



Syntheses, structures, photoluminescence, and magnetism of a series of lanthanide 1,3-adamantanedicarboxylate coordination polymers



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ABSTRACT

Five one-dimensional (1D) lanthanide dicarboxylate coordination polymers (CPs) have been successfully synthesized under hydrothermal conditions, namely, $[\text{Ln}_2(1,3\text{-adc})_3(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ [$\text{Ln} = \text{Eu}$ (**1**, $x = 1$), Tb (**2**, $x = 1$), Dy (**3**, $x = 2$), and Er (**4**, $x = 1$), 1,3- $\text{H}_2\text{adc} = 1,3\text{-adamantanedicarboxylic acid}$] and $[\text{Yb}(1,3\text{-adc})(1,3\text{-Hadc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**5**). Structural characterization reveals that CPs **1–4** exhibit isostructural 1D chain formed by 1,3- adc linking alternately two mononuclear $\text{Ln}(\text{COO})_4$ units and one dinuclear $\text{Ln}_2(\text{COO})_4$ cluster. CP **5** shows a 1D zigzag chain constructed from 1,3- adc connecting $\text{Yb}(\text{III})$, and the 1,3- Hadc anions are regularly arranged on two sides of the 1D chain. In **1–5**, the neighboring 1D chains are extended into a two-dimensional (2D) supramolecular layer by hydrogen-bonding interactions. Property investigation indicates that CPs **1–3** and **5** display characteristic luminescence of the $\text{Eu}(\text{III})$, $\text{Tb}(\text{III})$, $\text{Dy}(\text{III})$, and $\text{Yb}(\text{III})$ ions, respectively. CP **3** shows a field-induced slow magnetic relaxation behavior.

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1. Introduction

Over the past two decades, metal–organic complexes, as the most fascinating compounds, have been of special interest for chemists because of their diversity and variability as well as potential application value in catalysis [1–3], adsorption [4,5], photoluminescence [6,7], magnetism [8,9], and so on. Especially, the photoluminescent properties of lanthanide–organic complexes have been comprehensively investigated owing to the high color purity and long lifetimes of excited states of lanthanide(III) ions [10]. However, lanthanide(III) ions show small molar absorption coefficients and weak ultraviolet absorption with low luminescent efficiency due to the forbidden $f-f$ transitions [11]. Therefore, organic ligands with strong ultraviolet absorption were often used to sensitize luminescence of lanthanide(III) ions through an intramolecular energy-transfer process [12–14]. In recent years, some carboxylate ligands have been significantly utilized for sensitizing luminescence of lanthanide(III) ions [15–17].

As an important organic carboxylic acid ligand, 1,3-adamantanedicarboxylic acid (1,3- H_2adc) has been used for the construction of metal–organic complexes [18]. However, to our knowledge, lanthanide 1,3-adamantanedicarboxylate complexes

have rarely reported [19–21]. Especially, study on 1,3-adamantanedicarboxylate sensitizing luminescence of lanthanide(III) ions has not been observed up to now. Therefore, in this work, we chose 1,3- H_2adc as the main ligand and 2,2'-bipyridine as the auxiliary ligand to construct a series of lanthanide 1,3-adamantanedicarboxylate CPs $[\text{Ln}_2(1,3\text{-adc})_3(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ [$\text{Ln} = \text{Eu}$ (**1**, $x = 1$), Tb (**2**, $x = 1$), Dy (**3**, $x = 2$), and Er (**4**, $x = 1$)] and $[\text{Yb}(1,3\text{-adc})(1,3\text{-Hadc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**5**). Meanwhile, the photoluminescent properties of **1–5** were investigated. In addition, considering that complexes involving the highly anisotropic $\text{Dy}(\text{III})$ ion generally display slow magnetic relaxation behavior [22], the magnetic properties of **3** were also studied.

