2D lanthanide-based pyridine-substituted triazole benzoate coordination polymers: Structure, optical and magnetic properties

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A series of novel lanthanide-based coordination polymers, \( \text{Ln}[(\text{atpa})(\text{H}_2\text{O})_2] \cdot 1.5n\text{H}_2\text{O} \) (HL = 4-(3-methyl-5-(pyridin-4-yl)-1,2,4-triazol-4-yl)benzoic acid, H\text{atpa} = 2-aminoterephthalic acid and Ln = Tb(1), Dy(2), Ho(3), Er(4), Tm(5), Yb(6)) have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, optical and magnetic measurements. Compounds 1-6 are isomorphous, which can be described as 2D network based on \( \text{Ln}_2(\text{CO}_2)_2 \) units. The magnetic properties of compound 1 (Tb) show typical antiferromagnetic interaction, while compound 2 (Dy) has ferromagnetic behavior. The room-temperature photoluminescence spectra of 1 exhibit strong characteristic emissions in the visible region, whereas compounds of Dy(2), Er(4) and Yb(6) display NIR luminescence upon irradiation at the ligand band.

Lanthanide-based polymers continue to attract considerable attention because of their fascinating architectures and rich optical and magnetic properties [1-4]. The advantages of lanthanide luminescence are characteristic narrow emission bands mostly in the visible and near-infrared spectral regions, long lifetimes (µs to ms), and high quantum yields [5,6]. Tb\(^{3+}\) compounds are used generally as optical materials for their strong, visible, and easily detected emissions, while NIR emitting lanthanide ions Yb\(^{3+}\) and Er\(^{3+}\) are ever-growing studied in biological analysis, because of their almost-transparent emissions in biological issues [7]. The large anisotropic magnetic moment for some of the Ln\(^{3+}\) ions makes them very appealing for the preparation of magnetic materials (for instance, Tb\(^{3+}\) and Dy\(^{3+}\)) [8-26].

The association of modulable functionalized (carboxylates, phosphonates...) organic moieties with rare-earth metals allows the creation of a large number of compounds with dimensions and sometimes unique physical properties [27,28]. While pure carboxylate ligands have been extensively studied, less investigated nitrogen-containing heterocycles such as pyrazoles, 1,2,4-triazoles, and tetrazoles were found to possess promising coordination abilities [29,30]. Given the important potential applications of lanthanide-based polymers and the fascinating properties of the HL ligand, we have investigated a series of lanthanide-based polymers, \( \text{Ln}[(\text{atpa})(\text{H}_2\text{O})_2] \cdot 1.5n\text{H}_2\text{O} \) (H\text{atpa} = 2-aminoterephthalic acid and Ln = Tb(1), Dy(2), Ho(3), Er(4), Tm(5), Yb(6)) based on 4-(3-methyl-5-(pyridin-4-yl)-1,2,4-triazol-4-yl)benzoic acid (HL) and 2-aminoterephthalic acid (H\text{atpa}).

Compounds 1-6 are isomorphous, so compound 6 is employed as a representative to be discussed in detail. In compound 6, ligands L\(^{-}\) and atpa\(^{2-}\) both present only one coordination mode (see Scheme 1: configuration \( \mu_2 \) for L\(^{-}\), and each carboxylate group coordinates to two Yb\(^{3+}\) ions; configuration \( \mu_2 \) for atpa\(^{2-}\), and each carboxylate group coordinates to one Yb\(^{3+}\) ion). Compound 6, crystallizing in the triclinic system with the P1 space group. As shown in Fig. 1A, the asymmetric unit of 6 consists of one crystallographically independent Yb\(^{3+}\) ion, one L\(^{-}\) ligand, one atpa\(^{2-}\) ligand, two coordinated water molecules and one and a half lattice water molecules. Each Yb\(^{3+}\) is surrounded by an O8 donor set, formed by two oxygen atoms from two different L\(^{-}\) ligands, four oxygen atoms from two atpa\(^{2-}\) ligands, and two terminal water molecules. The coordination geometry around the metal center can be described as a distorted triagonal dodacahedron. This type of configuration of eight-coordinated Yb\(^{3+}\) ion is rarely reported, compared to the square antiprism, which is confirmed by comparing chosen ideal and observed pertinent dihedral angles based on calculations of the shape factor S to evaluate the degree of distortion from an ideal geometry [7,32]. The Yb-O bond lengths vary from 2.199(3) Å to 2.435(3) Å. Yb1 and its corresponding centresymmetric generated atom Yb1A are joined by two \( \mu_2 \)O atoms of carboxylate groups to form a binuclear unit, Yb\(_{2}(\text{CO}_2)_{12}\) units (Fig. 1B), in which the distance of Yb1-Yb1A is 4.822 Å. Atpa\(^{2-}\) ligands and Yb\(^{3+}\) ions connected to 1D chain (Fig. 1C). And the 1D chains were connected to a 2D sheet by the connection of the binuclear unit formed by two L\(^{-}\) ligands and two Yb\(^{3+}\) ions (Fig. S1). Each Yb\(_{2}(\text{CO}_2)_{12}\) unit is connected...
with four adjacent units through four atpa\(\text{2}^-\) ligands sustaining a 2D sheet, as illustrated in Figs. 1D and S2. The Yb-Yb distance across the bridging atpa\(\text{2}^-\) ligand is 11.178 Å. The atpa\(\text{2}^-\) ligands connect the units, which play a vital role in the extension of the dimensionality for \(\text{6}\). However, L\(^-\) ligands coordinate to the metal centers with terminal bridging-bidentate binding mode. As shown in Fig. 1E, hydrogen bonds form among the oxygen atoms from carboxylate groups, the nitrogen atoms from amino groups and coordinated water molecules. The crystallization O9w and O10w water molecules are placed in the intermellar region, establishing strong hydrogen bonding interactions with the layer network. The structures of \(\text{1–6}\) show the effect of lanthanide contraction: Ln–O bond length and Ln–Ln separations decrease along with the decrease of ionic radii from Tb(1) to Yb(6).

