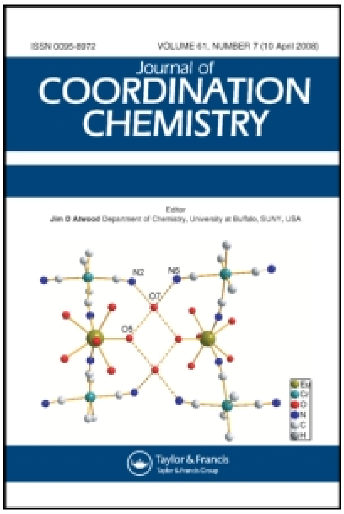

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Syntheses, crystal structures, and luminescence of carboxylato-bridged coordination compounds

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Two 2-D metal carboxylate coordination compounds $[Tb(pydc)(ox)_{1/2}(H_2O)_2]$ (**1**) and $[Cd(pydc)(me)(H_2O)]_2 \cdot H_2O$ (**2**) (pyridine-2,5-dicarboxylic acid = pydc, oxalic acid = ox, me = methanol) have been synthesized under hydrothermal conditions. Carboxylates are building blocks in the formation of zigzag chain and cockle stair-like chain structures for **1** and **2**, respectively. Both the compounds have been structurally determined by single-crystal X-ray diffraction, and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and fluorescence spectra.

Keywords: Hydrothermal condition; Coordination compounds; Pyridine-2,5-dicarboxylic acid; Oxalic acid; Luminescence

1. Introduction

Metal-organic frameworks (MOFs) have been of interest in supramolecular chemistry and crystal engineering for potential applications in molecular magnetism, catalysis, gas sorption, electrical conductivity, and optics [1] and also intriguing architectures and topologies [2]. Lanthanide ions have been of considerable interest in constructing MOF structures due to their high coordination numbers, flexible coordination magnetism, and luminescence [3]. MOF structures can be tuned by introducing different bridging ligands and carboxylates which are very important [4]. We establish lanthanide MOFs with pyridine-2,5-dicarboxylate (pydc) and oxalate (ox) bridging ligands. Both bridging ligands are excellent spacers in constructing MOF structures [5, 6]. Herein, we report hydrothermal synthesis, crystal structure, thermal stability, and luminescence of two new MOFs, $Tb(pydc)(ox)_{1/2}(H_2O)_2$ (**1**) and $[Cd(pydc)(me)(H_2O)]_2 \cdot H_2O$ (**2**).

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2. Experimental

2.1. *Materials and methods*

All chemicals employed were commercially available and used as received without purification. Elemental (C, H, N) analysis was performed on a Perkin-Elmer 2400 element analyzer. The infrared (IR) spectra were recorded from 400 to 4000 cm^{-1} on a Perkin-Elmer 17300 FT-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with the heating rate of $10^\circ C\,min^{-1}$ from 50 to 850°C under nitrogen. Fluorescence spectra were recorded with an F-2500 FL Spectrophotometer analyzer.

2.2. *Hydrothermal synthesis*

2.2.1. $Tb(pydc)(ox)_{1/2}(H_2O)_2$ (1). A mixture of $Tb(NO_3)_3$ (690 mg, 0.2 mmol), pydc (668 mg, 0.4 mmol), and oxalic acid (270 mg, 0.3 mmol) in H_2O (10 mL) was sealed in a 25-mL Teflon-lined autoclave at 150°C for 3 days, and then slowly cooled to room temperature at a cooling rate of $5^\circ C\,h^{-1}$. Colorless crystals of **1** were obtained by filtration, and air dried, with yield of 78%. Elem. Anal. Calcd for $C_8H_7NO_8Tb$ (404.07): C, 23.78; H, 1.75; N, 3.47. Found: C, 23.68; H, 1.79; N, 3.45%. IR(KBr): ν(O–H) 3388 s, ν_{as} (CO_2) 1676 s, ν_{as} (CO_2) 1610 vs, ν_s (CO_2) 1429 m, ν_s (CO_2) 1357 s.

