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Three-dimensional lanthanide coordination polymers with *p*-phenylenediacrylates: Syntheses, structures, and properties

Xin-Hui Zhou[a,b,*], Hong-Hui Li[a], Wei Huang[a,*]

[a] *Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210046, China*
[b] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

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ABSTRACT

Three three-dimensional lanthanide coordination polymers $[Ln_2(pda)_2(HCOO)(OH)(H_2O)]_n$ (Ln = Dy, **1**; Tb, **2**; Ho, **3**; H_2pda = *p*-phenylenediacrylic acid) have been solvothermally synthesized and their structures have been determined using either X-ray powder or single-crystal diffraction data. They are isostructural and possess a 3D architecture with the **pcu** (α-Po) net topology based on the parallel 1D lanthanide–oxygen rod-shaped secondary building units, each of which is connected to four other rods by the pda ligands. The photoluminescent properties of **1–3** have been investigated. Complexes **1–3** all display the intense blue emission in the solid state at room temperature. Especially, compared with the free H_2pda ligands, **1** shows the strong fluorescence enhancement due to the complexation.

1. Introduction

Compared with the transition metal coordination polymers, reports about the lanthanide coordination polymers are relatively scarce, due to the intrinsic variable and high coordination numbers of the trivalent lanthanide ions interfering the rational design for the self-assembly of lanthanide complexes. However, they have still attracted much attention in view of their interesting magnetic and luminescent properties [1–8] as well as great potential applications [9–14], for example, catalysis, adsorption, separation, sensor, and molecular recognition. The lanthanide-based luminescence emission has narrow line-type spectra, however, is typically weak due to low light-absorption efficiency, so it requires an antenna molecule in the framework for energy transfer [15]. Lanthanide coordination polymers constructed from the lanthanide ions and organic chromophore can generate the Ln-based luminescence and/or the linker-based emission, etc. Furthermore, the rigidity of the 3D framework can reduce the vibration of lanthanide ions and organic linkers, inhibit the non-radiative deactivation and increase the fluorescence quantum yields [16]. The crucial point for preparing the luminescent lanthanide coordination polymers is the careful selection of appropriate organic bridging ligands. The π-conjugated organic compounds are commonly used as linkers in lanthanide coordination polymers, owing to their usually strong absorption and emission resulting from the electronic transitions involving the extended π system. *p*-Phenylenediacrylic acid (H_2pda, Scheme 1) and its derivatives or analogs have wide applications in the field of solid-state photosensitive materials [17,18]. H_2pda is an extended conjugated rigid dicarboxylate ligand with long spacers (≈11 Å) between the carboxylate groups and displays the weak blue photoluminescence [19]. However, in search of the Cambridge Structural Database (using ConQuest Version 1.3, updated August 2011), nine complexes based H_2pda have been reported, of which only one is lanthanide coordination polymer [19–24]. In this article, we report the syntheses and structures of three lanthanide coordination polymers based on the pda ligands and lanthanide ions, formulated as $[Ln_2(pda)_2(HCOO)(OH)(H_2O)]_n$ (Ln = Dy, **1**; Tb, **2**; Ho, **3**; H_2pda = *p*-phenylenediacrylic acid). Their thermal and photoluminescent properties are also included.

2. Experimental

2.1. General

The lanthanide(III) nitrates were converted from their oxides by nitric acid. Other reagents and solvents were purchased from commercial sources and used as received. *p*-Phenylenediacrylic acid was purchased from Aldrich Chemical Co. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. Infrared spectra were recorded on a Vector22 Bruker Spectrophotometer

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* Corresponding authors. Address: Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210046, China. Fax: +86 25 85866396.

E-mail addresses: iamxhzhou@njupt.edu.cn (X.-H. Zhou), iamwhuang@njupt.edu.cn (W. Huang).

