

Fig. 3 Topological representation of the 6-fold interpenetrating network of **1**.

H_3L in DMF–H_2O at 180 °C for 72 h (see the ESI for details†). **1** crystallizes in the *C*2/*c* monoclinic space group.[15] As shown in Fig. 1, each Cd(II) atom is coordinated by three COO– groups from three individual L^{3-} ligands and one CO– group from DMF with a distorted pentagonal bipyramid coordination geometry. The distances of the Cd–O bonds fall between 2.257(4) Å and 2.496(4) Å and the O–Cd–O bond angles range between 54.51(12)° and 163.46(15)°, which is within the range reported in the previous reports[11*d*,16] (detailed data for the bond lengths and angles of **1** are in Table S1†). Each L^{3-} ligand adopt a *cis*,*trans*,*trans*-conformation and acts as a tripodal chelate ligand linking three Cd(II) atoms, giving rise to a unique 3-connected network. Furthermore, the average distance between two neighbouring Cd(II) atoms that are bridged by the same tricarboxyl ligand is ∼1.9 nm (Fig. 1). Topological analysis (using TOPOS software[17]) shows that **1** is a (10,3)-b net (sometimes referred to as a $ThSi_2$-related net) composed of 3-connected Cd(II) and L^{3-} nodes (Fig. 2 and Fig. 3). To our surprise, there are six individual 3D $ThSi_2$ nets interpenetrated together due to the large void in the single net of compound **1**. Compared with the few reported MOFs of the $ThSi_2$ topological type, this is the first MOF constructed from a tripodal aromatic acid ligand. It is worth mentioning that **1** is also the first example of a 6-fold interpenetrated anionic net with (10,3)-b topology. As a matter of fact, $[(CH_3)_2NH_2]^+$, one of the hydrolysis products of DMF, is a cation lying within the cages of the 3D framework and keeps the framework neutral. Nonetheless, there are still voids even though 6-fold interpenetration has occurred. The effective free volume of **1**, calculated by PLATON[18] analysis,

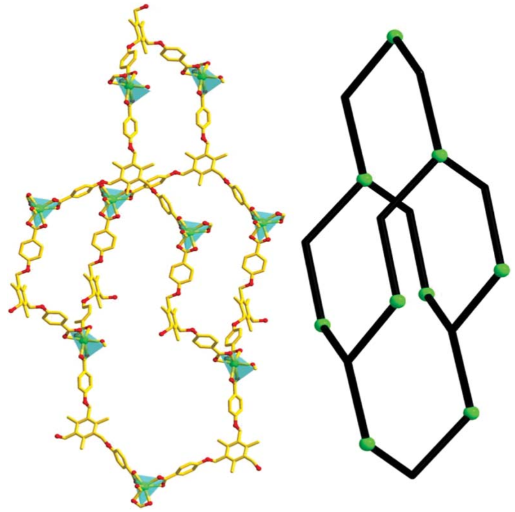

Fig. 2 A single $ThSi_2$ cage unit of **1** with (10,3)-b topology.

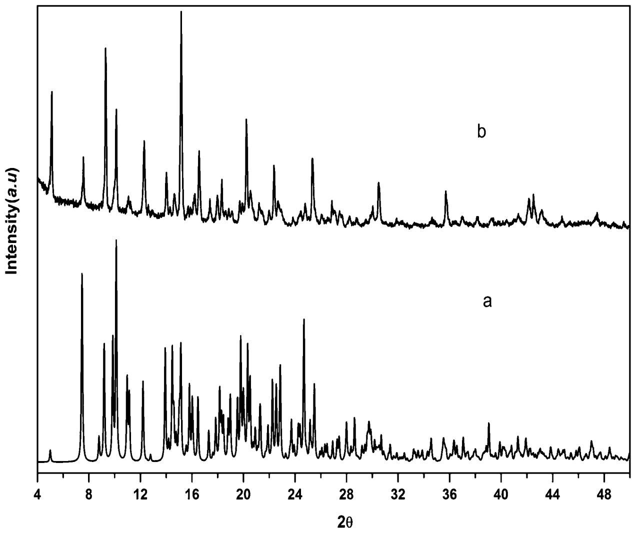

Fig. 4 Experimental X-ray powder pattern of **1**: (a) calculated pattern and (b) experimental pattern.

