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A New 3D Lanthanide Metal-Organic Framework Based on Fluorescent Whitener: Synthesis, Structures, and Luminescent Properties[1]

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Abstract—A new 3D lanthanide metal-organic framework, $[Sm(L)(Bpdc)_{0.5}(Phen)]_\infty$ (**I**) (L = 4,4'-bis(2-sulfonatostyryl)biphenyl; Bpdc = 4,4'-biphenyldicarboxylate; Phen = 1,10-phenanthroline), has been synthesized hydrothermally and characterized by IR spectroscopy, elemental analysis, thermogravimetric analysis and single-crystal X-ray diffraction (CIF file CCDC no. 990856). Compound **I** crystallizes in monoclinic, space group $P2_1/n$ with $a = 13.070(3)$, $b = 21.365(4)$, $c = 14.947(3)$ Å, $\beta = 101.65(3)°$, $V = 4087.8(15)$ Å^3, $\rho_c = 1.572$ g/cm^3, $Z = 4$, $\mu = 1.597$ mm^{-1}, $F(000) = 1944$, and the final $R = 0.0573$ and $wR = 0.1238$ for 9304 observed reflections ($I > 2\sigma(I)$). It is evident that there is a face-to-face π–π stacking interaction between each L ligand with adjacent Phen groups at a plane-plane distance of 3.482 Å. The ring normal and the vector between the ring centroids form an angle of 11.6° up to centroid-centroid distances of 3.555 Å. The experimental result shows that compound **I** exhibits good thermal stability and luminescent property.

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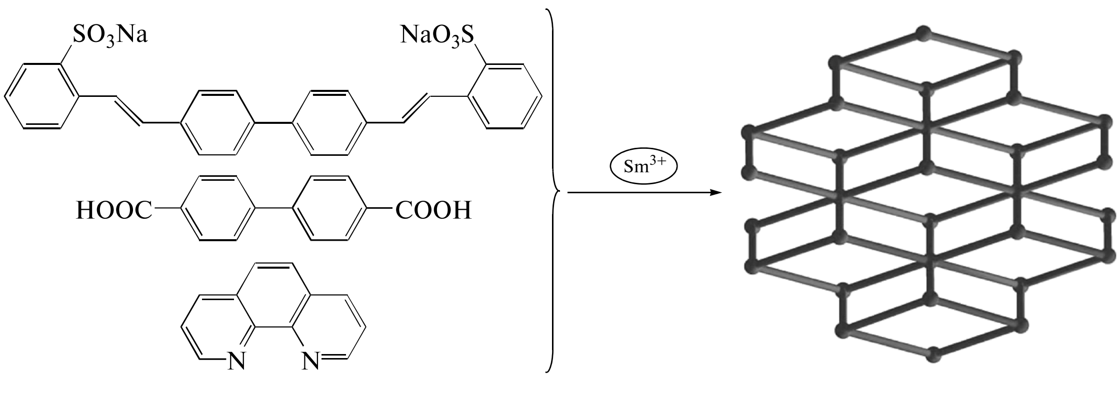
INTRODUCTION

