

Cite this: *Chem. Commun.*, 2011, **47**, 9834–9836www.rsc.org/chemcomm

COMMUNICATION

Influence of halide ions on the chirality and luminescent property of ionothermally synthesized lanthanide-based metal–organic frameworks†

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Received 3rd June 2011, Accepted 20th July 2011

DOI: 10.1039/c1cc13297k

Four lanthanide-based metal–organic frameworks, [Emim][Ln_{1.5}(2,5-tdc)₂]Cl_{1.5-x}Br_x (Ln = Nd 1, Eu 2) and [Emim][Ln(2,5-tdc)₂] (Ln = Nd 3, Eu 4) (2,5-tdc = thiophene-2,5-dicarboxylate, Emim = 1-methyl-3-ethylimidazolium), were synthesized under ionothermal conditions. Compounds 1 and 2 crystallize in the polar space group *P*2₁2₁2, while 3 and 4 crystallize in the central symmetry space group *P*2₁/*c*. Luminescence studies revealed a significantly higher quantum yield of 4 than that of 2, with similar lifetimes. It is clear that the coordination of the halide ions has profound effects on the structures and properties of these lanthanide-based metal–organic frameworks.

Syntheses using ionic liquids (IL) as solvents have received increasing interest for the preparation of functional materials in the context of crystal engineering. Syntheses under ionothermal conditions are unique; in addition to being the solvents, ILs frequently function as structure-directing agents, leading to framework structures that are different from those obtained by the more extensively utilized hydro/solvothermal methods.^{1,2} While most of the works focus on the influence of the component cations and/or anions of ILs on the structures of ionothermally synthesized materials,^{3–8} little is known as to how to construct chiral frameworks using achiral building units under ionothermal conditions.⁹ On the other hand, how to adjust the properties of ionothermally synthesized materials remains an essentially uncharted territory.¹⁰ Here we report the syntheses and crystal structures of four lanthanide-based metal–organic frameworks synthesized using 1-methyl-3-ethylimidazolium bromide (Emim-Br) as solvent: [Emim][Ln_{1.5}(2,5-tdc)₂]Cl_{1.5-x}Br_x (Ln = Nd 1, *x* = 0.5; Eu 2, *x* = 0.25) and [Emim][Ln(2,5-tdc)₂] (Ln = Nd 3, Eu 4)

(2,5-tdc = thiophene-2,5-dicarboxylate). Studies of their structures and luminescence properties revealed that both the chirality and luminescent property of the metal–organic frameworks can be affected through introducing halide ions into the frameworks.

Compounds 1 and 2 were synthesized through the reaction of LnCl₃·6H₂O (0.5 mmol) and thiophene-2,5-dicarboxylic acid (0.167 g, 1.0 mmol) in Emim-Br (0.955 g, 5.0 mmol) and 40 mg H₂O at 170 °C for 3 days. Compounds 3 and 4 were synthesized analogously using Ln₂O₃ in place of LnCl₃·6H₂O (ESI†, S1).

All compounds were analyzed by single-crystal X-ray diffraction. Compounds 1 and 2 are isomorphous, crystallize in the orthorhombic system, space group *P*2₁2₁2 (ESI†, S2). Thus, only the structure of 1 is described here in detail. Present in the asymmetric unit of 1 are 1.5 Nd³⁺, 2 2,5-tdc ligands, 2.5 Cl⁻, 0.5 Br⁻, and 1 Emim⁺ cation. The Cl⁻ to Br⁻ ratio is supported by the XPS spectrum (ESI†, S2, Fig. S1 and S2) and elemental analysis of 1. The coordination environment of Nd³⁺ is shown in Fig. 1a. Nd1 is octa-coordinate with contributions from two chelating carboxylate groups of two different 2,5-tdc ligands and four monodentate carboxylate groups of four different 2,5-tdc ligands. The bond lengths of Nd–O are 2.403(3)–2.466(3) Å and are comparable to those reported for similar octa-coordinate Nd complexes.¹¹ Nd2 is also octa-coordinate with contribution from one chelating carboxylate from a 2,5-tdc ligand, four monodentate carboxylate groups from different 2,5-tdc ligands, 1 Cl⁻, and 0.5 Cl⁻ and Br⁻ occupying the same position (Fig. 1a). The bond

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† Electronic supplementary information (ESI) available: Preparation of complexes 1 to 4, crystal data for 1 to 4 as well as refinement details, PXRD and TG analysis for complexes 1 to 4, X-ray photoelectron spectroscopy for 1 and 2, Room-temperature excitation and emission spectra for compounds 2, 4, and [(Eu₂(2,5-tdc)₃(CH₃OH)₂·(CH₃OH)], luminescence decay curves and luminescence quantum yields for compounds 2, 4 and [(Eu₂(2,5-tdc)₃(CH₃OH)₂·(CH₃OH)], and X-ray crystallographic files in cif format for complexes 1–4. CCDC 822460–822463. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc13297k

