Design and Synthesis of Enantiomerically Pure Chiral Sandwichlike Lamellar Structure: New Explorations from Molecular Building Blocks to Three-Dimensional Morphology

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Ⓢ *Supporting Information*

ABSTRACT: This article reports a pair of novel chiral sandwichlike complexes for the first time. In the two complexes, lanthanide Eu^{3+} ions and Na^+ ions are sandwiched between Schiff base ligands, resulting in a two-dimensional plane. For both of the complexes, the intraplane and interplane interactions are utterly different. The adjacent planes are held together by weak van der Waals forces, while the single plane is formed by covalently bonded intraplane N−Eu−O, O−Eu−O, and O−Na−O atoms. On the basis of this characteristic information derived from their molecular building blocks, we studied three-dimensional morphology which has good agreement with expected lamellar morphology. Furthermore, to examine the chiroptical and stable activities, the CD spectra were investigated in the solution of methanol and five different solid forms.

The exploration from molecular building blocks to the three-dimensional (3D) morphology is of utmost importance, not only from the viewpoint of scientific curiosity but also for the development of next-generation organic devices with electrical, optical, chemical, or biological functions.[1,2] With the help of modern analysis instruments and technology, we can get a large amount of information from molecular structure that involves the lattice positions of atoms, bond length and bond angle, dihedral angle, valence of element, and so on. In comparison, 3D morphology is a way in which substances behave. Micro- and macrolevels belong to two domains with vast differences, so it is not easy to figure out the cohesion between micromolecule and 3D morphology. Thanks to crystal engineering,[3] its conceptions undoubtedly help to shed light on the connection. By means of crystal engineering, we can get a wealth of knowledge that can now be used to help design and synthesize new materials. Besides, it also gives us the opportunity to get the predictable results after reasonable analysis. Thus, by selecting the right molecular building blocks, and armed with a detailed knowledge of the preferred interactions likely to be undertaken by these molecules, it is at least, in principle, possible to synthesize target products in a predictable way.[4]

In recent years, chiral inorganic−organic materials have received considerable attention, not only because of their numerous potential applications in nonlinear optics, enantio-

selective catalysis, and enantiopure medicine but also because of their intriguing variety of architectures and topologies.[5−7] Controlling the chirality in coordination complexes and in materials is an important way of relating their properties and reactivity to their structure and composition in a rational and predictive way. Lanthanide-based complexes are ideal candidates for their fascinating self-assembled structures and potential applications in magnetic, optical, electronic, and catalytic processes.[8] However, Ln ions inherent nature, such as their kinetic lability and weak stereochemical preference, often cause the design and preparation of lanthanide-based chiral materials to be very difficult. Thus, how to circumvent this target has become a big challenge.

After years of development, our research group has accumulated rich experience in the synthesis of lanthanide compounds.[9] Herein, we intend to design and synthesize enantiomerically chiral materials in which Ln ions are indispensable. Until now, three distinct approaches have been exploited to get the chiral materials: (1) utilizing chiral ligands to bridge metal ions or secondary building units,[10] (2) utilizing chiral coligands (templates) that do not participate in the framework but direct formation of a chiral structure,[11] and (3)

utilizing achiral ligands that crystallize in chiral space groups.[12] Among these three strategies, unambiguously, the first one provides the most straightforward and reliable way to synthesize chiral materials, and our attention in the chiral multidentate ligands are illustrative of this approach. As shown in Scheme S1 of the Supporting Information, (S)-L and (R)-L in enantiomeric form not only retain the chirality of the amino acids but also have versatile coordination behaviors. Besides, in the view of the structure, the functional groups with oxygen atoms allow extensive cross-linking between the metallic ions and organic moieties, but part of the methyl group and benzene ring are hindered in yielding high-dimensional architectures. Both helpful and hindering functions exist in one ligand, and that, in and of itself which have seemingly contradictory factors, provides the possible conditions to get unexpected crystal structures. Fortunately, the expectation has been supported via experiment, and a pair of novel sandwichlike complexes which were rarely reported in the literature was obtained.

Reaction of $Eu(NO_3)_3 \cdot 6H_2O$, NaOH, (S)-L^{3-} or (R)-L^{3-} in the solvent of methanol afforded pale yellow single crystals of complexes $\{Eu[(S)\text{-}L]_2\}_2Na_6$ (**1a**) and $\{Eu[(R)\text{-}L]_2\}_2Na_6$ (**1b**).[13] Single crystal X-ray diffraction data for complexes **1a** and **1b** were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 185 K. The crystal structures were solved by means of direct methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).[14] All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. All nonhydrogen atoms were refined with anisotropic displacement parameters.

