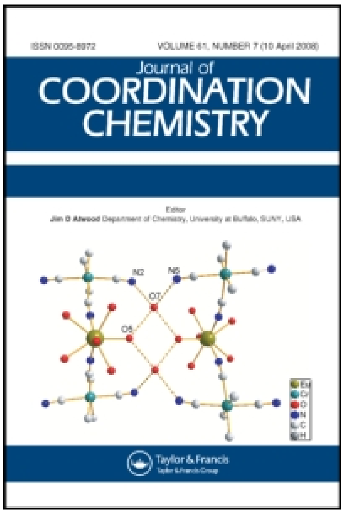

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Synthesis, structures and photoluminescence of two Er(III) coordination polymers

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Synthesis, structures and photoluminescence of two Er(III) coordination polymers

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Two new erbium compounds, $[Er_2(BDC)_3(DMF)_2]$ (**1**) and $[Er_2(CQC)_3(DMF)_3(H_2O)]\cdot DMF\cdot H_2O$ (**2**), where BDC stands for 1,4-benzenedicarboxylate, CQC for 2-(4-carboxyquinolin-2-yl)quinoline-4-carboxylate, and DMF for *N*,*N*-dimethylformamide, have been synthesized through pre-heating and cooling-down crystallization. In **1** the Er(III) is seven-coordinate with oxygen atoms from six BDC and one DMF, forming a three-dimensional open-framework structure. Compound **2** possesses a 2D structure based on dinuclear Er(III) building units. The photoluminescence of **1** has also been investigated.

Keywords: Erbium; Coordination polymer; Crystal structure; IR spectrum; Photoluminescence

1. Introduction

Rare earth coordination polymers attract attention due to properties such as magnetism and photoluminescence [1–4]. A number of rare-earth complexes have been synthesized using carboxylate-containing ligands such as 1,2,4,5-benzenetetracarboxylic acid, trimesic acid, benzenedicarboxylic acid and 2,6-naphalenedicarboxylic acid as the ligands [5]. Among the carboxylate ligands, 1,4-benzenedicarboxylic acid (H_2BDC) and 2-(4-carboxyquinolin-2-yl)quinoline-4-carboxylic acid (H_2CQC) are also promising organic linkers for rare-earth ions (scheme 1). For BDC ligand, the two carboxylates with an 180° angle establish bridges between several metal centers through various coordination modes, and the presence of the aromatic ring renders this molecule rather rigid. Compared with the *d*-block transition metal compounds, lanthanide coordination polymers containing BDC are less-common [6]. CQC is a 4-quinolinecarboxylic acid-based ligand, where quinoline rings can freely twist to meet the requirement of coordination geometries of metal ions in the assembly process. Thus, the CQC ligand

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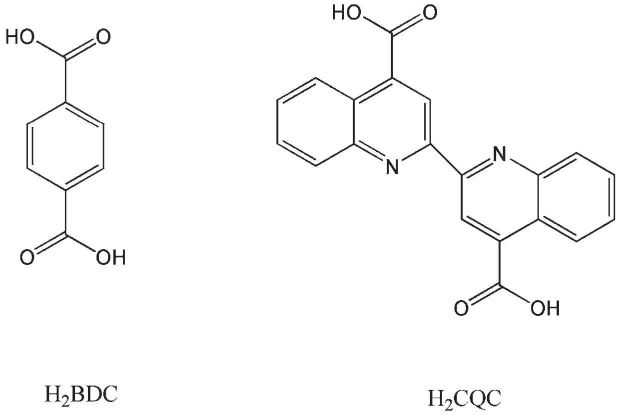

Scheme 1. Ligands used in syntheses of **1** and **2**.

allows two carboxylate groups to bridge metal centers from different directions. However, coordination chemistry of the CQC ligand is rarely observed in the literature.

Synthesis of rare earth carboxylate coordination polymers is performed in aqueous media, where water coordinates to the rare earth centers and quenches the luminescence intensity of the products [7]. In order to obtain single crystals of lanthanide aromatic carboxylate coordination polymers, we have tried an unconventional synthetic approach, where DMF (DMF = *N*,*N*-dimethylformamide) was used as the solvent and the crystallization was realized through a pre-heating and cooling-down approach. In this article, we describe the syntheses of two Er(III) compounds with 2D and 3D structures, $[Er_2(BDC)_3(DMF)_2]$ (**1**) and $[Er_2(CQC)_3(DMF)_3(H_2O)] \cdot DMF \cdot H_2O$ (**2**) in the presence of DMF as the solvent and BDC or CQC as ligands. The photoluminescence of **1** has also been elucidated.

