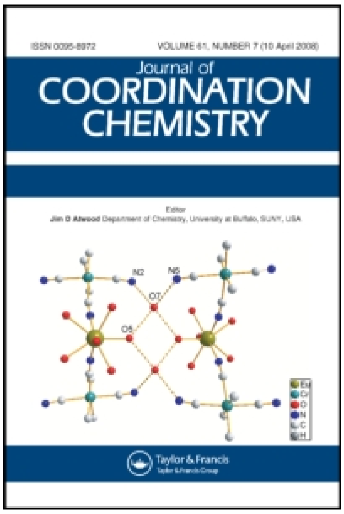

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Synthesis, crystal structures and luminescent properties of two new Ln(III)-dicarboxylate (Ln=Eu, Tb) complexes exhibiting three dimensional networks

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Synthesis, crystal structures and luminescent properties of two new Ln(III)-dicarboxylate (Ln = Eu, Tb) complexes exhibiting three dimensional networks

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Two new coordination polymers, $\{[Eu_2(L_1)_3(H_2O)_2] \cdot H_2O\}_n$ (**1**), $(Cu(II) \cdots Cu(II)$, $[Tb(H_2O)]_2(L_2)_3 \cdot 4H_2O$ (**2**) (H_2L_1 = succinic acid, H_2L_2 = glutaric acid) have been hydrothermally synthesized and characterized by elemental analysis, IR, luminescence spectra and single crystal X-ray diffraction. The complexes are constructed by dicarboxylates bridging chains of edge-sharing $EuO_8(H_2O)$ and $TbO_8(H_2O)$ polyhedra to form 3D network structures. Complexes **1** and **2** exhibit intense red and green photoluminescence upon UV excitation in the solid state at room temperature.

Keywords: Crystal structures; Rare earth; Photoluminescence; TGA

1. Introduction

Research on open metal-organic coordination frameworks [1, 2] is justified not only by their intriguing structural motifs but also their potential applications in selective catalysis, separations, magnetic, and luminescent properties [3–6]. One approach has been to design open coordination frameworks with suitable rigid multidentate ligands; long chain dicarboxylates present interesting behavior due to their conformational flexibility and coordination diversity. Lanthanide ions exhibit high affinity for oxygen and have diverse coordination modes, along with special fluorescent properties [7]. We present here the hydrothermal synthesis, crystal structures and luminescent properties of two new rare earth dicarboxylate complexes, $\{[Eu_2(L_1)_3(H_2O)_2] \cdot H_2O\}_n$ (**1**) and $[Tb(H_2O)]_2(L_2)_3 \cdot 4H_2O$ (**2**).

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2. Experimental

2.1. Synthesis of $\{[Eu_2(L_1)_3(H_2O)_2] \cdot H_2O\}_n$ (1)

A mixture of $Eu(NO_3)_3 \cdot nH_2O$ (1 mmol), succinic acid (H_2L_1, 118 mg, 1 mmol) and 1,10-phenanthroline (phen, 198 mg, 1mmol) in H_2O (15 mL) was placed in a Teflon-lined stainless vessel and heated to 433 K for 72 h. The reaction system was slowly cooled to room temperature at a rate of $10\,K\,h^{-1}$. Colorless crystals with X-ray diffraction quality were obtained and washed with water. Yield, 0.0918 g (26% based on Eu). Anal. Calcd for $C_{12}H_{18}Eu_2O_{15}$ (706.18) (%): C, 20.41; H, 2.57. Found: C, 20.36; H, 2.35. IR (KBr pellets, cm^{-1}): 3602m, 3342s, 2983m, 2948w, 2925w, 1567s, 1453s, 1426s, 1305s, 1215m, 1176m, 1049w, 1001w, 951w, 908m, 878w, 811m, 756w, 690m, 652m, 572m, 526w.

