

Synthesis, Structure and Luminescent Properties of Rare Earth Coordination Polymers Constructed from Paddle-Wheel Building Blocks

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A series of three-dimensional (3D) novel coordination polymers $M(\text{bpdc})_{1.5}(\text{H}_2\text{O}) \cdot 0.5\text{DMF}$ ($M = \text{Tb}$ (1), Ho (2), Er (3), or Y (4)) have been synthesized by reaction of the rare earth ions (M^{3+}) with 4,4'-biphenyldicarboxylic acid (H_2bpdc) in a mixed solution of DMF and $\text{C}_2\text{H}_5\text{OH}$. They possess the same 3D architectures and crystallize in monoclinic space group $C2/c$. Two seven-coordinated metal centers and four didmonodentate bpdc groups construct a paddle-wheel building block. These building blocks connect with two carboxyl groups to lead to a one-dimensional inorganic chain, $\text{---M---O---C---O---M---}$, along the [001] direction. The inorganic chains are linked with two biphenyl groups to form $25.15 \text{ \AA} \times 17.09 \text{ \AA}$ rhombic channels along the c axis without interpenetration. These complexes exhibit strong fluorescence in the visible region, and complex 3 shows Er^{3+} characteristic emission in the range of 1450–1650 nm at room temperature. These complexes could be anticipated as potential fluorescent probes and an IR-emitter, respectively.

Introduction

Metal–organic framework (MOF) coordination polymers with rigid and open frameworks have received intense attention for their potential applications in catalysis, gas storage, molecular recognition, optics, and magnetism.¹ To get designed and predictable frameworks and properties, an enormous amount of research is being focused on constructing novel coordination polymers by choosing versatile organic ligands and functional metal ions.² As functional metal centers, rare earth metals are attracting more and more attention from synthesis chemists for their fantastic coordination properties and special chemical characteristics arising from 4f electrons and the propensity to form isostructural complexes.^{2c,3} Many coordination polymers based on rare earths have been synthesized, and most of them exhibit

amazing optical and magnetic properties, enabling them as fluorescent probes and IR-emitters.^{2c,4} However, as the high-coordination number and flexible coordination geometry of rare earth ions make it difficult to control the preparation of rare earth complexes, the analogous complexes based on rare earth ions are still uncommon compared with those of transition metals.⁵ As known, rare earth ions have high affinity for hard donor atoms and ligands containing oxygen or hybrid oxygen–nitrogen atoms, especially multicarboxylate ligands, which are usually employed in the architectures for lanthanide coordination polymers.⁶ As a dicarboxylate

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Table 1. Crystallographic Data for Complexes 1–4

	1	2	3	4
empirical formula	C _{22.5} H _{17.5} TbO _{7.5} N _{0.5}	C _{22.5} H _{17.5} HoO _{7.5} N _{0.5}	C _{22.5} H _{17.5} ErO _{7.5} N _{0.5}	C _{22.5} H _{17.5} YO _{7.5} N _{0.5}
fw	573.8	579.8	582.2	503.8
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/c	C2/c	C2/c	C2/c
a (Å)	25.3477(8)	25.2219(14)	25.1508(11)	25.1904(14)
b (Å)	17.1399(8)	17.0779(14)	17.0903(11)	17.1122(14)
c (Å)	18.4904(8)	18.5141(12)	18.5354(10)	18.5799(12)
α (deg)	90	90	90	90
β (deg)	107.3250(10)	106.887(2)	106.6730(10)	106.789(2)
γ (deg)	90	90	90	90
V (Å ³)	7668.8(5)	7630.8(9)	7632.2(7)	7667.7(9)
Z	8	8	8	8
T (K)	298(2)	298(2)	298(2)	298(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ _{calc} (g·cm ⁻³)	0.931	0.946	0.946	0.960
μ (mm ⁻¹)	1.865	2.094	2.220	1.542
R ^a (I > 20σ(I))	0.0733	0.0613	0.0599	0.0745
R _w ^b	0.1917	0.1333	0.1355	0.1868

