

Coordination polymers from 1-D to 3-D assembled from disulfonate ligands: Structures and luminescent properties



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ABSTRACT

Four rare earth organodisulfonate coordination polymers, $\{[\text{Tb}_2(\text{phen})_4(\text{nds})_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Ln}(\text{phen})(\text{nds})(\text{OH})]\}_n$ [$\text{Ln} = \text{Sm}$ (**2**), Nd (**3**)], $\{[\text{Tb}(\text{phen})_2(\text{nds})_{0.5}(\text{OH}) \cdot \text{H}_2\text{O}] \cdot (\text{nds})_{0.5}\}_n$ (**4**), were synthesized under the solvothermal conditions by using ligands 2,6-naphthalenedisulfonate ($\text{L} = \text{nds}$) and 1,10-phenanthroline ($\text{L}' = \text{phen}$). Single-crystal X-ray diffraction reveals that compounds **1** and **4** exhibit different 1-D and 2-D crystal structures just owing to the single difference of stoichiometric ratio of the reactants in the synthesis process. Compounds **2** and **3** show 3-D structures with similar Ln coordination mode. Besides, the photoluminescent property in solid state of **1** was investigated in detail.

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Sulfonates, RSO_3^- , as structural analogues of phosphonates, RPO_3^{2-} , have not received so much attention due to the weak coordination strength of sulfonate group to metal atoms [1,2]. Actually, sulfonates are incapable of replacing coordinated water molecules thereby can be used to stabilize the framework behaving as guest molecules [3,4]. On the other hand, the weak interactions, however, are taken advantage to coordinate more flexibly and ultimately gaining much more various structures, especially for disulfonate and polysulfonate ligands [5]. 2,6-Naphthalenedisulfonate is one of the flexible ligands, which has six potential coordination O-donors and is an excellent bridging spacer for the construction of diverse structures.

We choose nds ($\text{nds} = 2, 6\text{-naphthalenedisulfonate}$) as the first ligand [6–10]. The second turns to phen ($\text{phen} = 1, 10\text{-phenanthroline}$) whose two nitrogen atoms can be simultaneously coordinated from one side in the plane [11,12]. Besides, the fluorescent

emissions of some complexes are due to the metal-disturbed ligand centered $\pi^* \rightarrow \pi$ transitions [13,14], so the ligand phen has come into notice. Many references showed that existing studies of rare earth organic luminescence material mainly focused on the complexes of Eu(III) and Tb(III) [15–18], relatively few references centralizing on Sm(III) [19]. Therefore, intriguing 1-D to 3-D structures: $\{[\text{Tb}_2(\text{phen})_4(\text{nds})_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Sm}(\text{phen})(\text{nds})(\text{OH})]\}_n$ (**2**), $\{[\text{Nd}(\text{phen})(\text{nds})(\text{OH})]\}_n$ (**3**), and $\{[\text{Tb}(\text{phen})_2(\text{nds})_{0.5}(\text{OH}) \cdot \text{H}_2\text{O}] \cdot (\text{nds})_{0.5}\}_n$ (**4**), were synthesized with various stoichiometric ratios of the ligands nds and phen.

Light yellow block crystals of **1** were obtained under hydrothermal reaction and autogenous pressure by mixing $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, nds, and phen in a 1:0.5:2 molar ratio at 180 °C for 72 h. Compound **4** was synthesized in a procedure similar to that of **1**, except for the different molar ratio 1:1:1.33. Compounds **2** and **3** were synthesized similarly, except for the kinds of metal salt. A mixture of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.6 mmol), nds (0.6 mmol), phen (0.6 mmol), and distilled water (14 mL) was stirred for 1 h and then it was transferred into a 25 mL