2.2. Synthesis of $[Tb(H_2O)]_2(L_2)_3 \cdot 4H_2O$ (2)

A mixture of $Tb(NO_3)_3 \cdot nH_2O$(1 mmol), glutaric acid (H_2L_2, 118 mg, 1 mmol) and NaOH (80 mg, 2 mmol) in H_2O (15 mL) was placed in a Teflon-lined stainless vessel and heated to 433 K for 72 h. Then the reaction system was slowly cooled to room temperature at a rate of $10\,K\,h^{-1}$. Colorless crystals of X-ray diffraction quality were obtained and washed with water. Yield, 0.1469 g (36% based on Tb). Anal. Calcd for $C_{15}H_{30}Tb_2O_{18}$ (816.23) (%): C, 22.07; H, 3.70. Found: C, 22.36; H, 3.35. IR (KBr pellets, cm^{-1}): 3588m, 3415s, 2999m, 2975w, 2951w, 2893w, 1541s, 1462s, 1414s, 1358m, 1272m, 1222m, 1197m, 1059m, 1010w, 925w, 882w, 816m, 755m, 699w, 654m, 546w, 481w.

2.3. Physical measurements

All chemicals were commercially available and used as received. Elemental analyses were carried out on a Perkin–Elmer 240C analyzer. IR spectra (KBr pellets) were taken on an AVATAR 360 FT–IR E.SP (Nicolet) spectrometer. Thermal analyses were performed in the temperature range of 25–700°C on a Rigaku standard TG-DTA analyzer. The luminescence spectra were measured with a Perkin Elmer LS 55 Luminescence Spectrometer.

2.4. X-ray crystallography

The room temperature (294 ± 1 K) single-crystal X-ray experiments were performed on a Bruker P4 diffractometer equipped with graphite monochromatized Mo-Kα radiation. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements and structures were solved by direct methods [10a]. All non-hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms of methylenes were generated geometically with C–H bond distances of 0.97 Å and hydrogen atoms of water were found on difference Fourier maps with O–H bond distances to be standard (0.85 Å). They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}$ (C or O). The final full-matric least-square refinement on F^2 converged with $R_1 = 0.0190$, 0.0264 and $wR_2 = 0.0472$, 0.0660 for 2049, 1989 observed

Table 1. Crystal data and refinement parameters of **1** and **2**.

Empirical formula	$C_{12}H_{18}Eu_2O_{15}$	$C_{15}H_{30}O_{18}Tb_2$
Molecular weight	706.18	816.23
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Unit cell parameters (Å, °)		
a	19.988(4)	7.942(2)
b	7.7808(16)	14.950(2)
c	13.890(3)	19.644(4)
β	121.37(3)	94.544(14)
Volume (Å^3)	1844.5(6)	2325.0(8)
Z	4	4
Calculated density (Mg cm^{-3})	2.543	2.332
Absorption coefficient (mm^{-1})	6.817	6.121
$F(000)$	1344	1576
Crystal size (mm^3)	$0.23 \times 0.17 \times 0.15$	$0.4 \times 0.4 \times 0.28$
θ range for data collection (°)	3.02–25.50	2.73–12.49
Limiting indices	$-25 \le h \le 20$, $-10 \le k \le 10$, $-15 \le l \le 17$	$-1 \le h \le 9$, $-18 \le k \le 1$, $-23 \le l \le 23$
Reflections collected/unique	8808/2101 [R(int) = 0.0375]	2899/2173 [R(int) = 0.0321]
Completeness to $\theta = 25.50$ (%)	99.6	100
Absorption correction	Multi scans	Empirical
Maximum and minimum transmission	0.4360 and 0.2995	0.3428 and 0.1444
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2101/0/132	2173/0/159
Goodness-of-fit on F^2	1.077	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0190$, $\omega R_2 = 0.0472$	$R_1 = 0.0264$, $\omega R_2 = 0.0660$
R indices (all data)	$R_1 = 0.0198$, $\omega R_2 = 0.0476$	$R_1 = 0.0295$, $\omega R_2 = 0.0689$
Largest different peak and hole (e Å^{-3})	0.806 and −1.048	0.575 and −1.106

reflections [$I \geq 2\sigma(I)$], respectively. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 [10b]. Details of crystal parameters, data collection and structure refinement are given in table 1.

