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Homochiral Lanthanide Phosphonates with Brick-Wall-Shaped Layer Structures Showing Chiroptical and Catalytical Properties

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Based on enantiopure *S*- or *R*-(1-phenylethylamino)methylphosphonic acid (pempH$_2$), homochiral lanthanide phosphonates (*S*)-[Ln(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (***S*-Ln**) and (*R*)-[Ln(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (***R*-Ln**) (Ln = Eu, Tb, Ho) are obtained successfully. All six compounds are isostructural, showing chiral brick-wall-shaped layer structures. They are all optically active, exhibiting second harmonic generation responses 0.7 times that of urea. The Eu and Tb compounds display strong red and green luminescent properties, respectively, with long luminescent lifetimes at the level of milliseconds. The catalytic properties of the dehydrated ***S*-Tb** are studied.

Introduction

The lanthanide ions have unique reactivity and magnetic and optical properties which are fundamental to most of their applications.[1,2] Enantiomerically pure lanthanide complexes, which combine the unique properties of the lanthanide ions with chiral coordination spheres, have great potential in applications as chiral NMR shift reagents for resolving NMR spectra of chiral Lewis bases,[3] as luminescence probes for circularly polarized luminescence spectroscopy,[4] and as enantioselective catalysts.[5] Although great efforts have been made in synthesizing new chiral lanthanide complexes with different purposes, very few compounds are concerned with organophosphonate ligands.[6] As far as we are aware, the only examples of chiral lanthanide phosphonates include Ln[(*S*)-HO$_3$PCH$_2$NHC$_4$H$_7$CO$_2$]$_3$·2H$_2$O (Ln = Tb, Dy, Eu, Gd) with chain structures[7] and those based on derivatives of 1,1′-binaphthalene-6,6′-bisphosphonic acid with lamellar or pillared layered structures.[8] In the latter cases, heterogeneous asymmetric catalytic properties have been explored, which resulted in racemic products with good yields.

Our interest in metal phosphonate chemistry has also been extended to the lanthanide compounds in recent years.[9] A series of lanthanide compounds containing 1,4,7- triazacyclononane-1,4,7-triyl-tris(methylenephosphonic acid) (notpH$_6$)[9a] or 1,4,7,10- tetraazacyclododecane-1,4,7,10-tetrakis-(methylenephosphonic acid) (dotpH$_8$)[9d] have been obtained. The dehydrated Gd-notp and Ln-dotp show interesting catalytic activities toward the Biginelli reaction. In this paper, we select a flexible chiral monophosphonic acid, e.g., (*S*)-

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or (*R*)-(1-phenylethylamino)methylphosphonic acid (pempH$_2$), to react with lanthanide ions in solution. Six homochiral lanthanide complexes with formulas (*S*)-[Ln(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (***S*-Ln**) and (*R*)-[Ln(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (***R*-Ln**) (Ln = Eu, Tb, Ho) are obtained successfully. Their chiroptical, luminescent, and catalytic properties are investigated.

Experimental Section

Materials and Measurements. (*S*)- or (*R*)-(1-phenylethylamino)methylphosphonic acid (pempH$_2$) was prepared by reactions of (*S*)- or (*R*)-1-phenylethylamine, diethyl phosphite, and paraformaldehyde, according to literature methods.[10] (*S*)- and (*R*)-1-phenylethylamine were purchased from Aldrich without further purification, and all of the other starting materials were of reagent-grade quality. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. CD spectra were measured on a JASCO J-720W spectrophotometer at room temperature. Approximate estimations of second-order-nonlinear optical intensity were obtained by comparison of the results obtained from a powder sample (80 ± 150 mm diameter) in the form of a pellet (Kurtz powder test[11]) with those obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. Thermal analyses were performed in nitrogen in the temperature range 25−650 °C with a heating rate of 10 °C min^{-1} on a TGA-DTA V1.1b Inst 2100 instrument. The fluorescent spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer with polycrystalline samples.

