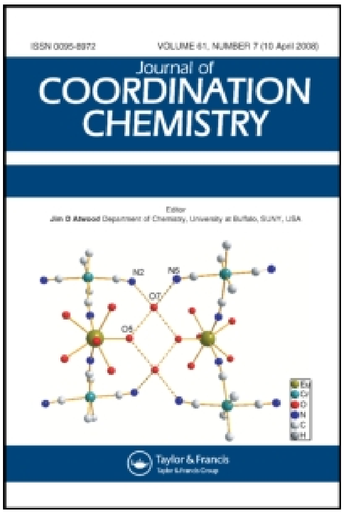

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Two lanthanide luminescent coordination compounds based on 3,5-pyrazoledicarboxylate and oxalic acid

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Two lanthanide luminescent coordination compounds based on 3,5-pyrazoledicarboxylate and oxalic acid

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Two isostructural 3-D complexes $[Ln(pdc)(ox)_{0.5}(H_2O)_2]\cdot H_2O$ (Ln = Tb(**1**), Eu(**2**); pdc = 3,5-pyrazoledicarboxylate; ox = oxalate) have been synthesized under hydrothermal conditions. Both are characterized by single crystal X-ray diffraction, elemental analysis, and IR. Compounds **1** and **2** possess a 3-D framework with 1-D rectangular channels built from 2-D, brick-like networks, and pdc ligands. The photoluminescence and lifetimes of **1** and **2** in the solid state have been studied.

Keywords: Hydrothermal synthesis; Lanthanide compounds; 3,5-Pyrazoledicarboxylate; Oxalic acid; Luminescence

1. Introduction

Metal-organic frameworks (MOFs) have potential applications in molecular magnetism, catalysis, gas sorption, electrical conductivity, and optics [1], and intriguing architectures and topologies [2]. Lanthanide ions have attractive physical properties [3]. Carboxylate ligands play an important role in coordination chemistry as spacers [4]; small bridging oxalate, along with lanthanide ions, have been widely used to construct multidimensional frameworks [5]; oxalate-carboxylate mixed-ligand complexes have also been reported to exhibit interesting structures and attractive properties [6]. The 3,5-pyrazoledicarboxylate (pdc, figure 1a) has proven to be a good spacer in constructing MOFs [7]. For example, the Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er complexes with 3,5-pyrazoledicarboxylic acid ligands, reported by Cheng *et al.* [7a], exhibited three different MOFs with different photophysical and magnetic properties, during which the 3,5-pyrazoledicarboxylic acid functioned as effective bridging ligand to assemble lanthanide-based coordination polymers. However, lanthanide coordination polymers with mixed 3,5-pyrazoledicarboxylic acid and oxalate are rarely reported. Herein, we report the hydrothermal synthesis, crystal structures,

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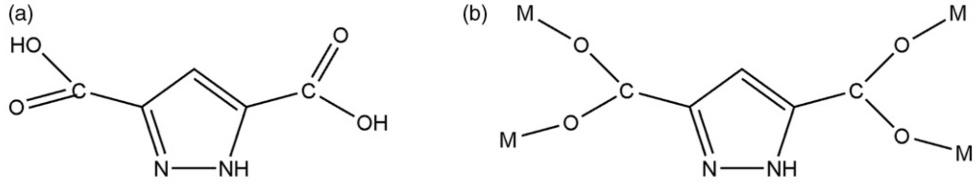

Figure 1. The structure (a) and coordination mode (b) for pdc.

and luminescence of two isostructural lanthanide complexes [Ln(pdc)$(ox)_{0.5}(H_2O)_2] \cdot H_2O$ [Ln = Tb(**1**), Eu(**2**)].

2. Experimental

2.1. *Materials and methods*

All chemicals employed were commercially available and used as received. Elemental (C, H, and N) analysis was performed on a Perkin-Elmer 2400 element analyzer. IR spectra were recorded from 400 to 4000 cm^{-1} on a Perkin-Elmer 17,300 FT-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with heating rate of 10°C min^{-1} from 50 to 850°C under nitrogen. Fluorescence spectra were recorded with an Edinburgh FLS920 phosphorimeter.