3. Results and discussion

3.1. *Crystal structure*

The two complexes consist of 3D open frameworks built from Ln(III) and dicarboxylate ligands. The selected bond lengths and angles of 1 and 2 are listed in table 2. Complex **1** is isostructural with Ln–succinate (Ln = La, Y, Pr, Tb, Gd) analogs [8], so only a brief structural description will be given here. It consists of edge-sharing $EuO_8(H_2O)$ polyhedral (figure 1) chains along the [010] direction linked together through the COO^- groups. These chains are then cross-linked by succinic acid backbones to form a three-dimensional framework (figure 2). The Eu(III) ion is nine-coordinate by a coordinated water and eight oxygen atoms from six carboxylate groups forming a tricapped trigonal prism. Two succinate groups chelate the europium ion and four share one oxygen atom. Each succinate anion binds a total of five or six Eu atoms. Each carboxylate group

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

1			
Eu(1)–O(1B)	2.324(2)	Eu(1)–O(5)	2.463(2)
Eu(1)–O(2D)	2.448(3)	Eu(1)–O(5C)	2.421(2)
Eu(1)–O(3)	2.537(2)	Eu(1)–O(6)	2.488(3)
Eu(1)–O(3C)	2.424(2)	Eu(1)–O(1W)	2.485(2)
Eu(1)–O(4)	2.497(2)		
O(4)–Eu(1)–O(3)	51.14(7)	O(5)–Eu(1)–O(6)	52.31(7)
2			
Tb(1)–O(1)	2.407(4)	Tb(1)–O(5B)	2.359(4)
Tb(1)–O(2)	2.456(4)	Tb(1)–O(5C)	2.656(4)
Tb(1)–O(3)	2.439(4)	Tb(1)–O(6C)	2.405(4)
Tb(1)–O(4)	2.530(4)	Tb(1)–O(7)	2.369(4)
Tb(1)–O(4A)	2.364(4)	O(1)–Tb(1)–O(2)	53.31(13)
O(3)–Tb(1)–O(4)	52.30(12)	O(5C)–Tb(1)–O(6C)	51.07(12)

Symmetry codes: For **1**: (A) $1-x$, $1-y$, $1-z$; (B) $1/2-x$, $1/2-y$, $-z$; (C) $1/2-x$, $y-1/2$, $1/2-z$; (D) x, $1-y$, $z+1/2$; For **2**: (A) $1-x$, $1-y$, $1-z$; (B) $x+1/2$, $y-1/2$, z; (C) $1.5-x$, $1.5-y$, $1-z$.

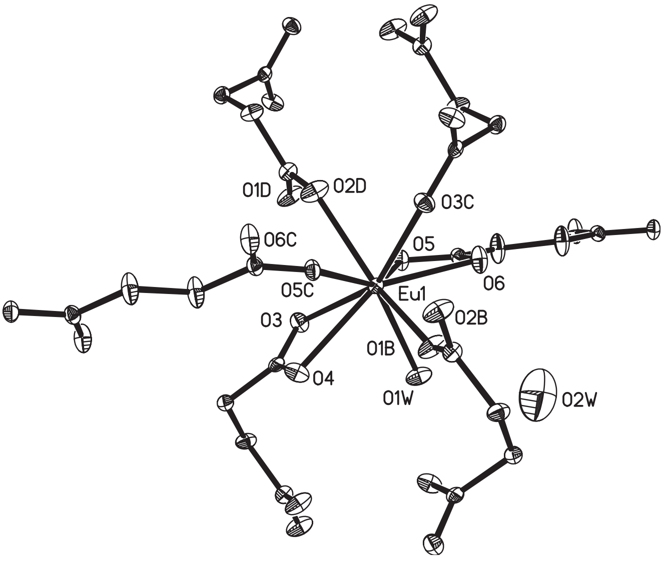

Figure 1. Coordination environment of Eu(III) in **1** (50% thermal ellipsoid probability showing atom labeling), symmetric codes: (A) $-x+1$, $-y+1$, $-z+1$; (B) $-x+1/2$, $-y+1/2$, $-z$; (C) $-x+1/2$, $y-1/2$, $-z+1/2$; (D) x, $-y+1$, $z+1/2$.

of the centrosymmetric anion chelates one Eu center and at the same time uses one oxygen atom, O5, to bridge a symmetry-related Eu atom. A similar coordination mode is found for the carboxylate group containing atoms O3 and O4 of the second succinate anion, whereas the other end is bidentate bridging. The polyhedra are joined in a chain parallel to the b direction (figure 2) by sharing one edge with each neighbor, the distances between adjacent metal centres in a row being 4.056(3) Å (Eu–Eu). The Eu(1)–O bond distances of Eu(1)O_8(H_2O) range from 2.324(2) to 2.537(2) Å and the average value is 2.454(2) Å.