Preparation of (*S*)-[Eu(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (*S*-Eu). An aqueous solution of *S*-pempH$_2$ (0.1 mmol, 0.0215 g) and Gd(NO$_3$)$_3$·6H$_2$O (0.10 mmol, 0.044 g) was stirred for one day, then adjusted to pH ≈ 1.0 with 1 M HNO$_3$. After evaporation at room temperature for two weeks, colorless platelike crystals of ***S*-Eu** were obtained. Yield: 68%. Anal. calcd for $C_{18}H_{34}N_6O_{22}P_2Eu_2$: C, 20.54; H, 3.26; N, 7.99%. Found: C, 20.51; H, 3.21; N, 8.04%. IR (KBr, cm^{-1}): 3394(w), 3169(w), 1635(w), 1520(w), 1478(w), 1456(w), 1384(s), 1305(m), 1156(w), 1131(w), 1089(m), 1033(w), 925(w), 813(w), 760(w), 699(w), 569(w), 484(w). Thermal analysis shows a weight loss of 7.7% in the temperature range 25−150 °C, close to the calculated value for the release of two coordination water molecules (6.9%).

(*R*)-[Eu(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (*R*-Eu). Complex ***R*-Eu** was obtained similarly except that *R*-pempH$_2$ was used. Yield: 63%. Anal. calcd for $C_{18}H_{34}N_6O_{22}P_2Eu_2$: C, 20.54; H, 3.26; N, 7.99%. Found: C, 20.57; H, 3.27; N, 8.07%. IR (KBr, cm^{-1}): 3410(w), 3165(w), 2977(w), 1646(w), 1571(w), 1522(w1478(w), 1456(w), 1384(s), 1305(m), 1156(w), 1131(w), 1089(m), 1033(w), 925(w), 813(w), 760(w), 699(w), 569(w), 484(w). Thermal analysis shows a weight loss of 7.8% in the 25−165 °C temperature range, close to the calculated value for the release of two coordination water molecules (6.9%).

(*S*)-[Tb(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (*S*-Tb). The preparation of ***S*-Tb** follows the same procedure as for ***S*-Eu** except that Tb(NO$_3$)$_3$·6H$_2$O (0.10 mmol, 0.044 g), instead of Eu(NO$_3$)$_3$·6H$_2$O, was used as the starting material. Colorless platelike crystals of ***S*-Tb** were obtained in a yield of 61%. Anal. calcd for $C_{18}H_{34}N_6O_{22}P_2Tb_2$: C, 20.28; H, 3.21; N, 7.88%. Found: C, 20.27; H, 3.24; N, 7.87%. IR (KBr, cm^{-1}): 3346(m), 2289(w), 1650(w), 1572(w), 1523(s), 1480(m), 1384(m), 1306(s), 1158(w), 1132(s), 1089(s), 1035(m), 812(w), 782(w), 759(w), 700(w), 580(w), 531(w). Thermal analysis shows a weight loss of 7.3% in the temperature range 25−165 °C, close to the calculated value for the release of two coordination water molecules (6.8%).

(*R*)-[Tb(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (*R*-Tb). Complex ***R*-Tb** was obtained similarly except that *R*-pempH$_2$ and Tb(NO$_3$)$_3$·6H$_2$O were used. Yield: 58%. Anal. calcd for $C_{18}H_{34}N_6O_{22}P_2Tb_2$: C, 20.28; H, 3.21; N, 7.88%. Found: C, 20.21; H, 3.27; N, 7.89%. IR (KBr, cm^{-1}): 3345(m), 3159(m), 2290(w), 1649(w), 1572(w), 1522(s), 1480(m), 1383(m), 1306(s), 1158(w), 1132(s), 1089(s), 1034(m), 812(w), 782(w), 760(w), 699(w), 580(w), 530(w). Thermal analysis shows a weight loss of 7.5% in the 25−160 °C temperature range, close to the calculated value for the release of two coordination water molecules (6.8%).