2.2. *Hydrothermal synthesis*

2.2.1. $[Tb(pdc)(ox)_{0.5}(H_2O)_2] \cdot H_2O$ (1). About 0.2 mM $Tb(NO_3)_3 \cdot nH_2O$, 0.2 mM pdc, 0.6 mM oxalic acid, and 10 mL deionized water were mixed, followed by the addition of NaOH (0.5 M L^{-1}) to adjust the pH to 4. After stirring 30 min, the mixture was heated at 150°C for 3 days in a 20 mL Teflon-lined autoclave under autogenous pressure. Colorless crystals of **1** were obtained by filtration and air dried, with yield of 73%. IR (KBr): 3430(s), 1678(s), 1577(m), 1469(m), 1371(s), 1217(w), 1008(w), 835(m), 783(m), and 594(w) cm^{-1}; Elemental Anal. Calcd for $C_6H_8TbN_2O_9$ (%) (411.06): C, 17.53; H, 1.96; and N, 6.81. Found (%): C, 17.59; H, 1.95; and N, 6.84.

2.2.2. $[Eu(pdc)(ox)_{0.5}(H_2O)_2] \cdot H_2O$ (2). A similar procedure with **1** was followed to prepare **2** except that $Eu(NO_3)_3$ was used instead of $Tb(NO_3)_3$, then colorless crystals of **2** were obtained with a yield of 70% by filtration, washed by distilled water, and air dried. IR (KBr): 3410(s), 1672(m), 1575(s), 1369(s), 1008(m), 804(w), and 667(w) cm^{-1}; Elemental Anal. Calcd for $C_6H_8EuN_2O_9$ (%) (404.10): C, 17.83; H, 2.00; and N, 6.93. Found (%): C, 17.82; H, 1.96; and N, 7.00.

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_6H_8N_2O_9Tb$	$C_6H_8N_2O_9Eu$
Formula weight	411.07	404.10
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	8.2997(17)	8.3194(3)
b	17.436(3)	17.4760(5)
c	7.8550(16)	7.9219(3)
α	90	90
β	108.63(3)	109.008(2)
γ	90	90
Volume (Å^3), Z	1077.2(4), 4	1088.96(6), 4
Calculated density (g cm^{-3})	2.535	2.465
Absorption coefficient (Mo-Kα) (mm^{-1})	6.612	5.806
Crystal size (mm^3)	0.21 × 0.18 × 0.15	0.21 × 0.15 × 0.14
θ range for data collection (°)	2.34–25.19	2.33–27.92
Independent reflections	[R(int) = 0.0303]	[R(int) = 0.0338]
R indices	$R_1{}^a = 0.0558$, $wR_2{}^b = 0.1419$	$R_1{}^a = 0.0622$, $wR_2{}^b = 0.1587$

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

2.3. *X-ray crystallography*

Single crystal X-ray diffraction data collections of **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 293 K. Data collection and reduction were performed using SMART and SAINT software [8]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL [9]. Hydrogens were located from difference Fourier maps and refined in a riding mode. A summary of crystal parameters and details of the data collection and refinement are given in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure of 1*

Single crystal X-ray analysis reveals that **1** and **2** are isostructural, hence only **1** is selected to discuss in detail. Complex **1** crystallizes in the monoclinic crystal system, $P2_1/c$ space group. One Tb, one monodentate pdc, half of ox, one free, and two coordinated waters are included in the asymmetric unit of **1** (figure 2). Each Tb^{III} is eight-coordinated by four oxygens from four different pdc ligands, two oxygens from one ox, and two oxygens from water. The Tb–O bond lengths range from 2.301–2.516 Å, typical for lanthanide carboxylates [3, 4], and is in good agreement with the ionic radius of Tb^{III}, while O–Tb–O bond angles range from 66.7(3) to 145.9(4)°. The coordination geometry of Tb(III) can be described as a distorted square antiprism.

As shown in figure 3(a), two adjacent Tb centers are bridged *via* two COO– groups from pdc, forming two eight-member closed rings: Tb1–O7–C7–O8–Tb1A–O7A–C7A–O8A and Tb1–O6–C3–O5–Tb1A–O6A–C3A–O5A. The eight-member rings link