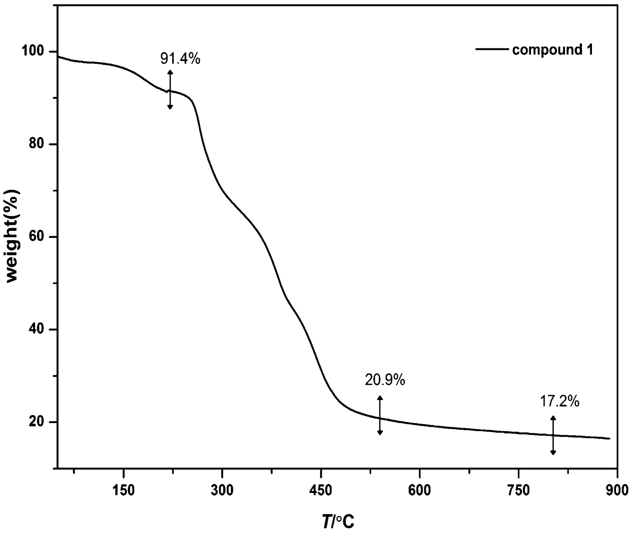

Fig. 5 TG curve of compound **1**.

is 9.2% (8113.4 Å^3 per unit) in spite of the C_3H_7NO (DMF) molecules and $[(CH_3)_2NH_2]^+$ cations.

X-ray powder diffraction (XRPD) data was collected on a Bruker D8 Advance instrument using a Cu–Kα radiation (λ = 1.54056 Å) at room temperature to check the phase purity of **1**. The peak positions of the simulated and experimental XRPD patterns are in good agreement with each other, as shown in Fig. 4, demonstrating the good phase purity of **1**.

TG was performed to verify the thermal stability of **1**. As depicted in Fig. 5, a total weight loss of 9.2% was observed for **1** in the temperature range of 100–216 °C, which is ascribed to the loss of one guest DMF molecule (calcd. 8.6%). Upon heating up, the framework decomposed and left 16.1% of a CdO (calcd. 17.2%) residue. It is a pity that we failed to investigate the hydrogen uptake in compound **1** due to its poor thermostability.

The luminescence properties of **1** and the free H_3L ligand were investigated in the solid state at room temperature. As depicted in Fig. 6, compound **1** exhibits a strong emission band at approximately 315 nm upon excitation at 250 nm, which may be assigned to intralinker (n→π*or π→π*) emission as similar emissions are observed at 370 nm for the free H_3L ligand.[19] In compound **1**, guests (DMF) or counter ions ($[(CH_3)_2NH_2]^+$) in the lattice may prevent the efficient energy transfer from the linker to the metal centers, resulting in linker-centered luminescence in the UV region.[20] Furthermore, the emission peak of **1** exhibits a blue-shift with respect to the free H_3L ligand, which may be attributed to guests or counter ions, together with the highly-dimensional interpenetrated structure.[21]

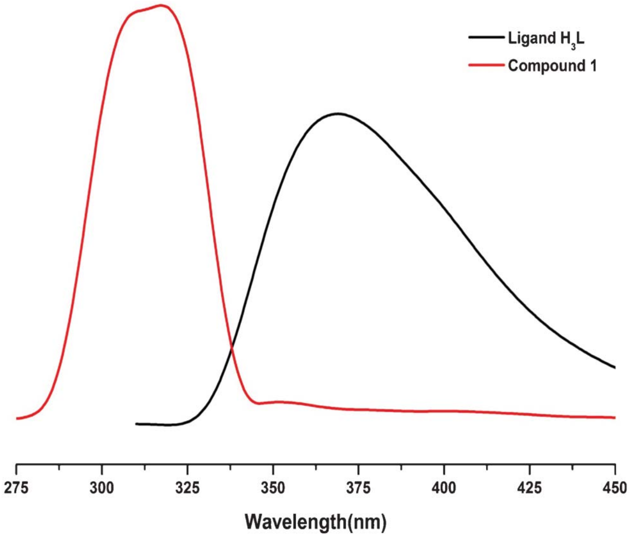

Fig. 6 Emission spectra of **1** and the free H_3L ligand in the solid state at room temperature.

In summary, a unique Cd(II) coordination framework was obtained using a novel nanosized tripodal aromatic acid H_3L ligand. This new MOF exhibits a rare anionic 6-fold-interpenetrated open framework with (10,3)-b topology, in which DMF molecules and cations fill the vacancies. **1** displays intense and blue-shifted photoluminescence compared to that of the free H_3L ligand. The use of the nanosized organic H_3L ligand containing efficiently flexible $–CH_2–O–$ linkages is a rational method for the construction of flexible open-framework materials. Currently, further investigations on the use of the H_3L ligand for the isolation of new porous MOFs are in progress and these results will be presented in the near future.

Acknowledgements

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15 Crystal data for compound **1**: $C_{38}H_{43}CdN_2O_{10\cdot50}$, M = 808.14, monoclinic, a = 23.681(2) Å, b = 9.6928(7) Å, c = 35.389(3) Å, α = 90.00°, β = 92.7890(10)°, γ = 90.00°, V = 8113.5(12) Å^3, T = 298(2) K, space group $C2/c$, Z = 8, 20001 reflections measured, 7161 independent reflections (R_{int} = 0.0754). The final R_1 values were 0.0715 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1895 ($I > 2\sigma(I)$). The final R_1 values were 0.1083 (all data). The final $wR(F^2)$ values were 0.2026 (all data). The goodness of fit on F^2 was 1.238.

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