(*S*)-[Ho(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (*S*-Ho). The preparation of ***S*-Ho** follows the same procedure as for ***S*-Eu** except that Ho(NO$_3$)$_3$·6H$_2$O (0.10 mmol, 0.044 g) instead of Eu(NO$_3$)$_3$·6H$_2$O was used as the starting material. Colorless platelike crystals of ***S*-Ho** were obtained. Yield: 58%. Anal. calcd for $C_{18}H_{34}N_6O_{22}P_2Ho_2$: C, 20.05; H, 3.18; N, 7.79%. Found: C, 20.07; H, 3.17; N, 7.80%. IR (KBr, cm^{-1}): 3481 (w), 3155 (w), 1652(w), 1573(w), 1524(s), 1480(w), 1384(m), 1308(s), 1270(w), 1209(w), 1160(w), 1134(s), 1091(s), 1035(s), 926(w), 811(w), 759(m), 740(w), 700(m), 580(w), 531(w), 484(w). Thermal analysis shows a weight loss of 7.3% in the 25−165 °C temperature range, close to the calculated value for the release of two coordination water molecules (6.7%).

(*R*)-[Ho(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (*R*-Ho). Complex ***R*-Ho** was obtained similarly except that *R*-pempH$_2$ and Ho(NO$_3$)$_3$·6H$_2$O were used. Yield: 63%. Anal. calcd for $C_{18}H_{34}N_6O_{22}P_2Ho_2$: C, 20.05; H, 3.18; N, 7.79%. Found: C, 19.99; H, 3.18; N, 7.77%. IR (KBr, cm^{-1}): 3405 (w), 3156 (w), 3033(w), 2848(w), 1591(w), 1521(m), 1478(w), 1384(s), 1308(s), 1287(w), 1209(w), 1164(w), 1136(w), 1090(s), 1036(m), 923(w), 814(w), 759(m), 699(m), 563(w), 536(w), 491(w). Thermal analysis shows a weight loss of 7.5% in the 25−150 °C temperature range, close to the calculated value for the release of two coordination water molecules (6.7%).

Crystallographic Studies. Data collections for complexes ***S*-Eu**, ***S*-Tb**, and ***S*-Ho** were carried out on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation (see Table 1 for crystallographic data and Table 2 for bond lengths and angles). Hemispheres of data were collected in the θ range of 2.73−26.00° for ***S*-Eu**, 2.74−25.00° for ***S*-Tb**, and 2.75−26.00° for ***S*-Ho**, using a narrow-frame method with scan widths of 0.308 in ω and an exposure time of 5 s per frame. The data were integrated using the Siemens SAINT program,[12] with the intensities corrected for the Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL.[13] All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms except those attaching to water molecules were put in calculated positions. The H atoms of water molecules were found from the Fourier maps. All H atoms

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Table 1. Crystallographic Data for Compounds ***S*-Eu**, ***S*-Tb**, and ***S*-Ho**

	***S*-Eu**	***S*-Tb**	***S*-Ho**
formula	$C_9H_{17}N_3O_{11}PEu$	$C_9H_{17}N_3O_{11}PTb$	$C_9H_{17}N_3O_{11}PHo$
M	526.19	533.15	539.16
crystal dimensions (mm)	0.14 × 0.12 × 0.04	0.16 × 0.12 × 0.04	0.12 × 0.10 × 0.04
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	6.875 (1)	6.832(1)	6.792(1)
b (Å)	8.715(1)	8.686(2)	8.661(2)
c (Å)	14.386(2)	14.368(3)	14.372(4)
β (deg)	93.130(3)	93.169(4)	93.098(5)
V (Å^3)	860.7(2)	851.4(3)	844.2(4)
Z	2	2	2
D_{calcd} (g cm^{-3})	2.030	2.080	2.121
μ (mm^{-1})	3.797	4.308	4.842
F(000)	516	520	524
R_{int}	0.0482	0.0479	0.0403
T_{max}, T_{min}	0.736, 0.472	0.844, 0.541	0.826, 0.563
GoF on F^2	1.054	1.057	0.991
R_1, $wR_2{}^a$ [$I > 2\sigma(I)$]	0.0481, 0.1066	0.0382, 0.0969	0.0342, 0.0719
R_1, $wR_2{}^a$ (all data)	0.0515, 0.1082	0.0384, 0.0971	0.0364, 0.0728
Flack parameter	−0.01(3)	−0.02(2)	0.01 (1)
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e Å^{-3}	1.360, −1.744	1.314, −1.916	0.978, −1.117

