

Hydrothermal Synthesis and Characterization of Novel Lanthanide 2,2'-Diphenyldicarboxylate Complexes

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Lanthanide complexes with a one-dimensional chain, $[\text{Ln}_2(\text{dpdc})_3(\text{H}_2\text{O})_2]_n$ [$\text{Ln} = \text{La}$ (**1**), Pr (**2**), Eu (**3**), Tb (**4**); $\text{dpdc} = 2,2'$ -diphenyldicarboxylate] were obtained by hydrothermal reaction of lanthanide(III) chlorides and 2,2'-diphenyldicarboxylic acid, and characterized by X-ray diffraction. The crystal structure data reveal that they are isostructural. In the asymmetric unit, the two Ln^{3+} ions are both eight-coordinate but they have different coordination environments. Lanthanide ions arranged in a zigzag manner are bridged by the

dpdc ligands into a 1-D chain, while the structure appears like a pinwheel viewed along the c axis. In these complexes, 2,2'-diphenyldicarboxylate anions exhibit tetradentate and pentadentate coordination modes. A laser-induced high-resolution spectrum (resolution: 0.2 cm^{-1}) of **3** was obtained, which shows two Eu^{3+} sites in **3**. This is in agreement with the results of single-crystal X-ray diffraction studies of **3**. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

The crystal engineering and synthesis of one-, two-, and three-dimensional coordination polymers have been areas of renewed interest and have undergone explosive growth in recent years.^[1–11] In principle, the physical and chemical properties of polymer networks are decisively dependent on the properties of the individual molecular components and their distribution within the crystal lattice. In terms of molecular composition, the inorganic-organic coordination polymers have many advantages over simple inorganic and organic materials. This is because varieties of organic ligands coordinating to metal atoms construct coordination polymers with many fascinating structures, in which the metal atoms display many kinds of coordination geometries,^[12–17] and these polymers may possess distinctive and attractive properties. Therefore, the choice of appropriate bridging ligands is a key step in forming interesting structures.

The coordination chemistry of aromatic polycarboxylic acids coordinated to metal atoms has been extensively investigated for their potential applications such as magnetic,^[18–20] luminescent,^[21,22] and microporous materials.^[23,24] In constructing coordination polymers with networks or channels, 2,2'-diphenyldicarboxylic acid (H_2dpdc) is a useful starting material and possesses several interesting structural features. Two carboxyl groups may be partially or completely deprotonated, resulting in novel structures of coordination polymers by various coordination modes. Dpdc is a flexible ligand in which the carboxyl groups may

not be coplanar with the phenyl ring due to steric hindrance in the coordination process. It can form an infinite variety of architectures in different directions. In the crystal structures of many reported transition metal complexes with 2,2'-diphenyldicarboxylate, the dpdc ligand exhibits diverse types of coordination modes^[25–29] with multiple coordination sites. Owing to the higher coordination number and attractive luminescent properties, applied in fluorescent probes, the reactions of dpdc and lanthanide ions may generate polymers with different coordination modes and properties distinct from transition metal complexes of dpdc . To the best of our knowledge, lanthanide 2,2'-diphenyldicarboxylate complexes have never been reported.

To obtain the coordination polymers, reaction of the lanthanide chloride and sodium 2,2'-diphenyldicarboxylate was carried out by the conventional solution method. The uncharacterized precipitate is insoluble in water and common organic solvents. This led us to adopt hydrothermal synthesis to obtain single crystals suitable for X-ray structure analysis. It is well known that hydrothermal reactions are useful in the synthesis of zeolites, phosphates, phosphonates, and polyoxalkoxometalates.^[30,31] Hydrothermal methods are also an effective approach to produce metastable compounds and promote the growth of crystals.^[32] More recently, we have used this method in the synthesis of lanthanide coordination polymers. Herein, we report the synthesis and structural characterization of lanthanide 2,2'-diphenyldicarboxylate complexes.