2. Experimental

2.1. Materials and measurements

All chemicals and reagents were commercially available and were used without further purification. Elemental analyses (C and H) were done with a Perkin-Elmer 2400 CHN elemental analyzer. IR data were recorded with a Magna FT-IR 560 spectrometer using KBr plate. Powder X-ray diffraction (PXRD) data were obtained on a Bruker AXS D8-Advanced diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermogravimetric analyses (TGA) were performed on a Pyris-Diamond thermal analyzer in the

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temperature range of 30–980 °C at a heating rate of 10 °C min⁻¹ under a flowing N₂ atmosphere. Photoluminescence measurements were performed on an FLS 920 Combined Steady State Fluorescence and Phosphorescence Lifetime spectrometer. Magnetic measurements were performed on a Quantum Design MPMS XL-7 SQUID-VSM magnetometer. Pascal's constants were used to determine the diamagnetic corrections.

2.2. Syntheses of 1–5

A mixture of Ln(NO₃)₃·nH₂O [0.1 mmol, Ln = Eu (**1**), Tb (**2**), Dy (**3**), Er (**4**), or Yb (**5**)], 1,3-H₂adc (0.1 mmol), 2,2'-bipyridine (0.1 mmol), H₂O (10 mL), and aqueous NaOH solution (1 mL, 0.1 mol L⁻¹) was sealed in a 25 mL Teflon reactor. The Teflon reactor was heated to 140 °C for 3 days, and then cooled to room temperature. Block crystal products were obtained. The crystal products were collected and dried in air. Yield: 75–85% (based on Ln). Elem. Anal. Calcd. for **1**: C, 40.76; H, 4.94. Found: C, 40.50; H, 4.89%. Calcd. for **2**: C, 40.24; H, 4.88. Found: C, 40.06; H, 4.82%. Calcd. for **3**: C, 39.31; H, 4.95. Found: C, 39.09; H, 4.88%. Calcd. for **4**: C, 39.62; H, 4.80. Found: C, 39.38; H, 4.75%. Calcd. for **5**: C, 41.80; H, 5.26. Found: C, 41.55; H, 5.19%. IR (KBr, cm⁻¹) for **1**: 3412 (s), 2897 (s), 2839 (m), 2356 (w), 1644 (s), 1513 (s), 1414 (s), 1219 (w), 1128 (w), 1038 (w), 1005 (w), 981 (w), 948 (w), 940 (w), 883 (m), 825 (m), 698 (m), 481 (m). For **2**: 3412 (s), 2897 (s), 2848 (m), 2356 (w), 1648 (s), 1513 (s), 1407 (s), 1219 (w), 1128 (w), 1045 (w), 1005 (w), 989 (w), 948 (w), 940 (w), 883 (m), 825 (m), 702 (m), 481 (m). For **3**: 3415 (s), 2904 (s), 2840 (m), 2360 (w), 1646 (s), 1519 (s), 1415 (s), 1220 (w), 1128 (w), 1045 (w), 1002 (w), 989 (w), 952 (w), 940 (w), 887 (m), 833 (m), 698 (m), 482 (m). For **4**: 3414 (s), 2905 (s), 2839 (m), 2360 (w), 1645 (s), 1513 (s), 1407 (s), 1219 (w), 1128 (w), 1046 (w), 1002 (w), 981 (w), 952 (w), 940 (w), 883 (m), 825 (m), 702 (m), 481 (m). For **5**: 3322 (s), 2913 (s), 2356 (w), 1693 (s), 1529 (s), 1423 (s), 1316 (m), 1235 (m), 1153 (w), 1111 (m), 1014 (w), 989 (w), 956 (w), 932 (w), 883 (w), 817 (m), 695 (m), 538 (w).

2.3. X-ray crystallographic study

Single-crystal X-ray diffraction data of **2–5** were collected with a Bruker Smart APEX II diffractometer with Mo K α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and

refined by the full-matrix least-squares methods on F^2 using the SHELXTL package [23]. All non-hydrogen atoms were refined with anisotropic parameters. Relevant crystal data and refinement parameters for **2–5** are summarized in Table 1. Selected bond lengths for **2–5** are given in Table S1.

