involving weak intermolecular forces, the much stronger interactions between metal ions and polydentate organic ligands make the contribution of weak interactions less significant.\[1,2\] Thus, the number of factors to be considered in the process is substantially decreased, and the outcome is often predictable. Many efforts were successfully directed to obtaining geometrically intriguing supramolecules such as molecular polygons,\[3\] highly symmetrical cage molecules,\[4\] and metal–organic frameworks\[5\] by rational design of metal–ligand motifs. However, precise prediction of the outcome is still not always possible, and there is more to be explored, especially for the $\text{f}$-block elements because of their versatile coordination numbers.\[6\] Potential applications of self-assembled lanthanide-containing nanoparticles in catalytic reactions, optoelectronics, and magnetic materials have attracted much interest.\[7]\] Despite intensive studies, enantiopure lanthanide coordination compounds still represent a formidable challenge.\[8]\]

We herein report a unique chiral lanthanum-containing supramolecule, dubbed lanthanitin because it forms by ferritin-like assembly.\[9]\] In addition, its incorporation into a chiral double helix in crystals in an unprecedented manner constitutes a new class of crystal packing other than that of the helicates.\[10]\] Chiral ligands (S,S)-H1 and (R,R)-H1 (acid forms of 1) used in this study were both synthesized from 4,4'-dibromostilbene in optically pure form by taking advantage of Sharpless asymmetric dihydroxylation (Scheme 1).\[11]\] Chirality is introduced on the ethylene bridge. The ditopic carboxyl groups on para positions of the aromatic rings will serve to bridge various metal ions. Tying up the two hydroxyl groups with a 1,1'-dimethylmethylene group eliminated the flexibility of the molecule. Thus, the molecule has a fixed conformation and a dihedral angle between the two benzoic acid groups of about $80^\circ$.

Colorless antiprismatic crystals of (S)-lanthanitin suitable for X-ray diffraction were grown from a mixture of (S,S)-H1 and LaCl$_3$$\cdot$6H$_2$O in N,N-diethylformamide (DEF) solution at 60°C over two weeks (Figure 1a). X-ray crystallographic studies revealed that the crystal belongs to the enantiomorphous space group $P4_12$2. The asymmetric unit containing a trigonal arrangement of nine La$^{III}$ ions and 12 (S,S)-1 linking ligands forms a supramolecular hemisphere. When the crystallographic twofold symmetry is applied to the asymmetric unit, two hemispheres fuse to form a spherical molecule with a diameter of 3.0 nm.

Twenty four ligands encompass the metal ions in a unit having the formula $[\text{La}_{18}(\text{S,S})_{12}((\text{CO}_3)_{3}(\text{H}_2\text{O})_{3})]^{2+}$ (Figure 1b). In the core of the molecule, two carbonate anions (Figure 2) each bind three lanthanum ions. The presence of the carbonate core as a seed is critical for the formation of crystals, even though the origin of carbonate is not clear. It may come from atmospheric carbon dioxide. This unusual kind of nucleation was reported previously only in two cases, one of which includes a Gd$^{III}$ complex.\[12]\]

One of the most notable structural features of (S)-lanthanitin is that the 18 La$^{III}$ ions form an octahedral arrangement with six sets of three lanthanide ions. The three La$^{III}$ ions in each set are arranged linearly with average interatomic distances of 4.145 Å. These sets are, if we consider...
ions in the core of the molecule and their symmetry-related partners form hydrogen bonds among themselves and leave no void space. The $\text{La}^{III}$ ions on the second sphere, $\{\text{La}(4), \text{La}(5), \text{and La}(6)\}$, have eight oxygen atoms as ligands, all of which are from carboxylates. The coordination between $\text{La}^{III}$ and carboxylate exhibits three different modes: monodentate, bis-monodentate, and chelating, $\mu-O$ tridentate, except for one carboxylate group (Figure 3). For the $\text{La}^{III}$ ions on the third sphere, additional water molecules are required to complete the respective coordination numbers besides oxygen atoms from carboxylates in bis-monodentate and bidentate chelating modes.

