Coordination Polymers

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Porous Lanthanide–Organic Open Frameworks with Helical Tubes Constructed from Interweaving Triple-Helical and Double-Helical Chains**

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In recent years, the construction of metal-organic coordination polymers has attracted considerable attention in supramolecular and materials chemistry due to the formation of fascinating structures and potential applications as optoelectronic, magnetic, and porous materials.[1] However, most of the work has so far focused on the assembly of the d-block metal-organic open frameworks,[2] while the analogous chemistry of the lanthanides remains less developed.[3] This is attributed to the tendency of the lanthanide ions for high coordination, which favors the formation of condensed structures with[4] or without guest species.[3b,5] To date, no systematic investigation on lanthanide-based porous materials with luminescent properties has been documented.[6] In addition, lanthanide-organic frameworks with channels from which the guest species can be removed and reintroduced reversibly without collapse of the framework are rare.[7]

Among the reported network lanthanide carboxylates, 4,5-imidazoledicarboxylic acid (H_3ImDC), which remains largely unexplored,[8] was chosen as the multidentate ligand for the following reasons: 1) The flexible, multifunctional coordination sites provide a high likelihood for generation of structures with high dimensions. 2) It can be deprotonated to generate H_2ImDC^-, $HImDC^{2-}$, and $ImDC^{3-}$, which allow various, acidity-dependent coordination modes. 3) The skew coordination orientation of the carboxy groups is favorable for constructing a helical structure.

Accordingly, our aim was to synthesize novel lanthanide-organic open frameworks by using the H_3ImDC ligand. Here we report the syntheses, structures, and luminescent and magnetic properties of two novel lanthanide-organic coordination polymers of $[Ln_2(ImDC)_2(H_2O)_3]\cdot 1.625\,H_2O$ (Ln = Eu (**1**) and Dy (**2**)). The structures of **1** and **2** not only display one-dimensional achiral channels, but also contain alternately arranged left- and right-handed helical tubular channels.

White prism crystals of **1** and **2** were obtained by the hydrothermal reaction of Ln_2O_3 and H_3ImDC in water in the presence of HNO_3 at pH 2 and 170 °C. The X-ray crystal structure analyses reveal that **1** and **2** are isostructural and crystallize in the high symmetry tetragonal space group $I4_1/a$.[9] Therefore, only the structure of **1** is described in detail. In the asymmetrical unit of **1**, there are two crystallographically independent Eu^{3+} ions and two unique ImDC ligands with two different coordination modes (Figure 1 and see the Supporting Information). The Eu1 ion (mode **I**, Scheme 1) is eight-coordinate and is described as a dodecahedron (see the Supporting Information): Two imidazole nitrogen (N_{Im}) and four carboxylate oxygen (O_{COO^-}) atoms from three ImDC moieties as well as two terminal water molecules. The coordination geometry for the nine-coordinate Eu2 ion (mode **II** in Scheme 1) is close to that of a tricapped trigonal prism (see the Supporting Information): six O_{COO^-} and two

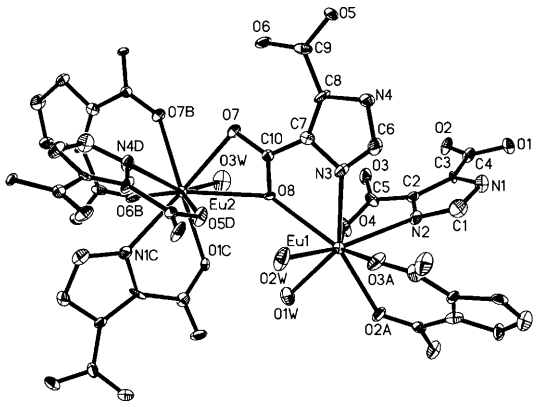
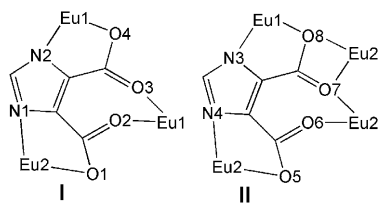


Figure 1. The coordination environments of Eu1 and Eu2 atoms in **1**. Atoms with "A" or "B" in their labels are symmetry-generated.



Scheme 1. Coordination modes of the ImDC ligands in **1**.

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N_{Im} atoms from four ImDC units as well as one terminal water molecule. The O7 and O8 atoms in mode **II** are simultaneously coordinated to two Eu^{3+} ions, while the O3 and O4 atoms in mode **I** are not further coordinated (Scheme 1). Thus, the O7/O8 atoms play a key role in the formation of **1** with an open framework. The Eu–O bond lengths range from 2.328(9) to 2.702(8) Å, whereas the Eu–N distances vary from 2.432(11) to 2.572 (10) Å.