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_w = [\sum w(F_o^2 - F_c^2) / \sum w(F_o^2)]^{1/2}.$$

ligand, 4,4'-biphenyldicarboxylic acid (H₂bpdc) possesses the following interesting characteristics: (a) There are only two carboxyl groups with a 180° angle, which is helpful to reduce space hindrance. (b) Biphenyl groups could form rigid frameworks and large channels.^{2a,7} Recently, a series of coordination polymers based on rare earth metals with 4,4'-biphenyldicarboxylic acid prepared by solvothermal synthesis were reported, but they were shown to be three-dimensional (3D) sandwich structures without any channels.⁷ Taking account of the above, we employ a vapor diffusion method at a lower temperature to assemble 4,4'-biphenyldicarboxylic acid and rare earth ions into coordination polymers with an open framework. We hope that a lower temperature may be helpful for the formation of lower coordination number rare earth ions and open frameworks. In this paper, we report four 3D coordination polymers with 25.15 Å × 17.09 Å rhombic channels, M(bpdc)_{1.5}(H₂O)·0.5DMF (M = Tb (**1**), Ho (**2**), Er (**3**), or Y (**4**)), successfully synthesized by a vapor diffusion method at a lower temperature than previously reported.

Experimental Section

All chemicals purchased were of reagent grade or better and were used without further purification. Rare earth nitrate salts were prepared via dissolving rare earth oxides with 6 M HNO₃ while adding a bit of H₂O₂ for Tb₄O₇ and then evaporated at 100 °C until the crystal film formed. Fluorescence spectroscopy data were recorded on a LS55 luminescence spectrometer. The elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer. Emission spectra of solid-state samples were obtained (1450–1650 nm) with a J-Y TR550 single spectrometer equipped with a R928 photomultiplier tube. The infrared (IR) spectra were recorded (400–4000 cm⁻¹ region) on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. TGA (thermal gravimetric analyses) were performed under nitrogen with a heating rate of 10 °C/min using a Perkin-Elmer TGA 7 thermogravimetric analyzer.

Synthesis of Tb(bpdc)_{1.5}(H₂O)·0.5DMF (1**).** A mixture of Tb(NO₃)₃·nH₂O (40 mg, 0.10 mmol) and 4,4'-H₂bpdc (10 mg, 0.05 mmol) was dissolved in *N,N'*-dimethylformamide (DMF) (10 mL) and ethanol (2 mL) at room temperature, and this new mixture was placed in a 20 mL test tube. Then a small vial containing triethylamine (0.1 mL) and DMF (1.5 mL) was put in the test tube. The test tube was left undisturbed at 4 °C for 15 days and 55 °C

for 7 days to give colorless crystals. Yield: 62%. Anal. Calcd for C_{22.5}H_{17.5}TbO_{7.5}N_{0.5} (*M_r* = 573.8): C, 47.08; H, 3.08; N, 1.22. Found: C, 45.48; H, 3.18; N, 1.17.

Synthesis of Ho(bpdc)_{1.5}(H₂O)·0.5DMF (2**).** The procedure was the same as that for **1** except that Tb(NO₃)₂·nH₂O was replaced by Ho(NO₃)₃·nH₂O (40 mg, 0.1 mmol). Yield: 67%. Anal. Calcd for C_{22.5}H_{17.5}HoO_{7.5}N_{0.5} (*M_r* = 579.8): C, 46.59; H, 3.04; N, 1.21. Found: C, 45.08; H, 3.16; N, 1.26.

Synthesis of Er(bpdc)_{1.5}(H₂O)·0.5DMF (3**).** The procedure was the same as that for **1** except that Tb(NO₃)₂·nH₂O was replaced by Er(NO₃)₃·nH₂O (40 mg, 0.1 mmol). Yield: 55%. Anal. Calcd for C_{22.5}H_{17.5}ErO_{7.5}N_{0.5} (*M_r* = 582.2): C, 46.51; H, 3.04; N, 1.21. Found: C, 44.88; H, 3.26; N, 1.06.