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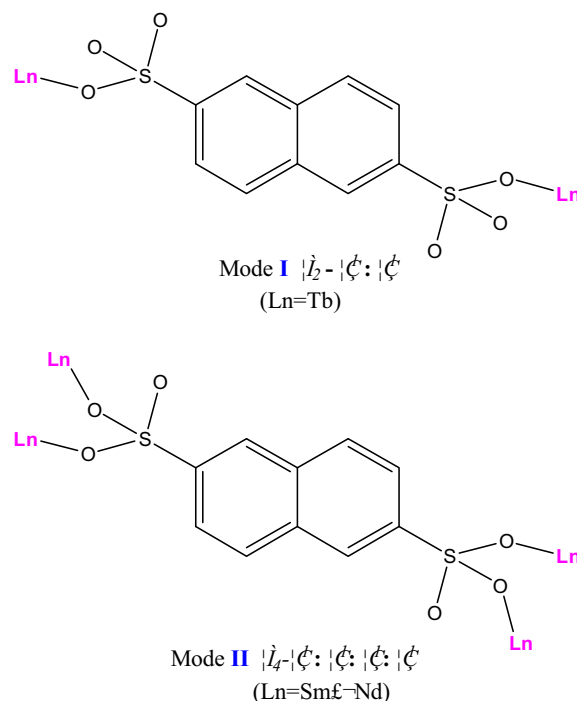
E-mail address: yuesht@scnu.edu.cn (S.-T. Yue).

Teflon reactor and heated in the same condition as **1**. Colorless block crystals of compound **2** were obtained after the mixture was slowly cooled to room temperature over 3 days.

Complex **1** exhibits a 2-D pillared-chained coordination framework constructed from μ_2 -(η^1 : η^1)-bridging L^- pillars (Mode I). In complex **2**, Sm1 and Sm2 are coordinated in the same way, where in the symmetric unit, O1 and O2 both link two Sm(III) ions (O1–Sm1 and O1–Sm2; O2–Sm1 and O2–Sm2) with the μ_2 -coordination modes forming a dinuclear unit [Sm_2O_2], outside of which, O3–S1–O4, O7–S2–O8 from two nds ligands connect these two Sm(III) ions forming an eight-membered unit [$Sm_2O_4S_2$] (Scheme 1 (A)). Ultimately, two rings are formed, which are surrounded by four L ligands and two L' ligands. According to this mode (Mode II), L tends to link two Sm(III) ions (Scheme 2). Complex **3** tends to construct 3-D networks which is similar to **2** (Scheme 1 (B)). Complex **4** also shows the coordination mode in Mode I, and it is a μ_2 -OH bridged dinuclear compound in which an inverse center locates between Tb(III) ions (Scheme 1 (C)).

In **1** (Fig. 1.A), the Tb(III) center is eight-coordinated by three oxygen atoms from three nds ligands, one oxygen atom from a coordinated water molecule and four nitrogen atoms from two bidentate chelating phen ligands, respectively, developing a bicapped trigonal prismatic coordination geometry. The Tb–O bond distances range from 2.295(4) to 2.341(4) Å and the Tb–N bond lengths range from 2.550(4) to 2.572(5) Å. The torsion angles of C(36)–S(1)–O(3)–Tb(1), C(30)–S(2)–O(6)–Tb(1) and C(27)–S(3)–O(9)–Tb(1) are 108.681(786)°, –37.981(138)° and 53.668(817)°, respectively. The adjacent Tb(III) ions are connected by nds-sulfonate linkers adopting the $\eta^3\mu^1$ – $\eta^3\mu^1$ mode, forming an infinite 1D chain (Fig. 2.(A)). Furthermore, six Tb(III) ions are connected by six nds bridges giving rise to the formation of a 2D sheet by repeating [$Tb_6(L)_6$] subunit, which can be interpreted as a 6³-net, as depicted in Fig. 2.(B).