2.2.2. $[Cd(pydc)(me)(H_2O)]_2 \cdot H_2O$ (2). A mixture of $CdCl_2 \cdot 2.5H_2O$ (684 mg, 0.3 mmol) and pydc (668 mg, 0.4 mmol) in a methanol solution ($CH_3OH/H_2O = 5$ mL: 5 mL) with pH = 6, adjusted by triethylamine, was sealed in a 25-mL Teflon-lined autoclave at 160°C for 3 days and then slowly cooled to room temperature at a cooling rate of $5^\circ C\,h^{-1}$. Colorless crystals of **2** were obtained by filtration, and air dried, with yield of 70%. Elem. Anal. Calcd for $C_{16}H_{20}Cd_2N_2O_{13}$ (673.16): C, 28.55; H, 2.99; N, 4.16. Found: C, 28.66; H, 2.89; N, 4.15%. IR(KBr): ν(O–H) 3326 s, ν_{as} (CO_2) 1625 s, ν_s (CO_2) 1392 m, ν_s (CO_2) 1357 s.

2.3. *X-ray crystallography*

Single crystal X-ray diffraction data collection for **1** 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 [7]. The compound structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package [8]. Hydrogens were located from difference Fourier maps and 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*

Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$. X-ray crystallographic analysis shows a 2-D structure. The structure unit of **1** contains one Tb(III), one pydc,

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

	1	**2**
Formula	$C_8H_7NO_8Tb$	$C_{16}H_{20}Cd_2N_2O_{13}$
M	404.08	673.16
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pca2_1$
Units of dimensions (Å, °)		
a	7.49440(1)	7.6166(15)
b	8.49660(1)	11.083(2)
c	9.56550(1)	21.141(4)
α	77.4560(1)	90
β	75.9420(1)	90
γ	69.6190(1)	90
V (Å^3)	547.950(1)	1784.6(6)
T (K)	298(2)	293(2)
D_c (g cm^{-3})	2.449	2.468
Z	2	4
μ(Mo-Kα) (mm^{-1})	6.488	2.468
Crystal size (mm^3)	0.201 × 0.199 × 0.187	0.31 × 0.25 × 0.19
θ range for data collection (°)	2.22–27.92	1.84–27.90
Independent reflections (R_{int})	0.0241	0.0675
R_1[a]/wR_2[b]	0.0188/0.0408	0.0478/0.1456

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

one half of ox and coordinated water molecules (figure 1a). The Tb(III) ion is eight-coordinated by one pydc–N atom, three pydc–O atoms, two ox–O atoms, and two aqua ligands. The coordination geometry of Tb(III) can be described as a distorted square antiprism. The Tb–O (carboxylate) bond lengths range from 2.285(2) to 2.389(2) Å, and Tb–O (aqua) are 2.377(3) and 2.423(3) Å. The Tb–N bond length is 2.530(2) Å. The O–Tb–O bond angle ranges from 67.37(7) to 144.09(8)°, while the O–Tb–N bond angle ranges from 64.92(7) to 143.31(8)°.

There is only one coordination mode for pydc in the structure for **1**, as shown in figure 2(a), a chelate-bridging mode chelating one Tb(III) ion and bridging two Tb(III) ions. Each Tb(III) chelates one N and one O and also bridges two O atoms. Adjacent Tb(III) are bridged *via* two carboxylate groups of pydc, giving a eight-membered chelating ring; the rings form an infinite 1-D chain alternately (A) *via* pydc bridges (figure 3b). The A-type chains connect through hydrogen bonds [O1–H3W, 1.91(4) Å, table 3] to form a 2-D layer.

Oxalic acid has the second ligand bridge, the eight-membered ring (figure 3b) by chelating the Tb(III) ions resulting in a 1-D zigzag chain (B), then neighboring chains are linked by pydc ligands leading to wavelike 2-D networks (figure 3c). The two types of 2-D layers intersect at Tb(III) (figure 3), thus forming a 3-D (6,5)-connected block-like framework network. The topology of this compound is shown in figure 3(d).

3.2. *Crystal structure of 2*

Compound **2** crystallizes in the orthorhombic system, space group *Pca2₁*. The asymmetric unit of **2** is a binuclear structure with two Cd(II) ions, two pydc,

Table 2. Selected bond distances (Å) and angles (°) for **1**[a] and **2**[b].