Metal-organic frameworks (MOFs) are well-known for their highly designable framework [1–3], which play an important role in numerous potential application areas including photoluminescence [4, 5], heterogeneous catalysis [6–8], gas storages [9–11], and magnetism [12], etc. Multicarboxylate and mutisulfonate ligands are usually used to construct many different kinds of MOFs with various dimensionality and topologies. In particular, MOFs consisted of just multicarboxylate ligands (terephthalic acid, 4,4'-biphenyldicarboxylic acid, etc.), or single mutisulfonate ligands (1,4-naphthalenedisulfonic acid, 2,5-naphthalenedisulfonic acid, etc.) have been studied [13–16], but lanthanide-containing MOFs with both mixed multicarboxylate and mutisulfonate ligands are less developed. In addition, 1,10-phenanthroline used as an auxiliary ligand to build supramolecular nodes was much reported due to its excellent coordinating ability and large conjugated system that can easily form π–π interactions [17, 18]. The disodium 4,4'-bis(2-sulfonatostyryl)biphenyl (Na_2L) of about 2.0 nm length is an attractive formula for its intensive fluorescent emission. Compared with free organic ligands, MOFs constructed from this length ligand will exhibit higher thermal stability and stronger emissive intensity [19]. Here we first report synthesis, structural and fluorescent investigations of a new non-interpenetrated LMOFs, $[Sm(L)(Bpdc)_{0.5}(Phen)]_\infty$ (**I**) (L = 4,4'-bis(2-sulfonatostyryl)biphenyl; Bpdc = 4,4'-biphenyldicarboxylate; Phen = 1,10-phenanthroline), which has a 3D framework formed by mixed ligands. The formula was established based on single-crystal X-ray diffraction studies, powder X-ray diffraction studies, elemental analysis and thermogravimetric analysis (TGA) results. Furthermore, the experimental result shows that compound **I** exhibits blue fluorescence in the solid state at room temperature.



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EXPERIMENTAL

Material and methods. All solvents and reagents were commercially available and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40 kV, 40 mA with CuK_α radiation (λ = 1.5406 Å) with a scan speed of 17.7 s/step and a step size of 0.02° (2θ). Elemental analyses for C, H, N, and S were carried out by using a Vario EL III Elemental Analyzer. TGAs were performed on a Q600 SDT instrument under a flow of N_2 at a heating rate of 10°C min^{-1} between ambient temperature and 700°C. Room-temperature UV-Vis spectra measurements were recorded using quartz cuvettes (1 cm) with Teflon stopper on a U-3100 UV-Vis spectrophotometer. IR spectra were measured from a KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer in the range 4000–400 cm^{-1}. Luminescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer.

Synthesis of compound I. A mixture of $Sm(NO_3)_3 \cdot 6H_2O$ (0.082 g, 0.2 mmol), Na_2L (0.112 g, 0.2 mmol), 4,4'-biphenyldicarboxylic acid (0.05 g, 0.2 mmol), Phen · H_2O (0.04 g, 0.2 mmol), one drop triethylamine and H_2O (15.0 mL) in a 25 mL Teflon-lined autoclave was heated at 150°C for 33 h. After the mixture was cooled slowly to ambient temperature, yellow block crystals were obtained. The crystals were filtered, washed with distilled water and dried at ambient temperature. The yield of the reaction, determined from the weight of the solvent-free material (0.132 g), is 70.5% based on Na_2L.

For $C_{47}H_{32}O_8N_2S_2Sm$ (**I**)

anal. calcd., %:	C, 58.32;	H, 3.38;	N, 2.91,	S, 6.63.
Found, %:	C, 58.25;	H, 3.46;	N, 2.82,	S, 6.56.

IR bands (KBr; ν, cm^{-1}): 3062 w, 3021 w, 2668 m, 2551 m, 1685 s, 1598 s, 1417 s, 1252 s, 1125 v.s, 1076 m, 759 m, 607 m.

X-ray structure determination. A yellow single crystal with dimensions of 0.05 × 0.1 × 0.15 mm was selected for X-ray diffraction studies. The data were collected on a Rigaku Mercury CCD diffractometer operated at 90 kV and 50 mA using MoK_α radiation (λ = 0.71073 Å) at room temperature. The structure was solved by direct methods [20] and refined on F^2 by full-matrix least-squares technique using the SHELX-97 program package [21]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located from a difference Fourier map and refined isotropically.