2. Experimental

2.1. *Materials*

$ErCl_3 \cdot 6H_2O$ was prepared by dissolving Er_2O_3 in hydrochloric acid followed by drying and crystallization. H_2BDC, H_2CQC, *N*,*N*-dimethylformamide (DMF) and other reagents of analytical grade were purchased commercially and used without further purification.

2.2. *Preparation*

2.2.1. Synthesis of $[Er_2(BDC)_3(DMF)_2]$ (1). $ErCl_3 \cdot 6H_2O$ (0.33 mmol) and H_2BDC (0.5 mmol) were dissolved in DMF (10 mL). The resulting mixture was stirred for about 1 h at room temperature, sealed in a 23 mL Teflon-lined stainless steel autoclave and heated at 85°C for 6 days under autogenous pressure. Afterward, the reaction system was gradually cooled to room temperature at a rate of 10°C h^{-1}. Colorless crystals of **1** suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with DMF and dried in air at ambient temperature. Yield: 49% based on Er(III). Elemental and ICP analysis results for $C_{15}H_{12}ErNO_7$: Calcd (%): C 37.10, H 2.49, N 2.89, Er 34.45; Found (%): C 37.14, H 2.43, N 2.93, Er 34.42.

2.2.2. Synthesis of $[Er_2(CQC)_3(DMF)_3(H_2O)] \cdot DMF \cdot H_2O$ (2). Complex **2** was synthesized by a method similar to that of **1**, using H_2CQC (0.5 mmol) instead of H_2BDC as the dicarboxylate ligand. Yield: 34% based on Er(III).

2.3. *Characterization*

The infrared spectra were recorded within the 400–4000 cm^{-1} region on a Bruker IFS 66V/S FTIR spectrometer using KBr pellets. The thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a Netzsch STA 449C thermogravimetric analyzer under air at a heating rate of 20°C min^{-1}. The near-IR emission spectrum of compound **1** was recorded on an Edinburgh Analytical Instruments FLS920 spectrometer equipped with a laser diode (LD) from the PicoQuant Company as the light source. The C, H, N elemental analysis was conducted on a Perkin-Elmer 240°C element analyzer, whereas the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP spectrometer. The powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) and the recording speed was 0.3° min^{-1} over the 2θ range of 4–40° at room temperature. All the spectroscopic characterization of **1** has been performed on the isolated crystals.

2.4. *Crystal structure determination*

Crystallographic data of **1** and **2** were collected on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å) at a temperature of 20 ± 2°C. The data processing was accomplished with the PROCESS-AUTO processing program. The structure was solved by direct methods using *SHELXS-97* [8] and refined by full-matrix least-squares techniques against F^2 using the *SHELXTL-97* [9] crystallographic software package. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and added to the structure factor calculation. The detailed crystallographic data and structure refinement parameters for **1** and **2** are summarized in table 1. Selected bond distances and angles for **1** and **2** are listed in table 2.

Table 1. Crystallograplic data and structure refinements for **1** and **2**.

Compounds	**1**	**2**
Formula	$C_{15}H_{12}ErNO_7$	$C_{72}H_{62}Er_2N_{10}O_{18}$
Formula weight	485.52	1689.84
Crytsal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a (Å)	18.654(4)	12.062(2)
b (Å)	10.738(2)	16.590(3)
c (Å)	18.547(4)	19.389(4)
α (°)	90	78.75(3)
β (°)	108.46(3)	75.43(3)
γ (°)	90	87.96(3)
V (Å^3)	3524.0(12)	3682.6(13)
Z	8	2
D_c (g cm^{-3})	1.830	1.524
F(000)	1864	1688
μ (Mo-Kα) (mm^{-1})	4.796	2.338
$R_1(I > 2\sigma(I))$	0.0484	0.0754
$wR_2(I > 2\sigma(I))$	0.1063	0.1929