1			
Tb(1)–O(7)#1	2.285(2)	Tb(1)–O(8)#2	2.333(2)
Tb(1)–O(2)	2.344(2)	Tb(1)–O(2W)	2.377(3)
Tb(1)–O(4)	2.389(2)	Tb(1)–O(1W)	2.423(3)
Tb(1)–O(3)#3	2.442(2)	Tb(1)–N(1)	2.530(2)
O(7)#1–Tb(1)–O(8)#2	108.25(8)	O(7)#1–Tb(1)–O(2)	87.98(8)
O(2W)–Tb(1)–O(4)	137.39(9)	O(2)–Tb(1)–O(4)	109.79(8)
O(8)#2–Tb(1)–O(4)	77.24(8)	O(2)–Tb(1)–O(2W)	78.83(10)
O(8)#2–Tb(1)–O(2W)	72.67(10)	O(7)#1–Tb(1)–O(4)	144.09(8)
O(7)#1–Tb(1)–O(2W)	75.26(9)	O(8)#2–Tb(1)–O(2)	141.78(8)
O(3)#3–Tb(1)–N(1)	136.52(7)	O(1W)–Tb(1)–N(1)	112.38(9)
O(4)–Tb(1)–N(1)	71.65(7)	O(2W)–Tb(1)–N(1)	75.52(9)
O(2)–Tb(1)–N(1)	64.92(7)	O(8)#2–Tb(1)–N(1)	83.42(8)
O(7)#1–Tb(1)–N(1)	143.31(8)	O(1W)–Tb(1)–O(3)#3	72.38(9)
O(4)–Tb(1)–O(3)#3	67.37(7)	O(2W)–Tb(1)–O(3)#3	129.04(9)
O(2)–Tb(1)–O(3)#3	143.92(8)	O(8)#2–Tb(1)–O(3)#3	74.13(8)
O(7)#1–Tb(1)–O(3)#3	79.84(7)	O(4)–Tb(1)–O(1W)	77.53(9)
O(2W)–Tb(1)–O(1W)	141.41(10)	O(2)–Tb(1)–O(1W)	71.99(9)
O(8)#2–Tb(1)–O(1W)	143.79(9)	O(7)#1–Tb(1)–O(1W)	78.97(9)
2			
Cd(1)–O(3W)	2.207(6)	Cd(1)–O(10)	2.240(8)
Cd(1)–O(7)#2	2.280(11)	Cd(1)–O(5)	2.306(11)
Cd(1)–O(1)	2.342(10)	Cd(1)–N(1)	2.367(8)
Cd(2)–O(2W)	2.216(8)	Cd(2)–O(9)	2.267(7)
Cd(2)–O(4)#3	2.273(10)	Cd(2)–N(2)	2.303(9)
O(3W)–Cd(1)–O(10)	150.3(3)	O(3W)–Cd(1)–O(7)#2	83.5(3)
O(10)–Cd(1)–O(7)#2	88.8(3)	O(3W)–Cd(1)–O(5)	82.2(3)
O(10)–Cd(1)–O(5)	85.4(3)	O(7)#2–Cd(1)–O(5)	139.6(2)
O(3W)–Cd(1)–O(1)	92.1(3)	O(10)–Cd(1)–O(1)	109.5(3)
O(7) #2–Cd(1)–O(1)	146.2(4)	O(5)–Cd(1)–O(1)	72.0(4)
O(3W)–Cd(1)–N(1)	116.8(3)	O(10)–Cd(1)–N(1)	90.4(3)
O(7)#2–Cd(1)–N(1)	83.0(4)	O(5)–Cd(1)–N(1)	136.8(3)
O(1)–Cd(1)–N(1)	69.1(3)	O(2W)–Cd(2)–O(9)	153.9(3)
O(2W)–Cd(2)–O(4)#3	89.3(4)	O(9)–Cd(2)–O(4)#3	82.4(4)
O(2W)–Cd(2)–N(2)	89.5(3)	O(9)–Cd(2)–N(2)	114.5(4)
O(4)#3–Cd(2)–N(2)	86.2(3)	O(2W)–Cd(2)–O(1)	85.7(4)
O(9)–Cd(2)–O(1)	83.9(4)	O(4)#3–Cd(2)–O(1)	137.6(3)
N(2)–Cd(2)–O(1)	135.7(3)	O(2W)–Cd(2)–O(5)	107.8(3)
O(9)–Cd(2)–O(5)	91.0(3)	O(4)#3–Cd(2)–O(5)	149.9(3)
N(2)–Cd(2)–O(5)	69.8(3)	O(1)–Cd(2)–O(5)	70.0(3)

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

two methanols, two coordinated water molecules and one lattice water (figure 3a). Each cadmium is six-coordinate with distorted octahedral coordination. The Cd1–O and Cd2–O bond lengths are in the range of 2.207–2.342 and 2.216–2.416 Å, respectively. The Cd1–N and Cd2–N bond lengths are 2.367 and 2.303 Å; O–Cd–O angles range from 70.0(3) to 150.3(3)°, and the O–Cd–N bond angles range from 69.1(3) to 136.8(3)°.