Synthesis of Y(bpdc)_{1.5}(H₂O)·0.5DMF (4**).** The procedure was the same as that for **1** except that Tb(NO₃)₂·nH₂O was replaced by Y(NO₃)₃·nH₂O (40 mg, 0.1 mmol). Yield: 58%. Anal. Calcd for C_{22.5}H_{17.5}YO_{7.5}N_{0.5} (*M_r* = 503.8): C, 53.62; H, 3.50; N, 1.39. Found: C, 52.01; H, 3.66; N, 1.46.

X-ray Crystallographic Study. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at room temperature in the ω–2θ scan mode. An empirical absorption correction was applied to the data using the SADABS program.⁹ The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. All calculations were performed using the SHELXL program.¹⁰ The crystallographic data are summarized in Table 1, and selected bond lengths and bond angles of the four complexes are listed in Tables 2 and 3, respectively.

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Table 2. Selected Bond Lengths (Å) for Complexes 1–4

Complex 1 ^a			
Tb(1)–O(1)	2.363(4)	Tb(1)–O(2) ^{#2}	2.299(4)
Tb(1)–O(3)	2.313(4)	Tb(1)–O(4) ^{#2}	2.332(4)
Tb(1)–O(5)	2.307(4)	Tb(1)–O(6) ^{#1}	2.269(4)
Tb(1)–O(7)	2.415(5)	Tb(1)–O(2) ^{#2}	2.298(4)
Tb(1)–O(4) ^{#2}	2.333(4)	Tb(1)–O(6) ^{#1}	2.269(4)
Complex 2			
Ho(1)–O(1)	2.269(6)	Ho(1)–O(2)	2.274(5)
Ho(1)–O(3)	2.303(5)	Ho(1)–O(4)	2.264(6)
Ho(1)–O(5)	2.314(6)	Ho(1)–O(6)	2.301(6)
Ho(1)–O(7)	2.405(7)		
Complex 3 ^b			
Er(1)–O(1) ^{#2}	2.295(5)	Er(1)–O(2)	2.280(5)
Er(1)–O(3) ^{#2}	2.251(6)	Er(1)–O(4)	2.331(5)
Er(1)–O(5) ^{#3}	2.271(4)	Er(1)–O(6) ^{#1}	2.229(5)
Er(1)–O(7)	2.374(7)	O(1)–Er(1) ^{#2}	2.295(5)
O(3)–Er(1) ^{#2}	2.251(6)	O(5)–Er(1) ^{#4}	2.272(4)
O(6)–Er(1) ^{#5}	2.229(5)		
Complex 4			
Y(1)–O(1)	2.323(3)	Y(1)–O(2)	2.239(4)
Y(1)–O(3)	2.295(4)	Y(1)–O(4)	2.282(3)
Y(1)–O(5)	2.381(4)	Y(1)–O(6)	2.263(4)
Y(1)–O(7)	2.310(3)		

^a Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, y, -z + 1/2$; (#2) $-x + 1, -y + 1, -z$. ^b Symmetry transformations used to generate equivalent atoms: (#1) $-x + 5/2, y + 1/2, -z + 1/2$; (#2) $-x + 2, -y + 2, -z$; (#3) $x - 1/2, y + 1/2, z$; (#4) $x + 1/2, y - 1/2, z$; (#5) $-x + 5/2, y - 1/2, -z + 1/2$.

Results and Discussion

Complexes 1–4 have been successfully synthesized by the vapor diffusion method. Single-crystal X-ray diffraction, elemental analysis, and TGA analysis studies performed on the complexes 1–4 reveal that they are identical in structure with the formula $M(\text{bpdc})_{1.5}(\text{H}_2\text{O}) \cdot 0.5\text{DMF}$ ($M = \text{Tb}$ (1), Ho (2), Er (3), or Y (4)). Thus, we will restrict our presentation and discussion to the terbium complex.