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds ***S*-Eu**, ***S*-Tb**, and ***S*-Ho**[a]

	***S*-Eu**	***S*-Tb**	***S*-Ho**
Ln−O3B	2.229(1)	2.208(7)	2.185(5)
Ln−O2A	2.314(6)	2.290(5)	2.266(4)
Ln−O1	2.379(7)	2.355(6)	2.324(4)
Ln−O1W	2.429(8)	2.387(7)	2.347(5)
Ln−O8	2.519(1)	2.488(7)	2.446(7)
Ln−O4	2.540(1)	2.532(1)	2.509(9)
Ln−O2W	2.552(8)	2.531(7)	2.493(6)
Ln−O5	2.592(1)	2.560(9)	2.523(8)
Ln−O7	2.619(9)	2.600(7)	2.593(6)
P1−O2	1.498(1)	1.512(8)	1.503(6)
P1−O3	1.519(1)	1.512(7)	1.518(6)
P1−O1	1.542(1)	1.530(9)	1.526(7)
O3B−Ln−O2A	98.2(5)	97.9(4)	98.0(3)
O3B−Ln−O1	81.9(5)	82.4(4)	83.2(3)
O2A−Ln−O1	138.5(3)	139.2(2)	139.3(1)
O3B−Ln−O1W	148.1(3)	148.3(2)	148.4(2)
O2A−Ln−O1W	79.3(4)	80.0(4)	79.6(3)
O1−Ln−O1W	79.6(4)	79.3(3)	79.0(3)
O3B−Ln−O8	77.6(3)	77.6(3)	77.9(2)
O2A−Ln−O8	139.8(3)	140.2(2)	140.1(2)
O1−Ln−O8	81.1(3)	80.1(2)	80.1(2)
O1W−Ln−O8	124.4(2)	123.6(2)	123.6(1)
O3B−Ln−O4	121.8(3)	122.0(3)	122.6(2)
O2A−Ln−O4	75.6(4)	75.6(3)	75.7(3)
O1−Ln−O4	138.9(4)	138.1(3)	137.0(3)
O1W−Ln−O4	88.7(3)	88.4(3)	87.7(2)
O8−Ln−O4	73.3(3)	73.9(3)	73.8(2)
O3B−Ln−O2W	74.4(3)	74.5(2)	74.6(1)
O2A−Ln−O2W	69.8(3)	69.7(2)	69.7(1)
O1−Ln−O2W	70.3(3)	71.1(2)	71.6(1)
O1W−Ln−O2W	75.0(3)	75.2(2)	75.0(1)
O8−Ln−O2W	142.2(3)	142.0(2)	142.4(2)
O4−Ln−O2W	143.8(3)	143.7(3)	143.4(2)
O3B−Ln−O5	72.2(3)	72.0(3)	71.7(2)
O2A−Ln−O5	74.3(3)	74.2(3)	74.2(2)
O1−Ln−O5	141.7(4)	141.4(3)	141.6(3)
O1W−Ln−O5	135.2(3)	135.5(3)	135.5(2)
O8−Ln−O5	66.2(3)	66.7(3)	66.8(2)
O4−Ln−O5	50.1(4)	50.4(3)	51.4(3)
O2W−Ln−O5	125.9(3)	125.9(3)	125.7(2)
O3B−Ln−O7	124.0(3)	124.1(2)	124.9(2)
O2A−Ln−O7	132.5(4)	132.7(4)	131.9(3)
O1−Ln−O7	74.4(4)	73.6(3)	73.1(2)
O1W−Ln−O7	75.2(3)	74.7(2)	74.1(1)
O8−Ln−O7	49.4(3)	49.3(2)	49.8(2)
O4−Ln−O7	64.5(3)	64.5(3)	63.9(2)
O2W−Ln−O7	137.0(3)	136.9(2)	136.5 (1)
O5−Ln−O7	97.0(3)	97.2(3)	97.7(2)

[a] A: $x + 1, y, z$. B: $-x + 1, y - 1/2, -z$.

were refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded.

