

Short communication

Isostructural lanthanide metal-organic frameworks comprised of left-handed helical chains: Synthesis, structure and luminescent properties

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ABSTRACT

Six isostructural three-dimensional (3D) lanthanide metal-organic frameworks (Ln-MOFs), $[\text{Ln}(\mu_2\text{-OH})(\text{PDC})(\text{H}_2\text{O})_2]\cdot\text{DMF}$ (Ln = Pr (**1**), Nd (**2**), Eu (**3**), Tb (**4**), Ho (**5**), and Yb (**6**), H₂PDC = pyridine-3,5-dicarboxylic acid), have been successfully synthesized under solvothermal conditions and characterized by single crystal X-ray diffraction, IR spectroscopy, elemental analysis and thermal gravimetric analysis. The framework contains unusual Ln-carboxylate/ μ_2 -OH left-handed helical chains, which are extended by PDC²⁻ linkers to form 3D networks with 1D hexagonal channel. The lanthanide contraction effect induces the decreases of average Ln-distances from Pr to Yb. Due to the efficient sensitization of PDC²⁻ ligand, complexes **2** and **6** display strong characteristic luminescence in the near-infrared (NIR) region, respectively. Moreover, the luminescent properties of complexes **3** and **4** are also studied in the solid state at room temperature.

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1. Introduction

Lanthanide metal-organic frameworks (Ln-MOFs) have been compelling research direction due to diversified topological structures [1–4], superior properties and gigantic prospective applications in numerous domains, such as luminescence [5–8], molecular magnetism [9], gas storage/separation [10–13], proton conductivity [14] and catalysis [15]. It is universally acknowledged that trivalent lanthanide ions are promising candidates for constructing unique luminescent materials owing to their high luminescence quantum yield, narrow and intense band emission, giant Stokes shift, and long luminescence lifetimes [16–19]. A lot of aromatic-carboxylic groups or pyridine-carboxylate ligands have been demonstrated to be good luminescent chromophores, which are good sensitizers to stimulate lanthanide ion luminescence [20–22].

Ln-MOFs bearing active recognized sites are generally considered as great luminescent probes and sensors for the recognition and sensing of cations, anions, small molecules, vapors, pH values and even temperature [23–26]. Additionally, combining different lanthanide ions into isostructural Ln-MOFs is an effective method to generate functional

Ln-MOFs [27–29]. In order to further investigate 3D Ln-MOFs and their intrinsic properties, we have been bent on synthesizing diversified Ln-MOFs with various aromatic-carboxylic groups or pyridine-carboxylate ligands and luminescent ions under solvothermal reactions and exhibited excellent luminescent properties [30–35]. Herein, we successively report the synthesis, structural and luminescent investigations of six isostructural Ln-MOFs, $[\text{Ln}(\mu_2\text{-OH})(\text{PDC})(\text{H}_2\text{O})_2]\cdot\text{DMF}$ (Ln = Pr (**1**), Nd (**2**), Eu (**3**), Tb (**4**), Ho (**5**), and Yb (**6**), H₂PDC = pyridine-3,5-dicarboxylic acid) based on the unusual Ln-carboxylate/ μ_2 -OH left-handed helical chain. Meanwhile, complexes **2**, **3**, **4**, and **6** exhibit strong luminescence from the Ln³⁺ centers because of the sensitization of PDC²⁻ ligand.

Complexes **1–6** were prepared by a mixture of Ln(NO₃)₃·6H₂O (0.5 mmol), H₂PDC (0.5 mmol), two drops of HOAc, DMF (4 mL) and H₂O (4 mL) sealed in a Teflon-lined autoclave and heated under autogenous pressure at 120 °C for 3 days. After being cooled to room temperature, six isostructural Ln-MOFs were obtained and washed with DMF. The formula of $[\text{Ln}(\mu_2\text{-OH})(\text{PDC})(\text{H}_2\text{O})_2]\cdot\text{DMF}$ was further confirmed by elemental analysis and thermal gravimetric analysis (TGA). Single crystal X-ray structure analyses reveal that complexes **1–6** are isostructural and crystallize in the hexagonal spontaneous resolution P6₁22 space group. As a representative example, the crystal structure of **1** is described in detail. Complex **1** has a three-dimensional framework, the asymmetric unit of which consists of one Pr(III) ion, one fully deprotonated PDC²⁻ ligand, one μ_2 -OH, two coordinated water molecules, and one lattice DMF molecule. As shown in Fig. 1, Pr(III)