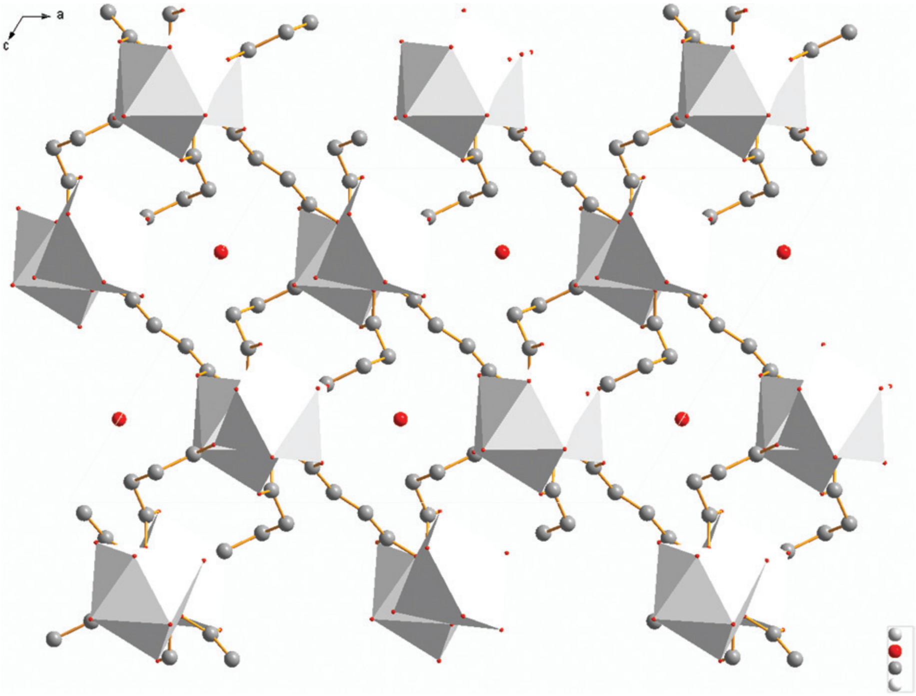

Figure 2. View of packing in **1**, showing Eu(III) coordination polyhedra and water guests.

Complex **2** is the first Tb–glutarate complex and isostructural to Nd–glutarate analogs [9], so only a brief structural description will be given here. Complex **2** is three-dimensional, consisting of chains of edge-sharing $TbO_8(H_2O)$ polyhedra, along the a direction, linked together by carbon chains to form a three-dimensional framework (figure 3). The Tb(III) ion is coordinated by a water molecule and eight oxygen atoms from five carboxylate groups forming a tricapped trigonal prism. Three glutarate groups chelate the terbium ion and two share one oxygen atom. The polyhedra are joined in a chain parallel to the a direction (figure 4) by sharing one edge with each neighbor, the distances between adjacent metal centres in a row being 4.211(7) and 4.092(6) Å (Tb–Tb). The Tb(1)–O distances range from 2.359(4) to 2.656(4) Å and the average is 2.398(4) Å.

3.2. *IR, luminescence and TGA spectra*

The IR spectra of both complexes are similar, each showing strong absorption bands at 1462–1403 cm^{-1} assigned to the symmetric C=O vibrations, and the asymmetric vibrations at 1615–1541 cm^{-1}. The bands ν_{sym}(O–C–O) and δ(O–C–O) were observed at 1215 and 811 cm^{-1} for **1**, 1222 and 816 cm^{-1} for **2**. The presence of coordinated water is confirmed by the appearance of a narrow band at 3602, 3588 cm^{-1} in **1** and **2**, respectively. The complicated pattern of carboxylic bands in the range of 1309–1615 cm^{-1} is consistent with the carboxylate groups bidentate bridging and bidentate chelating-bridging coordination modes.