Scheme 1. Preparation of ligands (S,S)-$H_2$ and (R,R)-$H_2$. See the Supporting Information. PTSA $=$ para-toluenesulfonic acid.

Figure 1. a) Preparation of lanthanitin enantiomers. b) Molecular structures of lanthanitins with octahedral arrangement of 18 La ions as large blue balls and the central carbonate carbon atoms as small green balls. Hydrogen atoms are omitted for clarity. Color code: C gray, O red.

The asymmetric unit, $\{\text{La}(1), \text{La}(4), \text{La}(7)\}$, $\{\text{La}(2), \text{La}(5), \text{La}(8)\}$, and $\{\text{La}(3), \text{La}(6), \text{La}(9)\}$ which together form a pyramidal shape with a small triangle $\{\text{La}(1), \text{La}(2), \text{La}(3)\}$ linked by a carbonate anion at the apex (Figure 2b). The interplanar distance among the sets is 1.90 Å. The outer lanthanum ions $\{\text{La}(7), \text{La}(8), \text{La}(9)\}$ and their twofold symmetry pairs define a slightly distorted octahedron with an average edge length of 17.624 Å (16.818–18.794 Å).

The average diagonal distance between La vertices is 24.886 Å. Most $\text{La}^{III}$ ions in the hemisphere have a coordination number of eight, except for $\text{La}(8)$ and $\text{La}(9)$, which are ten-coordinate (Figure 3). All three central lanthanum ions located on the first sphere, $\{\text{La}(1), \text{La}(2), \text{and La}(3)\}$, are coordinated by three kinds of ligands: two oxygen atoms of $\text{CO}_3^{2-}$, four oxygen atoms from carboxylate in bis-monodentate fashion, and two water molecules. The water molecules are engaged in hydrogen bonds with adjacent water molecules. All six water molecules are bound to three $\text{La}^{III}$ ions in the core of the molecule and
To grasp the framework structure, the molecule can be disassembled schematically into six \( \text{La}^3(\text{S},\text{S})\text{-I} \) units which are related with each other by pseudo-octahedral symmetry (Figure 4a). Each unit is interconnected with another four equatorial units by four organic ligands to form a completely integrated assembly. This assembly pattern endows lanthanitinin with a close structural resemblance to ferritin.\(^9\) The arrangement of the organic linkers in lanthanitinin is the same as that of the protein subunits in ferritin (Figure 4b and c).

Neglecting the minor distortions around the \( \text{La}^3\) coordination sphere, the lanthanum ions are aligned along three pseudomolecular fourfold rotational axes that pass through the molecule. In addition, three pseudo-threefold axes penetrate a set of trigonal-antiprismatic triangles, and six pseudo-twofold axes penetrate six sets of edges. The symmetry of the molecule is close to point group \( O \) or crystallographic 432, because there is no inversion center due to the chirality. Such an analogy to the well-known 432 molecular symmetry of ferritin is rarely seen in synthetic supramolecules.

Interestingly, (S)-lanthanitinin molecules form a right-handed double helix with pitch length of 80.460 Å and radius of 13.829 Å around the helical axis at (0.5,0.5,\( z \)) (Figure 5a). (S)-Lanthanitin units contact each other through 1,1'-dimethylmethylene (DMM) groups. Two DMM groups form a chiral cavity in which the two methyl groups of the DMM moieties of neighboring balls are incorporated (Figure 5b and c). The hydrogen atoms on the stereogenic carbon atoms are in good van der Waals contacts with the neighboring DMM groups.

\((R)\)-Lanthanitin, the chiral counterpart of (S)-lanthanitin, was prepared by employing \((R,R)\text{-IH}_2\) in place of \((S,S)\text{-IH}_2\). As we expected, \((R)\)-lanthanitin belongs to space group \( P4_122 \) of \((S)\)-lanthanitin. Furthermore, \((R)\)-lanthanitin also forms a double helix in the crystal lattice, with opposite handedness (Figure 5a). As confirmed by solid-state circular dichroism (CD), the chirality derived from the ligands is preserved in the crystals (Figure 6). Both \((S)\)- and \((R)\)-lanthanitin crystals in KBr pellet give mirror-symmetrical CD spectra with opposite signs, that is, each crystal has only one sense of helical structure. In addition, although there is an example of self-assembly of spherical colloids into single helical chains by capillary forces,\(^{13}\) it is very unusual that supramolecular double helices are formed by discrete entities through
nondirectional van der Waals interactions. Usually most artificial helices or double helices, denoted as helicates, have been guided by relatively strong interactions such as hydrogen bonds or coordination bonds.[14]