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ion is nine-coordinated by four carboxylate O atoms from four carboxylate groups of distinct PDC^{2-} ligands, one N from pyridyl group of the fifth different PDC^{2-} ligand, two O atoms from a μ_2 -OH, and two oxygen atoms from coordinated water molecules, forming a distorted tricapped trigonal prism coordination geometry (Fig. 1b). Each PDC^{2-} ligand bridges five Pr(III) ions through carboxylate groups or pyridyl groups with the unique μ_5 - η^1 : η^1 : η^1 : η^1 : η^1 mode (Fig. 1c). Interestingly, the interlinkage between Pr(III) ions and PDC^{2-} ligands through monodentate/bridging carboxylate groups give rise to an infinite 1D Pr-carboxylate left-handed helical chain along the *ac* plane (Fig. 1d) and *c*-axis (Fig. 1e). Followed by the further coordination of Pr(III) ions and N atoms from PDC^{2-} ligands, 1D Pr-carboxylate left-handed helical chains are extended to a 3D framework with the window sizes of $\sim 9.4 \times 9.4 \text{ \AA}^2$ (Fig. 1f). Furthermore, the chains are strengthened by μ_2 -OH atom bridging adjacent Pr(III) ions, resulting in unusual Pr-carboxylate/ μ_2 -OH chains (Fig. 1g and h). Meanwhile, a narrower 1D hexagonal channel with the effective dimensions of $\sim 3.1 \times 3.1 \text{ \AA}^2$ is observed along the *c*-axis (excluding van der Waals radii of the atoms). PLATON analysis reveals that the 3D framework is composed of voids of 42.5% that represent 1972.3 \AA^3 per unit cell volume and 838.3 \AA^3 total potential solvent area volume. Based on above description of the crystal structures, complexes **1–6** are isomorphous. The average Ln—O and Ln—N bond lengths and Ln···Ln separations decrease from Pr^{3+} to Yb^{3+} ions, consistent with the decreasing sequence of ionic radii due to the effect of lanthanide contraction. The average bond lengths of Ln—O for **1–6** continuously decrease from 2.481 (for **1**), 2.477 (for **2**), 2.447 (for **3**), 2.427 (for **4**), 2.405 (for **5**) to 2.377 Å (for **6**). Generally,

as the sizes of the Ln^{3+} ions decrease, the repulsions among the coordination atoms around one metal center increase, until the crystal structure becomes unstable and then forms a new structure [36,37]. Around the nine-coordinated Ln^{3+} centers from **1** to **6**, the Ln—N separations decrease significantly from 2.75 to 2.52 Å, which is also imitated by Ln···Ln separations from 4.540 to 4.422 Å.

Thermal gravimetric analysis (TGA) of **1–6** was carried out to examine the stability of the framework. TGA measurement was performed in the temperature range of 25–800 °C in the air atmosphere. In line with the isostructural structures of **1–6**, TGA curves of **1** and **6** are herein discussed. As shown in Fig. S1, their TGA curves display the similar thermal decomposition behaviors. The TGA curves in the range of 25–200 °C show a first weight loss of 16.83 (for **1**), and 15.62% (for **6**), respectively, corresponding to loss of one guest DMF molecule (calcd. 16.91, and 15.74%, respectively). The second weight loss occurred from 200 to 350 °C, which could be attributed to the loss of two coordinated H_2O molecules for **1** (calcd/found = 8.33/8.41%) and for **6** (calcd/found = 7.75/7.71%). The further heating above 400 °C leads to the framework decomposition due to the loss of PDC^{2-} ligands.