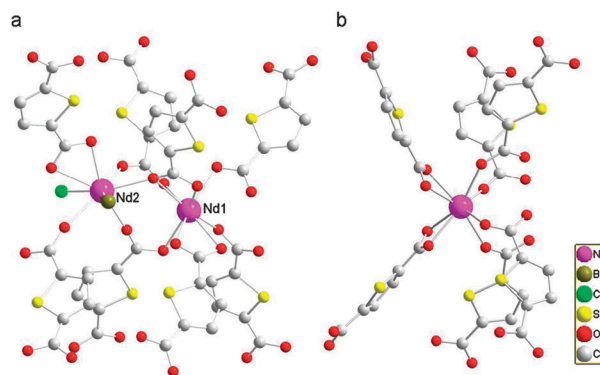


Fig. 1 Coordination environments of Nd centers in 1 (a) and in 3 (b). Hydrogen atoms in the organic ligands are omitted for clarity.

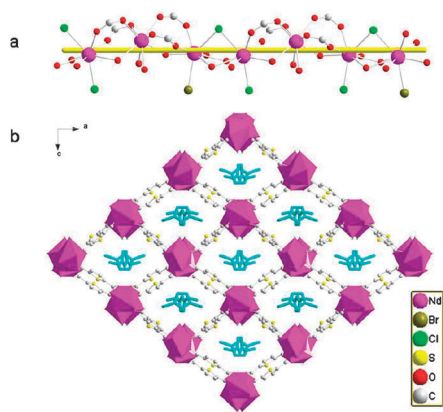


Fig. 2 (a) Ball-and-stick plot showing the 1D helical chain in **1**; (b) ball-and-stick and polyhedral representations of the crystal structure of **1** viewed along the *ac* plane (Emim⁺ is shown by blue stick with its H atoms omitted for clarity).

lengths of Nd–O, Nd–Cl and Nd–Br are 2.346(3)–2.658(3), 2.837(10)–2.839(10) and 2.846(2) Å, respectively, and are comparable to those found in analogous Nd complexes.^{11,12}

Each independent Nd1 center is linked to two adjacent Nd2 centers through a pair of bidentate carboxylate groups of two 2,5-tdc ligands and 1 μ–O bridge from one 2,5-tdc ligand, forming a trinuclear unit of [Ln₃(2,5-tdc)₄Cl₂Br]^{2–}. Connection of adjacent trinuclear units through one μ–Cl and two μ–O bridges generates a 1D left-handed helical chain, as shown in Fig. 2a. The helical chains extend along a crystallographic 2₁ screw axis in the *b* direction, and each is connected with four adjacent ones, leading to a 3D structure with all the helical chains exhibiting the same left-handed helicity (Fig. 2b). Consistent with its crystal structure, the CD (circular dichroism) spectra of single crystals of **1** indicate that individual crystals of **1** are indeed chiral (Fig. 3). However, the bulk sample is CD-inactive, indicating that the bulk sample is a conglomerate, a racemic mixture of both chiral forms.

Compounds **3** and **4** are isomorphous and crystallized in the monoclinic system, space group *P2₁/c* (ESI†, S2). The asymmetric unit of **3** consists of 1 Nd³⁺, 2 2,5-tdc ligands and 1 Emim⁺. Each Nd center is coordinated by two chelating carboxylate groups from different 2,5-tdc ligands, and four monodentate carboxylate groups from four different 2,5-tdc ligands (Fig. 4a). The bond lengths of Nd–O are 2.373(4)–2.528(4) Å, comparable to those of **2**. Two Nd centers connected through four

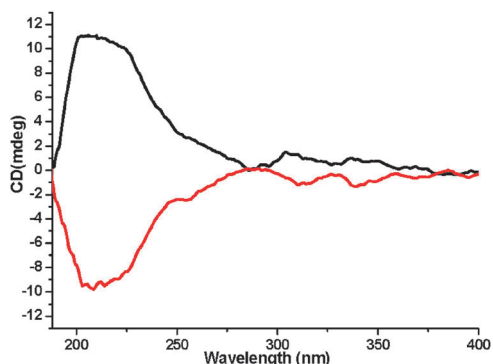


Fig. 3 The solid-state CD spectra of **1** measured with a single crystal.

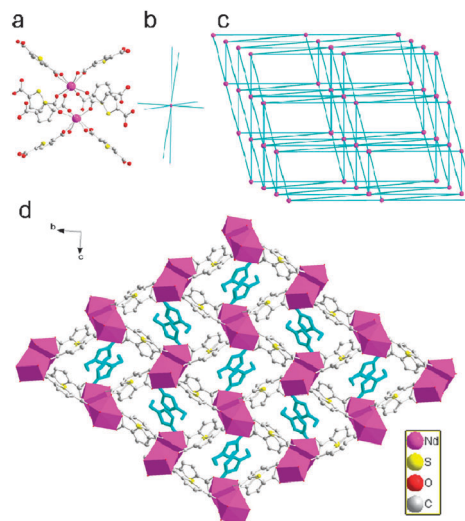


Fig. 4 (a) Plot showing the binuclear unit of {Nd₂} in **3**; (b) the schematic of the {Nd₂} unit as a node (● = {Nd₂}); (c) schematic view of the 3D framework based on the {Nd₂} unit as a node (● = {Nd₂}); (d) ball and stick plot showing the 3D structure in **3** viewed along the *bc* plane. The Emim⁺ is shown by blue sticks (hydrogen atoms are omitted for clarity).