Results and Discussions

Crystal Structures. Both ***S*-Ln** and ***R*-Ln** are isostructural on the basis of the XRD measurements (Figure S1, Supporting Information). Therefore, only compounds ***S*-Ln** (Ln = Eu, Tb, Ho) were selected for single-crystal structural analyses. It is found that all three compounds crystallize in the monoclinic system, chiral space group $P2_1$ (no. 4). Take compound ***S*-Eu** as an example. The asymmetric unit of ***S*-Eu** contains one Eu atom, one pempH$^-$ ligand, two $NO_3{}^-$ anions, and two coordinated water molecules (Figure 1). Each Eu atom is nine-coordinated with three positions occupied by phosphonate oxygen atoms (O1, O2A, and O3B) from three equivalent pempH$^-$ ligands, four positions occupied by oxygen atoms (O4, O5, O7, and O8) from two different $NO_3{}^-$ anions, and the remaining sites occupied by two water molecules (O1W and O2W). The bond lengths of Eu−O are between 2.229(1) and 2.619(9) Å, and the angles around the Eu atom are in the range of 50.1(4)−148.1(3)°. The $NO_3{}^-$ anions serve as bidentate ligands chelating with the same Eu atoms. However, the pempH$^-$ acts as a tridentate ligand, coordinating to three equivalent Eu atoms by its three phosphonate oxygen atoms. The amino nitrogen atom of pempH$^-$ is protonated. Each $\{EuO_9\}$ polyhedron is corner-shared with three $\{CPO_3\}$ tetrahedra and vice versa, leading to a chiral brick-wall-shaped inorganic layer (Figure 2). The layer contains 2_1 helical chains running along the b axis (Figure 2b). The neighboring layers are stacked along the c axis and repeat in an ···AA··· sequence, with a layer-to-layer separation of 14.386(2) Å. The organic groups are grafted on the two sides of the inorganic layer (Figure 3). An extensive hydrogen-bond network is found within the layer. The fundamental unit is a 14-membered ring, made up of two coordinated water molecules, two coordinated $NO_3{}^-$ anions, and one protonated N atom from the pempH$^-$ ligand. These rings are connected into chains through hydrogen-bond interactions between N1 and O2W (see Supporting Information). The four shortest contacts are 2.787 Å for O1W···O5^{i}, 2.786 Å for O2W···O7^{ii}, 2.984 Å for N1···O2W, and 2.993 Å for N1···O8^{iii} (symmetry codes: i, $-x + 2, y + 1/2, -z$; ii, $-x + 1, y - 1/2, -z$; iii, $-x + 1, y + 1/2, -z$).

The structures of compounds ***S*-Tb** and ***S*-Ho** are identical to that of ***S*-Eu**, except that the cell volumes decrease in the sequence ***S*-Eu** > ***S*-Tb** > ***S*-Ho** due to the effect of the lanthanide contraction.

Chiroptical and Luminescent Properties. Solid-state circular dichroism (CD) spectra were measured on KBr pellets for compounds ***S*-Ln** and ***R*-Ln** (Figure 4). Clearly, these compounds exhibit Cotton effects at the same wavelengths (256, 262, and 268 nm), reflecting that the optical activities of these compounds originate from the chiral

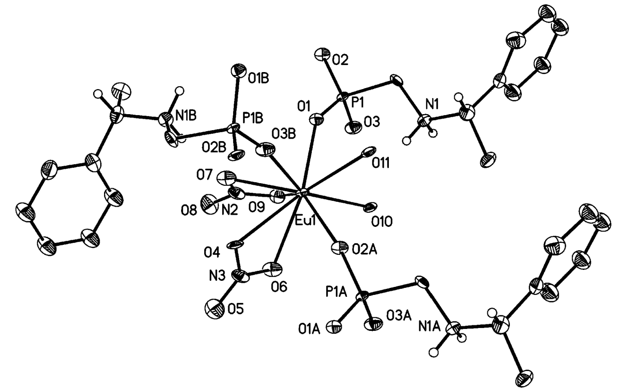

Figure 1. Coordination geometries of europium in ***S*-Eu** with atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.