A summary of the crystal data and relevant refinement parameters for compound **I** are given in Table 1. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 990856; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray analysis reveals that compound **I** is a three-dimensional framework built up by L, Bpdc and Phen ligands with Sm^{3+} ions. The asymmetric unit of compound **I** contains one eight-coordinated samarium ion, one L ligand, one-half of the Bpdc ligand and one Phen molecule. The coordination mode of the samarium ions is shown in Fig. 1. Selected bond lengths and bond angles for compound I are given in Table 2. Six oxygen atoms coordinated with Sm^{3+} ion are from two dimonodentate carboxyl groups (O(4) and O(5)) from Bpdc anions, one chelating bidentate SO_3^- groups (O(1) and O(3)) and two dimonodentate SO_3^- groups (O(6) and O(7)) from L, respectively. Two chelating nitrogen atoms (N(1) and N(2)) coordinated with Sm^{3+} ion are from one Phen molecule. The Sm–O (from L) and Sm–O (from Bpdc) bond lengths are in the range of 2.372(4)–2.537(5) and 2.300(6)–2.316(6) Å, respectively. The Sm–N bond lengths are 2.611(6) (Sm–N(1)) and 2.592(6) Å (Sm–N(2)), respectively. The OSmO bond angles vary from 56.03(16)° to 148.3(2)° and the OSmN bond angles vary from 69.8(2)° to 148.3(2)°. Each L ligand links three Sm^{3+} ions (Fig. 2a) (namely, two oxygen atoms of one SO_3^- group connect one metal ion in chelating bidentate fashion, two oxygen atoms of the other SO_3^- group connect two metal ions in dimomodentate fashion). Each Bpdc ligand acts as a four-connected node to link four Sm^{3+} ions (Fig. 2a). The dihedral angle is 7.401° between one benzene ring (C(13)–C(18)) from L ligand and one pyridine ring (C(7)–C(11), N(2)) from Phen ligand, that is to say, two rings are approximately coplanar. It is conspicuous that there is a face-to-face π–π stacking interaction between each L ligand with adjacent Phen groups at a plane-plane distance of 3.482 Å. The ring normal and the vector between the ring centroids form an angle of 11.6° up to centroid-centroid distances of 3.555 Å (Fig. 2b). Lanthanide metal ions center and its corresponding centrosymmetric atoms are interconnected through L ligands and Bpdc ligands to be assembled into a complicated 3D structure. Each Bpdc ligand links four metal ions to form a 1D infinite chain by means of four-connected node. Moreover, each L ligand links two dinuclear units and each dinuclear unit links four different L ligands, which finally form a complicated 3D structure as viewed along the *x* axis (Fig. 2c). The topology analysis of **I** shows that L and Bpdc ligands keep their 2-connectivity and each dinuclear SBU acts as a six-connected node. The resulting net has a vertex symbol ($4^6.6^6.8^3$) (Fig. 2d).

We examined the structural homogeneity of bulk as-synthesized pristine sample of compound **I** through comparison of the experimental and simulated PXRD

Table 1. Crystal data and structure refinement parameters of compound **I***

Parameter	Value
Formula weight	967.25
Temperature, K	293
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	13.070(3)
b, Å	21.365(4)
c, Å	14.947(3)
β, deg	101.65(3)
Volume, Å^3	4087.8(15)
Z	4
ρ_{calcd}, g/cm^3	1.572
μ, mm^{-1}	1.597
F(000)	1944
θ Range data collection, deg	3.00–27.45
Limiting indices	$-16 \le h \le 16$, $-27 \le k \le 27$, $-19 \le l \le 19$
Reflections collected/unique	39147/9304
Completeness to θ = 27.45, %	99.6
R_{int}	0.1243
Data/restraints/parameters	9304/0/542
Goodness-of-fit on F^2	1.091
Final R indices, $I > 2\sigma(I)$	$R_1 = 0.0409$, $wR_2 = 0.1238$
R indices, all data	$R_1 = 0.1288$, $wR_2 = 0.1794$

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

patterns. The peak intensities and positions of the experimental patterns are in excellent agreement with those of the simulated one generated from single-crystal X-ray diffraction data, suggesting that the product of compound **I** is pure single phase. We then carried out the PXRD measurement of **I** which was evacuated at 200°C for 8 h. The results still match very well with simulated data, indicating no obvious structural change, which demonstrates that **I** owns permanent high thermal stability.

