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Lanthanide Metal–Organic Frameworks Based on Octahedral
Secondary Building Units: Rare Net Topology and LuminescenceLi Yan,[†] Qi Yue,[†] Qin-Xiang Jia,[†] Gilles Lemerrier,^{*} and En-Qing Gao^{*,†}Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry,
East China Normal University, Shanghai 200062, China, and Université Reims Champagne-Ardenne,
Institute of Molecular Chemistry of Reims, UMR CNRS 6229, BP 1039 - 51687 Reims Cedex 2,
France

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ABSTRACT: Three isomorphous three-dimensional (3D) lanthanide metal–organic frameworks, $[\text{Ln}_2(\text{DBTDC-O}_2)_3(\text{DMF})_4] \cdot 3\text{DMF} \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{and Gd}$), have been solvothermally synthesized and characterized, where $\text{H}_2\text{DBTDC-O}_2$ is a sulfone-functionalized bridging ligand, *S,S*-dioxodibenzothiophen-3,7-dicarboxylic acid. In the structures, two lanthanide(III) ions are bridged by four *syn-syn* carboxylate groups and chelated by another two carboxylate groups to generate a $[\text{Ln}_2(\text{COO})_6]$ dinuclear moiety, which serves as octahedral secondary building units (SBUs) to produce the rare **sbx** 3D net ($4^85^46^3$), instead of the default primitive cubic (**pcu**) net. The frameworks possess relatively large solvent-occupied cavities despite the presence of 2-fold interpenetration. The Eu(III) compound displays intense luminescence as a result of the efficient ligand-to-metal energy transfer.

Lanthanide metal–organic frameworks (LMOFs) have evoked increasing interest not only for the general properties/applications of MOFs, such as tailorable porosity,^{1–3} but also for their special chemical/physical characteristics arising from 4f electrons, such as luminescence.^{4–6} Taking advantage of the high affinity of lanthanide ions for oxygen, a number of LMOFs with various dimensionality and topologies have been synthesized from multicarboxylate ligands.^{5,6} However, the rational design of LMOFs is more difficult and challenging than the design of MOFs with transition metal ions because lanthanide metal ions have high and variable coordination numbers and flexible coordination geometry. The net-based approach proposed by Robson et al.⁷ and the related “reticular synthesis” approach proposed by Yaghi et al.⁸ have proven very useful for the design of coordination networks. A plethora of transition metal MOFs with specifically shaped metal-carboxylate cluster motifs as secondary building units (SBUs) have been synthesized.⁹ For LMOFs, different binuclear $[\text{Ln}_2(\text{COO})_6]$ motifs containing different relative numbers of bridging and chelating carboxylate groups have been recognized as octahedral SBUs, and the combination of such SBUs with dicarboxylates, such as 1,4-benzenedicarboxylate and 4,4'-azodibenzoate, has led to several 3D coordination frameworks with the default primitive cubic (**pcu** or α -Po) net.¹⁰ “Default nets” refer to high-symmetry nets that are preferred overwhelmingly among the very large number of potential nets for an SBU with specific connectivity and geometry.⁸ Here we report a series of novel 3D LMOFs, $[\text{Ln}_2(\text{DBTDC-O}_2)_3(\text{DMF})_4] \cdot 3\text{DMF} \cdot 2\text{H}_2\text{O}$ (denoted as 1- Ln hereafter, $\text{Ln} = \text{Nd}, \text{Eu}, \text{and Gd}$), derived from a new dicarboxylate ligand bearing the sulfone functionality, 5,5-dioxodibenzothiophen-3,7-dicarboxylic acid ($\text{H}_2\text{DBTDC-O}_2$). These are the first coordination compounds with sulfone-functionalized DBTDC- O_2 ligand, and the 3D frameworks are based on octahedral $[\text{Ln}_2(\text{COO})_6]$ SBUs similar to those recognized in previous **pcu** structures but exhibit very rare **sbx** net topology (Schläfli symbol $4^85^46^3$).¹¹ Compound 1-Eu exhibits intense luminescence characteristic of Eu(III) materials with efficient ligand-to-metal energy transfer.