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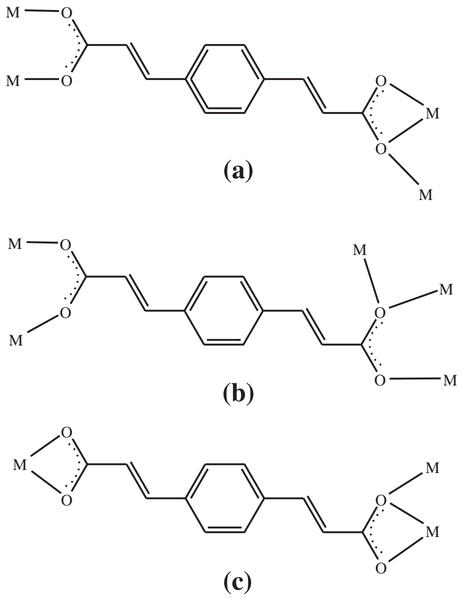

Scheme 1. Coordination modes of the ligand pda.

Table 1
Crystallographic data for complex **1**.

Formula	$C_{25}H_{20}Dy_2O_{12}$
Formula weight	837.41
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.691(4)
b (Å)	7.321(2)
c (Å)	29.609(9)
α (°)	90.00
β (°)	95.737(6)
γ (°)	90.00
V (Å^3)	2521.6(13)
Z	4
D_{calcd} (g cm^{-3})	2.206
T (K)	293(2)
μ (mm^{-1})	5.947
F(000)	1592
Reflections collected	12 026
Unique reflections	4431
Goodness-of-fit (GOF) on F^2	1.312
R_{int}	0.0501
R_1[a],wR_2[b] ($I > 2\sigma(I)$)	0.0835, 0.1595
R_1[a],wR_2[b] (all data)	0.0904, 0.1620

[a] $R_1 = \sum \|F_o - F_c\| / \sum |F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

with KBr pellets in the 400–4000 cm^{-1} region. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. Thermogravimetric analyses were collected on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 700 °C with a heating rate of 20 °C/min under nitrogen. Photoluminescent spectra were measured using a RF-5301PC spectrofluorophotometer.

2.2. Syntheses of complexes **1–3**

Since all the synthetic methods for **1–3** were similar, only the preparation of **1** is described here. A mixture of H_2pda (0.2 mmol, 43.6 mg), $Dy(NO_3)_3 \cdot 6H_2O$ (0.2 mmol, 91.4 mg), DMF (5 mL), and H_2O (5 mL) was sealed in a 15 mL Teflon-lined bomb and heated at 160 °C for 3 days. The reaction mixture was slowly cooled to room temperature. Colorless needle crystals of **1** suitable for X-ray diffraction analysis were isolated in 67% yield. Colorless needle crystals for **2** and pink needle crystals for **3** were obtained in 34% and 51% yields, respectively. *Anal.* Calc. for **1** $C_{25}H_{20}Dy_2O_{12}$: C, 35.86; H, 2.41. Found: C, 35.06; H, 2.79%. Calc. for **2** $C_{25}H_{20}Tb_2O_{12}$: C, 36.17; H, 2.43. Found: C, 35.64; H, 2.67%. Calc. for **3** $C_{25}H_{20}Ho_2O_{12}$: C, 35.65; H, 2.39. Found: C, 35.94; H, 2.19%. IR (KBr)/cm^{-1} for **1** (Dy): 713 m, 840 m, 889 w, 975 m, 1255 m, 1400 vs, 1427 vs, 1589 s, 1637 s, 3610 m. For **2** (Tb): 713 m, 840 m, 889 w, 975 s, 1255 s, 1398 vs, 1427 vs, 1587 s, 1633 s, 3604 m. For **3** (Ho): 715 m, 842 m, 889 w, 977 m, 1257 m, 1400 vs, 1427 vs, 1591 s, 1639 s, 3614 m.