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

1[a]					
Tb(1)–O(7)#1	2.301(10)	Tb(1)–O(8)#2	2.306(11)	Tb(1)–O(2)#3	2.414(10)
Tb(1)–O(5)	2.340(10)	Tb(1)–O(1W)	2.396(11)	Tb(1)–O(1)	2.459(10)
Tb(1)–O(6)#4	2.437(10)	Tb(1)–O(2W)	2.516(10)	O(5)–Tb(1)–O(6)#4	112.7(4)
O(7)#1–Tb(1)–O(8)#2	100.1(4)	O(7)#1–Tb(1)–O(5)	145.9(4)	O(2)#3–Tb(1)–O(6)#4	78.3(4)
O(8)#2–Tb(1)–O(5)	89.3(4)	O(5)–Tb(1)–O(1W)	78.6(4)	O(8)#2–Tb(1)–O(1)	72.0(4)
O(8)#2–Tb(1)–O(1W)	142.8(4)	O(1W)–Tb(1)–O(2)#3	131.2(3)	O(1W)–Tb(1)–O(1)	136.1(4)
O(7)#1–Tb(1)–O(2)#3	138.8(4)	O(1W)–Tb(1)–O(6)#4	74.8(4)	O(6)#4–Tb(1)–O(2W)	143.4(4)
O(5)–Tb(1)–O(2)#3	75.2(4)	O(7)#1–Tb(1)–O(1)	73.3(4)	O(2)#3–Tb(1)–O(2W)	136.1(3)
O(5)–Tb(1)–O(2W)	74.6(4)	O(5)–Tb(1)–O(1)	140.3(4)		
O(1)–Tb(1)–O(2W)	127.4(3)	O(2)#3–Tb(1)–O(1)	66.7(3)		
2[b]					
Eu(1)–O(3)#1	2.324(9)	Eu(1)–O(4)#2	2.330(9)	Eu(1)–O(3W)	2.431(9)
Eu(1)–O(1)#3	2.381(9)	Eu(1)–O(6)#4	2.440(9)	Eu(1)–O(5)	2.493(9)
Eu(1)–O(2)	2.453(9)	Eu(1)–O(2W)	2.545(10)	O(3)#1–Eu(1)–O(1)#3	88.8(4)
O(3)#1–Eu(1)–O(4)#2	100.0(4)	O(6)#4–Eu(1)–O(5)	66.2(3)	O(3)#1–Eu(1)–O(3W)	142.0(4)
O(4)#2–Eu(1)–O(1)#3	146.2(3)	O(3)#1–Eu(1)–O(2W)	70.5(4)	O(1)#3–Eu(1)–O(3W)	79.4(3)
O(3)#1–Eu(1)–O(2)	141.3(4)	O(1)#3–Eu(1)–O(2W)	75.0(3)	O(4)#2–Eu(1)–O(6)#4	138.3(3)
O(1)#3–Eu(1)–O(2)	114.1(3)	O(6)#4–Eu(1)–O(2W)	135.9(3)	O(3W)–Eu(1)–O(2)	75.4(3)
O(6)#4–Eu(1)–O(2)	79.2(3)	O(5)–Eu(1)–O(2W)	126.5(3)	O(2)–Eu(1)–O(5)	70.7(3)
O(3W)–Eu(1)–O(5)	136.4(3)	O(3W)–Eu(1)–O(2W)	71.6(3)		
O(4)#2–Eu(1)–O(2W)	77.4(3)	O(2)–Eu(1)–O(2W)	143.4(3)		

[a] Symmetry codes for **1**: #1 $-x+1, y-1/2, -z+1/2$; #2 $x+1, -y+1/2, z+1/2$; #3 $-x+1, -y, -z$; #4 $-x+1, -y, -z+1$.
[b] Symmetry codes for **2**: #1 $-x+2, y-1/2; -z+1/2$; #2 $x, -y+1/2, z+1/2$; #3 $-x+1, -y, -z+1$; #4 $-x+1, -y, -z$.

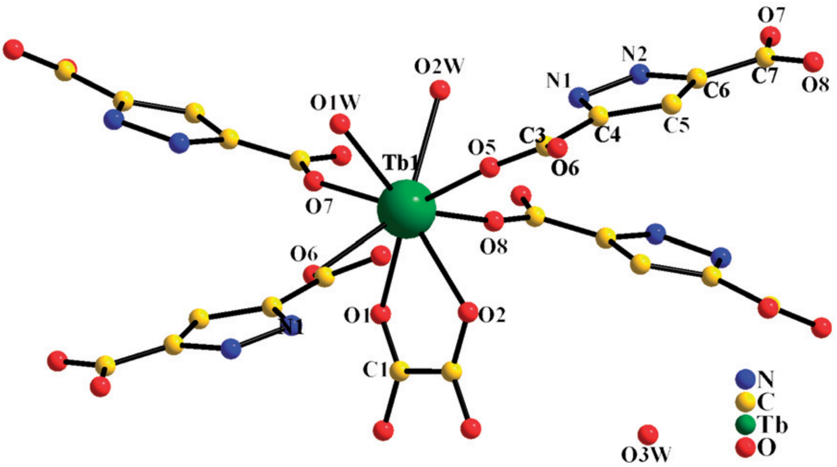

Figure 2. The coordination environment of Tb; all hydrogens are omitted for clarity.

to form 1-D Tb–O–C chains based on corner-sharing [TbO8] polyhedra along the *b*-axis, where the dihedral angle between the two neighboring planes is 43.93°. [Tb2O2C2] units are bridged by ox along the *b*-axis yielding a 2-D brick-like framework (figure 3b).