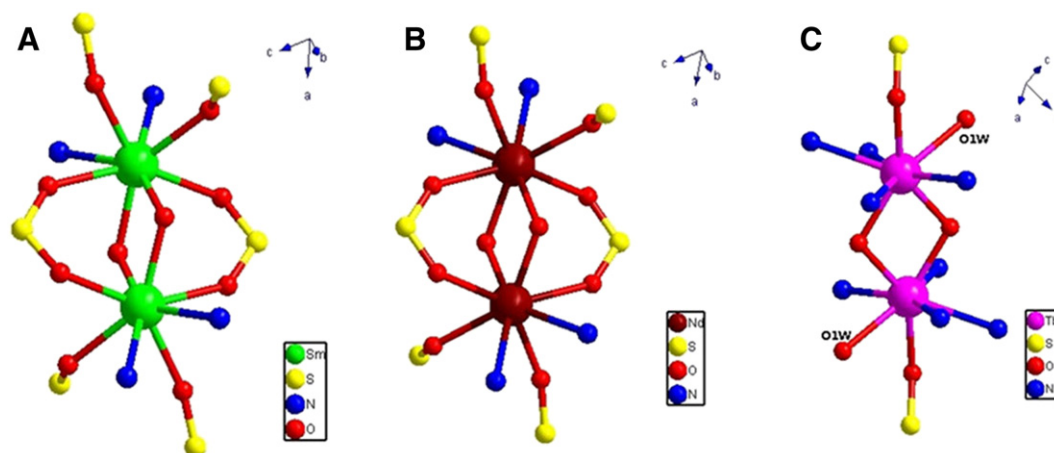
Single-crystal X-ray analysis reveals that the space groups of complexes **1** and **4** are the same, namely, triclinic *P*-1 space group [20]. Interestingly, single crystal of **4** shows completely different structure with **1**, although the reaction conditions are the same as **1** except the different stoichiometric ratio of the reactants. An ORTEP view of **4** is shown in Fig. 1.D. Each Tb(III) is in eight-coordinated antiprismatic geometry, which is completed by four nitrogen atoms from two chelating phen groups, two oxygen atoms from two hydroxide anions, one oxygen atom from water molecule and one oxygen atom from nds ligand. The Tb–O bond distances range from 2.255(2) to 2.508(2) Å and the Tb–N bond lengths range from 2.578(3) to 2.628(3) Å. The torsion angle of C(27)–S(2)–O(5)–Tb(1) is –160.641(208)°. The connection of adjacent dinuclear units through nds entities adopting symmetric $\eta^1\mu^1$ – $\eta^1\mu^1$ mode generates infinite 1D string. Furthermore, the units are connected by the nds ligands with H-bonds in another direction,



Scheme 2. Two coordination modes of L^- .

and the phen ligands are omitted for clarity (Fig. 3.(A)). For simplicity, the 3-D construction connected by nds ligands and weak interactions is built as Fig. 3.(B). In the dinuclear Tb unit, Tb1 and Tb2 are symmetric, which can be simplified as the μ_2 -coordination dinuclear unit [Tb_2O_2] (O1–Tb1 and O1–Tb2; O2–Tb1 and O2–Tb2) (Scheme 1 (C)), and the nds ligand can also be seemed as the symmetric connected bridge.

2 and **3** crystallize in the triclinic system, space group *P*-1 [20]. An ORTEP view of **2** and **3** is illustrated in Fig. 1.B and C. With the similar structure of **2** and **3**, complex **3** will be taken as a representative and be explained in detail. In **3**, the Nd(III) ion is eight-coordinated by two oxygen atoms from two μ_2 -OH groups, four oxygen atoms from the nds ligands, and two nitrogen atoms from one bidentate chelating phen ligand. The coordination geometry around the Nd(III) ion can be described as a bicapped trigonal prismatic geometry with the Nd–O bond distances ranging from 2.313(8) to 2.554(5) Å, Nd–N bond distances ranging from 2.654(2) to 2.671(2) Å and the O–Nd–O bond angles varying from 73.00(7) to 147.96(6)°, respectively. The torsion



Scheme 1. Three coordinated environments of metal atoms in **2**, **3**, and **4**.

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