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Enantioselective Resolutions and Circular Dichroism Studies of Lanthanide-Containing Keggin-Type $[Ln(PW_{11}O_{39})_2]^{11-}$ Polyoxometalates

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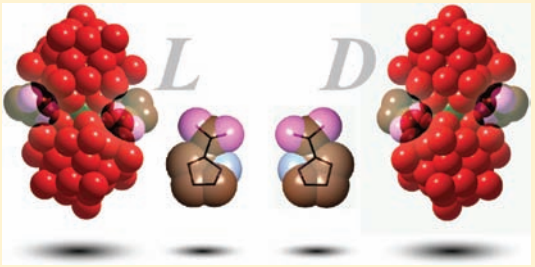
Supporting Information

ABSTRACT: Enantiopure crystals of $K_{1.3}Na_{3.2}H_{6.5}[L\text{-}Pr(PW_{11}O_{39})_2]\cdot 8.3L\text{-proline}\cdot 21.5H_2O$ (**1**), $K_{1.3}Na_{3.2}H_{6.5}[D\text{-}Pr(PW_{11}O_{39})_2]\cdot 8.3D\text{-proline}\cdot 17H_2O$ (**2**), and $K_{1.3}Na_{3.2}H_{6.5}[L\text{-}Er(PW_{11}O_{39})_2]\cdot 8.3L\text{-proline}\cdot 22.5H_2O$ (**3**) were successfully obtained by using L- and D-proline (pro) as chiral auxiliary agents. In these crystals, L- and D-$[Ln(PW_{11}O_{39})_2]^{11-}$ anions are attached by two L- and D-pro molecules, respectively, through a O···N hydrogen-bonding interaction between the square-antiprismatic LnO_8 center and amino-N atoms. The L- and D-$[Pr(PW_{11}O_{39})_2]^{11-}$ anions in aqueous solutions exhibited a couple of mirror-imaged CD spectra due to $^3H_{4/2}\rightarrow{}^3P_{0,1,2}$ and $^1D_2$ transitions in the stereogenic Pr^{3+} center. Chirality inductions by L- and D-pro from a racemic solution of $[Er(PW_{11}O_{39})_2]^{11-}$ was demonstrated by means of CD spectroscopy.



INTRODUCTION

Polyoxometalates (POMs)—metal−oxygen aggregates with discrete well-defined structures—show versatile properties such as catalysis, biological activities, and solid-state chemistry and physics.[1] The chiralities of POMs have received increasing interest,[2] as they would provide further development in applications. Significant current examples are asymmetric catalysts[3] and chiral recognition.[4] Studies of POM chirality in the biological field would raise expectations, because most of the biomolecules are optically active and many of their functional groups are known to interact with POMs with covalent and noncovalent interactions.

A chiral C_2-symmetric anion $[Ln(XW_{11}O_{39})_2]^{n-}$ ($Ln(XW_{11})_2$; Ln: lanthanide), first reported by Peacock and Weakley,[5] consists of a $Ln^{3+/4+}$ center octacoordinated by two tetradentate oxygen-donor $XW_{11}O_{39}^{n-}$ (XW_{11}) ligands with square-antiprismatic geometry.[6] The monovacant XW_{11} moiety, referred to as a "monolacunary" species, is derived from the parent Keggin-type $XW_{12}O_{40}^{n-}$ by removal of a W═O group. In crystalline solids, owing to the square-antiprismatic geometry for the LnO_8 coordination, the two XW_{11} subunits are ∼45°-twisted from each other, and the relative twist direction defines the two enantiomers of the $Ln(XW_{11})_2$ anion with C_2-symmetry. In aqueous solutions, ^{183}W NMR data for $Ln(PW_{11})_2$ showed spectra suggesting a C_{2v} or C_{2h} symmetry for the early Ln's (= La−Eu) and C_2-symmetry for the late Ln's (= Tb−Lu).[7] A temperature-controlled ^{183}W NMR study for $Lu(SiW_{11})_2$ solution allowed one to presume that two enantiomers are interchangeable at high temperatures (353−367 K) through rotation of the SiW_{11} moiety.[8] Recently, our attention has been focused on this structure, in which Ln plays roles of both stereogenic and $4f^n-4f^n$ transition centers. Generally, enantiopure Ln-centered complexes exhibit circular dichroism (CD)[9] and circularly polarized luminescence (CPL).[10] The flexible rotation of the XW_{11} moiety and $4f^n-4f^n$ transition of Ln^{3+} in chiral $Ln(XW_{11})_2$ anions would be applicable to optical materials and chiral sensing in catalytic and biological fields. However, to the best of our knowledge, most of the $Ln(XW_{11})_2$'s are racemized and crystallize in achiral space groups. A pioneering work by Pope and Termes[11] reported a Cotton effect of $(L\text{-brucine})_{7.6}Na_{2.4}[U^{IV}(PW_{11}O_{39})_2]$ in a DMF solution. Recently, spontaneous resolutions of $M(PW_{11})_2$ ($M = Ce^{4+}$,[6d] Zr^{4+},[12a] Hf^{4+}[12b]) were performed using the achiral dimethylammonium cation. The latter phenomenon is interesting but generally impractical for use because the products are an enantiomixture of crystals. Besides the Ln-containing POMs, $[Co_2Mo_{10}O_{34}(OH)_4]^{6-}$ is the first chiral POM that was isolated in an enantiopure form through a cation exchange with $[Co(en)_3]^{3+}$.[13] A recent example of asymmetric synthesis is $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]Zr_3O(H_2O)(tartH)[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$, the chirality of which is controlled by tartaric acid attached to two Zr sites with covalent-bonding.[14]