Based on the crystal data, we carried out the calculations of the shape factor \(S\) to estimate the degree of distortion of the coordination structure in first coordination sphere. The \(S\) value is given by Eq. (1):

\[
S = \min \left( \frac{1}{m} \sum_{i=1}^{m} (\delta_i - \theta_i)^2 \right)
\]

in which \(m\), \(\delta_i\) and \(\theta_i\) are the number of possible edges \((m = 18\) in this study\), the observed dihedral angle between planes along the ith edge and the dihedral angle for the ideal structure, respectively. The estimated \(S\) values of Yb\(^{III}\) ions are summarized (see Table S8 in the Supporting information). For \([\text{Yb}(...)](\text{atpa})(\text{H}_2\text{O})_2\text{n} \cdot 1.5\text{nH}_2\text{O}\), the \(S\) value for the eight-coordinated square antiprism structure (8-SAP, point group: \(D_{4d}\), \(S = 15^\circ\)) is bigger than that for the eight-coordinated trigonal dodecahedron structure (8-TDH, point group: \(D_{3d}\), \(S = 11^\circ\)), thereby...
suggested that the 8-TDH structure is less distorted than the 8-SAP structure. We thus determined that the coordination geometry of [Yb(L)(atpa)(H₂O)]₂⁺·1.5nH₂O is 8-TDH.

The TGA was carried out on crystalline samples of 1–6 in the flowing air with a heating rate of 10 °C/min in the temperature range of 25–800 °C. TG curves of isomorphous compounds 1–6 are, respectively, similar, exhibiting two main weight loss steps until the decomposition of the framework. Here, compound 3 is used as one representative as illustrated in Fig. S3 (Supporting information). The TG curve of compound 3 shows the first stage of weight loss from 25 °C to 160 °C (9.6% contrast to theoretical 9.2%), which is attributed to the release of the coordinated and guest water molecules and partial decomposition of the organic ligands. The second stage of weight loss occurs from 380 °C to 670 °C (72.43%). The remnants of compound 3 are close to the calculated values (27.83% base on the H₂O₂O₃).

The purity of the bulky crystalline samples was confirmed by PXRD. The PXRD patterns of compounds 1–6 are illustrated in Fig. S4 (Supporting information), which are in good agreement with simulated ones, confirming the phase purity of the as-synthesized products.

The solid-state photoluminescence spectra of 1 were recorded at room temperature and depicted in Fig. 2. Under excitation of 300 nm, compound 1 exhibits characteristic Tb³⁺ emission spectra at about 490 (5D₄ → 7F₅), 545 (5D₄ → 7F₅), 585 (5D₄ → 7F₅), and 621 nm (5D₄ → 7F₅). The dominant peak corresponding to the 5D₄ → 7F₅ transition at 545 nm is hypersensitive, which implies green luminescence of Tb³⁺ compound. The emission decay profiles of compound 1 in the solid state were obtained at room temperature. Fig. 3 shows the linear fit curve of compound 1. The fluorescence lifetime value of compound 1 was calculated by the single-exponential mode. From the result, it was found that the determined lifetimes for compound 1 are 0.57 µs (19.30%); 4.67 µs (51.79%) and 13.30 µs (28.91%), respectively, determined by monitoring the 5D₄ → 7F₅ transition. And that is close to the literature [7].