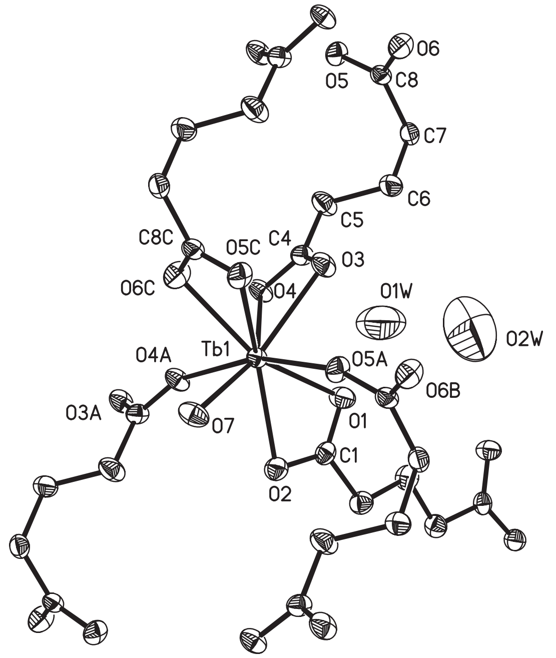

Figure 3. Coordination environment of Tb1(III) in **2** (50% thermal ellipsoid probability showing atom labeling), symmetric codes: (A) $1-x$, $1-y$, $1-z$; (B) $x+1/2$, $y-1/2$, z; (C) $1.5-x$, $1.5-y$, $1-z$.

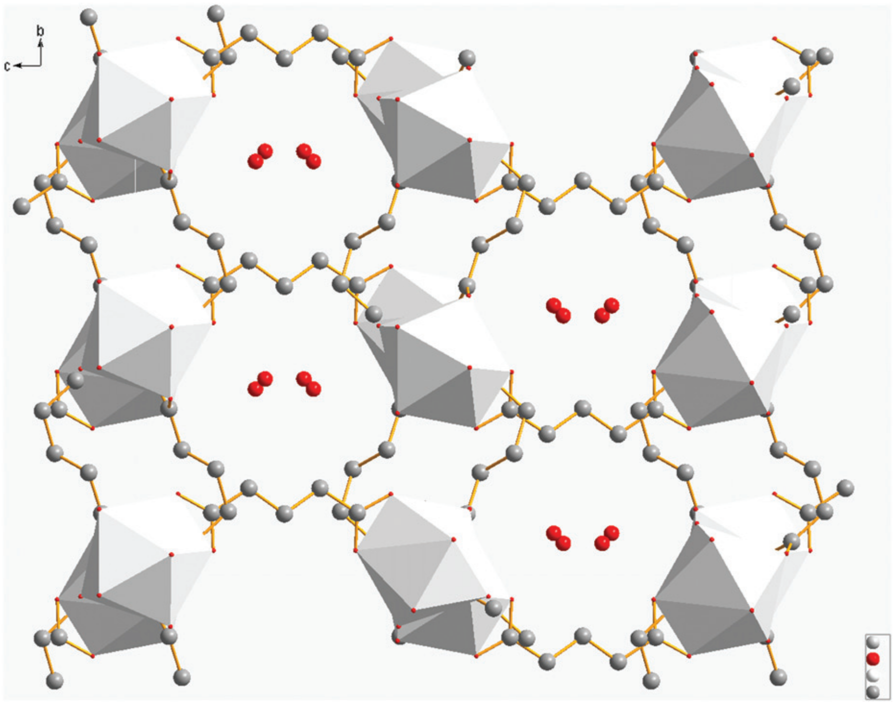

Figure 4. Chains built by polyhedra through edge sharing for **2**.

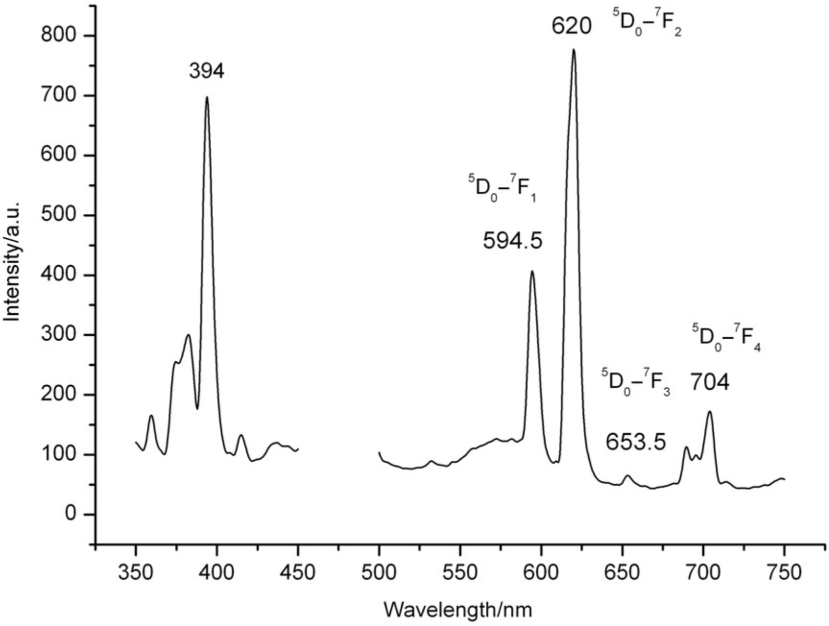

Figure 5. Fluorescence spectra for **1** in the solid state.