3. Results and discussion

3.1. Syntheses

In this work, a series of lanthanide 1,3-adamantanedicarboxylate CPs [Ln₂(1,3-*adc*)₃(H₂O)₄]·xH₂O [Ln = Eu (**1**, $x = 1$), Tb (**2**, $x = 1$), Dy (**3**, $x = 2$), and Er (**4**, $x = 1$)] and [Yb(1,3-*adc*)(1,3-*Hadc*)(H₂O)₃]·H₂O (**5**) were synthesized by the hydrothermal reactions of Ln(NO₃)₃·nH₂O, 1,3-H₂adc, 2,2'-bipyridine, and aqueous NaOH solution at 140 °C. CPs **1–4** are isostructural, and CPs **2** and **4** are different from [Tb₂(1,3-*adc*)₃(H₂O)₅][Tb₂(1,3-*adc*)₃(H₂O)₄]·3H₂O and [Er(1,3-*adc*)(1,3-*Hadc*)(H₂O)₃]·H₂O reported previously. This can be attributed to their different reaction conditions. [Tb₂(1,3-*adc*)₃(H₂O)₅][Tb₂(1,3-*adc*)₃(H₂O)₄]·3H₂O was prepared by the solvo-hydrothermal (DMA-H₂O) reaction of Tb(NO₃)₃·5H₂O and 1,3-H₂adc at 140 °C [19], whereas [Er(1,3-*adc*)(1,3-*Hadc*)(H₂O)₃]·H₂O was obtained by the hydrothermal reaction of ErCl₃·6H₂O, 1,3-H₂adc, and bpp at 160 °C [20]. Therefore, the reactant, solvent, and temperature played important roles in the formation of these lanthanide 1,3-adamantanedicarboxylate CPs.

3.2. Structural description of 1–4

X-ray single-crystal diffraction studies indicate that CPs **1–4** are isostructural and crystallize in the triclinic space group $P\bar{1}$. Thus, only the crystal structure of **3** is described here in detail. As shown in Fig. 1a, CP **3** consists of two crystallographically independent Dy (III) ions, three 1,3-*adc* anions, four coordinated water molecules, and two interstitial water molecules. The Dy1 ion is coordinated by nine oxygen atoms from four 1,3-*adc* anions and one water molecule. These nine oxygen atoms surround Dy1 to form a distorted monocapped square-antiprismatic coordination geometry, where the water molecule is in the capped position (Fig. S1). The Dy2 ion is seven-coordinated by four oxygen atoms from four 1,3-*adc* anions and three water molecules, displaying a distorted monocapped trigonal prismatic coordination geometry (Fig. S1).

Table 1
Crystal data and refinement parameters for **2–5**.

	2	3	4	5
formula	C ₃₆ H ₅₂ O ₁₇ Tb ₂	C ₃₆ H ₅₄ O ₁₈ Dy ₂	C ₃₆ H ₅₂ O ₁₇ Er ₂	C ₂₄ H ₃₆ O ₁₂ Yb
formula weight	1074.62	1099.79	1091.30	689.57
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	11.3055(12)	11.0183(6)	11.0109(6)	6.6585(3)
<i>b</i> (Å)	12.5943(14)	12.5932(7)	12.5794(7)	23.8546(11)
<i>c</i> (Å)	14.9697(16)	14.9540(8)	14.9360(8)	16.1452(7)
α (°)	70.541(2)	70.533(1)	70.425(1)	90
β (°)	81.947(2)	81.876(1)	81.807(1)	92.244(1)
γ (°)	85.205(2)	85.279(1)	85.491(1)	90
<i>V</i> (Å ³)	1940.8(4)	1935.32(18)	1928.27(18)	2562.5(2)
<i>Z</i>	2	2	2	4
<i>D</i> _{calcd.} (g cm ⁻³)	1.839	1.887	1.880	1.787
μ (mm ⁻¹)	3.689	3.910	4.398	3.713
<i>F</i> (000)	1068	1092	1080	1384
<i>R</i> _{int}	0.0453	0.0251	0.0322	0.0438
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0714	0.0407	0.0479	0.0308
<i>wR</i> ₂ ^b (all data)	0.2137	0.0970	0.1295	0.0673
GOF	1.023	1.031	1.017	0.989

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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