The most striking features of **1** are the linkages between the Eu^{3+} ions and the two unusual coordinate modes of the ImDC moieties to form a unprecedented three-dimensional framework with achiral channels and two types of helical tubes with opposite chirality (Figure 2a and see the Supporting Information). The helical tubes of **1** can be understood in terms of two distinct parts: The helical tubular walls and the fillers. Thus, the Eu^{3+} ions linked through four carboxyl groups of two types of ImDC units form the achiral channels and the helical tubular walls that are made of triple-helical chains and double-helical chains (Figure 2b,c and see the Supporting Information). In the structure, the left- and right-handed helical channels, which are made of triple-helical chains, are further weaved by double-helical chains having the reverse orientation to the triple-helical chains to make the tubular walls with opposite chirality (Figure 2b,c and see the Supporting Information). These tubular walls are further linked together by O7 and O8 atoms from mode **II** to form the achiral channels (Figure 2a, and Figures S5 and 6b in the Supporting Information). In addition, the helical channels constructed from the triple-helical chains have a 32-membered ring opening along the [001] direction (Figure 3). In fact, there is no closed 32-membered ring present in the structure. The open 32-membered ring consisting of four repeating O2-C4-O1-Eu2-O7-C10-O8-Eu1 linkages—which are built up from the Eu1 and Eu2 atoms as well as two bridging carboxy groups containing C4 and C10 atoms—gives rise to two types of helical ribbons of three equivalent helical chains with opposite chirality (Figure 2b,c and see the Supporting Information). The separation between the adjacent chains in the helical ribbon is the same as the length of the *c* axis (16.176 Å). The pitch of the helical ribbon running along the *c* axis is three times the length of the *c* axis. In contrast, the double-helical chain consists of two distinct helical chains with a 16-membered ring made of four repeating Eu1-O3-C5-O4 (Eu2-O5-C9-O6) linkages, which are only built up from Eu1 (Eu2) atoms and one carboxy bridge containing C5 (C9) atoms (see the Supporting Information). The shortest Eu···Eu distance, bridged by carboxy groups, is 4.24 Å.

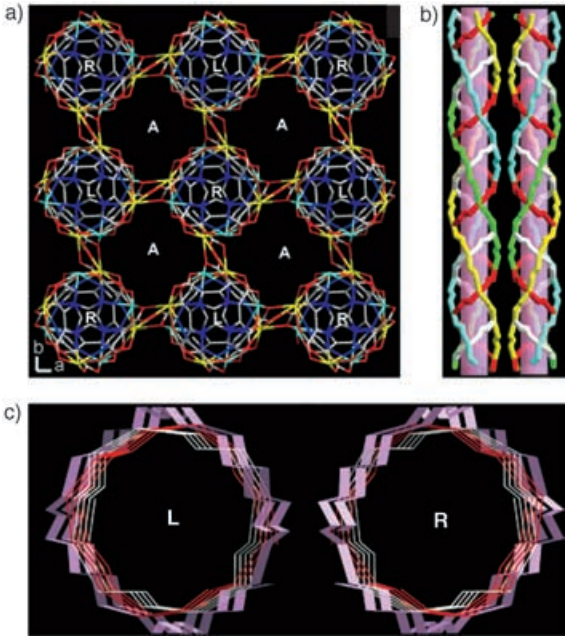

Figure 2. a) The framework of **1** viewed along the *c* axis, showing two types of helical tubular and achiral channels arranged alternately along the *a* and *b* axes. A: achiral channel, L and R indicate the left- and right-handed helical tubular channels. Hydrogen atoms are omitted for clarity. b) View of the helical tubular combination with opposite chirality, constructed from channels of triple-helical chains weaved by double-helical chains with the reverse helical orientation (*b* axis). The triple-helical chains are marked yellow, green, and cyan. The double-helical chains are displayed with red and white helical chains. The imidazole rings are omitted for clarity. c) The helical ribbon representation for the aggregate of triple-helical chains in the helical tube with opposite chirality along the [001] (left) and [00−1] directions (right). The white and red helical chains present two distinct helical chains of double-helical chains weaved across the ribbon.