Results and Discussion

Structural Description

The crystallographic data of **1–4** are shown in Table 1. The structural data show that the four coordination poly-

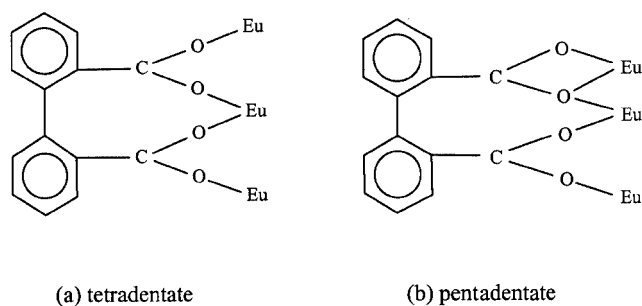
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Table 1. Crystal data for 1–4

Compound	1	2	3	4
Empirical formula	La ₂ C ₄₂ H ₂₈ O ₁₄	Pr ₂ C ₄₂ H ₂₈ O ₁₄	Eu ₂ C ₄₂ H ₂₈ O ₁₄	Tb ₂ C ₄₂ H ₂₈ O ₁₄
FW	1034.46	1038.46	1060.56	1074.48
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> , Å	20.970(7)	21.004(6)	20.914(6)	20.938(7)
<i>b</i> , Å	21.613(8)	21.587(7)	21.409(6)	21.363(7)
<i>c</i> , Å	8.377(3)	8.345(3)	8.234(2)	8.207(3)
α , deg	90	90	90	90
β , deg	103.773(7)	103.888(5)	104.028(5)	104.052(5)
γ , deg	90	90	90	90
<i>Z</i>	4	4	4	4
<i>V</i> , Å ³	3688(2)	3673(2)	3576.8(17)	3561(2)
ρ_{calcd} , g·cm ⁻³	1.863	1.878	1.969	2.004
Temp, K	293(2)	293(2)	293(2)	293(2)
μ , mm ⁻¹	2.360	2.696	3.551	4.016
Reflections collected	6320, 2657	7509, 3233	6187, 2573	7181, 3103
Total, independent, <i>R</i> _{int}	0.0504	0.0242	0.0558	0.0202
λ (Mo- <i>K</i> α), Å	0.71073	0.71073	0.71073	0.71073
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0314, 0.0682	0.0214, 0.0488	0.0340, 0.0810	0.0182, 0.0406

mers are isostructural. Each polymer can be regarded as a one-dimensional infinite chain composed of [Ln₂(dpdc)₃(H₂O)₂] units. Herein, only complex 3 will be described in detail. Complex 3 is composed of one-dimensional chains of [Eu₂(dpdc)₃(H₂O)₂]_{*n*}. Two carboxylate groups of each dpdc ligand are deprotonated, and the dpdc ligands adopt two types of coordination modes, as shown in Scheme 1. [Eu₂(dpdc)₃(H₂O)₂] consists of two crystallographically independent europium(III) ions as shown in Figure 1. Eu(1) is coordinated to eight oxygen atoms, two oxygen atoms [(O6A), (O6B)] from two bridging bidentate carboxylate groups of two tetradentate dpdc ligands, two oxygen atoms [O(3), O(3A)] from two bridging bidentate carboxylate groups of two pentadentate dpdc ligands, two oxygen atoms [O(1), O(1A)] from the two chelating-bridging tridentate carboxylate groups of the two pentadentate dpdc ligands, and two oxygen atoms [O(7), O(7A)] from two coordinated water molecules. The Eu(1)–O(carboxylate) bond lengths vary from 2.307 Å to 2.465 Å, and the Eu(1)–O(w) distances are both 2.521 Å. The O–Eu(1)–O bond angles range from 66.2° to 147.4°. Eu(2) is also ligated to eight oxygen atoms, two oxygen atoms [O(5), O(5A)] from two bridging bidentate carboxylate groups of a tetradentate dpdc ligand, four oxygen atoms [O(1), O(2), O(1B), O(2A)] from two chelating-bridging tridentate carboxylate groups of two pentadentate dpdc ligands, and two oxygen atoms [O(4A), O(4B)] from two bridging bidentate carboxylate groups of other two pentadentate dpdc ligands. The Eu(2)–O(carboxylate) distances fall in the range 2.318–2.594 Å, and the O–Eu(2)–O bond angles are in the range 35.8–150.7°. The results show that Eu(1) is surrounded by two tetradentate dpdc ligands, two pentadentate dpdc ligands, and two water molecules, while around Eu(2) there are one tetradentate dpdc ligand and four pentadentate dpdc ligands; the coordination environments of the two Eu^{III} ions are therefore different. However,

the coordination geometries of the two Eu^{III} ions can both be described as slightly distorted triangular dodecahedra.



