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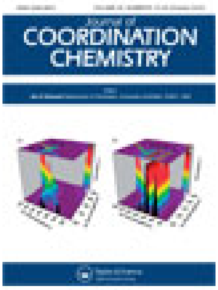

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1-D Chain lanthanide coordination polymers based on mixed 2,4-dichlorophenoxyacetate and 1,10-phenanthroline ligands: crystal structures and luminescent properties

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1-D Chain lanthanide coordination polymers based on mixed 2,4-dichlorophenoxyacetate and 1,10-phenanthroline ligands: crystal structures and luminescent properties

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Two new isostructural 1-D lanthanide coordination polymers, $\{[\mathrm{Ln(2,4\text{-}dcp)_3(phen)}]_n$ [(Ln = Eu (**1**); Tb (**2**)], [2,4-dcp = 2,4-dichlorophenoxyacetate, phen = 1,10-phenanthroline], were obtained under hydrothermal conditions and characterized by IR spectroscopy, elemental analyses, thermogravimetry analyses, powder X-ray diffraction, and single-crystal X-ray diffraction. Both structures exhibit similar 1-D infinite chains with a $\{\mathrm{Ln_2(2,4\text{-}dcp)_6(phen)_2}\}$ dimeric repeat unit, with lanthanides in an eight-coordinate environment. The results of thermal analysis indicate that **1** and **2** are quite stable to heat. 3-D fluorescence spectra of **1** and **2** were detected at room temperature under excitation and the emission wavelengths of 250–460 nm and 420–750 nm with the same interval of 5 nm, respectively. Interestingly, **1** and **2** possess longer fluorescence lifetimes than other complexes ($\tau = 1.61$ ms for **1** at 611 nm; 1.79 ms for **2** at 543 nm).

Keywords: Lanthanide coordination polymers; Hydrothermal synthesis; Crystal structures; Luminescent properties

1. Introduction

1-D Coordination polymers (CPs), which are the simplest topological type of coordination array, are generally considered to be the least interesting structurally; nevertheless, the polymers exhibit interesting magnetic, electrical, mechanical, and optical properties [1]. Luminescent lanthanide complexes have gained recognition owing to potential applications in biochemistry and materials science [2–7]. Lanthanide ions, especially Eu(III) and Tb(III), are excellent luminescent centers and the luminescent properties are influenced by ligands. Compared to first-row transition metals, lanthanides have a larger coordination sphere and more flexible coordination geometry, easily coordinating to various carboxylates and N-containing

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ligands to form complexes with diverse stereochemistries [8, 9]. Aromatic carboxylic acid, with versatile binding and coordination modes, are widely employed in construction of luminescent lanthanide coordination polymers, which usually exhibit high thermal stability and intense fluorescence because of a large conjugated π-electron system [10–12]. As a building block, 2,4-dichlorophenoxyacetate (2,4-dcp) can be multidentate and is an excellent candidate for construction of lanthanide coordination polymers. For example, Shi *et al.* obtained three lanthanide complexes based on 2,4-dcp with or without 1,10-phenanthroline ligands [13]. Guo *et al.* synthesized one 1-D neodymium coordination polymer based on 2,4-dcp [14]. Dendrinou-Samara *et al.* have reported a 1-D gadolinium(III) complex with 2,4-dcp [15]. However, construction of new lanthanide coordination polymers based on 2,4-dcp is scarce, especially involving N-containing ligands [13]. As part of an on-going study related to 2,4-dcp, we report the synthesis, structural characterization and luminescent properties of two new isostructural 1-D lanthanide coordination polymers, $\{[Ln(2,4\text{-dcp})_3(phen)]_n$ [(Ln = Eu (**1**); Tb (**2**)].

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were commercially available and used as received. Elemental analyses for C, H, and N were carried out using a Vario EL III Elemental Analyzer. Infrared spectra were recorded (4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) under a flow of N_2 and air environment at a heating rate of 10°C min^{-1} between ambient and 800°C, respectively. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with Cu-Kα ($\lambda = 1.5406$ Å) radiation. Luminescence spectra and lifetimes for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter.