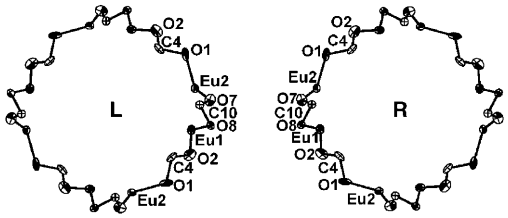

Figure 3. Views of the two types of helical channels containing triple-helical chains in **1** along the [001] (left) and [00−1] directions (right). L and R indicate the left- and right-handed helical channels.

Remarkably, the two types of imidazole rings of the ImDC ligands that act as the fillers are alternately trapped inside the helical tubes and coordinated to adjacent Eu1 and Eu2 atoms from the walls through N_{Im} atoms to form a pair of helical chains with the same helical orientation as the triple-helical chain (see the Supporting Information). The shortest Eu···Eu distance, bridged by an imidazole ring, is about 6.96 Å.

The guest water molecules are suspended in the achiral channels (dimensions 4.58 × 4.58 Å; see the Supporting Information), and the coordinated water molecules point away from the Eu–ImDC hybrid framework and into the achiral channels. There are strong hydrogen bonds between the guests, as well as between the guests and the oxygen atoms from the ImDC moieties and the coordinated water molecules (O···O 2.168(22)–3.344(15) and 2.735(19)–2.976(13) Å, respectively).

Complex **1** displays intense red luminescence (Figure 4a, and see the Supporting Information) and exhibits the characteristic transition of $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) of the Eu^{3+}

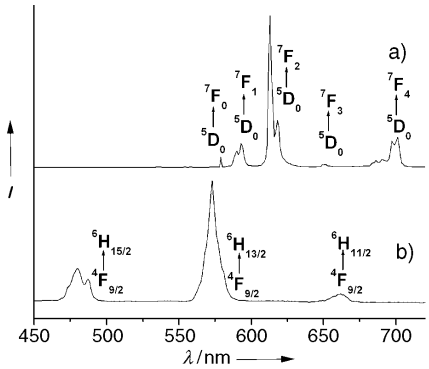

Figure 4. Emission spectra of **1** (a) and **2** (b) in the solid state at room temperature (excitation at 394 and 325 nm for **1** and **2**, respectively). *I* = intensity.

ion with a decay lifetime of 251.2 μs. The appearance of the symmetry-forbidden emission $^5D_0 \rightarrow {}^7F_0$ at 580 nm indicates that the Eu^{3+} ions in **1** occupy sites with low symmetry and have no inversion center,[10] which is further confirmed by the intensity ratio of about 5.5 for $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$.[11] This is in agreement with the result of the single-crystal X-ray analysis. Complex **2** is yellow-luminescent in the solid state with typical Dy^{3+} emissions at 480, 573, and 622 nm (decay lifetime 1.21 μs), corresponding to the characteristic emission $^4F_{9/2} \rightarrow {}^6H_J$ transitions of the Dy^{3+} ion ($J = 15/2$, 13/2, and 11/2; Figure 4b and Figure S11b in the Supporting Information). The yellow emission of the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition has a stronger intensity than the blue emission of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ for **2**, while the red emission of the $^5D_0 \rightarrow {}^7F_2$ transition is the most intense for **1**, suggesting that the ImDC ligand is suitable for the sensitization of yellow and red luminescence for Dy^{3+} and Eu^{3+}, respectively. With respect to H_3ImDC, the strongest emission peak is located at 490 nm ($\lambda_{ex} = 296$ nm; see Figure S11c in the Supporting Information). The absence of the ligand-based emission in the fluorescence spectra of **1** and **2** suggests that the energy transfer from the ligand to the lanthanide center is very effective and can sensitize the lanthanide emission to a large extent.

The magnetic susceptibilities of **1** and **2** were measured in the temperature range 5–300 K. For **1**, the room temperature value of $\chi_M T$ is 2.77 $cm^3 K mol^{-1}$, slightly less than the value of 3.0 $cm^3 K mol^{-1}$ for two Eu^{3+} ions calculated from the van Vleck equation allowing for population of the excited state with higher values of *J* at 293 K.[3d] As the sample is cooled, $\chi_M T$ continuously decreases due to the depopulation of the Stark levels for a single Eu^{3+} ion, and tends to a value very close to zero as the temperature approaches absolute zero, which indicates a $J = 0$ ground state for the Eu^{3+} ion ($^7F_0$) at the lowest temperature (see Figure S12a in the Supporting Information). The $\chi_M T$ value per molecule of **2** is 30.37 $cm^3 K mol^{-1}$ at room temperature, comparable to the expected value of 28.34 $cm^3 K mol^{-1}$ for two free Dy^{3+} ions with a $^6H_{15/2}$ ground state. As the temperature is lowered, the $\chi_M T$ product increases slightly to a maximum of 31.91 $cm^3 K mol^{-1}$ at about 120 K, and then decreases gradually to 24 $cm^3 K mol^{-1}$ at 5 K, suggesting a dominant ferromagnetic interaction between adjacent Dy^{3+} ions. The fitting above 100 K to Curie–Weiss equation yields a positive Weiss constant $\theta = 7.12$ K, which confirms a ferromagnetic coupling between Dy^{3+} centers (see Figure S12b in the Supporting Information). The further decrease of $\chi_M T$ at low temperature is mainly attributed to the splitting of the ligand field of the Dy^{3+} ion because of strong spin-orbital coupling.[12]