The pydc is quadridentate coordination (figure 2b) and links cadmium ions to form a 1-D cockle stair-like chain with Cd $\cdots$ Cd distances of 9.080 and 7.337 Å (figure 3b). While two pydc ligands link two cadmiums *via* two O to form a binuclear cluster $(CdO_4N)_2$ with a Cd $\cdots$ Cd separation of 3.831 Å, this distance is similar to those of reported cadmium complexes [9]. The adjacent 1-D chains are connected by Cd_2 clusters, and a 2-D grid layer is formed along the *b*-axis (figure 3c).

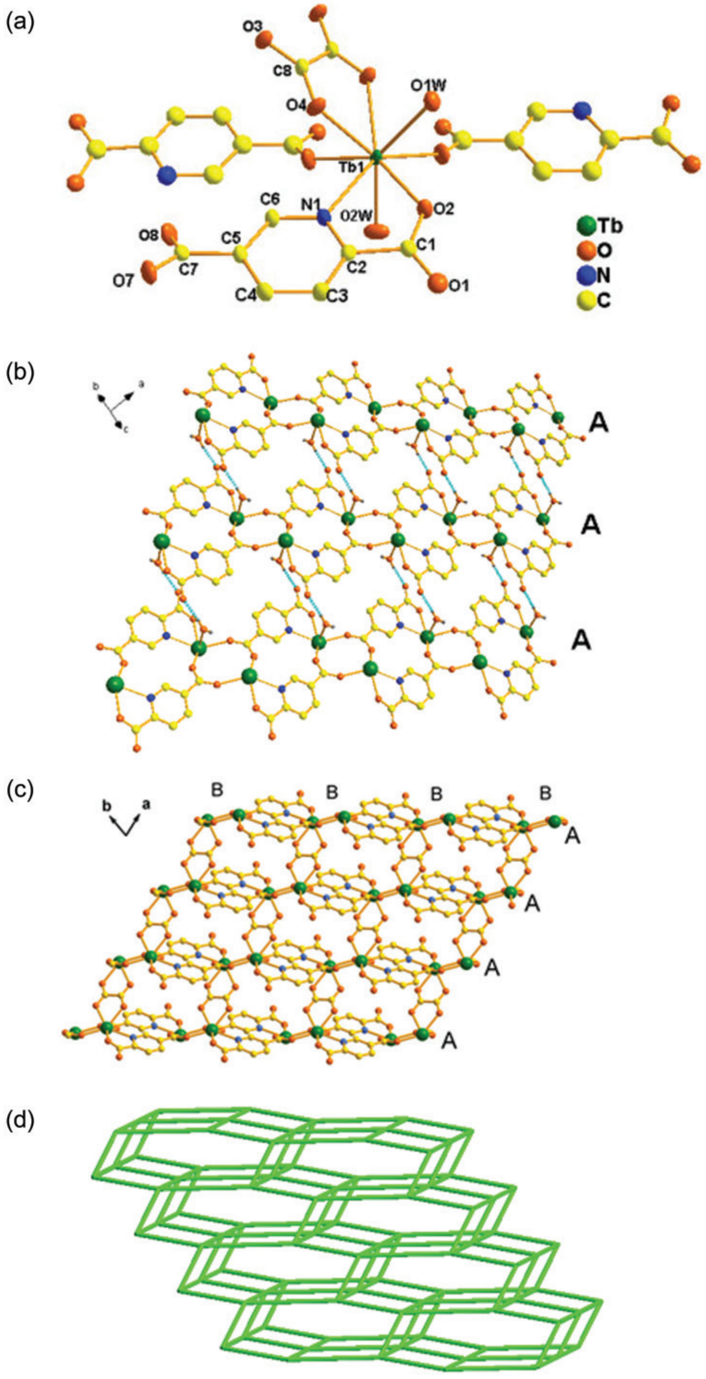

Figure 1. (a) The structure unit of **1**. (b) The 2-D layer formed by hydrogen bonds. (c) The wavelike 2-D layer based on oxalate bridges; and (d) Topology of the brick-wall framework for **1**.