The results of X-ray crystallographic analysis reveal that complexes **1a** and **1b** crystallize in the chiral space group $P2_1$. Both of them contain two types of cations (Eu^{3+} and Na^+) with different radii (Figure 1a). The Eu^{3+} ion is eight-coordinated with six oxygen atoms and two nitrogen atoms, forming a distorted square antiprism where three oxygen atoms plus one nitrogen atom create a local square plane, and three different oxygen atoms and one nitrogen atom form the other distorted square plane (Figure 1b). The bond angles for O−Eu−O, O−Eu−N, and N−Eu−N are in the range of 72.241−153.261°, 62.381−137.691°, and 148.341−152.441°, respectively. The average Eu−O bond length is 2.378 Å within the 2.286−2.503 Å range, while the Eu−N bond length ranges from 2.492 to 2.537 Å, slightly longer than those of the Eu−O bond. All O−Eu−O, O−Eu−N, and N−Eu−N bond angles and Eu−O and Eu−N bond lengths are within the expected ranges (Table S2 of the Supporting Information).

In each homochiral complex, two L^{3-} ligands and one Eu^{3+} ion form a EuL_2^{3-} unit, and each EuL_2^{3-} unit is connected with Na^+ ion, producing 2D planes (Figure 1, panels c and d). This 2D plane is novel with the sandwichlike lamellar structure. In both complexes, Eu^{3+} ions and Na^+ ions are sandwiched between Schiff base ligands; as shown in Figure 1 (panels e and f), L^{3-} ligands are the major components of two slices of extended "bread", while Eu^{3+} and Na^+ ions are the part of metallic "meat or fruit". Then, the bread and meat or fruit are connected by covalently bonded intraplane N−Eu−O, O−Eu−O, and O−Na−O atoms. In addition, there is one neutral aqua ligand which is coordinated with the Na ion in each complex. The hydrogen bonds related to H_2O, such as O34−H100···O26 and O34−H101···O23 in complex **1a** or O31−H31A···O16 and O31−H31B···O12 in complex **1b**, guarantee the stability of the 2D framework. The individual 2D plane is relatively stable
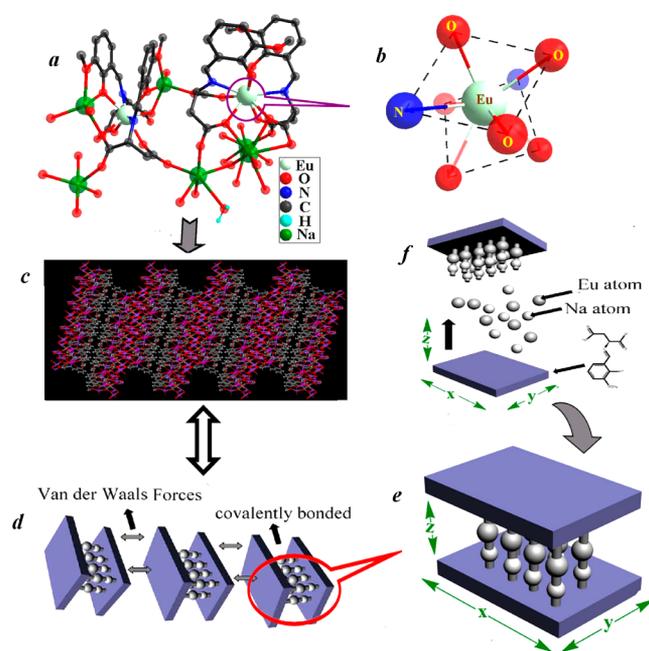
Figure 1. (a) Representation of the molecular structure of complex **1a** (all H atoms on carbon are omitted for clarity; complex **1a** and **1b** are similar to each other). (b) A distorted square antiprism which is formed by a Eu^{3+} ion. (c) The extended structure of complex **1a** viewed along the crystallographic *b* axis. (d) The schematic illustration of the extended structure. (e) The schematic presentation of the sandwichlike structure. (f) The vivid illustration of the basic components of the sandwichlike structure.

because of the dominant covalent interactions, while the adjacent planes only depend on weak van der Waals forces (Figure 1d). For **1a** or **1b**, it is not easy to construct a higher dimension (such as a 3D network), because the special sandwiched pattern may be the main resistance.

