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Unique (3,8)-connected lanthanide arenedisulfonate metal-organic frameworks containing benzimidazole-5,6-dicarboxylic acid co-ligand: Syntheses, structures and luminescence

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ABSTRACT

Two isostructural 3D lanthanide arenedisulfonate metal-organic frameworks (MOFs) $[Ln(\text{Hbidc})(\text{nds})_{0.5}(\text{H}_2\text{O})]_n$ ($Ln = \text{Eu}$ (**1**), La (**2**)) have been successfully synthesized by the hydrothermal reaction of lanthanide oxide with 2,6-naphthalenedisulfonate sodium (Na_2nds) and an auxiliary ligand, 1H-benzimidazole-5,6-dicarboxylic acid (H_3bidc). The two complexes are both constructed from 2D $[Ln(\text{Hbidc})]^+$ double layers pillared by nds^{2-} ligands to generate 3D (3, 8)-connected open-framework structures with 1D long narrow channels running along the a axis. From topological point of view, the 3D framework is a (3, 8)-connected $tfz-d$ net. The weak interactions including $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ stacking are observed in **1**. The 2D IR correlation spectroscopy was applied to study the molecular interactions induced by thermal perturbation. The emission spectra of **1** exhibit the characteristic transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 0-4$) of $\text{Eu}(\text{III})$.

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1. Introduction

In recent years, metal-organic frameworks (MOFs) [1–8], which have been applied in gas storage [2,3] and separation [4,5], as catalysts [6,7], as well as chemical sensors [8,9], have attracted considerable interests of chemists. Because of the various coordination numbers, luminescence and magnetic nature of lanthanide elements, more and more lanthanide MOFs are being synthesized with fascinating structures and particular properties [10,11]. As to the luminescence property of lanthanide MOFs, it is mostly contributed from the electronic configurations of lanthanide elements. The electronic configurations $[\text{Xe}]4f^n$ ($n = 0-14$) of lanthanide elements generate a variety of electronic energy levels, resulting in novel optical properties. Due to the shielding of $4f$ orbitals by $5s^25p^6$ subshells, the electronic energy levels are less sensitive to the chemical environment around the lanthanide ions [12]. This results in characteristic $4f-4f$ transitions of lanthanide elements. However, the light absorption of the lanthanide ions is very weak due to Laporte-forbidden $f-f$ transitions, making the direct excitation of the metals very inefficient unless high-power laser excitation is utilized. In order to solve this problem, organic

ligands with π -conjugate rings are coordinated to the lanthanide atoms and can participate in an energy transfer process, known as “antenna effect”. Then various organic ligands are used to prepare lanthanide MOFs to study their luminescent properties [12–17]. Among the most reported lanthanide MOFs, the lanthanide arenedisulfonate remains largely unexplored because organosulfonates are typical weak-bonded ligands [18]. However, the arenedisulfonate ligands are hard base and prefer to coordinate to Ln ions on the basis of the hard-soft acid/base classification; especially, 2, 6-naphthalenedisulfonate (nds^{2-}) ligand with two SO_3 groups has flexible coordination modes from μ_1 to μ_2 , making structural characterization, a hallmark property of Ln-MOFs, a challenge. To the best of our knowledge, there are several papers about lanthanide MOFs based on the nds^{2-} ligand [18–21]. Furthermore only isonicotinic acid [21] and 1,10-phenanthroline [20] have been served as second ligands to synthesize the hybrid lanthanide arenedisulfonate metal-organic frameworks. The 1H-benzimidazole-5,6-dicarboxylic (H_3bidc) as a second ligand into lanthanide arenedisulfonate frameworks remains unexplored.

The 1H-benzimidazole-5,6-dicarboxylic (H_3bidc) ligand was selected as a co-ligand to build novel lanthanide arenedisulfonate MOFs in this paper based on the following considerations: (i) It contains multifunctional coordination sites: N and O atoms, which might be used as good linkers in generating multidimensional structures. (ii) It can be successively deprotonated to generate H_2bidc^- , Hbidc^{2-} and bidc^{3-} depending on the pH level, and

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Table 1
Crystal data and structure refinement for **1** and **2**.