The compounds were synthesized from LnCl_3 and $\text{H}_2\text{DBTDC-O}_2$ under solvothermal conditions in DMF.¹² Single-crystal X-ray analyses¹³ suggested that 1-Eu, 1-Gd, and 1-Nd are isomorphous and exhibit isostructural 3D coordination frameworks with 2-fold

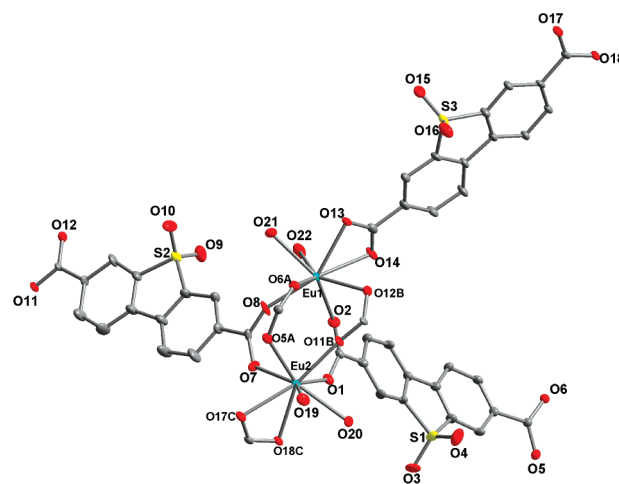


Figure 1. Coordination environments of Eu(III) ions in compound 1-Eu (30% probability thermal ellipsoids). For clarity, all hydrogen atoms are omitted, and for DMF molecules, only the coordinated oxygen atoms (O19, O20, O21, and O22) are shown. Symmetry codes: A = $x, -y + 1, z + 1/2$; B = $x, y - 1, z$; C = $x - 1/2, y + 1/2, z$.

interpenetration. The corresponding Ln–O distances follow the general trend of $\text{Nd-O} > \text{Eu-O} > \text{Gd-O}$ (Supporting Information), consistent with lanthanide contraction. The following description and discussion will be focused on 1-Eu. The asymmetric unit of the framework contains two independent Eu(III) ions, three DBTDC- O_2 ligands, and four DMF molecules (Figure 1). Each Eu atom is coordinated by eight oxygen atoms with a distorted square antiprismatic geometry. One basal face of the antiprism is defined by four carboxylate oxygen atoms from four DBTDC- O_2 ligands, with Eu–O in the range of 2.327(4)–2.498(4) Å. The other base is completed by another four oxygen atoms from a chelating carboxylate group and two DMF molecules, with Eu–O ranging from 2.320(4) to 2.523(4) Å. The above Eu–O distances fall in the usual range for Eu compounds with carboxylate ligands. The distortion of the antiprism is mainly due to the small bite angle (53.09° for Eu1 and 52.86° for Eu2) of the chelating carboxylate group. Two of the three independent DBTDC- O_2 ligands assume the μ_4 -bis(bridging) mode, with each carboxylate group bridging two metal atoms (Eu1 and Eu2) in *syn-syn* fashion. The third ligand adopts the μ_2 -bis(chelating) mode through the two carboxylate groups. All the ligands are quasi-linear and the two COO planes

* To whom correspondence should be addressed. E-mail: eqgao@chem.ecnu.edu.cn.

[†] East China Normal University.

^{*} Université Reims Champagne-Ardenne.