Crystal Structure of Complex 1. An X-ray diffraction study performed on complex 1 reveals that each asymmetric unit contains one seven-coordinated rare earth ion (Tb), one and a half bpdc ligands, and one water molecule. The terbium atom is coordinated with six oxygen atoms (O1–O6) from six bpdc groups and one oxygen atom (O7) from a terminal water molecule. The carboxylic O–Tb bond distances range 2.269(4)–2.363(4) Å and Tb–O_{wt} is 2.415(4) Å, all of which are comparable to those reported for other terbium–oxygen donor complexes.^{2c} Two crystallographically equivalent Tb atoms are bridged by four bpdc groups in a dimonodentate fashion to give a paddle-wheel building block, as seen in Figure 1. The paddle-wheel building blocks connect each other through two carboxyl groups along the [001] direction to lead to a one-dimensional (1D) inorganic chain, ---Tb–O–C–O–Tb---. Figure 2a and 2b are viewed along the [100] and [010] directions, respectively. The 1D inorganic chains are linked with biphenyl groups in the [110] and $[\bar{1}10]$ directions to form a 3D framework. It is notable that the 3D framework contains 25.15×17.09 Å rhombic channels along the diagonals (calculated from the distances of metal ion centers) (Figure 2c), which, to our best knowledge, is the largest one in this kind of material.

To fully understand the structure of complex 1 and how it prevents the construction of interpenetrated frameworks

Table 3. Selected Bond Angles (deg) for Complexes 1–4

Complex 1 ^a			
O(6) ^{#1} –Tb(1)–O(2) ^{#2}	153.53(17)	O(6) ^{#1} –Tb(1)–O(5)	85.77(13)
O(2) ^{#2} –Tb(1)–O(5)	97.48(14)	O(6) ^{#1} –Tb(1)–O(3)	131.09(15)
O(2) ^{#2} –Tb(1)–O(3)	74.46(15)	O(5)–Tb(1)–O(3)	73.83(13)
O(6) ^{#1} –Tb(1)–O(4) ^{#2}	84.77(14)	O(2) ^{#2} –Tb(1)–O(4) ^{#2}	81.35(14)
O(5)–Tb(1)–O(4) ^{#2}	154.95(14)	O(3)–Tb(1)–O(4) ^{#2}	128.79(14)
O(6) ^{#1} –Tb(1)–O(1)	74.85(15)	O(2) ^{#2} –Tb(1)–O(1)	125.35(16)
O(5)–Tb(1)–O(1)	116.08(14)	O(3)–Tb(1)–O(1)	75.33(13)