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

$[Er_2(BDC)_3(DMF)_2]$ (**1**)			
Er(1)–O(3)#1	2.283(6)	Er(1)–O(7)	2.341(8)
Er(1)#2–O(6)	2.324(6)	Er(1)–O(5)	2.275(6)
Er(1)#3–O(2)	2.242(6)	Er(1)#4–O(4)	2.272(6)
Er(1)–O(1)	2.243(5)		
O(2)#3–Er(1)–O(1)	84.0(2)	O(2)#3–Er(1)–O(4)#5	75.8(3)
O(1)–Er(1)–O(4)#5	110.1(2)	O(2)#3–Er(1)–O(5)	139.7(3)
O(1)–Er(1)–O(5)	78.5(2)	O(4)#5–Er(1)–O(5)	76.7(3)
O(2)#3–Er(1)–O(3)#1	145.6(3)	O(1)–Er(1)–O(3)#1	103.7(2)
O(4)#5–Er(1)–O(3)#1	129.4(3)	O(5)–Er(1)–O(3)#1	74.3(3)
O(2)#3–Er(1)–O(6)#2	78.7(2)	O(1)–Er(1)–O(6)#2	155.1(2)
O(4)#5–Er(1)–O(6)#2	83.0(3)	O(5)–Er(1)–O(6)#2	126.0(2)
O(3)#1–Er(1)–O(6)#2	81.7(3)	O(2)#3–Er(1)–O(7)	77.0(3)
O(1)–Er(1)–O(7)	78.1(2)	O(4)#5–Er(1)–O(7)	150.4(3)
O(5)–Er(1)–O(7)	132.6(3)	O(3)#1–Er(1)–O(7)	72.1(3)
O(6)#2–Er(1)–O(7)	80.6(3)		
$[Er_2(CQC)_3(DMF)_3(H_2O)] \cdot DMF \cdot H_2O$ (**2**)			
Er(1)–O(1)	2.521(7)	Er(1)–O(2)	2.374(8)
Er(2)–O(5)	2.317(7)	Er(2)–O(6)	2.424(8)
Er(2)–O(7)	2.434(7)	Er(2) –O(8)#2	2.296(7)
Er(2)–O(8)	2.830(8)	Er(1)–O(3)	2.328(6)
Er(1)–O(4)#1	2.352(7)	Er(2)–O(9)#2	2.343(6)
Er(2)–O(10)	2.385(7)	Er(1)–O(11)	2.303(7)
Er(1)–O(11)	2.728(8)	Er(1)–O(12)	2.395(7)
Er(2)–O(13)	2.390(7)	Er(2)–O(14)	2.334(10)
Er(1)–O(15)	2.375(7)	Er(1)–O(1W)	2.372(9)

Symmetry codes for **1**: 1 $-x-1/2$, $-y+1/2$, $-z$; #2 $-x$, $-y$, $-z$; #3$-x$, y, $-z+1/2$; #4 $x-1/2$, $y+1/2$, z; #5 $x+1/2$, $y-1/2$, z.
Symmetry codes for **2**: #1$-x$, $-y$, $-z+1$; #2 $-x-1$, $-y+1$, $-z$.

3. Results and discussion

3.1. *Crystal structures*

An atom numbering diagram of the fundamental unit for **1** is shown in figure 1. **1** crystallizes in the monoclinic system, space group *C*2/*c*. There is one