Scheme 1. Two coordination modes of dpdc ligand in 3

Each carboxylate moiety of the dpdc ligands bridges two adjacent Eu^{III} ions, and each ligand bridges three adjacent Eu^{III} ions through carboxylate oxygen atoms of these bridging dpdc groups, resulting in one-dimensional infinite polymeric chains along the *c* axis (Figure 2). The Eu^{III} ions are arranged in a zigzag manner, and the distance between two adjacent Eu^{III} ions is 4.459 Å. The tetradentate dpdc ligands and pentadentate dpdc ligands are located around the Eu^{III}...Eu^{III} chain and the number of pentadentate dpdc ligands is double the number of tetradentate ones. From Figure 2, we can see that the coordination environments of Eu(1A), Eu(1B), and Eu(1C) are the same as Eu(1) in Figure 1, and those of Eu(2A), Eu(2B), and Eu(2C) are the same as Eu(2) in Figure 1. In a tetradentate dpdc ligand, the two phenyl rings are not coplanar, and the dihedral angle is 56.2°. In addition, each of the two carboxylic groups of a tetradentate dpdc ligand is not coplanar with the connected phenyl ring, and the dihedral angles are both 122.5°; the two carboxylic groups of the tetradentate dpdc ligand are, however, coplanar. In the pentadentate dpdc ligand, one of the two carboxylate groups adopts a chelating-bridg-

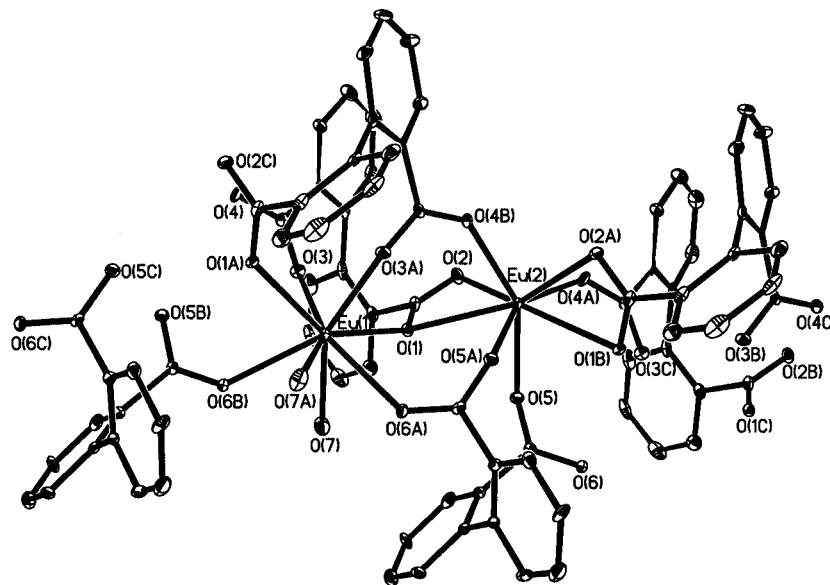


Figure 1. Coordination environment of the two Eu^{III} ions in **3** with thermal ellipsoids at 15% probability; all hydrogen atoms have been omitted for clarity