2.2. *Hydrothermal synthesis*

2.2.1. $\{[Eu(2,4\text{-dcp})_3(phen)]_n$ (1). Complex **1** was prepared by addition of stoichiometric amounts of $Eu(NO_3)_3 \cdot 6H_2O$ (0.223 g, 0.5 mmol) and 1,10-phenanthroline (0.09 g, 0.5 mmol) to a hot aqueous solution (12 mL) of 2,4-dichlorophenoxyacetic acid (0.110 g, 0.5 mmol). The pH was then adjusted to 9 with NaOH (0.016 g, 0.4 mmol). The resulting solution was sealed in a 23 mL Teflon-lined stainless steel autoclave and heated at 150°C for 3 days under autogenous pressure. Colorless single crystals (**1**) were obtained (yield: 83%, based on 2,4-dcp) upon cooling the solution to room temperature at 5°C h^{-1}. Anal. Calcd for $C_{36}H_{23}Cl_6EuN_2O_9$: C, 43.54; H, 2.32; N, 2.82. Found: C, 43.61; H, 2.29; N, 2.79. IR (KBr, cm^{-1}): 3460(s), 1694(s), 1602(s), 1516(w), 1480(s), 1451(w), 1428(s), 1342(w), 1291(s), 1263(m), 1234(m), 1141(w), 1104(m), 1074(s), 1043(w), 920(w), 869(w), 840(s), 798(m), 765(w), 725(s), 696(w), 645(m), 605(m), 560(w), 472(w).

Table 1. Crystal data and structure refinement details of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{36}H_{23}Cl_6EuN_2O_9$	$C_{36}H_{23}Cl_6TbN_2O_9$
Formula weight	992.22	999.18
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	17.430(7)	17.454(4)
b	8.081(3)	8.1139(18)
c	28.932(10)	28.933(5)
β	112.083(19)	112.051(11)
Volume (Å^3), Z	3776(2), 4	3797.8(14), 4
Calculated density (g cm^{-3})	1.745	1.748
Crystal size (mm^3)	$0.32 \times 0.30 \times 0.21$	$0.30 \times 0.22 \times 0.18$
θ range for data collection (°)	1.26–25.20	1.52–25.20
Reflections collected	27,019	27,037
Independent reflections	6754	6810
Goodness-of-fit on F^2	1.163	1.092
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0376$, $wR_2 = 0.1034$	$R_1 = 0.0327$, $wR_2 = 0.0881$
R indices (all data)	$R_1 = 0.0684$, $wR_2 = 0.1615$	$R_1 = 0.0544$, $wR_2 = 0.1131$

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$.
$wR = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^{1/2}$.

2.2.2. {[Tb(2,4-dcp)$_3$(phen)]$_n$ (2). Complex **2** was prepared by the same procedure as **1** except that $Eu(NO_3)_3 \cdot 6H_2O$ was replaced by $Tb(NO_3)_3 \cdot 6H_2O$. Yield: 85% (based on 2,4-dcp). Anal. Calcd for $C_{36}H_{23}Cl_6TbN_2O_9$: C, 43.24; H, 2.30; N, 2.80. Found: C, 43.20; H, 2.26; N, 2.85. IR (KBr, cm^{-1}): 3444(s), 1699(s), 1606(s), 1516(w), 1481(s), 1429(s), 1343(w), 1292(s), 1263(m), 1234(m), 1141(w), 1104(m), 1074(s), 1043(w), 920(w), 869(w), 840(s), 798(w), 766(w), 725(s), 696(w), 645(m), 605(m), 560(w), 472(w).