Thermal analyses show that water within the channels of **1** and **2** can be easily removed. The TG curve of **1** shows a two-step weight loss between 140 and 700°C. The first weight loss between 140 and 215°C is assigned to the loss of lattice water (observed 7.13%; expected 7.65%). No weight loss was observed from 216 to 390°C. The second weight loss between 391 and 700°C corresponds to decomposition of organic ligands (observed 41.20%, expected 42.15%). Complex **2** experienced three step weight loss with two successive losses of weight below 140°C. The first loss (Calcd, 8.8%; found 7.4%) between room temperature and 97°C corresponds to the loss of weakly bonded water in the tunnels along the crystallographic *a* axis. The second loss between 98 and 132°C corresponds to the loss of coordinated water (Calcd, 4.4%; found 4.2%). The third weight loss in the range of 370–700°C corresponds to decomposition of the organic part of the complexes.

Complex **1** exhibits red photoluminescence upon UV radiation in the solid state at room temperature, as shown in figure 5. The maximum excited wavelength is 394 nm and its emission spectrum involves three groups of narrow peaks, attributed to the $^5D_0 \rightarrow {}^7F_1$ (594 nm) and $^5D_0 \rightarrow {}^7F_2$ (620 nm), $^5D_0 \rightarrow {}^7F_3$ (653 nm), and $^5D_0 \rightarrow {}^7F_4$ (704 nm) transitions of Eu^{3+}. In the emission spectra, **1** exhibits a much higher $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ intensity ratio, in agreement with the lower degree of symmetry of a nine-coordinate europium in the crystal structure.

Complex **2** emits intense green light when excited at 351.5 nm in the solid state at room temperature (figure 6). The emission peaks of **2** correspond to the transitions from $^5D_4 \rightarrow {}^7F_n$ ($n = 6, 5, 4, 3$) transitions at 492, 546, 586 and 623 nm. Striking red emissions ($^5D_0 \rightarrow {}^7F_2$) and green luminescence ($^5D_4 \rightarrow {}^7F_5$) were observed in the spectra.

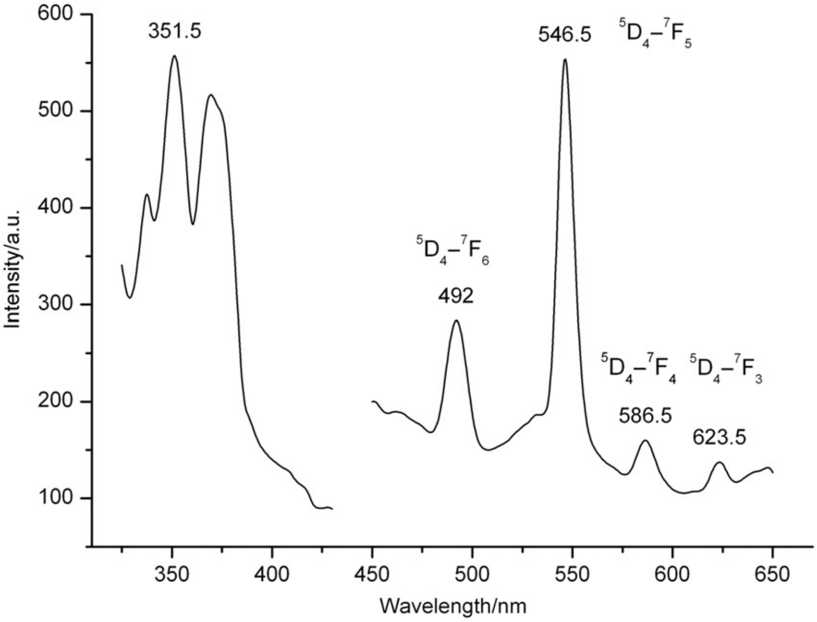

Figure 6. Fluorescence spectra of **2** in the solid state.

Supplementary material

The supplementary crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 294165, 298844. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: C44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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