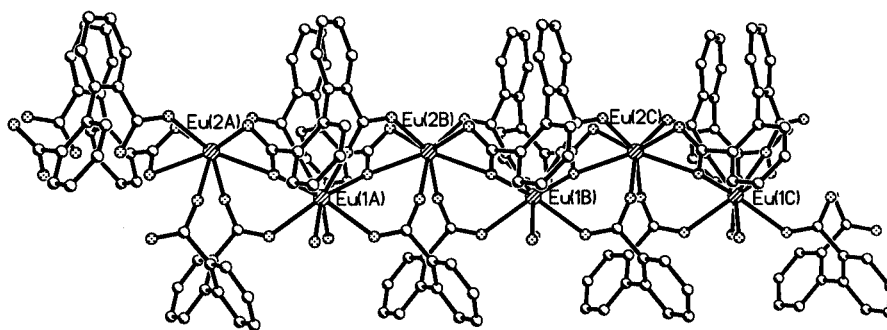


Figure 2. 1-D chain of **3** viewed along the a axis; all hydrogen atoms and uncoordinated water molecules have been omitted for clarity

ing tridentate mode, the other group adopts a bridging bidentate mode. Two oxygen atoms of the bridging bidentate carboxylate group coordinate to two Eu^{III} ions [Eu(1A), Eu(2B)], while two oxygen atoms of the other carboxylate group chelate to the third Eu^{III} ion [Eu(2A)] (see Figure 2) and, moreover, one oxygen atom of the chelating carboxylic group acts as a $\mu_2\text{-O}$ atom. In the pentadentate ligand, the bridging bidentate carboxylate group and the connected phenyl ring are not coplanar and the dihedral angle is 34.9° . The chelating-bridging tridentate carboxylate group and the connected phenyl ring are not coplanar either, and the dihedral angle is 67.4° . The two phenyl rings in a pentadentate dpdc ligand are not coplanar and the dihedral angle is 70.1° . This may result from the steric effect of the coordination. In the tetradentate ligand, the two bridging bidentate $\text{O}-\text{C}-\text{O}$ bond angles are 124.6° , whereas the chelating-bridging tridentate $\text{O}-\text{C}-\text{O}$ bond angles (122.6°) are all smaller than the bridging bidentate ones (123.9°) in the pentadentate ligand, as expected.

Every chain looks like a pinwheel viewed along the c axis (Figure 3). Eu^{III} ions reside at the centers of the pinwheel and are grouped into two parts, arranged in two rows. The ligands fall into three groups and are well distributed

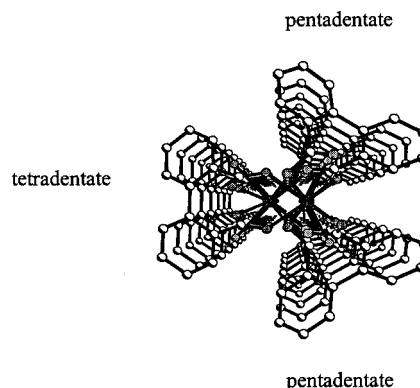


Figure 3. Pinwheel structure of **3**

around the centers of the Eu^{III} ions. The phenyl rings of the dpdc ligands belonging to the same group of a chain are all parallel to each other and the distances between the parallel phenyl rings are in the range of 6.4490 Å to 7.0314 Å.

The phenyl rings of dpdc ligands in adjacent 1-D chains of complex **3** are interdigitated, forming channels with a cavity of size 9.676×4.520 Å in the c direction (see Figure 4).

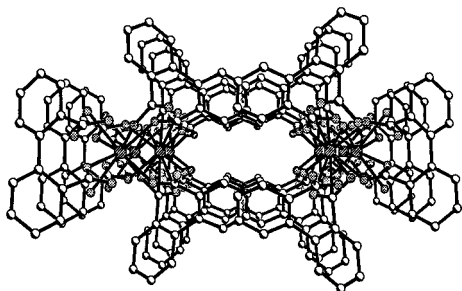


Figure 4. Packing of **3** viewed along the c axis

In the four lanthanide coordination polymers, the mean La–O(carboxylate), Pr–O(carboxylate), Eu–O(carboxylate), and Tb–O(carboxylate) distances are 2.501 Å, 2.470 Å, 2.413 Å, and 2.386 Å, respectively; the La–O(w), Pr–O(w), Eu–O(w), and Tb–O(w) distances are 2.633 Å, 2.579 Å, 2.521 Å, and 2.470 Å, respectively. The separations of La \cdots La, Pr \cdots Pr, Eu \cdots Eu, and Tb \cdots Tb are 4.555 Å, 4.529 Å, 4.459 Å, and 4.440 Å, respectively. We can thus conclude that the Ln $^{\text{III}}$ –O and Ln \cdots Ln distances decrease with the contraction of the ionic radii from La $^{\text{III}}$ to Tb $^{\text{III}}$ ions.