O(4) ^{#2} –Tb(1)–O(1)	83.58(15)	O(6) ^{#1} –Tb(1)–O(7)	76.72(17)
O(2) ^{#2} –Tb(1)–O(7)	78.54(17)	O(5)–Tb(1)–O(7)	76.42(16)
O(3)–Tb(1)–O(7)	136.30(15)	O(4) ^{#2} –Tb(1)–O(7)	78.85(17)
O(1)–Tb(1)–O(7)	147.71(15)		
Complex 2			
O(4)–Ho(1)–O(1)	153.4(2)	O(4)–Ho(1)–O(2)	85.0(2)
O(1)–Ho(1)–O(2)	96.8(2)	O(4)–Ho(1)–O(6)	130.4(2)
O(1)–Ho(1)–O(6)	75.1(2)	O(2)–Ho(1)–O(6)	74.8(2)
O(4)–Ho(1)–O(3)	85.7(2)	O(1)–Ho(1)–O(3)	81.5(2)
O(2)–Ho(1)–O(3)	154.8(2)	O(6)–Ho(1)–O(3)	128.0(2)
O(4)–Ho(1)–O(5)	74.6(2)	O(1)–Ho(1)–O(5)	126.1(2)
O(2)–Ho(1)–O(5)	117.2(2)	O(6)–Ho(1)–O(5)	75.4(2)
O(3)–Ho(1)–O(5)	82.6(2)	O(4)–Ho(1)–O(7)	77.5(2)
O(1)–Ho(1)–O(7)	77.2(3)	O(2)–Ho(1)–O(7)	76.0(2)
O(6)–Ho(1)–O(7)	136.5(2)	O(3)–Ho(1)–O(7)	79.1(2)
O(5)–Ho(1)–O(7)	147.6(2)		
Complex 3 ^b			
O(6) ^{#1} –Er(1)–O(3) ^{#2}	153.9(2)	O(6) ^{#1} –Er(1)–O(5) ^{#3}	85.25(18)
O(3) ^{#2} –Er(1)–O(5) ^{#3}	97.0(2)	O(6) ^{#1} –Er(1)–O(2)	130.1(2)
O(3) ^{#2} –Er(1)–O(2)	74.9(2)	O(5) ^{#3} –Er(1)–O(2)	74.20(18)
O(6) ^{#1} –Er(1)–O(1) ^{#2}	85.74(19)	O(3) ^{#2} –Er(1)–O(1) ^{#2}	81.9(2)
O(5) ^{#3} –Er(1)–O(1) ^{#2}	156.4(2)	O(2)–Er(1)–O(1) ^{#2}	127.37(19)
O(6) ^{#1} –Er(1)–O(4)	74.6(2)	O(3) ^{#2} –Er(1)–O(4)	125.7(2)
O(5) ^{#3} –Er(1)–O(4)	116.52(19)	O(2)–Er(1)–O(4)	75.0(2)
O(1) ^{#2} –Er(1)–O(4)	81.8(2)	O(6) ^{#1} –Er(1)–O(7)	77.6(3)
O(3) ^{#2} –Er(1)–O(7)	77.5(3)	O(5) ^{#3} –Er(1)–O(7)	77.8(2)
O(2)–Er(1)–O(7)	137.4(2)	O(1) ^{#2} –Er(1)–O(7)	79.0(2)
O(4)–Er(1)–O(7)	147.2(2)		
Complex 4			
O(2)–Y(1)–O(6)	153.14(16)	O(2)–Y(1)–O(4)	84.97(13)
O(6)–Y(1)–O(4)	97.56(14)	O(2)–Y(1)–O(3)	130.55(14)
O(6)–Y(1)–O(3)	75.37(15)	O(4)–Y(1)–O(3)	75.19(12)
O(2)–Y(1)–O(7)	85.39(13)	O(6)–Y(1)–O(7)	81.09(14)
O(4)–Y(1)–O(7)	154.72(13)	O(3)–Y(1)–O(7)	127.82(14)
O(2)–Y(1)–O(1)	75.17(15)	O(6)–Y(1)–O(1)	125.33(15)
O(4)–Y(1)–O(1)	117.27(14)	O(3)–Y(1)–O(1)	74.81(14)
O(7)–Y(1)–O(1)	82.51(15)	O(2)–Y(1)–O(5)	77.69(16)
O(6)–Y(1)–O(5)	76.94(16)	O(4)–Y(1)–O(5)	76.59(15)
O(3)–Y(1)–O(5)	136.98(15)	O(7)–Y(1)–O(5)	78.55(16)
O(1)–Y(1)–O(5)	147.92(16)		

