# Two novel luminescent lanthanide sulfate–carboxylates with an unusual 2-D bamboo-raft-like structure based on the linkages of left- and right-handed helical tubes involving *in situ* decarboxylation†

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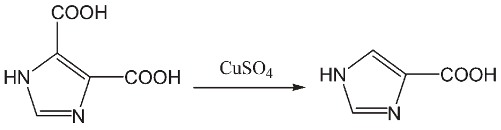
**Two novel 2-D bamboo-raft-like lanthanide luminescent materials [Ln(Himc)($SO_4$)($H_2O$)] (Ln = Dy, Eu; $H_2$imc = 4-imidazolecarboxylic acid), constructed from alternate left- and right-handed helical tubes, were synthesized and characterized; interestingly, $H_2$imc came from the *in situ* decarboxylation of the 4,5-imidazoledicarboxylic acid ($H_3$imdc) in the hydrothermal reactions.**

The synthesis and characterization of novel organic–inorganic hybrid materials are of great current interest because of their fascinating structural diversity and potential applications in many fields such as catalysis, material science, optoelectronic- and magnetic-chemistry.[1,2] A variety of families of inorganic frameworks involving tetrahedral anionic moieties such as silicates,[3] phosphate,[4] germanates[5] and arsenates[6] have been reported. The architectures formed by sulfates, on the other hand, have been less well investigated.[7] So far, few lanthanide sulfates have been structurally characterized. The reported lanthanide sulfate structures are mainly restricted to inorganic hydrates, species containing alkali metal or ammonium ions, or organic amines.[8,9] However, organic–inorganic hybrids by incorporating carboxylic acid ligands in the structure of lanthanide sulfates are rare.[10]

The decarboxylation of free carboxylic acids is often difficult, except for some activated acids such as aryl carboxylic acid. Even in this case, it was performed by palladium or nickel catalysts at a high temperature in the gas phase.[11] Recently, hydrothermal decarboxylation of multi-carboxylic acids containing N-donors has been shown to occur in the presence or absence of metal ions.[12,13] However, to the best of our knowledge, the decarboxylation of 4,5-imidazoledicarboxylic acid ($H_3$imdc) under hydrothermal conditions has not been documented so far. Herein, we report the first example of lanthanide sulfate–carboxylates, [Ln(Himc)($SO_4$)($H_2O$)] (Ln = Dy **1**, Eu **2**), involving *in situ* decarboxylation of $H_3$imdc.

White prism crystals of **1** and **2** were obtained by the hydrothermal reaction of $Ln_2O_3$, $CuSO_4{\cdot}5H_2O$ and $H_3$imdc in water at 170 °C for 10 days (Scheme 1),‡ but, so far, have not been obtained when $H_2$imc is used. The X-ray crystal structure analyses revealed that **1** and **2** are isomorphous. Therefore, only the structure of **1** is described in detail.§ It is interesting to note that decarboxylation occurred and $H_3$imdc was transformed into $H_2$imc under hydrothermal conditions in the presence of Cu(II) ions. Notably, decarboxylation did not occur in above reaction when copper salt was absent[2c] or transition metal ions other than Cu(II) were used. These results indicate that Cu(II) plays a catalytic role in the decarboxylation process. Other decarboxylations catalyzed by Cu(II) ions have also been reported.[12a,12d,14] In the asymmetrical unit of **1** there is one unique $Dy^{3+}$ ion, one $Himc^-$ ligand and one $SO_4^{2-}$ anion, respectively (Fig. 1). The $Dy^{3+}$ ion is eight-coordinate and described as a dodecahedron: one imidazole nitrogen, four sulfate oxygen atoms from three $SO_4^{2-}$ anions and one terminal water molecule. Each $Himc^-$ anion connects two $Dy^{3+}$ ions, one in monodentate mode and the other in bidentate mode, while each $SO_4^{2-}$ anion adopts a $\mu_3$-tetradentate coordination mode bridging three $Dy^{3+}$ ions. A pair of $Dy^{3+}$ ions are bridged by two $\mu_2$-O atoms of two $SO_4^{2-}$ anions to form a [$Dy_2O_2$] rhombic unit (Fig S1†). These units are linked up *via* carboxyl groups of Himc to give rise to two types of helical chain of opposite chirality, with a pitch of 6.479 (2) Å running along the