Herein, we describe the successful isolation of the following enantiopure crystals, $K_{1.3}Na_{3.2}H_{6.5}[L\text{-}Pr(PW_{11}O_{39})_2]\cdot 8.3L\text{-proline}\cdot 21.5H_2O$ (**1**), $K_{1.3}Na_{3.2}H_{6.5}[D\text{-}Pr(PW_{11}O_{39})_2]\cdot 8.3D\text{-proline}\cdot 17H_2O$ (**2**), and $K_{1.3}Na_{3.2}H_{6.5}[L\text{-}Er(PW_{11}O_{39})_2]\cdot 8.3L\text{-proline}\cdot 22.5H_2O$ (**3**) (proline = HNC_4H_7COOH). To date, chiral amino acids including proline (pro) have been used for the synthesis and recognition of chiral POMs. Interactions between a chiral $[\alpha_1\text{-}Ln^{III}(H_2O)_x(P_2W_{17}O_{61})]^{7-}$ and amino acids in solution were studied by means of ^{31}P and ^{183}W NMR, and interaction maps of W sites have been established.[15] In the

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Table 1. Crystallographic Data and Results for X-Ray Crystallography

	1	2	3
formula	$O_{116.1}PrP_2W_{22}K_{1.3}Na_{3.2}C_{41.5}N_{8.3}H_{124.2}$	$O_{111.6}PrP_2W_{22}K_{1.3}Na_{3.2}C_{41.5}N_{8.3}H_{115.2}$	$O_{117.1}ErP_2W_{22}K_{1.3}Na_{3.2}C_{41.5}N_{8.3}H_{126.2}$
fw	6969.37	6888.31	7013.74
cryst syst	triclinic	triclinic	triclinic
space group	*P*1	*P*1	*P*1
a (Å)	12.8544(3)	12.8016(4)	12.8505(5)
b (Å)	13.2986(3)	13.2173(5)	13.2454(5)
c (Å)	19.7777(4)	19.7108(7)	19.6811(7)
α (deg)	103.6597(7)	103.714(2)	103.7675(11)
β (deg)	92.6904(7)	92.569(2)	92.8707(10)
γ (deg)	97.6256(7)	97.660(2)	97.5486(11)
V (Å^3)	3245.44(12)	3201.0(2)	3214.0(2)
Z	1	1	1
θ range (deg)	3.1−27.5	3.1−27.5	3.1−27.5
limiting indices reflns	$-15 \le h \le 16$	$-15 \le h \le 16$	$-16 \le h \le 14$
	$-17 \le k \le 17$	$-17 \le k \le 17$	$-17 \le k \le 17$
	$-25 \le l \le 25$	$-25 \le l \le 25$	$-25 \le l \le 25$
cryst size (mm^3)	0.40 × 0.17 × 0.15	0.45 × 0.08 × 0.09	0.53 × 0.10 × 0.09
D_c (g cm^{-3})	3.566	3.573	3.623
F(000)	3137.00	3092.00	3156.00
μ (mm^{-1})	19.9926	20.2654	20.4633
total data	52693	52075	51805
unique data	25622	25513	25345
$R_{(int)}$	0.058	0.0465	0.072
goodness of fit	1.038	1.047	1.073
ρ_{max}, ρ_{min} (eÅ^{-3})	3.38, −2.76	3.01, −2.38	2.59, −3.02
R_1 [$I > 2\sigma(I)$][a]	0.0509	0.0429	0.083
wR_2[b]	0.1529	0.1425	0.1681
Flack parameter	−0.004(11)	0.023(10)	0.028(14)