bidentate carboxylate groups of four different 2,5-tdc ligands, forming a dinuclear unit as shown in Fig. 4a and b. Such dinuclear units, acting as 8-connected building blocks, are linked to their respective neighbors, generating a 3D structure with a topology represented by the Schläfli symbol (4²⁴)(6⁴) (Fig. 4c and d). We note that a Co-based metal–organic framework with the same topology as that of **1** has previously been reported.¹³

Compounds **1–4** are structurally distinct from those built from the same organic ligands and lanthanide ions under hydrothermal conditions.^{14,15} Clearly it is the use of ILs that causes the observed differences. A more detailed structural analysis may explain why compounds **1** and **2** crystallize in a polar space group, whereas **3** and **4** do not. It appears that the key lies in the different coordination spheres of the lanthanide ions. Specifically, the exclusive carboxylato coordination of **3** and **4** prevents the formation of a helical chain as observed in the cases of **1** and **2**; in the latter, the introduction of halide ions reduces the number of organic ligands necessary for the completion of the lanthanide coordination. As a result, the steric hindrance about the metal ion is significantly reduced, making it possible for the formation of the helical chain as observed in **1** and **2**. The present observation of halide facilitating the formation of helical chains of lanthanide-based coordination polymers is consistent with our previous findings.¹⁶

Fig. 5 shows the emission spectra of complexes **2** and **4** in the solid-state upon excitation at 395 nm under the same conditions (excitation and emission slits are both 1.4 nm). The shape of the emission spectra for **2** and **4** are similar, yet the intensity of **2** is significantly weaker than that of **4**. Referring to the previous work,^{14b} the peaks at 580, 592, 613, 650 and 700 nm are assigned to the ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ transitions, respectively. Luminescence quantum yields determined by the integration sphere method upon excitation at 395 nm (ESI†, S3) are 0.087 for **2** and 0.43 for **4**, and the decay lifetimes are 0.95 and 1.03 ms, respectively. This result

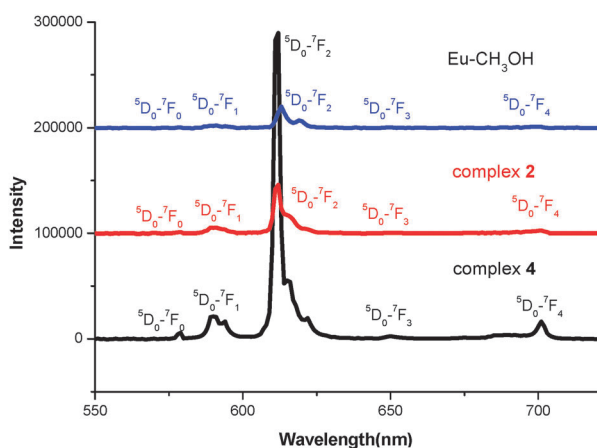


Fig. 5 The solid-state luminescence spectra of **2**, **4** and $[(\text{Eu}_2(2,5\text{-tdc})_3(\text{CH}_3\text{OH})_2 \cdot (\text{CH}_3\text{OH}))]$ measured under the same conditions.

indicates that the introduction of halide ions significantly decreases the luminescence efficiency of the halo-coordinated compound, since the PXRDs of **2** and **4** clearly demonstrated that both **2** and **4** crystallized in pure phase and TG analyses of **2** and **4** showed that both **2** and **4** were stable up to 300 °C (ESI†, Fig. S3–S6). It also deserves noting that the luminescence quantum yields of **2** and **4** are significantly higher than that of $[(\text{Eu}_2(2,5\text{-tdc})_3(\text{CH}_3\text{OH})_2 \cdot (\text{CH}_3\text{OH}))]^{14b}$ (luminescence quantum yield 0.048, decay lifetime 0.32 ms). In the latter case, the existence of two monodentate coordinated methanol molecules leads to luminescence quenching through high-energy OH-vibrations of the MeOH molecules. These results suggest that the luminescent property of lanthanide-based organic frameworks could be improved if synthesized under ionothermal conditions when the use of luminescence-quenching solvents/ligands can be avoided.

In summary, four lanthanide-based metal–organic frameworks were synthesized under ionothermal conditions. Crystal structure analysis reveals that compounds **1** and **2** crystallize in the polar space group $P2_12_12$, while **3** and **4** in the central symmetry space group $P2_1/c$. The Eu^{3+} -containing compounds **2** and **4** were shown to be luminescent, but the quantum yield of **4** is much higher than that of **2**. The observed differences in both structure and luminescence properties have been rationalized in terms of halide coordination in these compounds under ionothermal conditions.

This work was supported by the NNSFC (Grant Nos. 20825103 90922031 and 21021061), the 973 Project from MSTC (Grant No 2007CB815304).

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