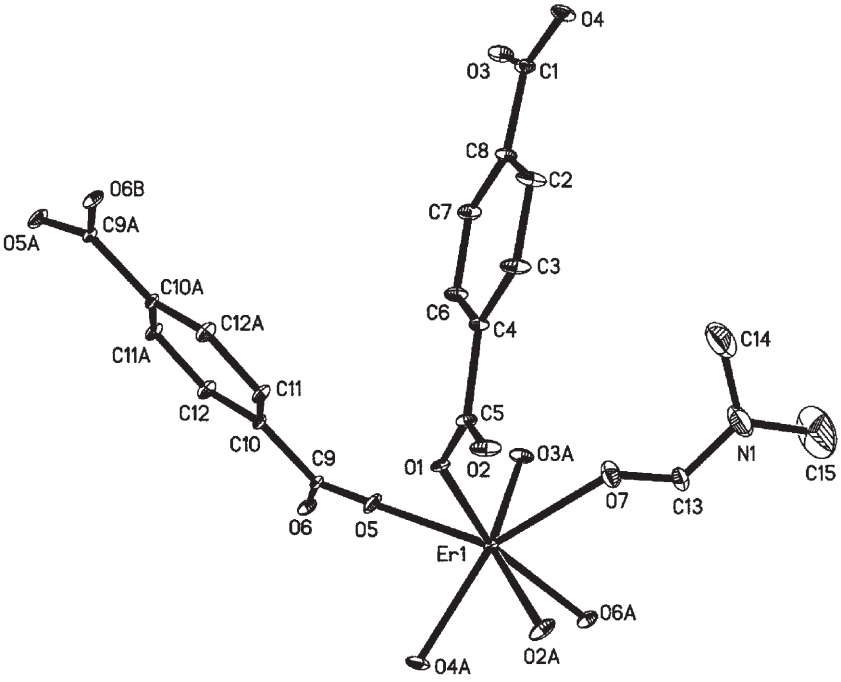

Figure 1. Thermal ellipsoid plot (30%) showing the asymmetric unit of **1**.

crystallographically independent Er(III) ion in the structure. The Er(III) is coordinated by seven oxygen atoms: six from the carboxylate groups of six BDC ligands, and one from a coordinating DMF. The Er–O distances range from 2.242 (6) to 2.341(8) Å, and the O–Er–O angles vary from 72.1(3) to 155.1(2)°, close to those in previously reported Er(III) complexes [10–11]. The dihedral angle between the benzene rings of two BDC ligands containing O1 and O5, respectively, is 56.8°; the two BDC ligands only exhibit one type of coordination mode in the asymmetric unit, with BDC linking four Er(III) ions using its two bridging carboxylate groups. In this coordination mode, the Er(III) atoms are linked through the carboxylate groups of the rod-shaped BDC ligands to generate a three-dimensional framework (figure 2).

Compound **2** features a 2D architecture constructed from dinuclear Er(III) motifs as a secondary building block. As depicted in figure 3, the asymmetric unit of **2** contains two crystallographically independent Er(III) ions. Er(1) is surrounded by nine oxygen atoms, of which seven are from four surrounding CQC ligands, one from a water molecule, and one from a DMF molecule. The Er(2) has a coordination environment similar to that of Er(1), and the Er–O distances for the two erbium atoms are also similar. Noticeably, in the structure of **2** one CQC ligand bridges four Er(III) centers, while the other CQC molecule adopts a new coordination mode in which one carboxylate bridges two Er(III) ions using one oxygen atom, while the other chelates one Er(III) ion. The coordination modes in **2** generate a 2D layer structure with (4, 4) grids (figure 4), each corner of which is occupied by a binuclear Er(III) subunit.

Pure phase of **1** was obtained through pre-heating and cooling-down crystallization process in the presence of DMF, whereas **2** failed to crystallize pure

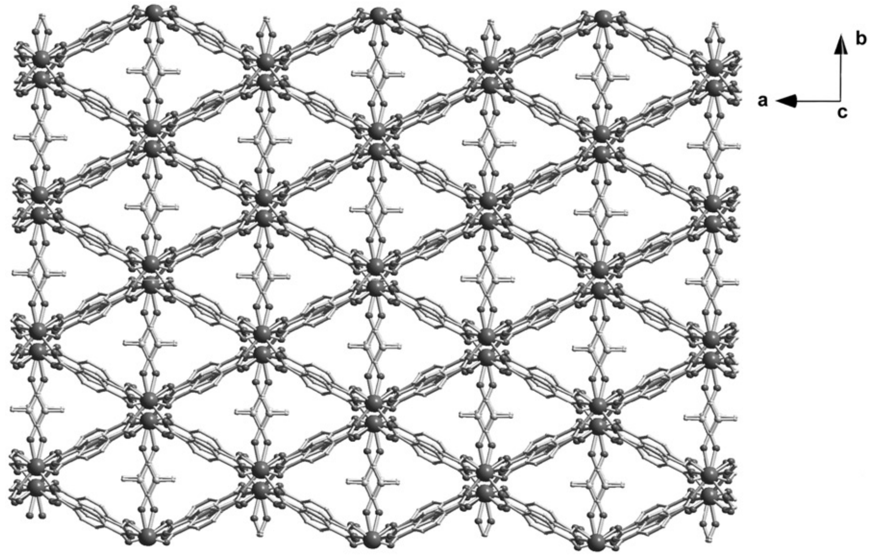

Figure 2. Three-dimensional framework of **1** viewed along the *c*-axis. Hydrogen atoms have been omitted for clarity.