^a Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, y, -z + 1/2$; (#2) $-x + 1, -y + 1, -z$. ^b Symmetry transformations used to generate equivalent atoms: (#1) $-x + 5/2, y + 1/2, -z + 1/2$; (#2) $-x + 2, -y + 2, -z$; (#3) $x - 1/2, y + 1/2, z$.

and forms such large channels, it is instructive to investigate the coordination number of metal centers and the steric configuration of ligands. The seven-coordinated Tb ion with a terminal water molecule makes it possible to construct the paddle-wheel building block via four of the coordination positions. Two oxygen atoms from two other bpdc ligands locate at the two left coordination position of metal centers, and these two bpdc ligands link paddle-wheel building blocks to lead to a 3D open framework. Two phenyl rings of a bpdc linker have a torsion angle of 29.4°, and phenyl rings of adjacent linkers mutually form a weak $\text{CH} \cdots \pi$ interaction to lead to an impenetrable organic wall of biphenyl groups (Figure 3).^{2a} It is metrically impossible for additional ligands to fill between adjacent biphenyl groups; thus, an interpenetration structure is prohibited. The relative low coordination

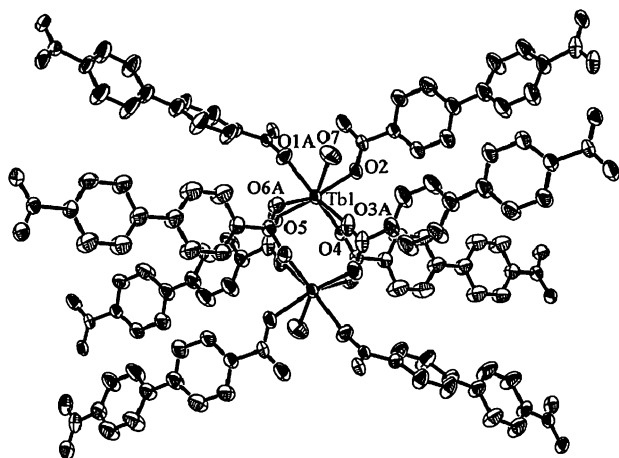


Figure 1. Paddle-wheel building block unit including asymmetric units of $\text{Tb}(\text{bpdc})_{1.5}(\text{H}_2\text{O})\cdot 0.5\text{DMF}$ with non-hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. Atoms labeled with an additional A are symmetrically equivalent to those atoms without such designation.

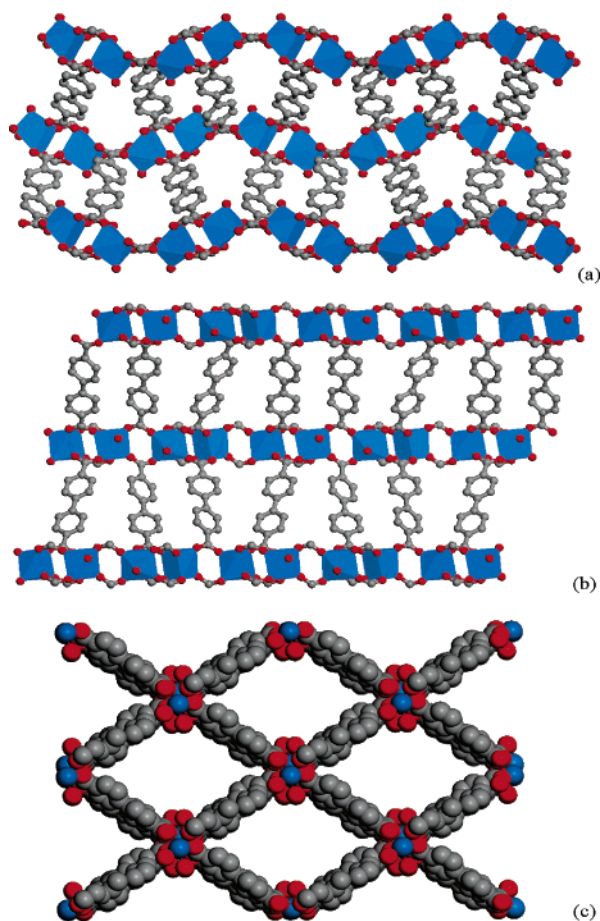


Figure 2. Crystal structure of complex $\text{Tb}(\text{bpdc})_{1.5}(\text{H}_2\text{O})\cdot 0.5\text{DMF}$, containing infinite ---Tb-O-C-O-Tb--- inorganic chains viewed (a) along the [100] direction and (b) along the [010] direction and (c) 1D large channels viewed along the [001] direction (Tb, blue; O, red; C, gray). H atoms were omitted for clarity.

number of the rare earth ions and the special steric configuration of the ligand result in the less condensed framework without interpenetration.

Photoluminescent Properties. The photoluminescent spectra of polymers and H_2bpdc are shown in Figure 4. Two emission groups for complex **1** in the range of 320–450 and