In the two reported isostructural complexes with 2,2'-diphenyldicarboxylic acid, $[\text{M}_2(\text{O}_2\text{CC}_{12}\text{H}_8\text{CO}_2)_2(\text{H}_2\text{O})_8]$, $[\text{M} = \text{cobalt(II)}, \text{nickel(II)}]$,^[25] the M–O distances of the two transition metal complexes are both shorter than those of complexes **1–4**. The coordination environments of the two transition metal ions are both slightly distorted octahedra, and the M $^{\text{II}}$ ions are all six-coordinate, with two oxygen atoms from two carboxylate groups of a dpdc ligand and four oxygen atoms from four coordinated water molecules. Obviously, there are two more atoms coordinated to the Ln $^{\text{III}}$ ion in **1–4**, producing an eight-coordinate metal center. The dihedral angles of the aromatic rings of the dpdc ligand in the two transition metal complexes are 85.96° and 87.2° for Co $^{\text{II}}$ and Ni $^{\text{II}}$, respectively, which are larger than those in the tetradentate dpdc ligand and pentadentate dpdc ligand of **3** (56.2° and 70.1°, respectively). This may be a result of the higher coordination number of the lanthanide ions and thus the steric hindrance effect re-

sults in the formation of coordination polymers. Similarly, compounds **1–4** exhibit more complicated coordination modes than the transition metal dpdc complexes. This is due to the larger radii of Ln $^{\text{III}}$ ions, and corresponding large coordination number, as well as the different coordination modes that are required by lanthanide ions.

Thermogravimetric Analyses

Thermogravimetric analyses of **1–4** were performed to observe their thermal behaviors. The thermogravimetric analysis data for **1**, **2**, **3**, and **4** are listed in Table 2. Loss of two coordinated water molecules of the four complexes was observed as the first weight loss. Their dehydration temperatures are in the range of 178.6 °C to 225.1 °C, and further decomposition processes begin at temperatures above 459 °C, giving the final products Ln $_2\text{O}_3$ (Ln = La, Eu), Pr $_6\text{O}_{11}$, and Tb $_4\text{O}_7$. Taking **1** as an example, the TGA curve shows that the process of first weight loss is between 178.6 and 221.5 °C with 3.5% total weight, which is in accordance with the removal of two water molecules per formula unit (calculated: 3.6%). Then, further decomposition of **1** begins at temperatures above 461.2 °C, giving rise to La $_2\text{O}_3$.

Photophysical Properties of **3**

Complex **3** emits intense red fluorescence when it is irradiated by UV light. Figure 5 shows its high-resolution emission spectrum excited at a wavelength of 355 nm at 77 K, corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions in

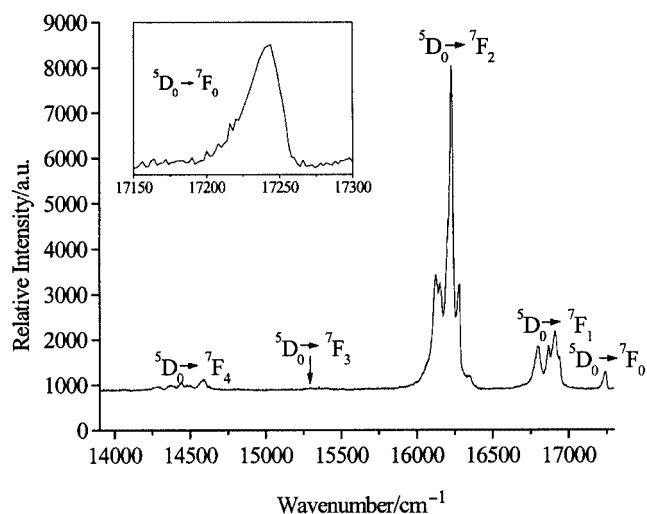


Figure 5. Emission spectrum of **3** corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions at 77 K, $\lambda_{\text{exc}} = 355$ nm