The thermal stability of compound **I** was investigated by TGA in nitrogen atmosphere at the heating rate of 10°C min^{-1} (Fig. 3). The TGA of compound **I** reveals two distinct thermal events. The first weight loss of 7.6% is in the 310–360°C range, possibly corresponding to the partial decomposition of L ligand (maybe C=C bonds of L ligand fracture). The other weight loss of 25.4% from 510 to 650°C displays the decomposition of the framework, giving rise to the final Sm_2O_3.

The luminescent properties of compound **I** was investigated in the solid state at room temperature. First, we investigated the ultraviolet-visible light (UV-Vis) absorption spectrum of compound **I**. The UV-Vis absorption spectrum of compound **I** shows a wide absorption band in the UV spectral region from 200 to 600 nm, in which the absorbance maxima is 328 nm (Fig. 4a). The absorption band could be mainly attributed to n–π* and π–π* transitions of L ligand. Subsequently, the solid-state photoluminescent properties of compound **I** was studied in solid state at room temperature. The excitation wavelengths of 328 was set from the absorption maximum determined from the UV-Vis spectral data of compound **I**. As shown in Fig. 4b, when excited at 328 nm wavelength, compound **I** exhibits intense emission spectrum. The most intense emission at 462 nm probably originates from a

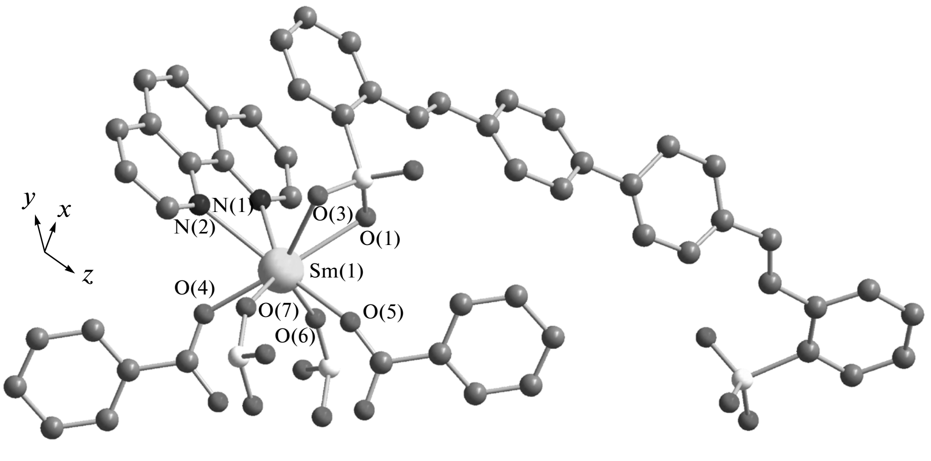

Fig. 1. Coordination environment of Sm in compound **I**. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and bond angles (deg) of compound **I***

Bond	d, Å	Bond	d, Å	Bond	d, Å
Sm(1)–O(4)	2.300(6)	Sm(1)–O(1)	2.537(5)	S(4)–C(40)$^{\#2}$	1.778(8)
Sm(1)–O(5)$^{\#1}$	2.316(6)	Sm(1)–N(2)	2.591(6)	C(45)–C(45)$^{\#3}$	1.474(15)
Sm(1)–O(7)	2.372(4)	Sm(1)–N(1)	2.611(6)	C(40)–S(4)$^{\#4}$	1.778(8)
Sm(1)–O(6)$^{\#1}$	2.392(4)	Sm(1)–S(5)	3.083(2)	N(1)–C(1)	1.329(10)
Angle	ω, eg	Angle	ω, deg	Angle	ω, deg
O(4)Sm(1)O(5)$^{\#1}$	118.3(2)	O(7)Sm(1)S(5)	111.67(14)	C(41)O(5)Sm(1)$^{\#1}$	155.2(6)
O(4)Sm(1)O(7)	78.0(2)	O(6)$^{\#1}$Sm(1)S(5)	105.77(14)	C(35)C(40)S(4)$^{\#4}$	119.8(6)
O(5)$^{\#1}$Sm(1) O(7)	73.8(2)	O(3)Sm(1)S(5)	27.88(13)	C(39)C(40)S(4)$^{\#4}$	118.6(5)
O(4)Sm(1)O(6)$^{\#1}$	79.05(19)	O(1)Sm(1)S(5)	28.26(11)	S(4)O(6)Sm(1)$^{\#1}$	153.8(4)