Luminescence spectra of Dy³⁺, Er³⁺ and Yb³⁺ compounds in solid state upon excitation at 333 nm, 375 nm, and 397 nm, display typical narrow band emissions in the NIR region at room temperature. The emission spectrum of Dy³⁺ compound peaked at 1308 nm, and 888 nm is attributed to the transition from the excited states 6F₁₅/₂(6H₁₃/₂) and 6F₁₁/₂(6H₁₃/₂), respectively (Fig. 4A) [33]. The Er³⁺ compound exhibits the emission band in the near-infrared region with the maximum at 1500 nm attributed to the transition from the excited state 4I₁₁/₂ to the ground state 4I₁₃/₂, respectively (Fig. 4B) [34]. The Yb³⁺ compound displays a strong absorption at 1003 nm (Fig. 4C), which is the characteristic transition 2F₅/₂ → 2F₇/₂ of the Yb³⁺ ion in near-infrared region [35]. However, the luminescence of Ho³⁺ and Tm³⁺ in compounds 3 and 5 is too weak to be measured with our instrument setup. The relative intensities of these emissions are sensitive to the detailed nature of the ligand environment. Furthermore, the intensity of the compounds based on the HL ligand is completely weak, possibly due to the coordinated water molecules, which reduces the luminescent intensity of the rare earth ions, and the energy transfer from the HL ligand to Ln³⁺ ions is inefficient in the theory of energy transfer [38].

The spin-orbital coupling in general plays an important role in the magnetism of lanthanide compounds due to the internal nature of the valence f orbitals. This large spin–orbit coupling partly removes the degeneracy of the 2S + 1L group term of lanthanide ions, giving 2S + 1L states, which further split into Stark levels under the crystal field perturbation [36]. The variable-temperature magnetic susceptibilities were measured at an applied magnetic field of 1000 Oe in the temperature range of 2.0–300 K for 1–2, and the χMT vs T plots are shown in Figs. 5 and 6. For compound 1, the χMT value at 300 K of 12.557 cm³ K mol⁻¹ is slightly larger than the expected value of 11.82 cm³ K mol⁻¹ of one isolated Tb³⁺ ion in the 7F₅ state, and it gradually decreases with decreasing temperature to reach a minimum of 8.29 cm³ K mol⁻¹ at 2 K. The decrease of the χMT product suggests the presence of weak antiferromagnetic interaction between Tb³⁺ ions. The low temperature decrease is likely due to a combination of the depopulation of Stark levels of Tb³⁺ ions and the presence of interlayer antiferromagnetic interactions. For compound 2, the χMT value at room temperature is 14.598 cm³ K mol⁻¹, slightly higher than the expected 14.17 cm³ K mol⁻¹ with the ground state 7F₅/₂ and g = 4/3. The χMT value decreases slowly with a minimum in temperature to ca. 12 K. The increase of the χMT value increases rapidly and reaches the maximum of 14.37 cm³ K mol⁻¹ at 2 K. The fact that the χMT value increases after reaching the minimum value at 12 K shows that a ferromagnetic interaction is expected to exist between the Dy³⁺ ions in 2 [37]. Because no out-of-phase (χ″MT) signals are observed in the ac magnetic susceptibility between 2 and 20 K, there is no evidence of slow-relaxation for 2 (see Fig. S5 in the Supporting information).

In conclusion, a series of novel lanthanide-based coordination polymers, [Ln(L)(atpa)(H₂O)]₂n·1.5nH₂O (HL = 4-[3-methyl-5-(pyridin-4-yl)-1,2,4-triazol-4-yl]benzoic acid, H₂atpa = 2-amino-terepthalic acid and Ln = Tb(1), Dy(2), Ho(3), Er(4), Tm(5), Yb(6)) have been hydrothermally synthesized. Compounds 1–6, crystallizing in the triclinic system with the P1 space group, feature a 2D network based on Ln(II)(CO₂)₆ units. Atpa⁻ ligands and Ln³⁺ ions connected to 1D chain, and the 1D chains were connected to a 2D sheet by the connection of two L⁻ ligands and two Ln³⁺ ions. Compound 1 exhibits the characteristic emission of Tb³⁺ ions, showing that the ligands are luminescence sensitizers. Compounds 2, 4, and 6 exhibit the characteristic transition of Dy³⁺, Er³⁺ and Yb³⁺ ions in near-infrared region. The magnetic properties of compound 1 show typical antiferromagnetic interaction, while compound 2 has ferromagnetic behavior.
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Appendix A. Supplementary material

CCDC 916887, 916883, 916886, 916884, 916888, 916889 for compounds 1–6 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.

References