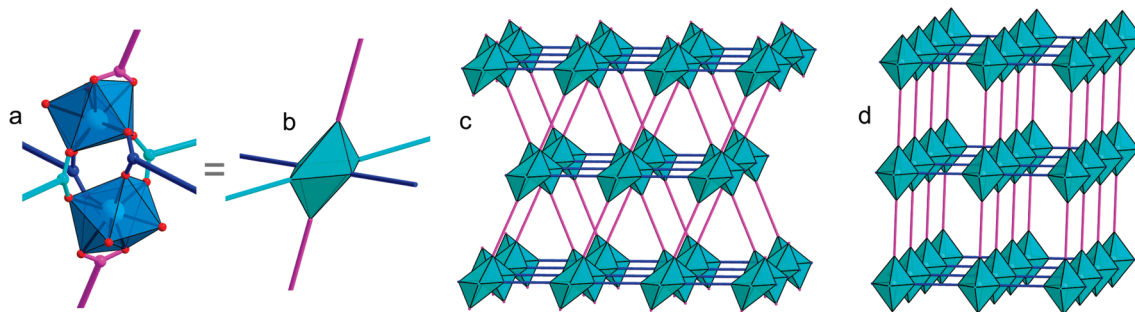


Figure 2. (a, b) Views showing that the binuclear SBU can be reduced to an octahedral node. The rods in cyan, blue, and purple represent the three different sets of linkers. (c) The 3D **sxb** net based on the octahedral node. (d) The default **pcu** net for octahedral nodes.

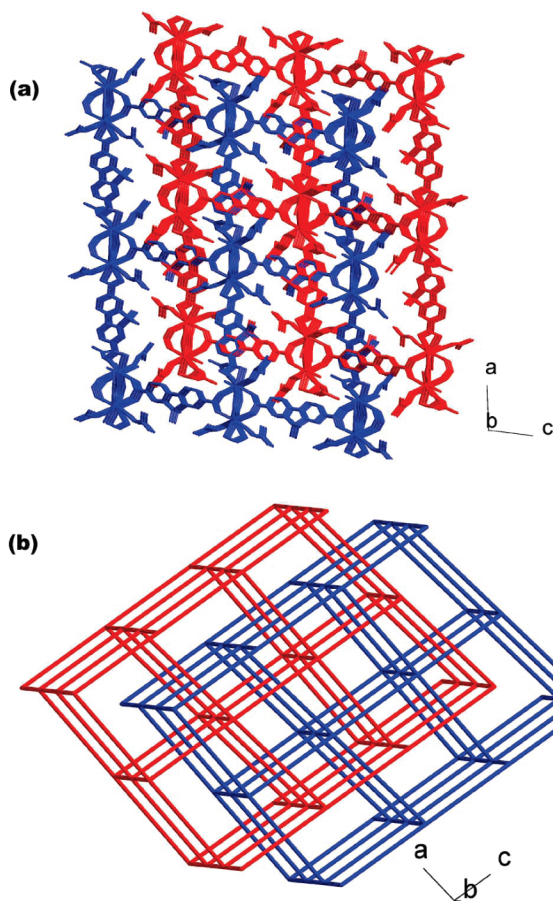


Figure 3. (a, b) Views showing the 2-fold interpenetration in **1-Eu**.

for each ligand are quasi-coplanar with the dihedral angle ranging from 3.7° to 24.6° . A pair of Eu1 and Eu2 is connected through four independent *syn-syn* carboxylate bridges to generate a binuclear unit, with an $\text{Eu}\cdots\text{Eu}$ distance of $4.2708(4)$ Å.

The binuclear $[\text{Ln}_2(\text{COO})_6]$ motif with four bridging and two chelating carboxylate groups has been recognized in a few discrete complex molecules with monocarboxylate ligands¹⁴ and a 3D Tb(III) MOF (numbered as **2** hereafter for the convenience of description) with 4,4'-azodibenzoate,^{10a} with similar coordination geometry and comparable bond parameters. The binuclear units can be regarded as six-connecting octahedral SBUs (Figure 2a,b), and as observed in **2**, each SBU in **1-Ln** is connected with six identical motifs through six DBTDC- O_2 ligands to yield a 3D framework. However, the net topology of **1-Ln** is quite different from that of **2**. While **2** adopts the default **pcu** net ($4^{12}6^3$) for octahedral nodes, topological analyses of **1-Ln** suggest an **sxb** topology with Schläfli vertex symbol $4^85^46^3$ (Figure 2c).¹¹ To the best of our knowledge, this six-connected uninodal net has not been described in the domain