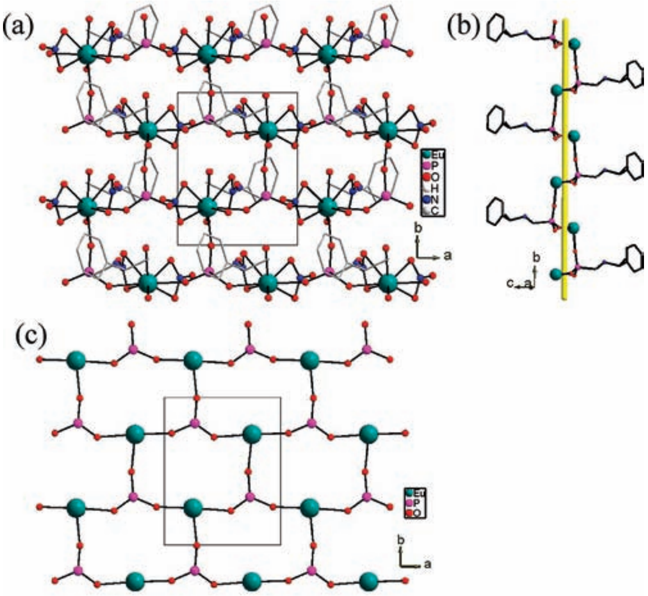

Figure 2. (a) One layer of structure ***S*-Eu**. All H atoms are omitted for clarity. (b) A helical chain within the layer running along the *b* axis. (c) The brick-wall-shaped inorganic layer of ***S*-Eu**.

organic phosphonate ligands.[14] For compounds ***S*-Ln** and ***R*-Ln** with the same lanthanide ion, the opposite signs of Cotton effects confirm that they are pairs of enantiomers. The second harmonic generation (SHG) properties of the powder samples of ***S*-Ln** and ***R*-Ln** were also studied. The results indicate that ***S*-Ln** and ***R*-Ln** (Ln = Eu, Tb, Ho) exhibit SHG responses about 0.7 times that of urea.

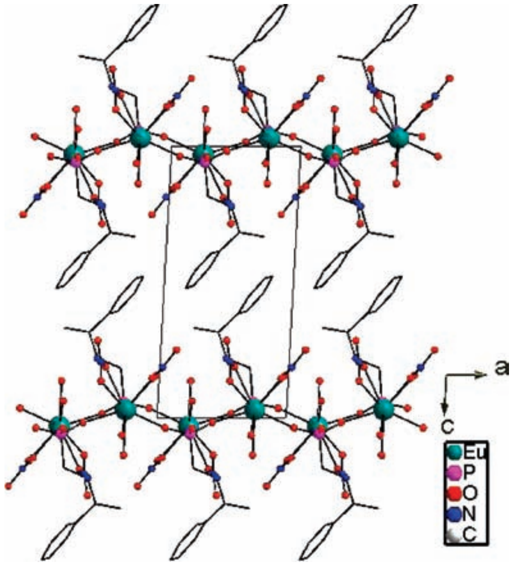

Figure 3. Packing diagram of ***S*-Eu** viewed along the *b* axis. All H atoms are omitted for clarity.

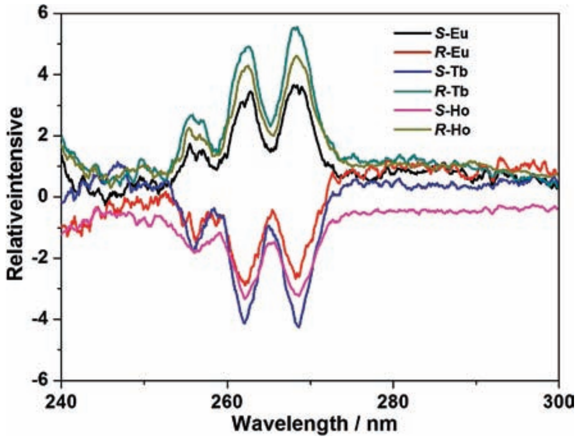

Figure 4. CD spectra of ***S*-Eu** (black), ***R*-Eu** (red), ***S*-Tb** (blue), ***R*-Tb** (cyan), ***S*-Ho** (purple), and ***R*-Ho** (celadon) in KBr pellets.