2.3. *X-ray crystallography*

X-ray diffraction analyses for **1** and **2** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Data collection and reduction were performed using APEX II software [16]. Multi-scan absorption corrections were applied for all data sets using the APEX II program [16]. Both structures were solved by direct methods and refined by least squares on F^2 using the SHELXTL program package [17]. Displacement ellipsoids of some atoms show prolate or oblate shapes, which may imply that the vibration of these molecules is stronger than others. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Crystallographic data for **1** and **2** are listed in table 1. Selected bond lengths and angles are given in table 2.

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

Complex **1**			
Eu(1)–N(1)	2.617(6)	O(7)$^{\text{ii}}$–Eu(1)–O(1)	82.5(2)
Eu(1)–N(2)	2.629(6)	O(1)–Eu(1)–O(5)$^{\text{ii}}$	148.45(19)
Eu(1)–O(1)	2.348(5)	O(5)$^{\text{ii}}$–Eu(1)–O(8)	74.25(19)
Eu(1)–O(2)$^{\text{i}}$	2.387(5)	O(1)–Eu(1)–O(2)$^{\text{i}}$	79.99(18)
Eu(1)–O(4)	2.436(5)	O(8)–Eu(1)–O(2)$^{\text{i}}$	133.99(18)
Eu(1)–O(5)$^{\text{ii}}$	2.371(5)	O(2)$^{\text{i}}$–Eu(1)–O(4)	149.38(18)
Eu(1)–O(7)$^{\text{ii}}$	2.323(5)	O(7)$^{\text{ii}}$–Eu(1)–N(1)	148.2(2)
Eu(1)–O(8)	2.371(5)	O(5)$^{\text{ii}}$–Eu(1)–N(2)	77.56(19)
Complex **2**			
Tb(2)–N(1)	2.611(4)	O(7)$^{\text{ii}}$–Tb(2)–O(1)	81.61(14)
Tb(2)–N(2)	2.604(4)	O(1)–Tb(2)–O(8)	137.58(13)
Tb(2)–O(1)	2.331(4)	O(7)$^{\text{ii}}$–Tb(2)–O(2)$^{\text{i}}$	80.89(14)
Tb(2)–O(2)$^{\text{i}}$	2.377(4)	O(8)–Tb(2)–O(2)$^{\text{i}}$	134.73(13)
Tb(2)–O(4)	2.412(4)	O(1)–Tb(2)–O(4)	75.96(14)
Tb(2)–O(5)$^{\text{ii}}$	2.350(4)	O(5)$^{\text{ii}}$–Tb(2)–O(4)	121.93(14)
Tb(2)–O(7)$^{\text{ii}}$	2.295(4)	O(7)$^{\text{ii}}$–Tb(2)–N(2)	147.08(14)
Tb(2)–O(8)	2.344(4)	O(1)–Tb(2)–N(1)	71.84(13)

Symmetry codes: $\text{i} = 1 - x,\ 1 - y,\ 1 - z$; $\text{ii} = 1 - x,\ -y,\ 1 - z$.

3. Results and discussion

3.1. *Synthesis of 1 and 2*

Hydrothermal synthesis has proved an effective method in self-assembly of metal-organic complexes. In this way, we synthesized **1** and **2**. In order to obtain suitable crystals for single-crystal X-ray diffraction analysis, many control experiments were conducted. The control experiments proved that the formation of title compounds is greatly influenced by the reaction temperature, solvent system and pH of the reaction systems. When the reaction temperature was set at 120°C or 180°C, no crystals can be obtained. When the temperature was set at 150°C, **1** and **2** in high yield were obtained. The mixed solvent (water : ethanol = 1 : 1) introduced during the synthesis of **1** and **2** gave small crystals, not suitable for single-crystal X-ray diffraction analysis. We obtain a 0-D complex when the pH was set between 4 and 6, which will be reported in another paper. Addition of NaOH (or KOH or $NaOCH_3$) in reaction systems not only changes the pH of solution, but also changes the ionic strength, which may be the main reason of forming polymeric complexes. Several polymeric compounds containing 2,4-dcp ligand are prepared at pH between 7 and 8 [15]. The pH close to 9 in preparing **1** and **2** is good for increasing the ionic strength and forming polymeric compounds.