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] Compound **1**: $w = 1/[\sigma^2(Fo^2) + (0.0920 \cdot P)^2 + 24.1757 \cdot P]$. Compound **2**: $w = 1/[\sigma^2(F_o^2) + (0.0955 \cdot P)^2 + 14.6824 \cdot P]$. Compound **3**: $w = 1/[\sigma^2(F_o^2) + (0.0809 \cdot P)^2 + 19.8623 \cdot P]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

present study, the X-ray crystallographic analyses of **1**−**3** revealed an association of pro molecules to the $Ln(PW_{11})_2$ anion with a hydrogen-bonding interaction in the solid state. The CD activity of the characteristic 4f−4f transitions in the Pr^{3+} and Er^{3+} centers was observed for the first time in Ln-POM complexes.

EXPERIMENTAL SECTION

Syntheses of $K_{1.3}Na_{3.2}H_{6.5}$[L-Pr($PW_{11}O_{39}$)$_2$]·8.3L-proline·21.5H_2O (1), $K_{1.3}Na_{3.2}H_{6.5}$[D-Pr($PW_{11}O_{39}$)$_2$]·8.3D-proline·17H_2O (2), and $K_{1.3}Na_{3.2}H_{6.5}$[L-Er($PW_{11}O_{39}$)$_2$]·8.3L-proline·22.5H_2O (3). L- or D-pro (9.0 mmol) was dissolved in an aqueous solution (20 mL) containing KCl (2.0 mmol), to which a $Ln(NO_3)_3 \cdot nH_2O$ solution (1.0 mmol in 5 mL of H_2O) was added. The mixture was stirred for 0.5 h at 60 °C, acidified to pH 1.5 with 1 M HCl, and reacted with aqueous $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 16H_2O$[16] (2.0 mmol in 15 mL H_2O) with boiling for 1 h. The solution was allowed to cool to room temperature, and residual fine powders were filtered off. The filtrate was boiled again to reduce the volume to ∼10 mL and stood at room temperature for slow evaporation to give block crystals of **1**, **2**, and **3** with 15, 15, and 37% yields (based on W), respectively, after several days. Elemental analyses of C, H, and N in **1**−**3** were performed on a Yanaco MT5 CHN CORDER. The contents of Na, P, K, Pr, Eu, Er, and W were determined using inductively coupled plasma (ICP) atomic emission spectroscopy on an ICPS-8100 spectrometer. Waters of crystallization were estimated thermogravimetrically (TG-DTA) using a ULVAC MTS9000 + TGD9600 system. Results for the elemental analyses are as follows.

Compound **1**. Found: C, 7.04; H, 1.34; N, 1.67; K, 0.81; Na, 1.18; P, 0.95; W, 56.50; Pr, 2.29; H_2O, 5.54 wt %. Calculated: C, 7.15; H, 1.80; N, 1.67; K, 0.73; Na, 1.06; P, 0.89; W, 58.0; Pr, 2.02; H_2O, 5.56 wt %.

Compound **2**. Found: C, 7.24; H, 1.44; N, 1.73; H_2O, 4.42 wt %. Calculated: C, 7.24; H, 1.69; N, 1.69; H_2O, 4.45 wt %.

Compound **3**. Found: C, 7.26; H, 1.36; N, 1.75; K, 0.77; Na, 1.14; P, 0.91; W, 57.0; Er, 2.55; H_2O, 5.77 wt %. Calculated: C, 7.11; H, 1.81; N, 1.66; K, 0.72; Na, 1.05; P, 0.88; W, 57.7; Er, 2.38; H_2O, 5.78 wt %.

Attempts to prepare compounds containing other amino acids, glycine, serine, threonine, and glutamine, under the same synthesis conditions resulted in the formation of poorly crystalline powders, for which no further characterization was made.