* Symmetry codes: $^{\#1}$ $-x + 2, -y, -z + 1$; $^{\#2}$ $-x + 3/2, y + 1/2, -z + 3/2$; $^{\#3}$ $-x + 2, -y, -z$; $^{\#4}$ $-x + 3/2, y - 1/2, -z + 3/2$.

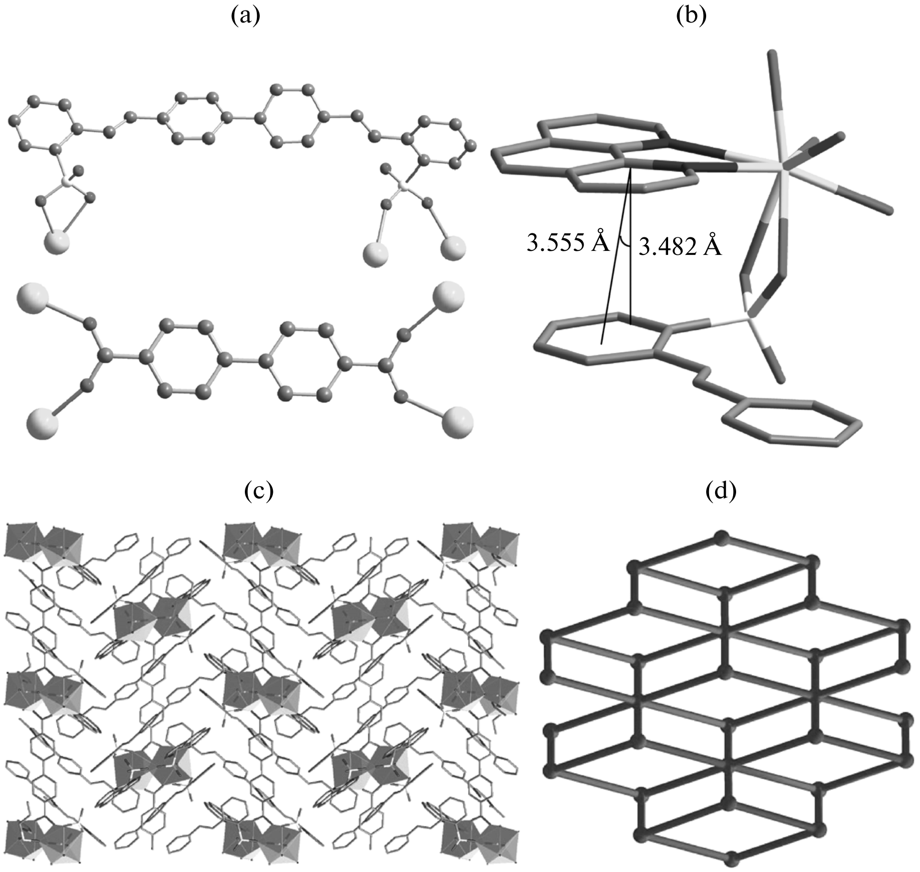

Fig. 2. Coordination modes of L and Bpdc ligand. (a); view of the π–π stacking interactions between Phen and the benzene ring of L ligand (b); sticks model of **I** as viewed along the a axis with polyhedron structures (c); 3D topological structure of **I** (d). The colors of red, blue, gray, yellow and green correspond to oxygen, nitrogen, carbon, sulfur, and samarium atoms, respectively. Hydrogen atoms are omitted for clarity.