3.2. *Structural description*

Single-crystal X-ray structure analysis revealed that **1** and **2** are isostructural. The structure of **1** is described in detail here. Compound **1** is a 1-D polymer with $\{Eu_2(2,4\text{-dcp})_6(\text{phen})_2\}$ dimeric repeat units. The asymmetric unit of **1** consists of one europium, three 2,4-dcp ligands and one phen as shown in figure 1(a). The Eu(III) is eight-coordinate by six O-donors of six different 2,4-dcp and two N-donors of phen. Eu1 can be described as having a square antiprism (SAP) geometry (figure 1b) with Eu–O, Eu–N bond distances and O–Eu–O, O–Eu–N bond angles ranging from 2.323(5) to 2.629(6) Å

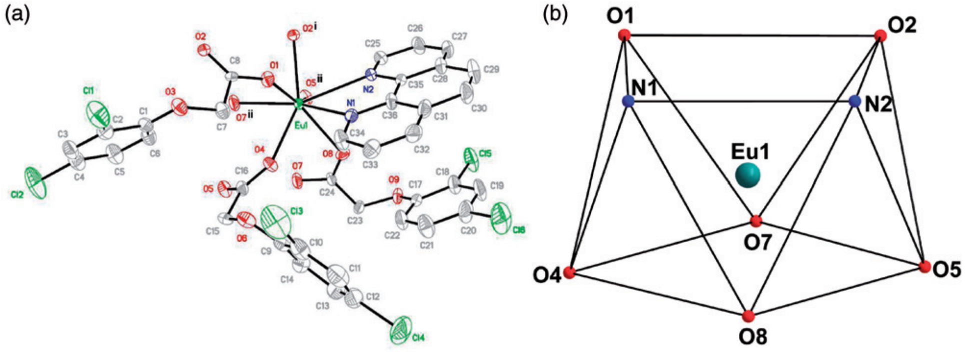

Figure 1. (a) Ball and stick plot showing coordination geometry around Eu(III) in **1** with 30% thermal ellipsoids. All hydrogen atoms were omitted for clarity (symmetry codes: i = 1 − x, 1 − y, 1 − z; ii = 1 − x, − y, 1 − z); (b) SAP geometry surrounding Eu.

and 61.7(2)° to 149.38(18)°, respectively, all of which are within the range of those observed for other eight-coordinate Eu(III) complexes with nitrogen and oxygen donors [18–21]. The average bond distances of Eu–O and Eu–N are 2.373 and 2.623 Å, respectively, which are close to the corresponding average distances 2.444 and 2.616 Å found in $[Eu(2,4\text{-dcp})_2(phen)_2]_2(ClO_4)_2$ [13]. This indicates that the interaction of europium with oxygen or nitrogen in **1** and $[Eu(2,4\text{-dcp})_2(phen)_2]_2(ClO_4)_2$ is very little different.

In the polymeric structure of **1**, the 2,4-dcp ligands are μ_2 bridging to link two Eu(III) ions, differing from those described in $[Gd(2,4\text{-dcp})_3(H_2O)\cdot 2dmf]_n$ (**a**), $[Nd(2,4\text{-dcp})_3(H_2O)]_n$ (**b**) and $[Eu(2,4\text{-dcp})_2(phen)_2]_2(ClO_4)_2$ (**c**), in which the carboxylate groups exhibit two or three different coordination modes [13–15]. Similar to $[\{Er(CCl_3CO_2)_2(H_2O)\}_2(CCl_3CO_2)_2(H_2O)]_n\cdot nH_2O$ (**d**) and $[La(Ben)_3(Pno)_{0.5}H_2O]$ (**e**), the binding mode of the carboxylates exhibit the same μ_2 bridging [22, 23]. This single coordination mode of the carboxylates in 1-D lanthanide complexes is rare. The carboxylates of 2,4-dcp connect Eu(III) ions to form a zigzag Eu-carboxylate chain parallel to the a-axis (figure 2). Distances between adjacent Eu(III) ions are 4.356(2) and 5.433(3) Å, respectively, and the angles among successive Eu(III) is 110.79(2)°. The corresponding values for complexes **a**, **b**, **c**, **d**, and **e** are 4.057 Å, 4.218 Å, 147.61°; 4.172 Å, 154.93°; 4.593 Å, 4.255 Å, 174.22°; 4.430 Å, 4.823 Å, 147.00°, 151.06° and 4.518 Å, 4.551 Å, 4.844 Å, 140.09°, 143.35°, respectively. Moreover, C–H···O hydrogen bonds and short $O_{carboxyl}\cdots O_{carboxyl}$ contacts were also observed [O2···O3 = 2.735(2) Å; O2···O5 = 2.834(3) Å; O5···O7 = 2.974(2) Å].