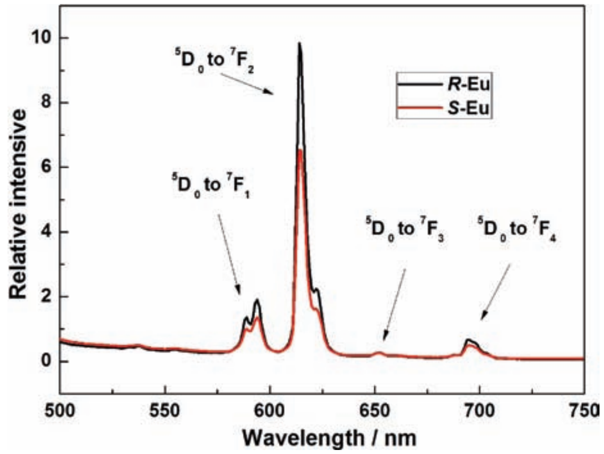

Figure 5. Emission spectra of ***S*-Eu** and ***R*-Eu** in the solid state.

Solid-state luminescence properties of ***S*-** or ***R*-Eu** and ***S*-** or ***R*-Tb** were investigated at room temperature, shown in Figures 5 and 6, respectively. Excited at 395 nm, ***S*-** and ***R*-Eu** display strong red luminescent properties characteristic of the Eu(III) ions. The emission spectra have four bands at about 588, 614, 652, and 695 nm, corresponding to the $^5D_0$ to ^7F_n ($n = 1-4$) transitions. Among them, the $^5D_0$-to-$^7F_2$ transitions dominate the emission spectrum, and their intensities are much stronger than those of $^5D_0$ to $^7F_1$ transitions, indicating that the first coordination spheres of Eu(III) ions in ***S*-Eu** and ***R*-Eu** do not possess an inversion center, in agreement with their crystal structures.[7] ***S*-Tb** and ***R*-Tb** emit green light excited at 375 nm, with emission bands at 621, 586, 544, and 489 nm corresponding to $^5D_4$-to-^7F_n ($n = 3-6$) transitions. The $^5D_4$-to-$^7F_5$ transitions at 544 nm are more intensive than the others, in accordance with the typical

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(14) Kaneko, W.; Kitagawa, S.; Ohba, M. *J. Am. Chem. Soc.* **2007**, *129*, 248.

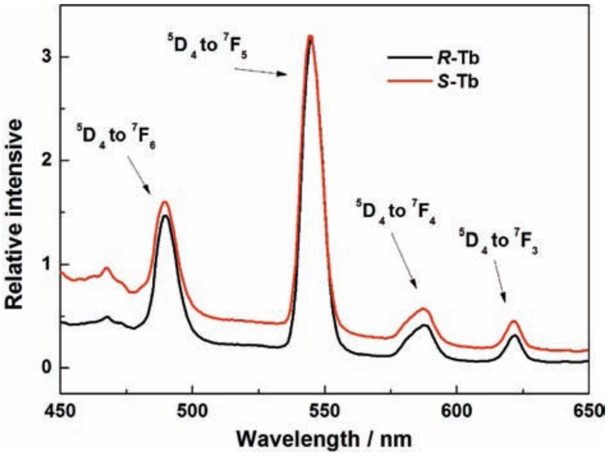
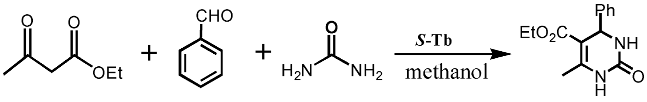


Figure 6. Emission spectra of ***S*-Tb** and ***R*-Tb** in the solid state.

Tb(III) ion emission spectrum. The Eu(III) ($^5D_0$) luminescence lifetimes ($\lambda_{ex,em} = 395, 614$ nm) are measured to be 0.360 ms for ***S*-Eu** and 0.345 ms for ***R*-Eu**, respectively. While the Tb(III) ($^5D_4$) luminescence lifetimes ($\lambda_{ex,em} = 373, 544$ nm) are 1.045 ms for ***S*-Tb** and 1.032 ms for ***R*-Tb**, respectively.