The solid-state emission spectra of complexes **2**, **3**, **4** and **6** at room temperature were measured from the visible to the near-infrared region. As shown in Fig. 2a, complex **2** displays three strong emission bands in the NIR region, derived from the typical f-f transitions of the Nd(III) ion at ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ (895 nm), ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ (1062 nm), and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ (1336 nm), respectively, indicating that PDC^{2-} sensitizes Nd^{3+} ions via the antenna effect. Similar to complex **2**, the NIR luminescent spectra of complex **6** ($\lambda_{\text{ex}} = 336 \text{ nm}$) exhibits a NIR emission at

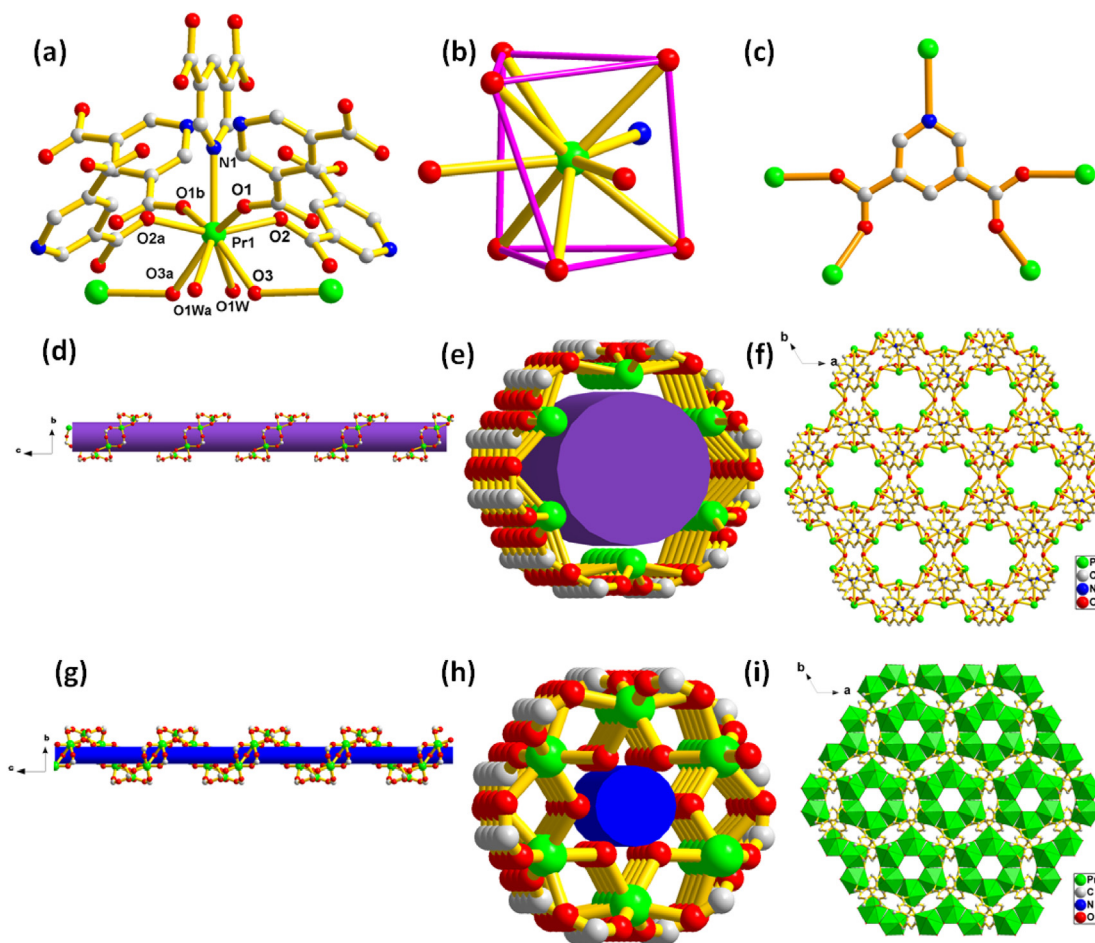


Fig. 1. (a) Coordination environment of the Pr(III) ion; (b) Tricapped trigonal prism coordination geometry of the Pr(III) ion; (c) Coordination modes of PDC^{2-} ligands; (d) and (e) 1D Pr-carboxylate left-handed helical chain; (f) 3D framework constructed by Pr^{3+} ions and PDC^{2-} ligands along the *c*-axis; (g) and (h) 1D Pr-carboxylate/ μ_2 -OH chain; (i) Polyhedral view of 3D frameworks showing the 1D hexagonal channels along the *c*-axis. All the lattice solvent molecules and H atoms are omitted for clarity.

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