Table 2. Thermogravimetric analysis data of **1–4**

	1	2	3	4
Dehydration temperature [°C]	178.6–221.5	197.6–208.3	209.1–225.1	199.3–215.3
Loss of water calcd. (found) [%]	3.6 (3.5)	3.5 (3.6)	3.4 (3.3)	3.3 (3.5)
Further decomposition temperature [°C]	461.2	460.9	459.5	463.8

the range 13900–17300 cm^{-1} . The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is the induced electric dipole transition, which is greatly affected by the coordination environment, while the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is the magnetic dipole transition, which is much less sensitive to the environment. The intensity ratio of $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ is 3.73, which shows that the Eu^{3+} ions are not at an inversion center. For the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, the peak number should obey the $(2J + 1)$ rule. However, the broad and asymmetric spectrum of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition (see inset in Figure 5), as well as the shoulder of the three peaks in the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition indicate that $2 \times (2J + 1)$ partly overlapping signals are expected in the low-temperature luminescence spectrum of **3**, and thus the europium ions in **3** are not located in the same chemical environment. To further study the local structural characteristics, a selective excitation technique has been applied. Setting 16213 cm^{-1} and 16143 cm^{-1} as the analyzing wave number, respectively, the excitation spectra *a* and *b* arising from the $^5\text{D}_0 \leftarrow ^7\text{F}_0$ transition were obtained, as shown in Figure 6. Obviously, there are two peaks located at 579.57 nm and 579.83 nm in both excitation spectra *a* and *b*, which confirms two Eu^{3+} ion sites in the complex **3**.^[33] This is in good agreement with the results of the single-crystal X-ray diffraction. It can be concluded that there are two different La^{3+} , Pr^{3+} , and Tb^{3+} ion sites in the complexes **1**, **2**, and **4**, respectively.

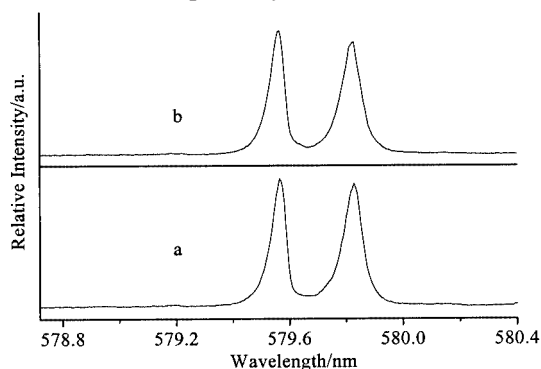


Figure 6. Excitation spectra of **3** at 77 K; analyzing wave number: (a) 16 213 cm^{-1} ; (b) 16 143 cm^{-1}

Conclusion

The first examples of structural characterization of lanthanide coordination polymers with 2,2'-biphenyldicarboxylic acid were obtained. The dpdc ligands in **1**, **2**, **3**, and **4** have two coordination modes, tetradentate and pentadentate. Coordination polymers **1–4** are isostructural, and 1-D chains of **1–4** are composed of $\text{Ln}_2(\text{dpdc})_3(\text{H}_2\text{O})_2$ building blocks, in which the lanthanide(III) ions have two chemical environments. The Ln–O bond lengths and Ln...Ln separations show a lanthanide contraction over the series.

Experimental Section

Materials: $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving their oxides in hydro-

chloric acid, and then drying. 2,2'-Diphenyldicarboxylic acid was purchased from Aldrich and used without further purification, while all the other reagents are commercially available and were used as received.