Catalyzed Biginelli Reaction. The Biginelli reaction is a one-pot cyclocondensation of aldehyde, 1,3-ketoester, and urea or thiourea.[15] Encouraged by our previous success in catalyzing the Biginelli reaction by using a dehydrated layer compound [Gd{$C_9H_{20}N_3(PO_3H)_2(PO_3)$}($H_2O$)]$ClO_4 \cdot 3H_2O$,[9] the enantiopure compound ***S*-Tb** was subjected to tests of its catalytic properties for the Biginelli reaction. In order to create good Lewis acid properties, ***S*-Tb** was dehydrated by heating at 140 °C for 2 h. The dehydrated sample retains the framework structure of ***S*-Tb**, confirmed by the XRD patterns (Figure S2, Supporting Information). The solid-state CD spectrum suggests that the dehydrated sample is also chiral (Figure S3, Supporting Information). The condensation of benzaldehyde, ethyl acetoacetate, and urea was tested in dehydrated methanol in the presence of 5 mol % dehydrated ***S*-Tb** for 24 h at room temperature, producing dihydropyrimidine in a yield of 50%.[16] No product can be obtained without catalysts. In addition, the catalyst could easily be recovered and reused without a loss of activity. Unfortunately, however, the products are essentially racemic (ee <5%), although the catalyst is chiral.



Conclusion

In this paper, we report six homochiral lanthanide phosphonates (*S*)-[Ln(pempH)$(NO_3)_2(H_2O)_2$] (***S*-Ln**) and (*R*)-[Ln(pempH)$(NO_3)_2(H_2O)_2$] (***R*-Ln**) [Ln = Eu, Tb, Ho; $pempH_2$ = *S*- or *R*-(1-phenylethylamino)methylphosphonic acid]. All show chiral brick-wall-shaped layer structures and are optically active. The Eu and Tb compounds display strong red and green luminescent properties as expected. The dehydrated ***S*-Tb** shows catalytic activities related to the Biginelli reaction.

It is noted that the layer structures of ***S*-Ln** and ***R*-Ln** are different from those of the related zinc compounds α-(*S*)- and α-(*R*)-[Zn_2(pemp)(pempH)Cl] and β-(*S*)- and β-(*R*)-[Zn_2(pemp)(pempH)Cl],[17] due to the different coordination modes of the lanthanide and zinc atoms. In the latter cases, the phosphonate ligand exists in deprotonated ($pemp^{2-}$) and singly protonated ($pempH^-$) forms. The amino nitrogen atom of the $pemp^{2-}$ ligand is incorporated in the coordination with the Zn atom. However, in ***S*-Ln** and ***R*-Ln**, the amino nitrogen atoms are all protonated. The protonated amino nitrogen could provide additional sites for catalysis and molecular recognition. Further work is in progress to produce new chiral lanthanide phosphonate compounds with multifunctional properties.

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Supporting Information Available: Additional figures in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Dehydrated compound ***S*-Tb** (10 mg 0.025 mmol) was added to a solution of benzaldehyde (50 μL, 0.5 mmol), ethyl acetoacetate (65 μL, 0.5 mmol), and thiourea (36 mg, 0.6 mmol) in methanol (2 mL). After the reaction mixture was stirred at room temperature for 48 h, water (1 mL) was added, and the product was extracted with ethyl acetate (3 × 5 mL). After the organic layer was dried with anhydrous Na_2SO_4 and evaporated, the residue was purified by prepared TLC (petroleum ether/ethyl acetate 3:1) to afford 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one. ^1H NMR (500 MHz, DMSO, TMS): δ 9.16 (s, 1H; NH), 7.73 (s, 1H; NH), 7.33−7.30 (m, 2H; Ar-H), 7.25−7.22 (m, 3H; Ar-H), 5.14 (s, 1H; CH), 3.99−3.95 (q, $J = 7.1$ Hz, 2H; $-OCH_2-$), 2.25 (s, 3H; $-CH_3$), 1.09−1.06 ppm (t, $J = 7.1$ Hz, 3H; $-CH_3$). EIMS *m/z*: 260.3 (M^+).

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