3.3. *Powder X-ray diffraction analysis*

Samples of **1** and **2** were measured by X-ray powder diffraction at room temperature. As shown in figure S1, the peak positions of the experimental patterns are in good agreement with simulated patterns, which clearly indicates the purity of the complexes.

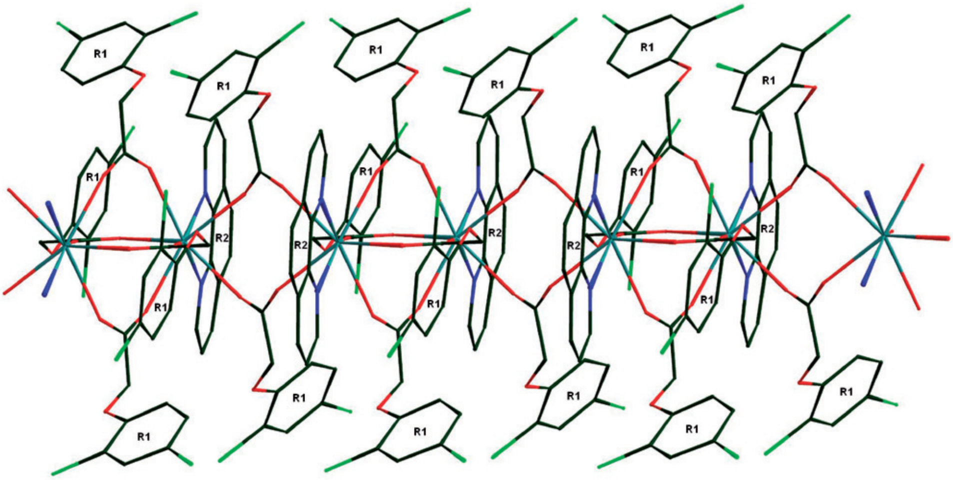

Figure 2. View of the 1-D chain structure of **1**. All hydrogen atoms were omitted for clarity.

3.4. *Infrared spectra*

FT-IR spectra of **1** and **2** are recorded as KBr pellets (figures S2 and S3). The IR spectra have strong, broad bands at 3460 cm^{-1} in **1** and 3444 cm^{-1} in **2**, which may be assigned to ν(O–H) of water (impurity). Features at 1602 and 1428 cm^{-1} for **1**, 1606 and 1429 cm^{-1} for **2**, are associated with asymmetric (C–O–C) and symmetric (C–O–C) stretching vibrations. The $\Delta\nu(\nu_{as}(COO^-)–\nu_s(COO^-))$ values are 174 cm^{-1} for **1** and 177 cm^{-1} for **2** (between 105 and 200 cm^{-1}), indicating coordination of 2,4-dcp with lanthanide in a bridging bidentate mode [24], consistent with the X-ray diffraction structural analysis.