$K_{1.3}Na_{3.2}H_{6.5}$[L-Er($PW_{11}O_{39}$)$_2$]·8.3L-proline·17H_2O (3s). A stoichiometric synthesis according to the method of Fedotov et al.[7] was also adopted for the preparation of **3**. An aqueous solution (20 mL) containing PW_{11} (2.0 mmol) at pH 4.8 was added to a mixture solution of H_2O (20 mL), KCl (2.0 mmol), NaCl (18 mmol), L-pro (9.0 mmol), and $ErCl_3$ (1.0 mmol), boiled with stirring for 1 h, and filtered after cooling. The filtrate was acidified to pH 2.9 with 1 M HCl, heated for slow evaporation to reduce the volume to ∼20 mL, and allowed to stand at 14 °C. A product, **3s**, crystallized within several days (yield 18% based on W). Found: C, 7.13; H, 1.50; N, 1.67 wt %. Calculated: C, 7.21; H, 1.68; N: 1.68 wt %. Compound **3s** is identical to **3** except for fewer waters of crystallization (17H_2O).

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Single Crystal X-Ray Crystallography for 1−3 and 3s. Single crystals were mounted on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). Reflection data were collected at ~200 K and subjected to numerical absorption corrections based on the crystal sizes and shapes.[17] Structures were solved by the direct method SHELXS-97[18] and refined by the full-matrix least-squares on F^2 using CrystalStructure.[19] The absolute structures were determined by the Flack parameter refinement.[20] The Ln, W, and P atoms in the $[Ln(PW_{11}O_{39})_2]^{11-}$ anion and Na and K cations were refined anisotropically. All of the H atoms were not included in the refinements. The crystallographic data and results for the refinements were listed in Table 1. The structure of **3s** was identical to that of **3**, and its crystallographic data are listed in Table S1, Supporting Information.

Of the number of pro's (8.3 equivalents of $[Ln(PW_{11}O_{39})_2]^{11-}$) estimated from the elemental analyses, only four molecules have been found in the crystallographic analysis. Note that the determined crystal structures of **1**−**3** have large voids in their lattices (Figure S1, Supporting Information). In difference Fourier maps around these void regions, one can observe residual electron density distributions which resemble those of pro molecules or their pyrrolidine-ring fragment (Figure S2, Supporting Information). All attempts to refine these peaks with rigid or partially restrained models failed in divergences because of low electron density residuals (Table 1). We concluded that the remaining pro molecules are in positional, orientational, and/or occupational disordering state(s) in these voids. Also, crystallographically undefined Na and K cations might be distributed in these voids.

The details on the structures of **1**−**3** can be obtained from Cambridge Crystallographic Data Center (CCDC), e-mail: deposit@ccdc.cam.ac.uk, depository numbers CCDC-812343 (**1**), CCDC-812344 (**2**), and CCDC-812345 (**3**).

Spectroscopic Measurements. The solution CD spectra were measured on a JASCO J-820 spectrometer at room temperature using quartz optical cells (diameters, 10 or 30 mm; path length, 100 mm) under the following conditions: scanning speed, 10 nm min^{-1}; wavelength resolution, 5 nm; response time, 16 ms. The obtained spectra were corrected by subtraction from the spectrum of distilled water.

A chiral induction by pro was tested on the basis of the "Pfeiffer effect"[21] (see Results and Discussion) using aqueous racemic solutions of $[Er(PW_{11}O_{39})_2]^{11-}$ which had been prepared stoichiometrically.[7] An aqueous solution of $ErCl_3 \cdot 6H_2O$ (1.0 mmol in 15 mL H_2O) acidified to pH 1.5 with 1 M HCl was mixed with a solution containing PW_{11} (2.0 mmol in 15 mL H_2O). The solution was stirred for 1 h at 60 °C and allowed to cool to room temperature. The resulting racemic solution of $[Er(PW_{11}O_{39})_2]^{11-}$ is CD-inactive, to which L- or D-pro (9.0 mmol in 10 mL H_2O) was added with stirring, and then subjected to CD spectroscopy. The chirality induction is evidenced when ellipticity is detected on the CD spectrum.

The ^{31}P NMR spectra for compounds **1** and **2** in D_2O were measured on a Bruker Biospin AVANCE III (400 MHz) at 298 K. H_3PO_4 (85%) was used as an external standard.