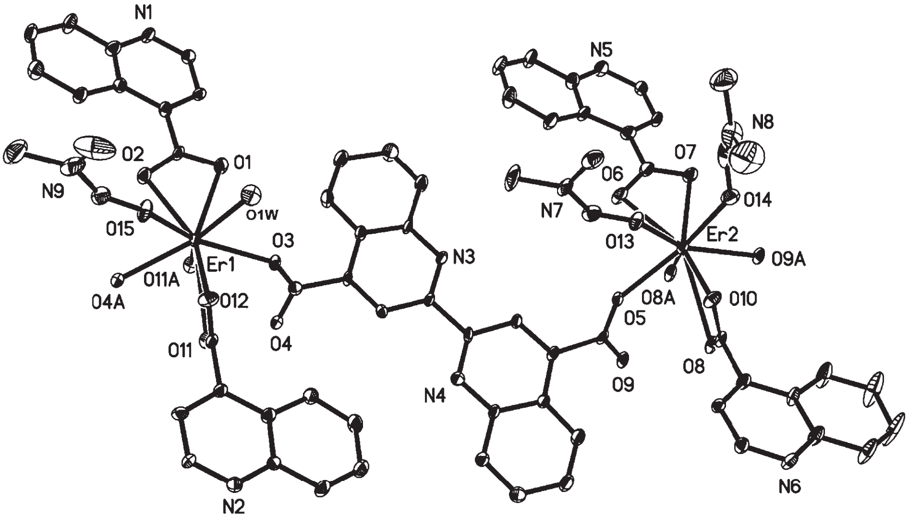

Figure 3. Thermal ellipsoid plot (30%) showing the asymmetric unit of **2**.

from the reaction system. Crystals of CQC always accompanied those of **2** in the final product because of the low solubility in DMF. Consequently, it was not possible to characterize the physico-chemical properties of **2**.

3.2. *X-ray powder diffraction*

The simulated and experimental X-ray powder diffraction patterns of **1** are shown in figure 5. The experimental pattern is in good agreement with the corresponding

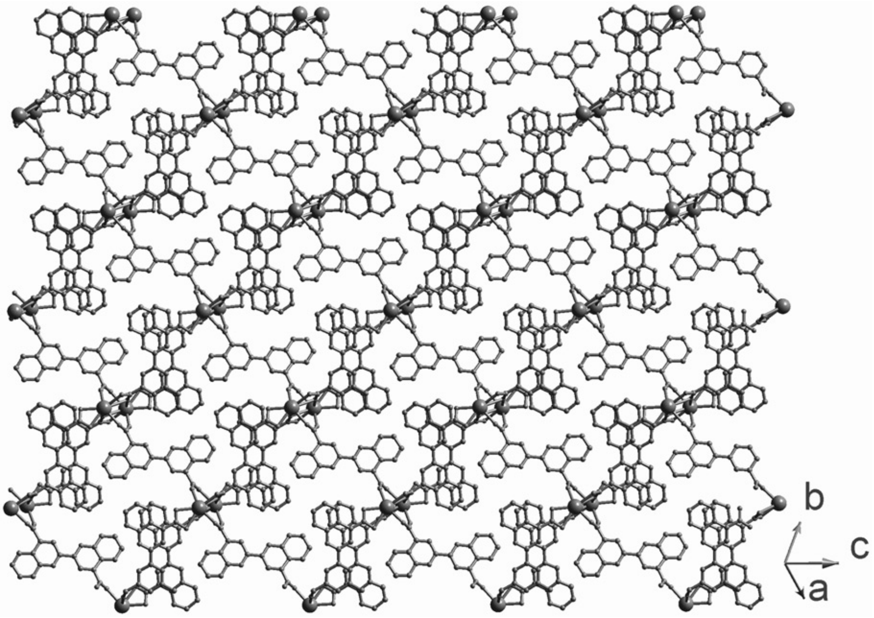

Figure 4. Two-dimensional network of **2**. Hydrogen atoms have been omitted for clarity.