3.5. *TG analyses*

TGA of **1** and **2** were performed in N_2 when the sample was heated to 800°C at a rate of 10°C min^{-1}. Complex **1** shows two weight loss steps (figure S4). The first corresponds to release of three 2,4-dcp from 280°C to 480°C (obsd 66.1%, Calcd 66.5%). The weight loss step above 480°C corresponds to one phen and decomposition of the framework structure. Thermal decomposition of **1** in air is also studied (figure S5), revealing that mass loss of **1** in air is larger than in N_2.

3.6. *Luminescent properties*

Metal-organic hybrid coordination polymers with lanthanide metal centers have been widely investigated for their fluorescence properties. The lanthanides only exhibit weak emissions under direct excitation due to their low molar absorptivity. Lanthanide-centered emission can be sensitized by coordinating ligands with π-systems, which can efficiently absorb and transfer the energy. 1-D fluorescences of **1** and **2** were investigated at room temperature under excitation and emission wavelengths of 250–460 and

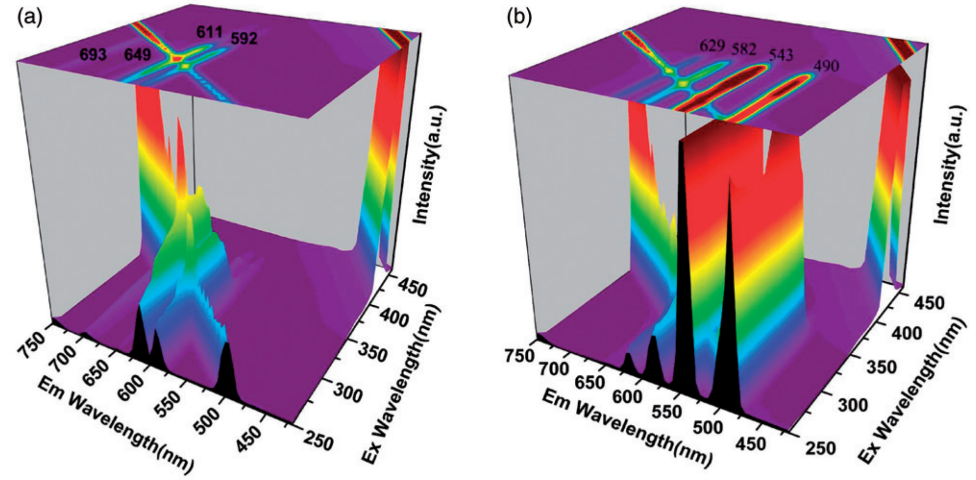

Figure 3. View of the 3-D fluorescence spectra of **1** (a) and **2** (b) under excitation of 250–450 nm at room temperature.

420–750 nm with the same interval of 5 nm, respectively. As shown in figure 3(a), emission peaks of **1** at 592, 611, 649, and 693 nm can be obtained under the excitation wavelength between 385–405 nm, which corresponds to $^5D_0\to{}^7F_n$ ($n=1\to 4$) transitions of Eu(III), respectively, indicating a moderately efficient ligand-to-metal (europium) energy transfer [25]. The emission band at 611 nm ($^5D_0\to{}^7F_2$) is the strongest emission, and the intensity increases as the site symmetry of Eu(III) decreases. Emission peak $^5D_0\to{}^7F_1$ at 592 nm is a magnetic dipole transition and its intensity should vary with the crystal field strength acting on Eu(III). The intensity ratio II($^5D_0\to{}^7F_2$)/($^5D_0\to{}^7F_1$), which is equal to *ca* 1.4, indicates that Eu(III) ions have a low-symmetry coordination environment [26], consistent with the single-crystal X-ray analysis. As shown in figure 3(b), there are four main emission peaks in the emission spectrum of **2** with excitation wavelength of 250–325 nm, ascribed to characteristic emission of Tb(III), and corresponding to electronic transitions from the emitting level $^5D_4$ to the ground multiplet ^7F_n ($n=6\to 3$) [27]. The most intense emission at 543 nm corresponds to $^5D_4\to{}^7F_5$ transition. The second most intense emission at 490 nm corresponds to $^5D_4\to{}^7F_6$. Bands at 582 and 629 nm correspond to $^5D_4\to{}^7F_4$ and $^5D_4\to{}^7F_3$ transitions of Tb(III), respectively. Emission spectra of **1** and **2** in the solid state are clearly red-shifted compared with the free ligands 2,4-dcp and phen (figure S6), attributed to interaction between the lanthanide and ligands. Complexes **1** and **2** possess longer fluorescence lifetimes than other lanthanide complexes, which also show long fluorescence lifetimes ($\tau=1.61$ ms for **1** at 611 nm; 1.79 ms for **2** at 543 nm) (figure 4) [28, 29]. The longer fluorescence lifetimes for **1** and **2** can be attributed to the structural motifs. The luminescent intensity of Ln(III) relies on the efficiency of energy transfer from the ligand to Ln(III) [30]. Presence of lattice and coordination water decreases the luminescent emission intensity of lanthanide coordination polymers, as the thermal oscillation of water molecules consume some excitation energy absorbed by "antenna" ligands. There are no lattice or coordination water molecules in **1** and **2**, thus the emission intensities are much stronger than those [28, 29] due to less deactivation in **1** and **2**.