of MOFs and has only been recognized in a couple of hydrogen-bonded nets.¹⁵

It is worthwhile to make a comparison between the **sxb** (in **1-Ln**) and **pcu** (in **2**) nets based on similar SBUs. For convenience, we distinguish three sets of linkers between the octahedral SBUs: two equatorial sets (blue and cyan rods in Figure 2) related to the two independent bis(bridging) ligands and an axial set (purple rods) corresponding to the bis(chelating) ligand. It should be noted that the three sets of linkers are topologically identical in a **pcu** net but independent in an **sxb** net. In both nets, the equatorial linkers connect the SBUs into parallel 2D square sheets with 4^4 net topology. The difference lies in the way the sheets are cross-linked by the axial linkers, which is closely related to the orientations of the octahedral SBUs within the sheet. In **2**, all octahedra have the same axial direction, which is nearly perpendicular to the equatorial sheet, and the intersheet linkers are all parallel to one another. By contrast, as is clearly shown in Figure 2c, the octahedra in the sheet of **1-Ln** have two different and inclined axial directions, which alternate along the crystallographic *c* direction (corresponding to the cyan linkers). Consequently, the intersheet axial linkers assume two different orientations to adapt to the different SBU orientations, accompanied by an offset stacking of the sheets.

The single **sxb** frameworks in **1-Ln** contain a large void space. To occupy the space, a pair of identical frameworks is mutually interpenetrated with each other (Figure 3). Despite the presence of two interpenetrating nets, there are still large pores in which guest DMF and water molecules are included. It is noted that the pore surface is lined with the sulfone groups from the ligands. For **1-Eu** as an example (the data for the other materials can be found in the Supporting Information), Platon calculations¹⁶ suggest that the free volume is 4704 Å³ per unit cell (30.9% of the crystal volume). The coordinated DMF molecules were considered as framework components in the calculations). Thermogravimetric analysis (see the Supporting Information) of as-synthesized samples of **1-Eu** revealed a rapid weight loss of 23% from room temperature to 180°C . Upon further heating, the weight decreases slowly until 460°C , and then the material undergoes rapid decomposition. The total weight loss of 30.9% from room temperature to 460°C corresponds to the loss of seven DMF and two water molecules per formula (calcd. 31.1%). The compound loses the crystallinity easily upon heating, and powder X-ray diffraction measurements (see the Supporting Information) revealed that the desolvated samples (even partially desolvated below 100°C) were amorphous and did not return to the original crystalline phase by being immersed in the solvent for several days, suggesting that the framework undergoes irreversible collapse if the solvent molecules occupying the pores are removed.

The solid-state luminescence of **1-Eu** was investigated at room temperature. The compound displays intense red luminescence and the characteristic sharp peaks attributed to the Eu(III) $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions ($j = 0-4$ at 578, 590, 616, 652, and 695 nm, respectively, Figure 4).^{4b,5,17} The presence of the weak symmetry-forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission indicates that the Eu(III) ions occupy

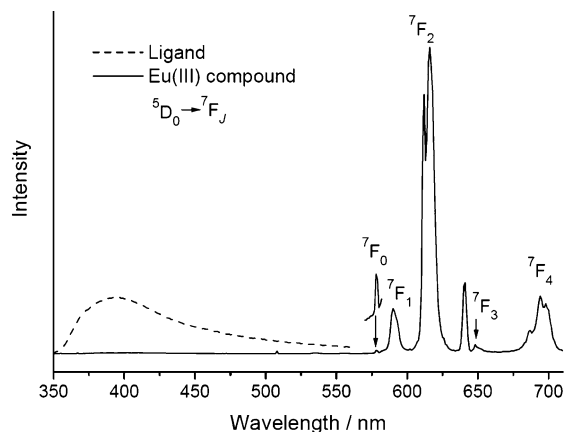


Figure 4. The solid-state luminescence spectra of the ligand and **1-Eu** (excited at 320 nm).