The pdc ligand is a tetra-connector to link four Tb centers by four carboxylate oxygens (figure 1b). The 2-D brick-like frameworks are bridged by pdc spacers along the *b*- and *c*-axis directions forming a 3-D framework, which contains 1-D rectanglar

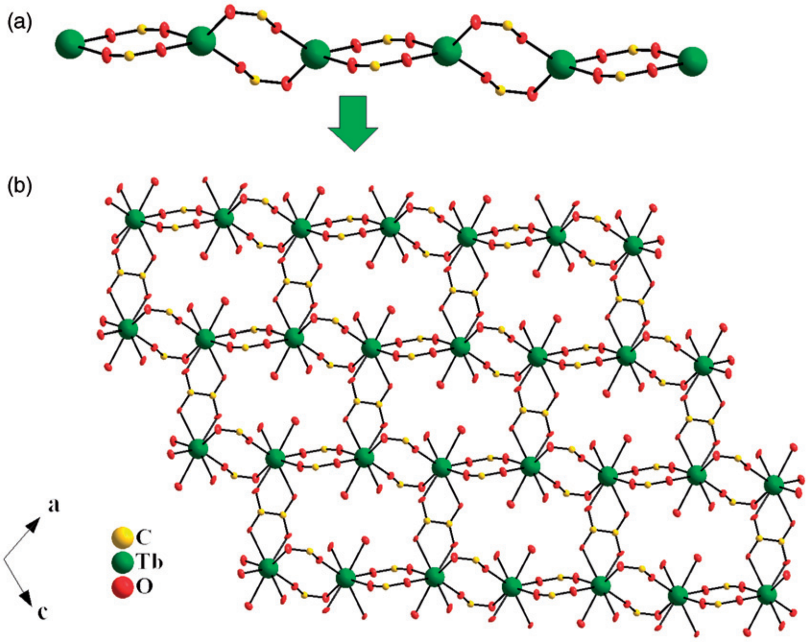

Figure 3. (a) 1-D chain of {Tb2O2C2} units. (b) Brick-like framework along the *b*-axis; some C, N, and O atoms of pdc, and all hydrogens are omitted for clarity.

channels, as shown in figure 4. In the channel, there exist hydrogen bonds between O3W and O1W with O(1W) ··· O(3W) = 2.837 Å (2.882 Å for **2**).

Although **1** and **2** are isostructural, there are several differences which can be classified according to the metal. Since the radius of Eu is bigger than that of Tb, most Eu–O bond distances in **2** are slightly larger than Tb–O bond distances in **1**, as shown in table 2. As a result, the cell volume of **2** is a little bigger than that of **1**.

3.2. *Luminescence*

Solid-state excitation and emission luminescence spectra of **1** and **2** at room temperature are shown in figure 5. The excitation spectrum for **1** showed a wide excitation band centered at 254 nm. Some narrow excitation peaks located at 352, 369, and 378 nm were ascribed to various f–f transitions of Tb^{III}. The emission spectrum of **1** revealed the characteristic emission of Tb with intense green-emission, attributed to $^5D_4 \rightarrow {}^7F_J$ ($J = 6$, 5, 4, and 3) centered at 490, 544, 584, and 621 nm, respectively; $^5D_4 \rightarrow {}^7F_5$ is the strongest emission, indicating efficient ligand-to-metal energy transfer (LMCT) [10]. Complex **2** showed two excitation bands ranging from 200 to 450 nm, centered at 249 and 394 nm. Emission of **2** ranging from 550 to 720 nm is ascribed to $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3, and 4). The emission at 617 nm is characteristic of the hypersensitive $^5D_0$–$^7F_2$ transition of Eu^{III}, which is much more intense than the $^5D_0$–$^7F_1$ transition at 591 nm. The symmetry-forbidden weak emission $^5D_0 \rightarrow {}^7F_0$ at 579 nm indicates that the Eu centers in **2** do not possess inversion symmetry [11], confirmed by crystallographic analyses. The luminescent lifetimes of solid **1** and **2** using an