Instrumentation: Elemental analyses were performed on an Elementar Vario EL analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique. Thermogravimetric analyses were performed on a ZRY-2P Thermal Analyzer. The excitation light source was a YAG-Nd laser that emits at 1.064 μm , and the excitation wavelength was 355 nm. The sample was placed in a Dewar and cooled with liquid nitrogen. The fluorescence was collected at right angles through a Spex 1403 monochromator with a photomultiplier tube, then averaged by a Boxcar integrator, and finally data were transferred to a computer.

X-ray Crystallographic Study: The single-crystal X-ray data collections for complexes **1**, **2**, **3**, and **4** were performed on a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on $|F|^2$ using the SHELXTL-97 program.^[34] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinements.

CCDC 195399–195402 (**1–4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[La₂(dpdc)₃(H₂O)₂]_n (1**):** A mixture of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.111 g, 0.3 mmol), 2,2'-diphenyldicarboxylic acid (0.109 g, 0.45 mmol), H_2O (10 mL), and an aqueous solution of NaOH (0.4 mL, 0.26 mmol) was sealed in a 25-mL stainless-steel reactor with a Teflon liner, heated to 170 $^\circ\text{C}$ for 72 h, and then slowly cooled to room temperature. The products were filtered, washed with ethanol, and then dried in air. Colorless transparent crystals of **1** were obtained in 70.4% yield (0.109 g). $\text{C}_{42}\text{H}_{28}\text{La}_2\text{O}_{14}$ (1034.44): calcd. C 48.77, H 2.73; found C 48.66, H 2.52. IR data (KBr pellet): $\tilde{\nu} = 3549(\text{m}) \text{ cm}^{-1}$, 1615(s), 1548(s), 1523(s), 1442(s), 1406 (s), 771(m), 760(m).

[Pr₂(dpdc)₃(H₂O)₂]_n (2**):** A mixture of $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.107 g, 0.3 mmol), 2,2'-diphenyldicarboxylic acid (0.109 g, 0.45 mmol), H_2O (10 mL), and an aqueous solution of NaOH (0.3 mL, 0.20 mmol) was sealed in a 25-mL stainless-steel reactor with a Teflon liner, heated to 200 $^\circ\text{C}$ for 72 h, and then slowly cooled to room temperature. The products were filtered, washed with ethanol, and then dried in air. Light green crystals of **2** were obtained in 71.5% yield (0.111 g). $\text{C}_{42}\text{H}_{28}\text{O}_{14}\text{Pr}_2$ (1038.44): calcd. C 48.58, H 2.91; found C 48.67, H 2.43. IR data (KBr pellet): $\tilde{\nu} = 3550(\text{m}) \text{ cm}^{-1}$, 1617(s), 1548(s), 1522(s), 1442(s), 1406 (s), 771(m), 761(m).

[Eu₂(dpdc)₃(H₂O)₂]_n (3**):** The synthesis of **3** was similar to that of **1**. The products were filtered, washed with ethanol, and then dried in air. Reddish brown transparent crystals of **3** were obtained in 67.4% yield (0.107 g). $\text{C}_{42}\text{H}_{28}\text{Eu}_2\text{O}_{14}$ (1060.64): calcd. C 47.54, H 2.66; found C 47.59, H 2.30. IR data (KBr pellet): $\tilde{\nu} = 3551(\text{m}) \text{ cm}^{-1}$, 1622(s), 1553(s), 1525(s), 1443(s), 1408(s), 772(m), 762(m).

[Tb₂(dpdc)₃(H₂O)₂]_n (4**):** The synthesis of **4** was similar to that of **2**. The products were filtered, washed with ethanol, and then dried in air. Colorless transparent crystals of **4** were obtained in 68.9%

yield (0.111 g). Calcd. for $C_{42}H_{28}Tb_2O_{14}$ (1074.44): calcd. C 46.95, H 2.81; found C 46.97, H 2.38. IR data (KBr pellet): $\tilde{\nu} = 3552(m)$ cm^{-1} , 1624(s), 1555(s), 1527(s), 1443(s), 1409(s), 763(m).

Acknowledgments

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