RESULTS AND DISCUSSION

Compounds **1**−**3** were prepared by the reaction between Ln^{3+} and $[\alpha\text{-}PW_9O_{34}]^{9-}$ in the presence of L- or D-pro to crystallize in *P*1 with similar unit cell parameters (Table 1). On the other hand, we confirmed that the stoichiometric synthesis of the Er analog prepared from PW_{11} resulted in the formation of **3s**, which is practically identical to **3**. Absolute structures of **1**−**3** could be determined by refinement of the Flack parameters. The crystal structures of **1** and **2** (Figure S1, Supporting Information) consist of different enantiomers of $Pr(PW_{11})_2$ (hereafter, we define them as L-$Pr(PW_{11})_2$ and D-$Pr(PW_{11})_2$, respectively),

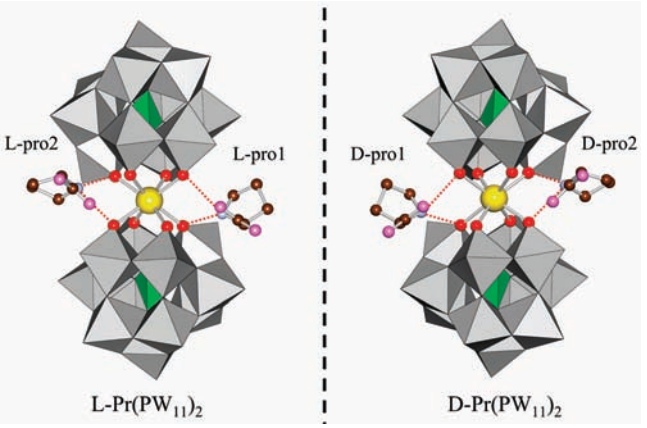

Figure 1. Structures of $Pr(PW_{11})_2$ anions in **1** (left) and **2** (right). Dark gray, WO_6 octahedra; green, PO_4 tetrahedra; yellow, Pr; red, O coordinating to Pr; pink, carboxyl O; brown, C; light gray, amino-N; red dotted lines, N···O hydrogen bonds.

L- and D-pro, alkaline cations (Na^+ and K^+), and waters of crystallization. Compound **3** is isostructural with **1**, containing L-$Er(PW_{11})_2$ anions. As mentioned in the Experimental Section, for all compounds **1**−**3**, a part of the L- and D-pro molecules and Na^+ and K^+ cations are highly disordered in the void regions among the $Ln(PW_{11})_2$ anions. The pK_a (1.95 and 10.47) of pro[22] and the preparative conditions (pH 2.6−2.9) of **1**−**3** allow one to infer that one or two pro molecules are protonated ($H_2N^+C_4H_7COOH$) and others are zwitterionic ($H_2N^+C_4H_7COO^-$).

Figure 1 represents the L- and D-$Pr(PW_{11})_2$ anions in **1** and **2**. The PW_{11} moieties in these anions are twisted in opposite directions, giving rise to the stereogenic centers on the Pr atoms. The geometrical parameters of $Pr(PW_{11})_2$ are comparable to those in the same anion in different compounds.[6c] The anion is attached by two pro molecules in the vicinity of the PrO_8 center; each of the amino N atoms is positioned with hydrogen(H)-bond distances d(N···O) = 2.82(2)−2.95(2) Å from two O atoms in the PrO_8 polyhedron. In the pro molecules, both of the H atoms on the amino-N would participate in the H-bonding. The carboxylate groups are directed outward from the anion to avoid an electrostatic repulsion. Unlike the H-bonding scheme in **1** and **2**, $[\alpha_1\text{-}Ce^{III}(H_2O)_x(PW_{17}O_{61})]^{7-}$ is presumed to interact with pro via a direct attachment between the Ce^{3+} center and carboxylate O.[15a]

Figure 2a displays the molecular association between L-Pr-$(PW_{11})_2$ and L-pro in **1**. The two pro molecules have slightly different conformations (Figure 2 inset). The C^{α}, C^{β}, C^{δ}, and N atoms are nearly planar for both molecules. The C^{γ} atom is in a *cis* position with respect to the carboxyl group in L-pro1, whereas that in L-pro2 is in a *trans* position. It is significant that the molecular surface of L-pro closely fits into the groove-forming O atoms (represented with red spheres in Figure 2a) in L-Pr-$(PW_{11})_2$. A hypothetical rigid model (Figure 2b right) composed of opposite chirality, i.e., L-$Pr(PW_{11})_2$ and *cis*-D-pro1, demonstrates a steric hindrance, in which an estimated shortest d(N···O) (= 3.4−4.1 Å) is longer than that in **1**. Therefore, the interaction appears to be stereoselective. Other L-pro molecules in **1** do not participate in a specific association with L-$Pr(PW_{11})_2$ but serve as chiral fillers positioned among the anions in the crystal. Compound **2** has the inverse structure of **1**;