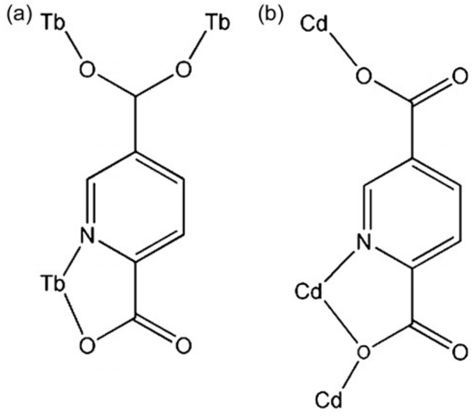

Figure 2. Coordination modes for pydc in (a) **1** and (b) **2**.

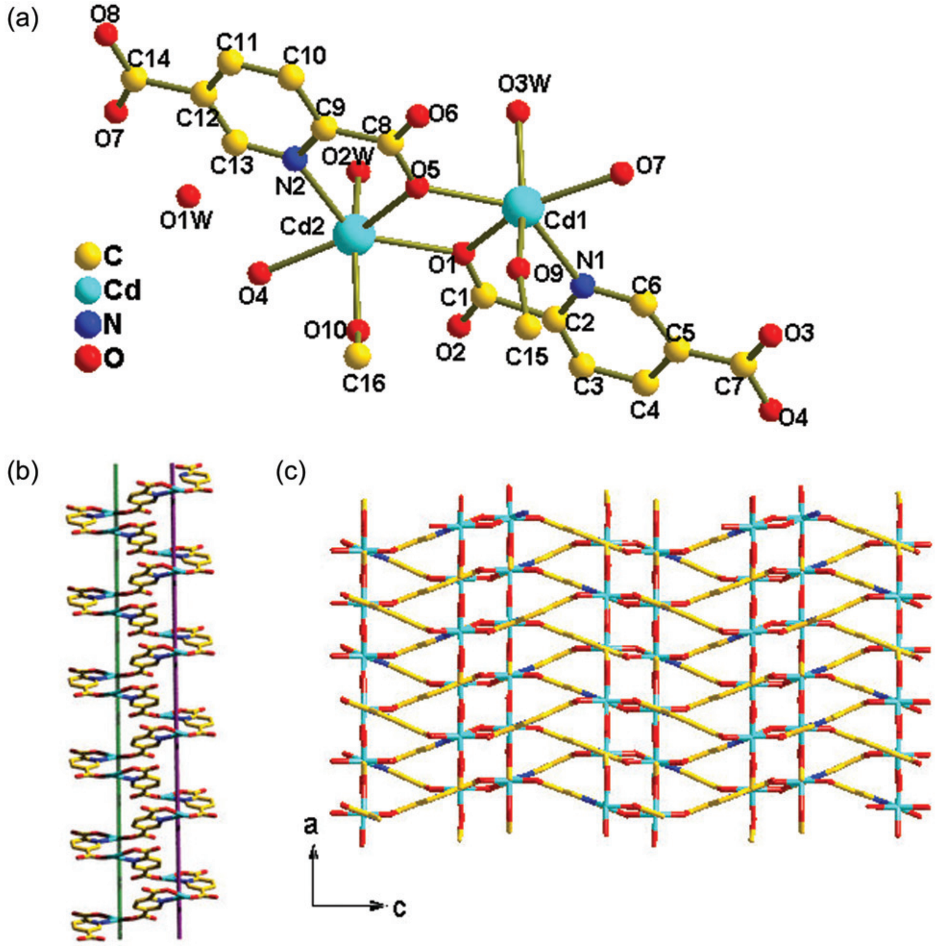

Figure 3. (a) The asymmetric unit of **2**. (b) The 1-D cockle stair-like chains; and (c) The 2-D grid layer running along the *b*-axis.