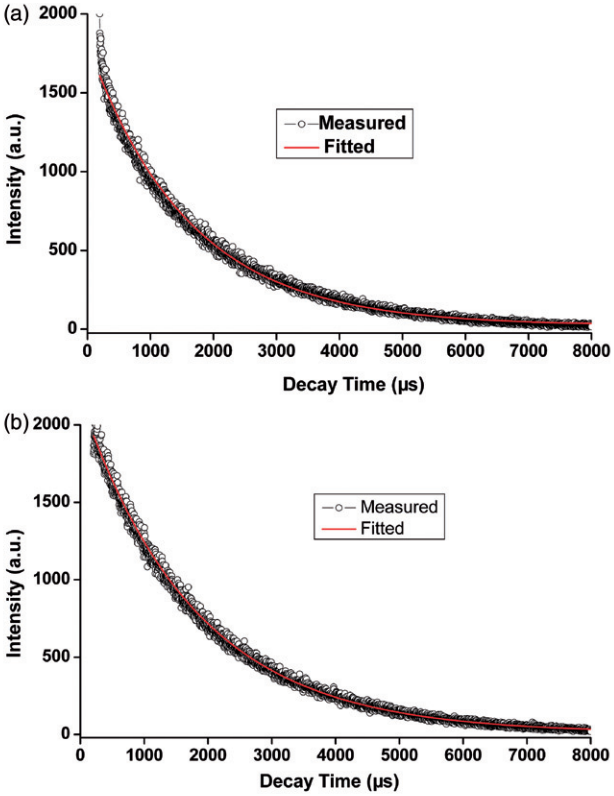

Figure 4. Luminescent lifetimes for **1** (a) and **2**.

4. Conclusion

Two 1-D lanthanide coordination polymers, $\{[\mathrm{Ln(2,4\text{-}dcp)_3(phen)}]_n$ [(Ln = Eu (**1**); Tb (**2**)], were obtained with high yield and purity. Both structures exhibit the same 1-D zigzag-like chain with a $\{\mathrm{Ln_2(2,4\text{-}dcp)_6(phen)_2}\}$ dimeric repeat unit. Complexes **1** and **2** emit bright red and green fluorescence under excitation of 385–405 nm and 250–325 nm, respectively. Moreover, **1** and **2** possess long fluorescence lifetimes ($\tau = 1.61$ ms for **1** at 611 nm; 1.79 ms for **2** at 543 nm) and are good candidates as light-emitting luminescent materials. Further work on the design and synthesis of other lanthanide coordination polymers with intriguing architectures and properties based on 2,4-dcp is ongoing in our laboratory.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC references numbers are 860762 and 860763 for **1** and **2**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The additional figures can be obtained from the web free of cost.

Acknowledgments

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