Compound	1	2
Empirical formula	C ₁₄ H ₉ N ₂ O ₈ SEu	C ₁₄ H ₉ N ₂ O ₈ SLa
Formula weight	517.25	504.20
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> –1	<i>P</i> –1
<i>a</i> (Å)	7.430(2)	7.531(2)
<i>b</i> (Å)	9.591(3)	9.737(2)
<i>c</i> (Å)	10.315(3)	10.379(2)
α (°)	98.582(5)	99.17(3)
β (°)	96.634(6)	97.18(3)
γ (°)	93.822(4)	93.76(3)
<i>V</i> (Å ³)	719.3(4)	742.5(3)
<i>D_c</i> (g/cm ³)	2.388	2.255
<i>Z</i>	2	2
<i>F</i> (000)	500	488
μ (mm ⁻¹)	4.559	3.070
Reflns collected/unique	6012/3172	6132/3271
<i>R</i> _{int}	0.0319	0.0477
GOOF on <i>F</i> ²	1.190	1.144
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0424, 0.1155	0.0475, 0.1322
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e ⁻³)	4.018/–2.479	2.141/–2.640

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$$

hence may supply neutral, mono-, di-, tri-cationic forms allowing designing of a broad range of neutral, anionic or cationic coordination networks. (iii) Its coupling fused-ring structure is favorable for participating in energy transfer processes as a luminescence sensitizer. Here we report two novel 3D lanthanide MOFs [Ln(Hbidc)(nds)_{0.5}(H₂O)]_n (Ln=Eu(**1**), La(**2**)), which is the first example of incorporating fused-ring aromatic carboxylic acid as the second ligand into the lanthanide arenedisulfonate MOFs. The two compounds are isostructural. The Hbidc²⁻ ligands connect the lanthanide ions to form 2D [Ln(Hbidc)]⁺ double layers, which are pillared by nds²⁻ ligands to generate 3D (3, 8)-connected lanthanide arenedisulfonates. The 2D IR correlation spectroscopy was applied to study the molecular interactions induced by thermal perturbation.

2. Experimental

2.1. Reagents and general techniques

All the chemicals used were available commercially and without further purification. The elemental analyses of C, H, and N were performed with an Elementar Vario EL III elemental analyzer. IR spectra were measured as KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR in the range 400–4000 cm⁻¹. The fluorescent spectra were recorded on an Edinburgh Instrument FL/FS-920 fluorescent spectrometer using Xe lamp for steady fluorescence. Thermogravimetric (TG) analyses were conducted on a Perkin-Elmer TGA7 Thermal analyzer in an N₂ atmosphere with a heating rate of 10 °C/min from 25 °C to 800 °C. The XRD spectrum was obtained on a Panalytical X'pert Pro with Cu K α radiation (λ =1.54056 Å).

2.2. Synthesis of [Ln(Hbidc)(nds)_{0.5}(H₂O)]_n (Ln=Eu (**1**), La(**2**))

A mixture of Ln₂O₃ (0.2 mmol: 0.071 g Eu₂O₃, 0.065 g La₂O₃), H₃bidc(0.042 g), and Na₂nds (0.067 g, 0.2 mmol) was added to 10 mL distilled H₂O. After being stirred for 1 h, the pH value was adjusted to 2.0 with HNO₃ (0.2 mol L⁻¹). The mixture was sealed in a 25 mL Teflon-lined stainless steel container and heated at 170 °C for 72 h, then cooled to room temperature. Accordingly