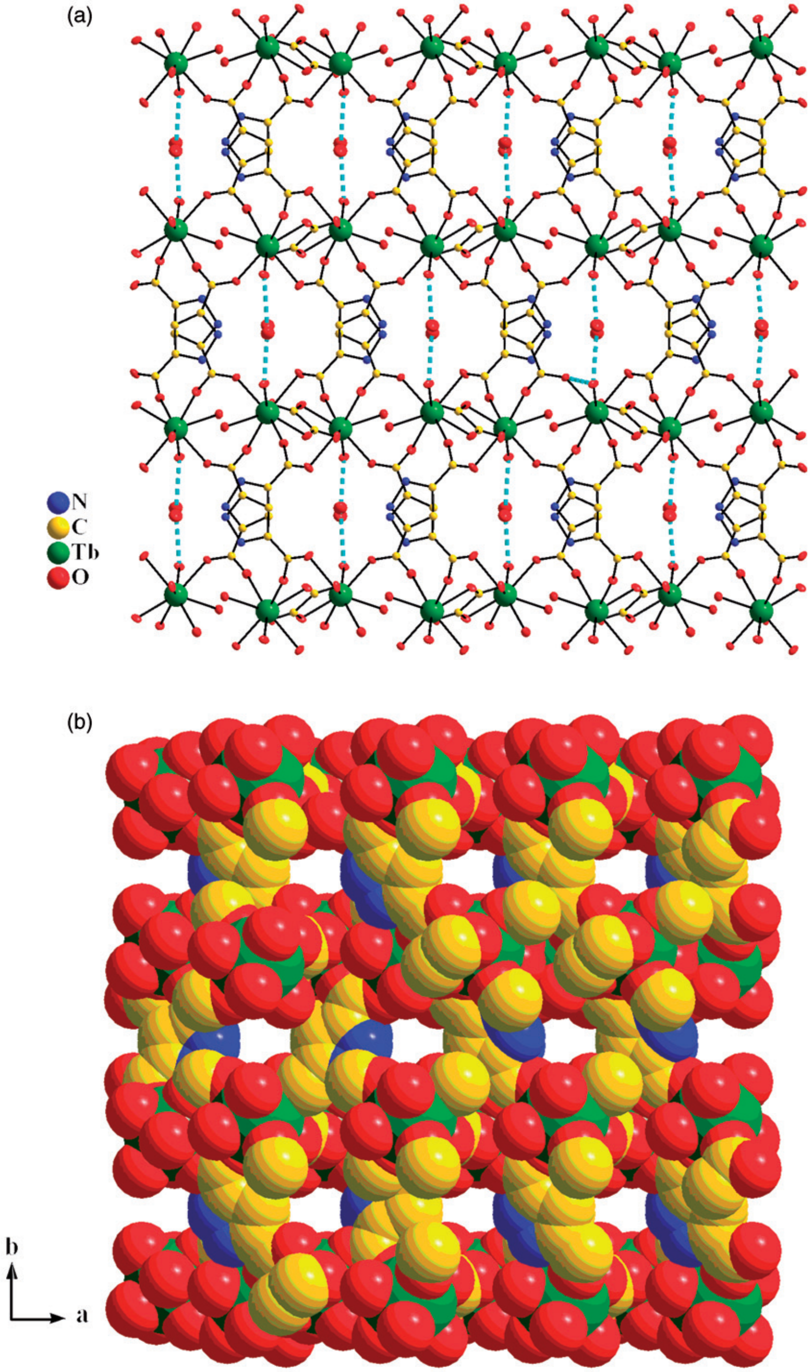

Figure 4. (a) 3-D frameworks of **1** along the *c*-axis. Blue broken lines are H bonds. (b) The space-filling of **1** with 1-D channels.