3.3. *Luminescent property*

The solid-state luminescent properties of **1** and **2** were investigated at room temperature. The emission spectra of **1**, **2**, and pydc are shown in figure 4. Excitation of **1** at 239 nm reveals the characteristic transition of the Tb(III) ion at 492, 543, 585, and 620 nm, attributed to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$, respectively. The most intense emission band at 543 nm suggests that the ligand sensitizes green luminescence for the Tb(III) ion. Compound **2** shows strong photoluminescent emission mainly from 400 to 500 nm ($\lambda_{max} = 450$ nm) with excitation at 311 nm, while the emission broadband of pydc mainly ranges from 350 to 450 nm with one peak at 392 nm. However, there is no ligand-based emission in the fluorescence spectra of **2**, suggesting that energy transfer from the ligand to the metal is effective, and assignment to ligand–metal charge transfer.

3.4. *Thermogravimetric analysis*

Thermogravimetric analysis curves have been obtained in N_2 for crystalline samples of **1** and **2** from 50 to 850°C. The first weight loss of 8.32% from 50 to 265°C for **1** corresponds to removal of lattice water. There is a flat line between 265 and 390°C, which

Table 3. Hydrogen bonds for **1** (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	(DHA)
O(2W)–H(3W)···O(1)#5	0.78(4)	1.91(4)	2.683(4)	175(4)
O(1W)–H(2W)···O(2)#6	0.93(4)	1.85(5)	2.737(3)	160(4)
O(2W)–H(4W)···O(3)#7	0.64(4)	2.18(5)	2.818(4)	173(5)
O(1W)–H(1W)···O(3)#3	0.73(5)	2.50(5)	2.873(4)	114(5)
O(1W)–H(1W)···O(1)#6	0.73(5)	2.51(5)	2.946(3)	120(5)

Symmetry transformations used to generate equivalent atoms: #3: $-x, -y, -z+1$; #5: $-x+1, -y+1, -z$; #6: $-x+1, -y, -z$; #7: $x+1, y, z$.

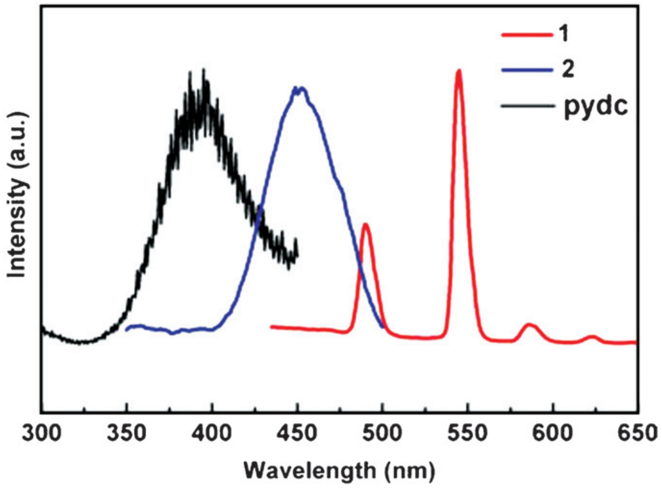

Figure 4. Solid-state emission spectrum for **1**, **2**, and pydc at room temperature.

means the dehydrated framework is stable. The second weight loss happens between 390 and 850°C, attributed to loss of all organic components. Compound **2** first loses lattice water below 100°C, and coordinated water from 100 to 175°C. The TG curve of the dehydrated product shows no weight loss to 325°C, followed by a step weight loss of 53.3% from 325 to 850°C. The final weight is 38.5% for CdO (Calcd: 38.2%).

4. Conclusions

We have synthesized two new coordination compounds $Tb(pydc)(ox)_{1/2}(H_2O)_2$ (**1**) and $[Cd(pydc)(me)(H_2O)]_2 \cdot H_2O$ (**2**) under hydrothermal conditions. Compound **1** exhibits a wavelike 2-D network with infinite 1-D zigzag chains (B), while weak hydrogen-bonding interactions make a 3-D network. Compound **2** possesses a 2-D grid layer, which contains 1-D cockle stair-like chains and binuclear $(CdO_4N)_2$. The difference in coordination modes of the pyridine-2,5-dicarboxylic acids and oxalic acids exert an important influence on the resulting frameworks. Moreover, **1** displays the characteristic transition of the Tb(III) ion ($\lambda_{max} = 543$ nm), and **2** shows the emission of $\lambda_{max} = 450$ nm at room temperature, suggesting energy transfer from the ligand to the metal.

Supplementary material

CCDC-694095 and 707334 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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