In summary, we have successfully constructed two novel lanthanide metal coordination polymers with an open framework under hydrothermal conditions from lanthanide oxide as the source of lanthanide and multidentate ImDC as a bridging ligand; the synthetic procedure has been well established.[13] The linkages between Ln centers through the ImDC ligands in two unique coordination modes result in a series of unusual lanthanide-organic open frameworks containing not only two types of helical tubular channels with opposite chirality but also achiral channels. To the best of our knowledge, this is the first time lanthanide metal coordination polymers with ImDC ligands have been prepared.

Experimental Section

1 and **2**: A mixture of Ln_2O_3 (0.5 mmol; Eu_2O_3, 0.176 g; Dy_2O_3, 0.187 g), H_3ImDC (1 mmol, 0.156 g), and H_2O (8 mL) in the presence of HNO_3 (0.33 mL 8.4 wt%) in a molar ratio of about 1:2:889:0.92 (pH 2) was sealed in a 30-mL stainless steel reactor with a Teflon liner and heated at 170 °C for 10 days, and then cooled to room temperature. White prismatic crystals of **1** and **2** were recovered by filtration, washed with distilled water, and dried in air.

1: Yield: 60% (based on Eu_2O_3); elemental analysis (%) calcd for $C_{10}H_{11.25}Eu_2N_4O_{12.63}$: C 17.32, H 1.64, N 8.08; found: C 17.31, H 1.63, N 8.14; IR (KBr pellet): $\tilde{\nu} = 1573$, 1389, 1108 cm^{-1}.

2: Yield: 37% (based on Dy_2O_3); elemental analysis (%) calcd for $C_{10}H_{11.25}Dy_2N_4O_{12.63}$: C 16.79, H 1.59, N 7.84; found: C 16.30, H 1.61, N 7.59; IR (KBr pellet): $\tilde{\nu} = 1579$, 1392, 1111 cm^{-1}.

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[9] Crystal data for **1** ($C_{10}H_{11.25}Eu_2N_4O_{12.63}$): $M_r = 693.40$, tetragonal, space group $I4_1/a$, $a = 20.2950$ (11), $b = 20.2950(11)$, $c = 16.1760(12)$ Å, $V = 6662.7(7)$ Å^3, $Z = 16$, $\rho = 2.765$ g cm^{-3}, $\mu = 7.543$ cm^{-1}, $F(000) = 5220$, GOF = 1.187. Of 7971 total reflections collected, 2947 were unique ($R_{int} = 0.0700$). $R1$ ($wR2$) = 0.0473 (0.0966) for 259 parameters and 2115 reflections [$I > 2\sigma(I)$]. Crystal data for **2** ($C_{10}H_{11.25}Dy_2N_4O_{12.63}$): $M_r = 714.48$, tetragonal, space group $I4_1/a$, $a = 20.187(3)$, $b = 20.187$ (3), $c = 15.992(3)$ Å, $V = 6517.0(19)$ Å^3, $Z = 16$, $\rho = 2.913$ g cm^{-3}, $\mu = 9.185$ cm^{-1}, $F(000) = 5316$, GOF = 1.191. Of 19395 total reflections collected, 2873 were unique ($R_{int} = 0.0353$). $R1(wR2)$ = 0.0265 (0.0568) for 264 parameters and 2783 reflections [$I > 2\sigma(I)$]. 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 by 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. CCDC-238992 (**1**) and CCDC-238946 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[13] Other phase-pure lanthanides polymers, $[Ln_2(ImDC)_2(H_2O)_3]\cdot n\,H_2O$ (Ln = Y, Pr, Nd, Sm, Gd, Tb, and Er; CCDC-271490–271496) were also obtained as single crystals. X-ray diffraction proves that these compounds are analogous to the title compound. Further investigation on the fluorescent, magnetic, and adsorption properties of these compounds is in progress.