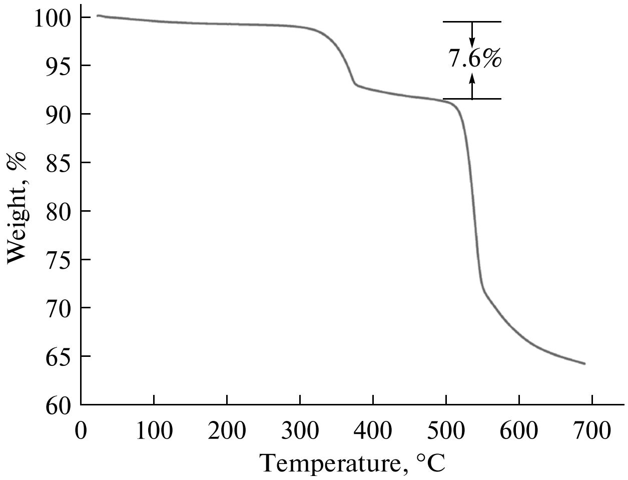

Fig. 3. TGA curves of **I** recorded under a N_2 atmosphere.

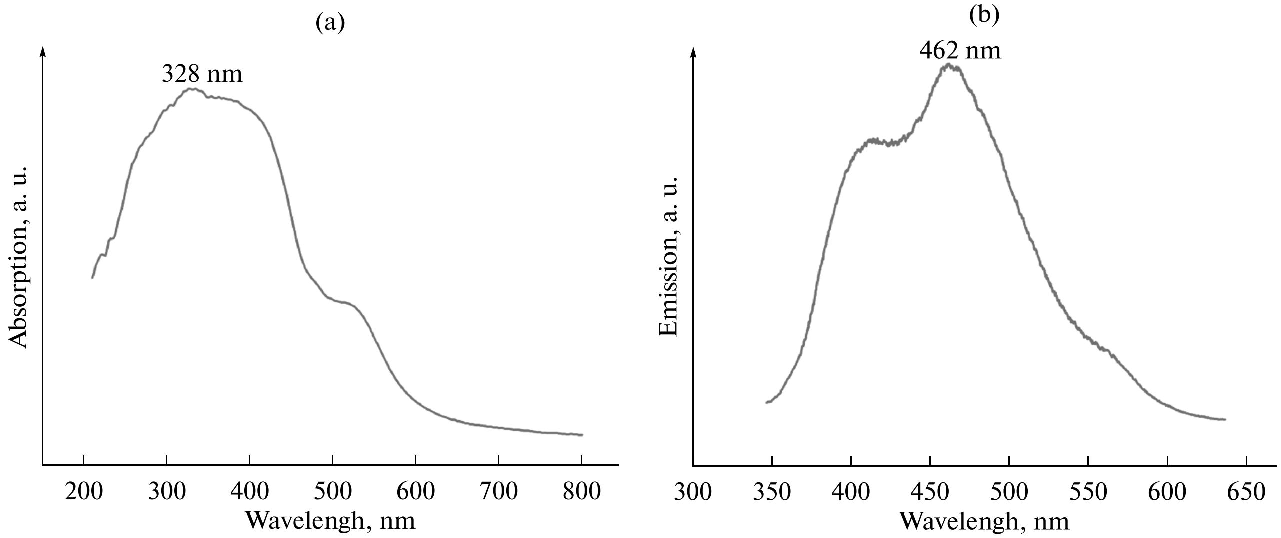

Fig. 4. Room-temperature UV-Vis spectra of **I** in the solid state (a); photoluminescence spectra of **I** in the solid state (b).

ligand-centred π–π* transition of L [22]. Compound **I** exhibits blue luminescent properties.

ACKNOWLEDGMENTS

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