As expected, the observed chirality indicated by their chiral space groups can be understood in terms of chirality transfer from the small chiral amino acids to the whole framework. To study the root of its chirality, the chirality is based on the absence of a planar symmetry or an inversion center in the molecules as a whole through the chiral carbon atom. To examine the chiroptical and stable activities of enantiopure complexes **1a** and **1b** in the solution state, their CD spectra in methanol were investigated. The CD spectra are mirror images of one another, and conclusively demonstrate that complexes **1a** and **1b** are enantiomers (see Figure S5, panels a−e of the Supporting Information). Besides, the CD spectra of complexes **1a** and **1b** are virtually unchanged with time, indicating that both compounds are enantiomerically stable in methanol solution. When $Eu(NO_3)_3 \cdot 6H_2O$, NaOH, and both (S)-L^{3-} and (R)-L^{3-} are reacted together in the methanol solvent, we got a racemic compound, and the correlational CD was shown in Figure S5f of the Supporting Information. Statistically, only 5 to 10%, based on probability, can be conglomerate crystals under these circumstances.[15] This means that homochiral interaction upon the formation of crystalline racemates is usually weaker than heterochiral interaction,[16] thus indicating the challenge in realizing spontaneous resolution.

In previous reports, the mechanism of formation of 3D morphology was mainly believed to originate from the intrinsic molecular structure. For lamellar structures, one of the most typical examples is MoS_2, which has attracted tremendous

interest during the past few years.[17] MoS_2 is built of atomic planes held together by weak van der Waals forces, and each plane is formed by covalently bonded intraplane S−Mo−S atoms (Figure S2 of the Supporting Information). Compared to the intraplane interaction, the interplane interaction is relatively weak, and this causes the shear resistance to be weak. Further, the interplane slippage is much more apt to occur when the shear force is existed, thus resulting in lamellar morphology. From the above, we can conclude that the formation of MoS_2 morphology can be well-illustrated with the help of the molecular structure. Such conjecture also remained valid when it was extended to carbon,[18] metal sulfides,[19] and boron nitride;[20] however, the inorganic−organic materials are rarely reported by researchers.

Structurally similar to MoS_2, the sandwichlike lamellar complexes which we synthesized are also built of atomic planes held together by weak van der Waals forces, and each plane is formed by covalently bonded intraplane atoms. In the sandwichlike lamellar complexes, the ligands and metal atoms are extended by strong covalent bonds only along the [001] plane. Along the [100], part of the methyl group and benzene ring in both complexes are almost intended to face outward mutually. This special structure causes different interactions between the intraplane and interplane, and if there is external force involvement, the interplane interaction of the complex will be broken more easily. With MoS_2, the micromechanical exfoliation has been used to fabricate and isolate thin sheets with the knowledge of crystal engineering.[21] For the sandwich-like complex, what will be the 3D morphology? Will the rules also cover a case like this? On the basis of a comprehensive analysis of the structural information and reported literature, we surmise that the 3D morphology of the sandwichlike complex should be inclined to be lamellar if they are accordant with the conceptions of crystal engineering. Surely, the results of our experiments verify the preceding ideas. No matter which method (ultrasonic treatment or agitation) is used, we deal with the sample without any surfactant or derivant. Together with the crystals, to observe their 3D morphology, the crystals are lamellar (Figure S6 of the Supporting Information), and the samples of ultrasonic treatment or agitation at different temperatures are also all lamellar (Figure 2a and Figure S3, panels a−c of the Supporting Information).

Figure 2b shows the small-angle X-ray diffraction pattern of the material of **1a**. Experimental methods and procedures are similar to the reported literature,[22] and the scattered intensities were measured as a function of **Q**, the scattering vector. From the positions of the peaks (Q_a), the repeat distance can be calculated by using the equation $Q_a = 2\pi n/d$, in which d is the repeat distance and n the order of the diffraction peak. Two strong diffraction peaks, which are located at $Q = 5.74$ and 11.48 nm^{-1}, are observed in the small-angle X-ray diffraction curve, indicating the second and fourth orders of a lamellar phase with a periodicity of 2.19 nm. The thickness of the sandwichlike structure which consists of two slices of extended bread and metallic meat or fruit is 22.337 Å in its crystal structure (Figure 2d). The small-angle X-ray diffraction shows good agreement with the crystal structure. To further study the relationship between the thickness and the d spacing, three samples were randomly selected from ten different samples. Interestingly, when the measured thickness of different samples were divided by d spacing, the results are all nearly round numbers (for Figure 2c, 65 nm is approximately equal to 30;
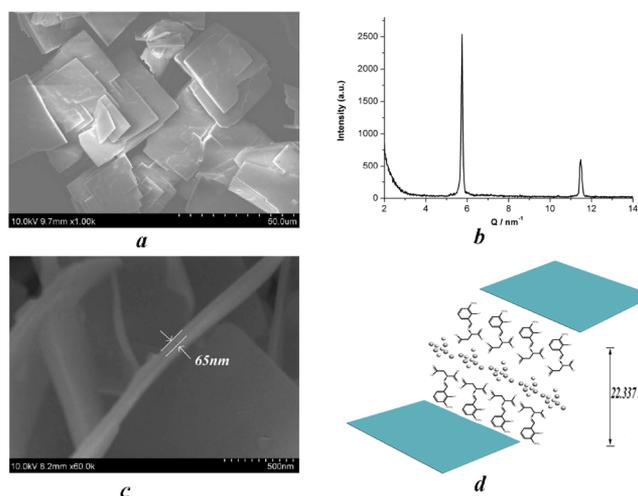
Figure 2. (a) The SEM image for the sample of ultrasonic treatment. (b) The small-angle X-ray diffraction curve of the sample **1a**. (c) The side view of the lamellar sample **1a**-1. d) The schematic presentation for the thickness of the sandwichlike structure.