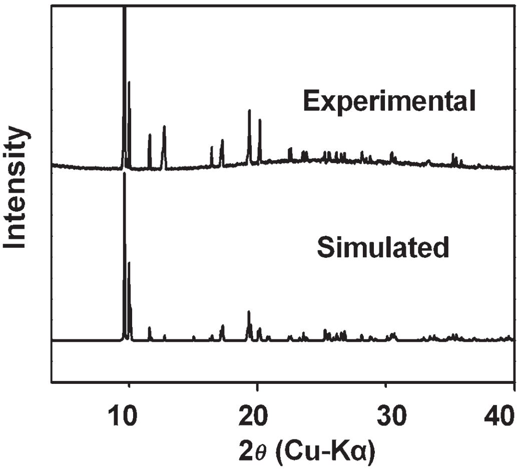

Figure 5. The simulated and experimental X-ray powder diffraction (XRPD) patterns of **1**.

simulated one, indicating phase purity of the as-synthesized product. Phase purity of **1** is also confirmed by elemental and ICP analysis which correspond to the calculated data from the structure formula.

3.3. *IR spectroscopy*

The IR spectrum of **1** shows characteristic bands of BDC at about 1600 cm^{-1} for the asymmetric vibration and at about 1410 cm^{-1} for the symmetric vibration of

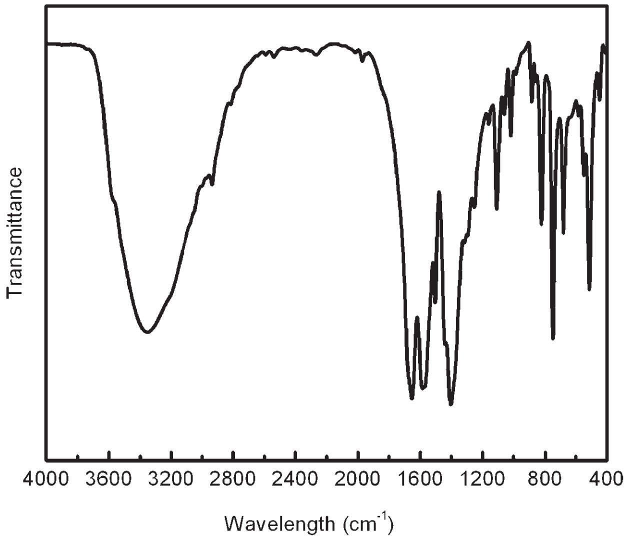

Figure 6. The infrared spectrum of **1**.

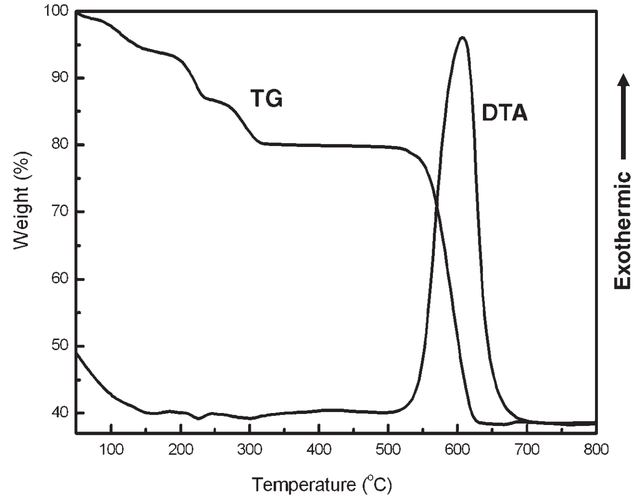

Figure 7. Thermogravimetric (TG) and differential thermal analysis (DTA) curves of **1**.

the aromatic skeleton of the benzene ring (figure 6) [12]. The C–H stretching mode for the phenyl ring is relatively weak at about 3000 cm^{-1}. The absence of the characteristic bands attributed to the protonated carboxylic groups at about 1800 cm^{-1} indicates complete deprotonation of BDC [13].