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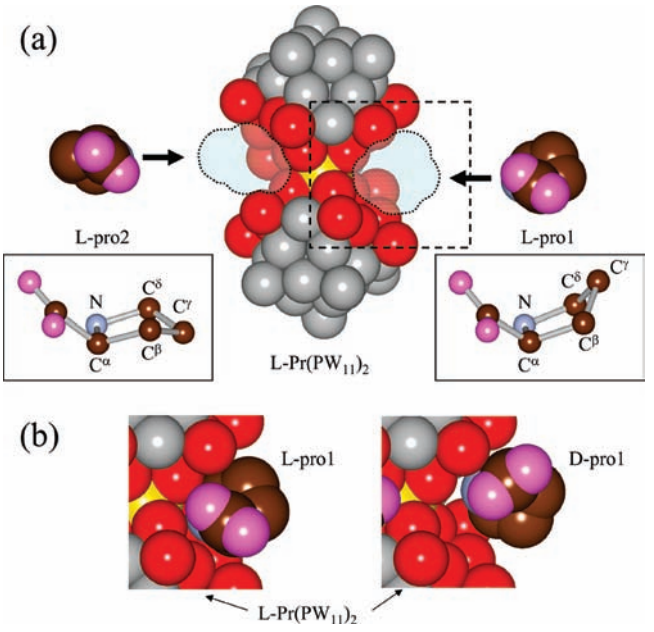

Figure 2. (a) Space-filling model of L-Pr$(PW_{11})_2$ attached by two L-pro molecules in **1**. The groove-forming O atoms capturing the pro molecules are shown by the red spheres. Insets: Conformations of the L-pro molecules. (b, left): Close-up view of the boxed area in (a). (b, right): Hypothetical association model between L-Pr$(PW_{11})_2$ and D-pro1.

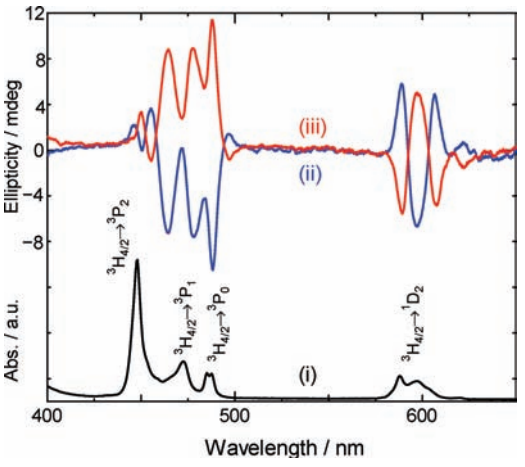

Figure 3. VIS absorption spectrum of **1** (i) and CD spectra of **1** (ii) and **2** (iii) in aqueous solutions ($[Pr(PW_{11})_2] = 2.0 \times 10^{-2}$ M).

the two D-pro1 and D-pro2 molecules attached to the D-Pr$(PW_{11})_2$ anion have *cis* and *trans* conformations (Figure 1, right). In the same manner, the association between L-Er$(PW_{11})_2$ and two L-pro's is established in **3** by slightly longer H-bonding d(N···O) (= 2.88(2)−3.06(2) Å) than those in **1** and **2**.