**Scheme 1** $H_2$imc, formed *via* the decarboxylation of $H_3$imdc.

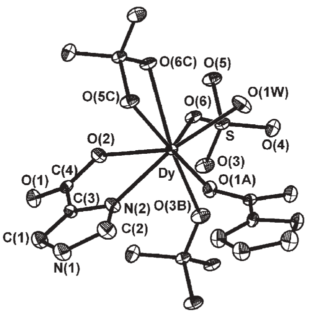


**Fig. 1** The coordination environments of $Dy^{3+}$ in **1**. Thermal ellipsoids are at 50% probability. Atoms having "A", "B" or "C" in their labels are symmetry-generated. A: $x$, ½ − $y$, ½ + $z$; B: −$x$, 1 − $y$, 1 − $z$; C: −$x$, −$y$, 1 − $z$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Dy–O(1A) 2.313(2), Dy–O(2) 2.390(3), Dy–O(3B) 2.318(3), Dy–O(5C) 2.405(3), Dy–O(6) 2.355(2), Dy–O(6C) 2.514(2), Dy–O(1W) 2.342(2), Dy–N(2) 2.455(3).

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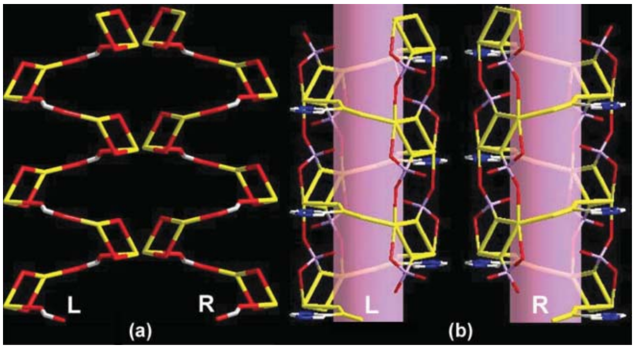

**Fig. 2** (a) View of the left- and right-handed helical chains along the b-axis. Color code: Dy, yellow; O, red; C, white; N, blue; S, purple. (b) The helical tubes constructed from the helical chains weaved by $SO_4^{2-}$ anions. The helical chain is marked yellow for identification. L/R: left/right-handed helical tube, respectively.

$2_1$-axis (Fig. 2a and Fig. S2†). The left- and right-handed helical chains are further weaved by $SO_4^{2-}$ anions through their remaining μ-O atoms to chelate the two $Dy^{3+}$ ions of adjacent $[Dy_2O_2]$ units to make the helical tubes of opposite chirality. The dimensions of the helical tube are about 4.64 × 5.71 Å (Fig. 2b and Fig. S3†). The coordinated water molecules point away from the Dy–$\{SO_4\}$–Himc hybrid framework and into the helical tubes. There are strong hydrogen bonds between the coordinated water molecules and the oxygen atoms of the $SO_4^{2-}$ anions, with O···O distances ranging from 2.77 to 2.87 Å (Fig S4†). These two types of helical tubes are alternately connected, with $[Dy_2O_2]$ units functioning as hinges. As a result, a novel 2-D bamboo-raft-like layered network, built from alternately arranged left- and right-handed helical tubes, forms in the bc-plane. The imidazole rings are above or below the layers (Fig. 3). The 2-D layers stack in –AAA– mode along the a-axis. The hydrogen bonds between the N atoms of the imidazole rings and the O atoms of the $SO_4^{2-}$ anions link the adjacent layers into a 3-D framework (N···O 2.93 Å). From the topological point of view, the 2-D layer of **1** is a (3,5)-connected net. Each Dy atom acts as a five-connected node and every $SO_4^{2-}$ anion functions as three-connected node in the ratio 1 : 1. The net is shown schematically in Fig. 4 and Fig. S5†. The Schäfli symbol is $(4^2{\cdot}6)$ $(4^2{\cdot}6^7{\cdot}8)$.