3.4. *TG–DTA analysis*

To characterize the thermal stability, we conducted thermogravimetric (TG) and differential thermal analyses (DTA) for **1**. The TG-DTA curves (figure 7) were obtained in air for the crystalline sample of **1** in the temperature range of 35 to 800°C. The TG

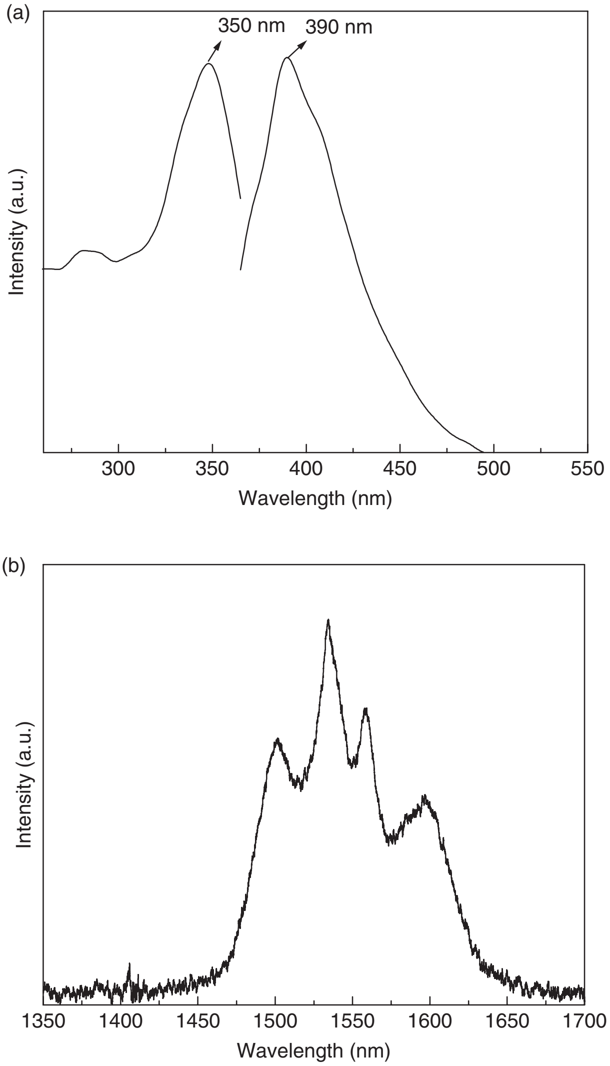

Figure 8. Photoluminescent spectra of free H_2BDC (a) and compound **1** (b) in the solid state at room temperature.

curve exhibits two major weight losses. The first corresponds to removal of DMF at the wide temperature range 35–300°C; the second was in the range 500–615°C attributable to decomposition of BDC. The thermal effect of the first weight is weak but the second loss is accompanied by a distinct exothermic effect, suggesting that the decomposition is intense.

3.5. *Photoluminescent property*

Near-IR-emitting materials based on rare-earth compounds have attracted attention as candidates for active components in near-IR-luminescent optical devices [14].

The solid-state photoluminescent spectra of **1** and free H_2BDC were recorded at room temperature and are shown in figure 8. The H_2BDC exhibits a fluorescent emission band at 390 nm ($\lambda_{ex} = 350$ nm), which is attributable to $\pi^* \rightarrow n$ transitions (figure 8a) [15]. The crystal sample of **1** shows the characteristic emission of Er(III) around 1535 nm upon excitation at 488 nm. This emission is associated with the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition (figure 8b). The emission arising from free ligand is not observed for **1**, suggesting energy transfer from the ligand to the Er(III) center during photoluminescence.

The hydrothermal method has been frequently used to synthesize carboxylate lanthanide complexes, whereas the pre-heating and cooling-down crystallization approach, in the presence of a non-aqueous solvent, was employed only occasionally. Hydrothermally formed lanthanide complex compounds usually contain coordinating water which quenches the luminescence of the lanthanide centers. Consequently lanthanide complexes synthesized from a hydrothermal system emit weak or no light upon excitation. Although **2** contains coordinating water, **1** is water-free, and exhibits significant photoluminescent intensity and may find applications as a photoactive material due to its strong near-IR emission.

4. Conclusion

Two rare-earth coordination polymers $[Er_2(BDC)_3(DMF)_2]$ (**1**) and $[Er_2(CQC)_3(DMF)_3(H_2O)] \cdot DMF \cdot H_2O$ (**2**) have been synthesized through pre-heating and cooling-down crystallization process in a non-aqueous medium. **1** possesses a three-dimensional framework structure in which the Er(III) centers are linked by rod-shaped BDC ligands, whereas **2** shows a 2D structure which is based on dinuclear Er(III) building units. The intense near-IR luminescence indicates that **1** is potentially useful as a photoactive material.

Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-609775 and 635806. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44) 1223 336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

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