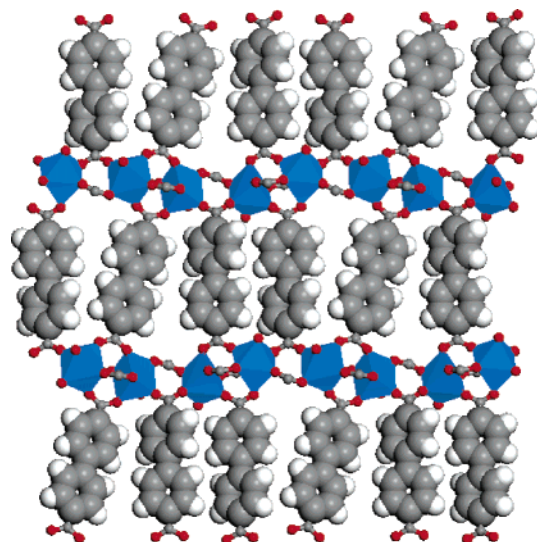


Figure 3. Projection along the [110] direction, showing the impenetrable walls of the channels adjacent to ligand weak $\text{CH}\cdots\pi$ interactions of bpdc^{2-} .

450–650 nm ($\lambda_{\text{ex}} = 236$ nm) are shown in Figure 4a. The emission ranging from 450 to 650 nm is attributed to terbium ions, corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J = 6, 5, 4, 3$).¹¹ As shown in Figure 4b, complex **1** exhibits three blue-shift emission bands and one red-shift emission peak with respect to free H_2bpdc . The blue-shift emission bands would be assigned to the emission of ligand-to-metal-charge-transfer (LMCT).¹² The red-shift emission peak at 422 nm probably is related to the intraligand fluorescent emission; similar red-shifts have been observed before.^{3a,13} The emission peak positions of complexes **2** and **3** are similar to those of complex **1**, which would be assigned to the emission of ligand-to-metal charge transfer (LMCT) and the intraligand fluorescent emission according to complex **1** (Figure 4c).

Interestingly, the intensity of the emission peak at 422 nm remarkably decreased with the augmentation of excited wavelength from 236 to 320 nm (Figure 5). A strong excitation band of complex **1** is observed at 236 nm when the emission band is fixed at 422 nm, which is coincident with the high emission peak at 422 nm excited by 236 nm.

Complex **3** exhibited the characteristic emission of Er^{3+} around 1540 nm excited at 980 nm, which would be assigned to the intraconfigurational $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition (Figure 6).^{4d,14}

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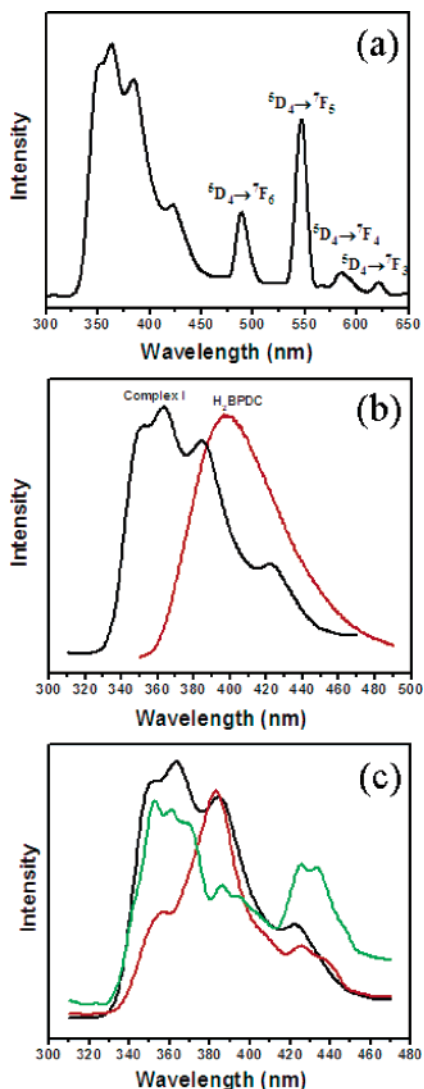


Figure 4. (a) Photoluminescence spectrum of complex **1** excited at 236 nm, (b) emission spectra of complex **1** (black) and H_2bpdc (red) excited at 236 nm, and (c) emission spectra of complex **1** (black), complex **2** (red), and complex **3** (green) excited at 236 nm.