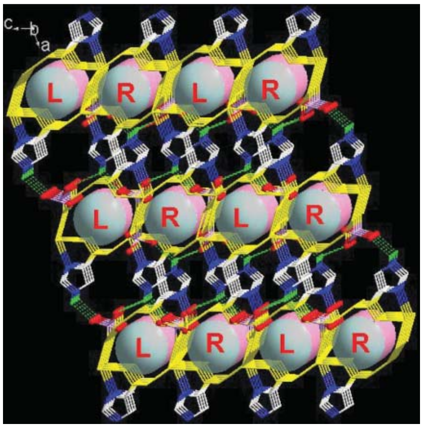

**Fig. 3** View of the 2-D bamboo-raft-like structure formed by the alternating assembly of helical tubes of opposite chirality. The helical chain is marked yellow for identification and the coordinated water molecules are omitted for clarity. L/R: left/right-handed helical tube, respectively.

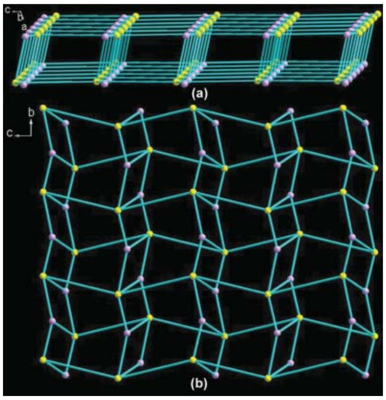

**Fig. 4** Schematic view of the $(4^2{\cdot}6)(4^2{\cdot}6^7{\cdot}8)$ net in the structure of **1** along (a) the b-axis and (b) the a-axis. The $Dy^{3+}/SO_4^{2-}$ units (yellow/purple) function as 5-/3-connected nodes, respectively.

The thermal stability of **1** and **2** were examined by TGA in a dry air atmosphere from 40 to 1000 °C. In the TG curve of **1**, the weight loss of 51.7% (calc. 51.9%) in the temperature range 150–900 °C corresponds to the successive release of individual coordination water molecules, the decomposition of one ligand and/or the departure of one sulfate as $SO_3$ per formula unit.[10a] The 48.3% white residue might be $Dy_2O_3$[15a] (calc. 48.1%). The TG curve of **2** displays a weight loss of 33.8% (calc. 32.1%) from 350–1000 °C, corresponding to the release of one coordination water molecule and one ligand per formula unit. The white residue might be $Eu_2O(SO_4)_2$[15b] (observed 66.2%, calc. 67.9%), a mixture containing ½ $Eu_2O_2(SO_4)$ and ½ $Eu_2(SO_4)_3$.

The two emission groups for complex **1** in the range 400–450 and 450–680 nm are shown in Fig. 5a. The emissions at 482, 574 and 662 nm (decay lifetime = 0.946 μs) are attributable to the

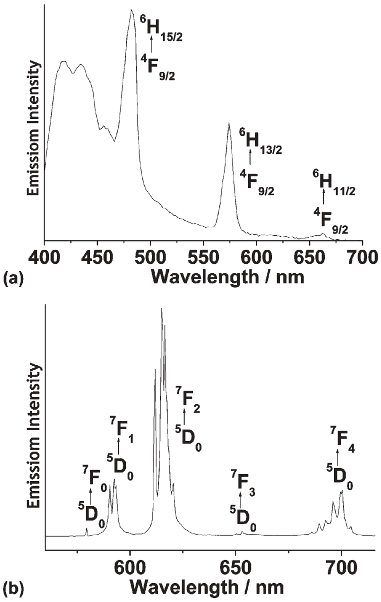

**Fig. 5** Emission spectra of (a) **1** and (b) **2** in solid state at room temperature (excitation at 352 and 394 nm for **1** and **2**, respectively).

characteristic emission of $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2 and 11/2) transitions of the $Dy^{3+}$ ion. It is obvious that the intensity of the blue emission, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition, is much stronger than that of the yellow one. This indicates that $H_2$imc acts as a better sensitizer to the blue $Dy^{3+}$ emission, unlike the previously reported $H_3$imdc-based $Dy^{3+}$ complex, which gives a predominantly yellow luminescence.[2c] The large broad blue-shift band ranging 400 to 450 nm could be assigned to the emission of ligand-to-metal charge transfer (LMCT).[16] The intensity of the metal-centered transitions is strong relative to that of the broad LMCT band, which implies that direct metal excitation is comparable with the sensitized process, as the extinction coefficients of the metal emission are much lower than that of the ligands. **2** yields intense red luminescence (Fig. 5b) and exhibits the characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transition of the $Eu^{3+}$ ion, with a decay lifetime of 256 μs. The $^5D_0 \rightarrow {}^7F_0$ transition, observed as a weak peak at 579 nm, reveals the presence of the $Eu^{3+}$ site with low symmetry.[17] The $^5D_0 \rightarrow {}^7F_2$ transition is clearly stronger than the $^5D_0 \rightarrow {}^7F_1$ transition, the intensity ratio of 3.9 for $I_{({}^5D_0 \rightarrow {}^7F_2)}/I_{({}^5D_0 \rightarrow {}^7F_1)}$ indicates the absence of an inversion center at the $Eu^{3+}$ site. This is in agreement with the result of single crystal X-ray analysis. No emission bands from the ligands or LMCT are observed, indicating that the ligands transfer the excitation energy efficiently to the $Eu^{3+}$.