low-symmetry coordination sites with no inversion centers, in agreement with the result of X-ray structural analysis. The relative intensities of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emissions have also been used as a diagnostic signal to probe site symmetry. While the intensity of the former (magnetic dipole transition) is independent of the coordination environment, the latter is electric-dipole allowed, and its intensity increases as the site symmetry is lowered. The high $(^5D_0 \rightarrow ^7F_2)/(^5D_0 \rightarrow ^7F_1)$ intensity ratio of 8.8 for **1-Eu** confirms the absence of centrosymmetry in the Eu(III) site. The local-ligand field splitting is particularly evident for the $^5D_0 \rightarrow ^7F_{1-2}$ and $^5D_0 \rightarrow ^7F_4$ transitions, presenting at least three Stark components. Lifetime measurements at room temperature provide the decay of the 5D_0 luminescence at 616 nm (excited at 320 nm). The decay curve is well fitted with a monoexponential function and yields a lifetime of ca. 0.32 ms, indicating that all the europium sites experience similar decay rates. This is consistent with the crystallographic observation that the two independent Eu(III) sites have almost identical environments. The luminescence of the free ligand was measured for comparison. While the free ligand displays a broadband centered around 395 nm, the emission is quenched in the spectra of **1-Eu**, revealing an efficient energy transfer from the ligand to the metal ion. Finally, the luminescence spectrum of the desolvated material is very similar to that of the as-synthesized sample, suggesting that the ligand-to-metal energy transfer process is essentially unaffected by the loss of solvent molecules, although the material becomes amorphous upon desolvation.

To summarize, we have described a novel type of 3D lanthanide metal–organic frameworks derived from a sulfone-functionalized dicarboxylate ligand. The 2-fold interpenetrated 3D framework is based on the octahedral $[Ln_2(COO)_6]$ secondary building units and exhibits very rare **sbx** net topology, instead of the default **pcu** net for octahedral nodes. The Eu(III) compound displays intense luminescence with efficient ligand-to-metal energy transfer. In addition, although the present materials do not possess permanent porosity, the functionalized ligand could be used to construct new porous materials with functions. Further studies along this line are underway.

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Supporting Information Available: X-ray crystallographic information files (CIF), supplementary tables and graphics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Synthesis: A mixture of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mmol, 7 mg), **L** (0.03 mmol, 12 mg), and DMF (3 mL) was stirred for 30 min at room temperature and then heated in a 23 mL Teflon-lined autoclave under autogenous pressure at 110 °C for 3 days. Colorless prism crystals of **1-Eu** were collected by filtration in a yield of 30.4% after cooling to room temperature. Elemental analysis found (%) for fresh samples: C 43.35, H 4.51, N 5.80. Calcd for $\text{C}_{63}\text{H}_{71}\text{N}_7\text{O}_{27}\text{S}_3\text{Eu}_2$: C 43.03, H 4.07, N 5.58. IR(KBr, cm^{-1}): $\nu(\text{H}_2\text{O})$, 3320 (br); $\nu(\text{C}=\text{O})_{\text{DMF}}$, 1650(s); $\nu(\text{CO}_2^-)$, 1590(s), 1540(s), 1420(s), 1390(s); $\nu(\text{SO}_2)$, 1300(m),

- 1170(m). The Nd and Gd compounds were synthesized by similar procedures (see Supporting Information).
- (13) All the three compounds have been characterized by single-crystal X-ray diffraction. The details are given in Supporting Information. As an example, the low-temperature crystal data for the Eu(III) compound are summarized as follows. $C_{63}H_{71}N_7O_{27}S_3Eu_2$, $M_w = 1758.37$, monoclinic, $C2/c$, $a = 34.8041(14)$ Å, $b = 14.8602(6)$ Å, $c = 29.7740(12)$ Å, $\beta = 98.8010(10)$, $V = 15217.7(11)$ Å³, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.779 \text{ mm}^{-1}$, $D_c = 1.535 \text{ g}\cdot\text{cm}^{-3}$, $T = 123(2)$ K. $R_1 = 0.0519$ for 11242 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1371$ for 14937 unique reflections ($R_{\text{int}} = 0.0768$). The solvent molecules in the large cavity of the structure could not be modeled owing to the heavy disorder of the molecules and the limited quality of the dataset. The final refinements were carried out using the data obtained by the SQUEEZE routine in the PLATON software package.¹⁶ The number of the guest molecules per formula was estimated from analytic and TGA results.
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