Figure S3d of the Supporting Information equals 10; Figure S3e of the Supporting Information equals 20).

As we were not able to obtain single crystals for the samples after ultrasonic treatment and agitation, X-ray powder diffraction experiments were used to characterize them. Figure 3 shows the powder X-ray diffraction pattern of the final
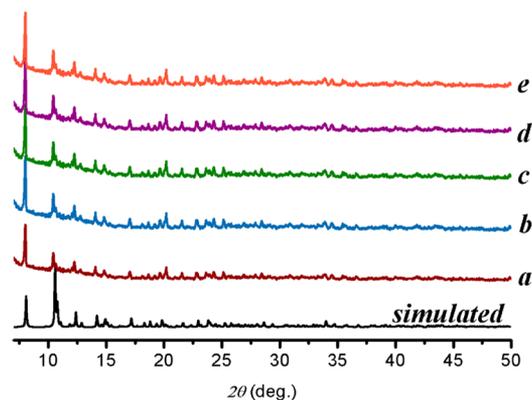
Figure 3. XRD curves of the complex **1a**. (a) XRD of crystals, (b) ultrasonic treatment, (c) agitation in 25 °C, (d) agitation in 60 °C, and (e) agitation in 70 °C.

products. From the results it can be seen that the peaks are strong and narrow, and the samples were crystalline in spite of different reaction conditions. All diffraction peaks of the samples which were ultrasonically treated or agitated at different temperatures can be well-indexed to the simulated peaks. Besides, in order to examine chiroptical and stable activities after ultrasonic treatment and agitation, the CD spectra were also studied. CD data were obtained from a transparent disk made from a mixture of **1a** or **1b** (5 mg) and KBr (100 mg). As shown in Figure S5 of the Supporting Information, the CD spectra of complexes **1a** and **1b** were basically kept under the conditions of ultrasonic treatment and agitation. The powder X-ray diffraction pattern and CD spectra show that the sandwichlike complexes have good stability in moderate reaction conditions.

In conclusion, a pair of enantiomerically chiral sandwichlike lamellar structures were synthesized with conventional methods. Accounting for the characteristic information derived from their molecular building blocks, we studied the 3D morphology. Furthermore, to examine the chiroptical and stable activities, the CD spectra were investigated in the solution of methanol and five different solid forms. Further work on the characteristic features of these complexes is by way of exploration and development.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files (CIF format) for complex **1a** and **1b**, and additional structural figures and physical characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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(13) Procedures for the preparation of ligands (S)-L and (R)-L are described in the Supporting Information. Synthesis of **1a**: A mixture of NaOH (40 mg, 1 mmol) and (S)-L^{3-} (333 mg, 1 mmol) in methanol (20 mL) was stirred for 5 min to obtain a transparent solution. Then, a solution of Eu(NO$_3$)$_3$·6H$_2$O (223 mg, 0.5 mmol) in methanol (10 mL) was added, and the mixture was rapidly stirred for 2 h. The solution is then left to slowly evaporate. A lot of microcrystalline powder was obtained by slow evaporation of methanol over a week at room temperature in air. Pale yellow single crystals, suitable for X-ray diffraction analysis, were obtained by the recrystallization of microcrystalline powder in methanol. These crystals were collected by filtration, washed with cold methanol, and dried in air. Yield: 63% (based on the ligand). Elemental analysis (%) calcd for C$_{96}$H$_{72}$Eu$_4$N$_8$Na$_{12}$O$_{63}$: C, 35.7; N, 3.4; Eu, 18.8; Na, 8.5. Found C, 36.3; N, 3.5; Eu, 18.2; Na, 8.1. Synthesis of **1b**: This complex was synthesized following the same procedure as described for **1a** but with (R)-L^{3-} (333 mg, 1 mmol) instead of (S)-L^{3-}. The crystals were obtained in a 59% yield (based on the ligand). Elemental analysis (%) calcd for C$_{96}$H$_{72}$Eu$_4$N$_8$Na$_{12}$O$_{63}$: C, 35.7; N, 3.4; Eu, 18.8; Na, 8.5. Found C, 36.1; N, 3.5; Eu, 18.6; Na, 8.2.

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