In summary, we have successfully constructed two novel coordination polymers based on inorganic lanthanide sulfate skeletons and an 4-imidazolecarboxylic acid under hydrothermal conditions, and the systematic synthetic procedures well established. The 2-D bamboo-raft-like architectures with $(4^2{\cdot}6)(4^2{\cdot}6^7{\cdot}8)$ topology are built from alternately arranged left- and right-handed helical tubes. Interestingly, decarboxylation occurred and 4,5-imidazoledicarboxylic acid was transformed into 4-imidazolecarboxylic acid in the presence of $Cu^{2+}$ ions under hydrothermal reaction conditions. Blue and red luminescence are observed in the $Dy^{3+}$ and $Eu^{3+}$ complexes, respectively. In addition, both metal and LMCT emission are observed for the $Dy^{3+}$ complex.

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## Notes and references

‡ Syntheses of **1** and **2**: A mixture of $Ln_2O_3$ (0.25 mmol: 0.093 g $Dy_2O_3$, 0.083 g $Eu_2O_3$), $H_3$imdc (1 mmol, 0.156 g) and $CuSO_4{\cdot}5H_2O$ (0.5 mmol, 0.125 g) in a molar ratio of about 1 : 4 : 2 and 10 mL $H_2O$ (pH = 3) were sealed in a 30 mL stainless steel reactor with a Teflon liner, heated at 170 °C for 10 d and then cooled to room temperature. Accordingly, white prismatic crystals of **1** or **2** were recovered by filtration, washed with distilled water and dried in air. Yield: 6% (**1**) and 5% (**2**) (based on $Ln_2O_3$). Anal. calc. for $C_4H_5DyN_2O_7S$ **1**: C, 12.39; H, 1.30; N, 7.23. Found: C, 12.35; H, 1.83; N, 7.15%. Anal. calc. for $C_4H_5EuN_2O_7S$ **2**: C, 12.73; H, 1.34; N, 7.43. Found: C, 13.02; H, 1.92; N, 7.40%.

§ Crystal data for **1**: $C_4H_5DyN_2O_7S$, $M_r = 387.66$, monoclinic, space group $P2_1/c$, $a = 11.157(3)$, $b = 6.4786(15)$, $c = 12.087(3)$ Å, $\beta = 107.808(1)^\circ$, $V = 831.8(4)$ Å$^3$, $Z = 4$, $\rho = 3.096$ g cm$^{-3}$, $\mu = 9.256$ mm$^{-1}$, $F(000) = 724$, GOF = 1.014, A total of 5902 reflections were collected, 1836 of which were unique ($R_{\text{int}} = 0.0290$). $R1(wR2) = 0.0204$ (0.0441) for 138 parameters and 1730 reflections ($I > 2\sigma(I)$). CCDC 293649. For **2**: $C_4H_5EuN_2O_7S$, $M_r = 377.12$, monoclinic, space group $P2_1/c$, $a = 11.209(2)$, $b = 6.5406(11)$, $c = 12.203$ (2) Å, $\beta = 107.922(2)^\circ$, $V = 851.2(3)$ Å$^3$, $Z = 4$, $\rho = 2.943$ g cm$^{-3}$, $\mu = 7.635$ mm$^{-1}$, $F(000) = 712$, GOF = 1.351 A total of 6227 reflections were collected, 1946 of which were unique ($R_{\text{int}} = 0.0178$). $R1(wR2) = 0.0174$ (0.0639) for 136 parameters and 1853 reflections ($I > 2\sigma(I)$). CCDC 293650. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELXTL-97 program package. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602034h

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