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

Dy1–O2a	2.295(11)	Dy1–O3	2.475(12)
Dy1–O4	2.402(11)	Dy1–O6	2.369(12)
Dy1–O7b	2.366(12)	Dy1–O9	2.414(13)
Dy1–O10	2.418(11)	Dy1–O11c	2.621(13)
Dy1–O12c	2.475(13)	Dy2–O1d	2.399(11)
Dy2–O3	2.377(11)	Dy2–O5	2.599(13)
Dy2–O5b	2.484(13)	Dy2–O7	2.390(11)
Dy2–O8	2.563(11)	Dy2–O10	2.323(11)
Dy2–O10c	2.384(11)	Dy2–O11	2.410(12)
Dy1–Dy2	3.809(1)	Dy2–Dy1c	3.882(1)
O2a–Dy1–O7b	77.7(4)	O2a–Dy1–O6	74.8(4)
O7b–Dy1–O6	134.2(4)	O2a–Dy1–O4	142.5(4)
O7b–Dy1–O4	79.4(4)	O6–Dy1–O4	140.5(4)
O2a–Dy1–O9	72.3(4)	O7b–Dy1–O9	75.8(4)
O6–Dy1–O9	127.2(4)	O4–Dy1–O9	73.5(4)
O2a–Dy1–O10	79.4(4)	O7b–Dy1–O10	67.8(4)
O6–Dy1–O10	71.7(4)	O4–Dy1–O10	118.1(4)
O9–Dy1–O10	137.7(4)	O2a–Dy1–O3	145.6(4)
O7b–Dy1–O3	78.1(4)	O6–Dy1–O3	106.3(4)
O4–Dy1–O3	53.5(4)	O9–Dy1–O3	124.1(4)
O10–Dy1–O3	69.0(4)	O2a–Dy1–O12c	99.3(4)
O7b–Dy1–O12c	144.8(4)	O6–Dy1–O12c	76.0(4)
O4–Dy1–O12c	83.1(4)	O9–Dy1–O12c	70.1(5)
O10–Dy1–O12c	146.9(4)	O3–Dy1–O12c	114.5(4)
O2a–Dy1–O11c	137.7(4)	O7b–Dy1–O11c	144.6(4)
O6–Dy1–O11c	69.7(4)	O4–Dy1–O11c	71.1(4)
O9–Dy1–O11c	112.6(4)	O10–Dy1–O11c	109.6(4)
O3–Dy1–O11c	68.7(4)	O12c–Dy1–O11c	50.5(4)
O10–Dy2–O3	72.2(4)	O10–Dy2–O10c	130.5(3)
O3–Dy2–O10c	75.4(4)	O10–Dy2–O7	125.2(4)
O3–Dy2–O7	141.7(4)	O10c–Dy2–O7	67.9(4)
O10–Dy2–O1d	140.0(4)	O3–Dy2–O1d	85.8(4)
O10c–Dy2–O1d	71.5(4)	O7–Dy2–O1d	92.7(4)
O10–Dy2–O11	100.2(4)	O3–Dy2–O11	141.8(4)
O10c–Dy2–O11	127.9(4)	O7–Dy2–O11	73.7(4)
O1d–Dy2–O11	76.6(4)	O10–Dy2–O5b	67.5(4)
O3–Dy2–O5b	75.5(4)	O10c–Dy2–O5b	136.7(4)
O7–Dy2–O5b	140.7(4)	O1d–Dy2–O5b	74.9(4)
O11–Dy2–O5b	67.2(4)	O10–Dy2–O8	74.1(4)
O3–Dy2–O8	137.3(4)	O10c–Dy2–O8	109.2(4)
O7–Dy2–O8	52.4(4)	O1d–Dy2–O8	136.6(4)
O11–Dy2–O8	69.7(4)	O5b–Dy2–O8	114.0(4)
O10–Dy2–O5	73.0(4)	O3–Dy2–O5	79.1(4)
O10c–Dy2–O5	64.7(4)	O7–Dy2–O5	75.7(4)
O1d–Dy2–O5	136.0(4)	O11–Dy2–O5	135.9(4)
O5b–Dy2–O5	137.9(3)	O8–Dy2–O5	66.5(4)

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

2.3. Crystal structure determination

The crystal structure of complex **1** was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT [25] on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were