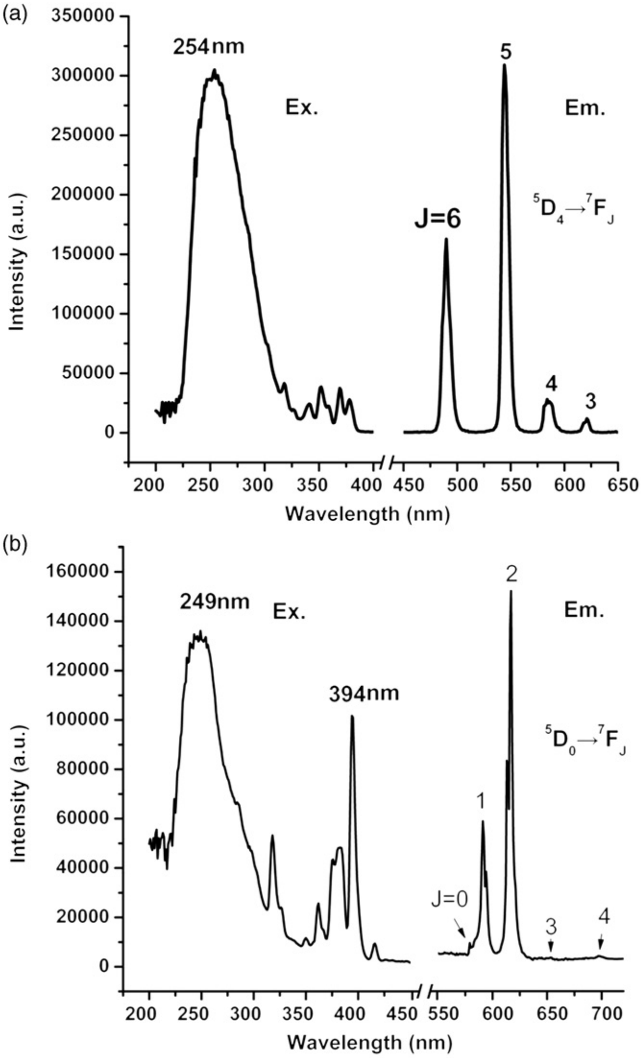

Figure 5. Excitation and emission spectra for **1** (a) and **2** (b) at room temperature.

Edinburgh FLS920 phosphorimeter with a 450 W xenon lamp as excitation source show lifetimes for **1** and **2** of 889 and 442 µs, respectively (figure 6).

3.3. *Thermogravimetric analysis*

Compounds **1** and **2** are isostructural and only **2** is selected to discuss stabilities. TGA curves in N_2 for crystalline **2** from 35 to 850°C show that between 35 and 150°C there is a flat line (no weight loss). The first weight loss of 13.35% from 150°C to 325°C corresponds to the removal of the coordination and lattice water (Calcd: 13.37%). The second weight loss of 10.75% happens between 325 and 410°C, attributed to the loss of oxalic acid (Calcd: 10.89%). The third weight loss is from 410 to 850°C, which

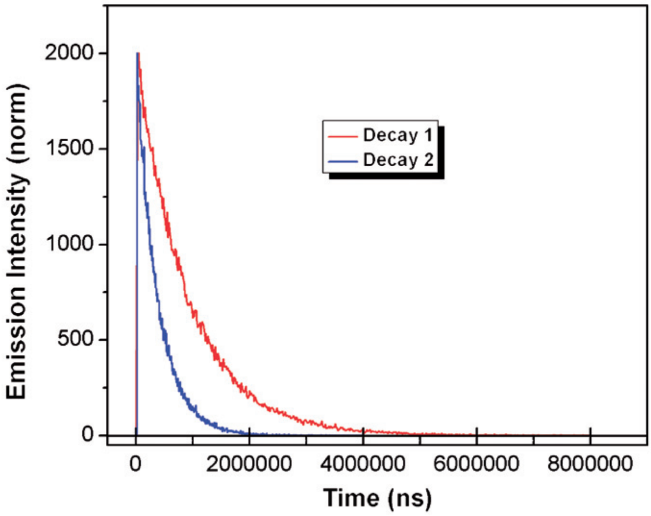

Figure 6. Luminescent lifetimes for **1** and **2**.

corresponds to the loss of the rest of organic components and collapse of the framework.

4. Conclusion

Two new 3-D complexes $[Ln(pdc)(ox)_{0.5}(H_2O)_2] \cdot H_2O$ (Ln = Tb(**1**), Eu(**2**)) have been synthesized by utilizing a 3,5-pyrazoledicarboxylate and oxalate as spacers. These complexes possess 3-D frameworks with crossed channels for the accommodation of guest water; pdc bridged lanthanide ions into 1-D chains as spacers and ox-bridged neighboring parallel chains form 2-D brick-like layers, pillared by pdc spacers forming a 3-D framework. Complexes **1** and **2** possess intense luminescence at room temperature. Polymers with important properties and charming topologies will be further synthesized by using different carboxylates or adding transition metals [12].

Supplementary material

CCDC Nos 683104 and 683105 contain the crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/datarequest/cif.

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