Figure 3i shows a visible-region absorption spectrum of L-Pr$(PW_{11})_2$ in aqueous solution. It consists of relatively broad bands, which can be assigned to $^3H_4 \rightarrow {}^3P_2$ (peak: 448 nm), $^3H_4 \rightarrow {}^3P_1$ (472 nm), $^3H_4 \rightarrow {}^3P_0$ (485−486 nm), and $^3H_4 \rightarrow {}^1D_2$ (588 and 596 nm) transitions of Pr^{3+}. The D-Pr$(PW_{11})_2$ solution showed a spectrum identical to that of Figure 3i (data not shown). The CD spectra for these solutions (Figure 3ii, iii) exhibit a couple of mirror-imaged bands. The observed CD activity is due to the stereogenic Pr^{3+} center in dominant L- or

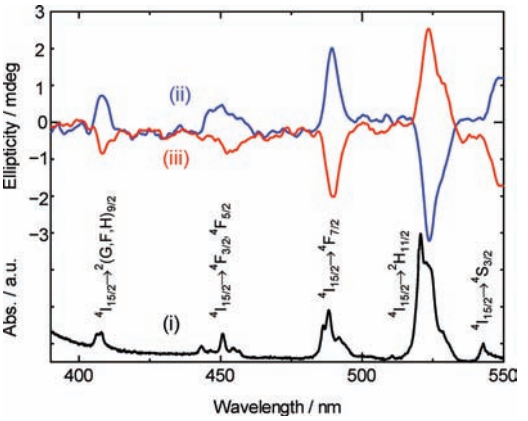

Figure 4. UV−vis absorption spectrum of racemic solution of Er$(PW_{11})_2$ (i) and CD spectra after treatment with L-pro (ii) and D-pro (iii) ($[Er(PW_{11})_2] = 2.5 \times 10^{-2}$ M; [pro] = 2.3×10^{-1} M).

D-Pr$(PW_{11})_2$ species induced by the coexistent L- or D-pro, respectively. ^{31}P NMR spectra of **1** and **2** (in D_2O solutions) have a singlet peak at −13.3 ppm (Figure S3, Supporting Information), indicating a stability of the Pr$(PW_{11})_2$ anion in solution.

To demonstrate the chirality induction by L- and D-pro, we examined the Pfeiffer effect[15] in Er$(PW_{11})_2$ solutions (see Experimental Section). The initial solution containing a racemic mixture of Er$(PW_{11})_2$ has sharp absorption bands (Figure 4i) assignable to f−f transitions of Er^{3+}: $^4I_{15/2} \rightarrow {}^2G_{9/2}$, $^2F_{9/2}$, $^2H_{9/2}$ (∼405 nm), $^4I_{15/2} \rightarrow {}^4F_{5/2,3/2}$ (380, 450 nm), $^4I_{15/2} \rightarrow {}^4F_{7/2}$ (480 nm), and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (520−530 nm). An addition of L-pro to this solution induced a clear CD band (Figure 4ii) corresponding to the above f−f transitions. On the other hand, treatment with D-pro resulted in a mirror-imaged spectrum (Figure 4iii). These results suggest that L- and D-Er$(PW_{11})_2$ species are exchangeable to establish a racemic equilibrium, and the equilibrium is shifted to either of the enantiomers as a result of interaction with L- or D-pro. Similar racemization of Ln$(XW_{11})_2$ in aqueous solution was presumed for Lu$(SiW_{11})_2$ at high temperatures (353−367 K), which may occur through a fast rotation of the SiW_{11} unit.[8]

■ CONCLUSIONS

In summary, we succeeded in obtaining enantiopure Ln$(PW_{11})_2$ compounds **1**−**3** using L- and D-pro as the chiral inducers. Structural characterization of the compounds revealed the H-bonding interaction between Ln$(PW_{11})_2$ and two pro molecules. The rigid molecular model composed of Ln$(PW_{11})_2$ and pro allowed us to speculate that the interaction in the crystal is stereoselective. The solution CD spectroscopy for **1**−**3** exhibited clear ellipticity at 4f−4f absorption bands of Pr^{3+}, demonstrating stereogenic Pr centers in the L- and D-Pr$(PW_{11})_2$ anions. The Pfeiffer effect in Er$(PW_{11})_2$ solutions proved the interexchange of the enantiomers and domination of either of them in the coexistence of L- or D-pro.

The Ln$(PW_{11})_2$−pro association found in the crystals is of great interest in view of stereo and chiral chemistry. However, we have no information on the interaction between Ln$(PW_{11})_2$ and pro in solutions and on the isolation mechanism. Further investigation on these points is a subject of our current study.

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■ ASSOCIATED CONTENT

Supporting Information. The X-ray crystallographic data for **3c** (Table S1), packing diagrams and difference Fourier maps for **1**−**3** (Figures S1 and S2), and solution ^{31}P NMR spectra for **1** and **2** (Figure S3) are available free of charge via the Internet at http://pubs.acs.org.

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