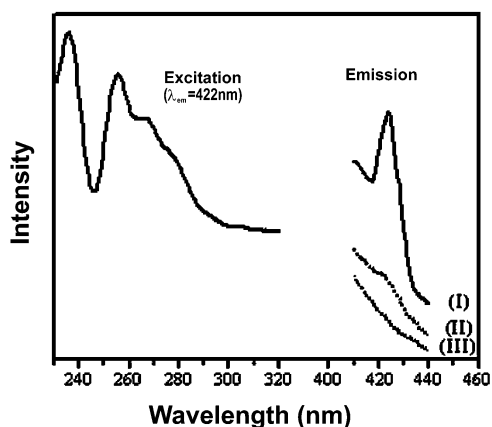


Figure 5. Excitation and emission spectra of complex **1** excited at (I) 236 nm, (II) 285 nm, and (III) 320 nm.

Given the excellent fluorescent properties and the IR emission spectrum being observed, it is not unreasonable to anticipate the use of such materials as fluorescent probes and IR-emitters.

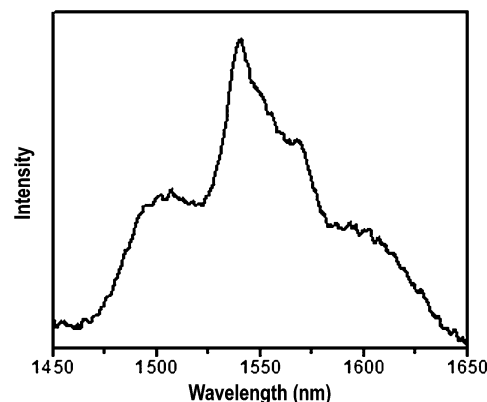


Figure 6. Photoluminescence spectra of complex **3** excited at 980 nm at room temperature.

Thermogravimetric Analysis. A thermogravimetric analysis of complex **1** displays the first weight loss of 6.61% between 50 and 150 °C corresponding to the loss of the half guest DMF molecule (calculated: 6.37%) and the second weight loss of 3.14% between 150 and 300 °C corresponding to the loss of one terminal water molecule (calculated: 3.14%). Then the decomposition of the complex starts above 350 °C. The remaining weight of 35.87% corresponds to the percentage (calculated: 32.58%) of the Tb and O component, Tb_4O_7 .

IR Spectrum. The complexes display similar IR spectra. The aromatic skeleton vibration of the benzene ring, ν_{C-H} of benzene, δ_{C-H} out of the face of benzene, and 1,4-substitution of the benzene ring have bands at 1610, 3058, 856, 680, and 771 cm^{-1} , respectively. The pair of bands at 1656 and 2920 cm^{-1} are due to ν_{C-O} and the asymmetric stretching vibration of the methyl group of the guest DMF molecule.¹⁵ The lack of the characteristics of the carboxylic groups of any protonated forms of bpdc (1715–1680 cm^{-1}) indicates the complete deprotonation of H_2bpdc after the reaction. The broad band at 3220 cm^{-1} is attributed to the vibrations of the water ligand.¹⁶

Conclusions

Four three-dimensional coordination polymers based on rare earths with the same architectures, $Tb(bpdc)_{1.5}(H_2O) \cdot 0.5DMF$ (**1**), $Ho(bpdc)_{1.5}(H_2O) \cdot 0.5DMF$ (**2**), $Er(bpdc)_{1.5}(H_2O) \cdot 0.5DMF$ (**3**), and $Y(bpdc)_{1.5}(H_2O) \cdot 0.5DMF$ (**4**), have been synthesized using a low-temperature solvent evaporation method. These coordination polymers are constructed from paddle-wheel building blocks, which are linked with carboxyl groups of the bpdc ligands to lead to inorganic chains. These inorganic chains connect with biphenyl groups to form 25.15 Å × 17.09 Å rhombic channels. Seven-coordinated rare earth metal centers and the special steric configuration of the ligand play important roles in forming the uncommonly large channels without interpenetration. These complexes exhibit strong fluorescence in the visible region, and complex **3**

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shows an Er^{3+} characteristic emission in the range 1450–1650 nm at room temperature. Thus, these complexes could be anticipated as potential fluorescent probes and an IR-emitter, respectively.

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Supporting Information Available: CIF files, TG curves, a nitrogen adsorption plot, and an emission spectrum for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>. IC0500457