tawny columnar crystals were isolated by filtering, washed with distilled water and dried in air. Yield: 40% (**1**) and 28% (**2**) (based on Ln₂O₃). Calc for C₁₄H₉N₂O₈SEu (**1**): C, 32.51; H, 1.75; N, 5.42; O, 24.74 wt%; Found: C, 32.48; H, 1.78; N, 5.38; O, 24.67 wt%. IR (KBr, cm⁻¹): 3364(m), 3139(s), 1646(s), 1592(s), 1567(s), 1474(m), 1463(m), 1405(s), 1356(s), 1263(s), 1151(s), 1130(s), 1021(s), 915(m), 872(w), 827(w), 625(s), 415(m) (Fig. S3 in the supporting information). Anal. Calc for C₁₄H₉N₂O₈SLa (**2**): C, 33.51; H, 1.80; N, 5.56; O, 25.39 wt%; Found: C, 33.58; H, 1.79; N, 5.55; O, 25.67 wt%. IR (KBr, cm⁻¹): 3353(m), 3135(s), 1648(s), 1591(s), 1565(s), 1519(m), 1474(m), 1462(m), 1400(s), 1351(s), 1258(s), 1150(s), 1128(s), 1020(s), 913(m), 872(w), 826(w), 625(s), 413(m) (Fig. S4).

2.3. X-ray crystallographic determination

Suitable single crystals were selected and mounted on a glass fiber. All data were collected at room temperature on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated MoK α (λ =0.71073 Å) radiation in the ω scanning mode at room temperature. An empirical absorption correction was applied using ABCOR program. The structures were solved by direct methods and refined by full-matrix least squares on *F*² using the SHELXTL-97 program package [22]. All non-hydrogen atoms of **1** and **2** were refined anisotropic except some disorder C atoms. The hydrogen atoms were generated geometrically. Crystallographic data and structure refinements for **1** and **2** are summarized in Table 1, selected bond lengths are listed in Table 2, and the hydrogen bond parameters of **1** are listed in Table 3.

3. Results and discussion

3.1. Structural description

Single crystal X-ray diffraction analysis reveals that **1** and **2** are isomorphous, belonging to the triclinic system with space group of *P*-1. Therefore, the structure of **1**-Eu is described here representatively. The asymmetric unit of **1** is composed of one crystallographically independent Eu(III) ion, one H₂bidc, half nds²⁻ and one water molecule (Fig. S5). The Eu(III) ion is nine-coordinated by five carboxylate O atoms and one N atom from four bidc²⁻ ligands, two O atoms from nds²⁻ ligand and one coordinated water molecule (Fig. 1). The coordination geometry for the Eu(III) ion is close to a tricapped trigonal prism (Fig. S6). The Eu–O bond distances are in the range of 2.292(5)–2.662(6) Å and the Eu–N bond length is 2.611(4) Å.

Table 2
Selected bond distances (Å) for **1** and **2**.

1			
Eu–O(2)#1	2.297 (5)	Eu–O (6)	2.529 (6)
Eu–O(4)#1	2.430 (5)	Eu–O (4)#2	2.612 (5)
Eu–O(1)	2.435 (5)	Eu–O (7)	2.667 (6)
Eu–O(3)#2	2.443 (5)	S (1)–O(5)	1.434 (6)
Eu–O(1W)	2.452 (6)	S (1)–O(7)	1.454 (6)
Eu–N(2)#3	2.521 (6)	S (1)–O(6)	1.475 (6)
2			
La–O(2)#4	2.400 (4)	La–N (2)	2.631 (5)
La–O(4)#4	2.503 (4)	La–O (7)	2.694 (5)
La–O(1)#5	2.516 (5)	La–O (4)#6	2.698 (5)
La–O(3)#6	2.557 (5)	S (1)–O(5)	1.447 (5)
La–O(1W)	2.558 (5)	S (1)–O(7)	1.459 (5)
La–O(6)	2.616 (5)	S (1)–O(6)	1.480 (5)

^aSymmetry codes: #1 –*x*, –*y*, –*z*+2; #2 *x*+1, *y*, *z*; #3 –*x*, –*y*+1, –*z*+2; #4 *x*, *y*–1, *z*; #5 –*x*, –*y*+1, –*z*+2; #6 –*x*, –*y*+1, –*z*+1.

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