In conclusion, we have obtained novel supramolecules containing lanthanum ions: (S) and (R)-lanthanitin, in which many ligands work together to bind numerous metal ions and form a spherical supramolecule with unique structural resemblance to ferritin. Furthermore, the chiral supramolecules resulting from the use of enantiomerically pure ligands form double helices in the crystal with a single handedness. Various combinations of lanthanides and chiral ligands could provide supramolecule lanthanide nanoparticles with potential optoelectronic, magnetic, and catalytic applications. Their solution properties and applications will be subjects of future study.

Experimental Section

Synthesis of (S)- and (R)-lanthanitin: Ligands (SS)-H2 and (RR)-H2 were prepared according to the methods described in the Supporting Information. A mixture of LaCl3·6H2O (0.010 g, 0.10 mmol) and (SS)-H2 or (RR)-H2 (0.010 g, 0.10 mmol) in DEF (3 mL) and H2O (3 mL) was heated at 60 °C for two weeks. Colorless prismatic crystals were obtained in 30% yield. The crystals were sparingly soluble in water before sonication, and insoluble in common organic solvents. Elemental analysis (%) calculated for (S)-lanthanitin [La18(OCOO)4(C6H4O2)-]·H2O: C 46.90, H 4.27, N 0.18; found: C 46.90, H 4.11, N 0.15.

X-ray structural analysis of (S)-lanthanitin: Prismatic colorless crystal, 0.50 x 0.30 x 0.30 mm2, C56H44Cl8La18O64S, M = 11945.6, tetragonal, space group P4_2/2 (No. 95), a = 27.5037(10), c = 80.460(3) A, V = 60864(4) A^3, Z = 4, ρcalc = 1.304 g cm^-3, ρ(MoKα) = 1.312 mm^-1. A crystal was attached to a glass capillary, which was positioned in a N1i0 stream at 243(2) K after mounting on a Bruker SMART CCD diffractometer equipped with a normal-focus and graphite-monochromated Mo-target X-ray tube (λ = 0.70137 Å). A total of 1315 frames were collected, and integrated with the SAINT software package with a narrow-frame algorithm. An absorption correction was applied by using SADABS. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELXTL software package. A total of 211188 reflections were collected in the range 1.05 ≤ θ ≤ 20.84°, of which 32002 were independent and 22331 were observed (I > 2σ(I)). All stages of weighted full-matrix least-squares refinement were conducted on F^2 data and converged to give R1 = 0.0835 (> 2σ(I)), wR2 = 0.2268 (all data), and GOF = 1.029. Most non-hydrogen atoms were refined anisotropically, except for six atoms with nonpositive-definite parameters. Hydrogen atoms were generated with the ideal geometry. The absolute configuration was confirmed by the Flack parameter of 0.060(19).

X-ray structural analysis of (R)-lanthanitin: prismatic colorless crystal, 0.35 x 0.30 x 0.25 mm2, C56H44Cl8La18O64S, M = 11945.6, tetragonal, space group P4_2/2 (No. 95), a = 27.2922(6), c = 79.728(3) Å, V = 59.386(4) Å^3, Z = 4, ρcalc = 1.336 g cm^-3, ρ(MoKα) = 1.345 mm^-1. Final refinement converged to R1 = 0.0921 (> 2σ(I)), wR2 = 0.2341 (all data), GOF = 1.076, and a Flack parameter of x = 0.13(3). CCDC 619112 ((S)-lanthanitin) and 619113 ((R)-lanthanitin) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

UV/Vis absorption spectra of various solutions were measured between 800 and 200 nm with a Jasco UVIDEC 650 spectrophotometer. CD spectra were recorded on a Jasco J-810 spectropolarimeter. DRCD spectra were obtained by inserting a diffuse-reflectance spectrophotometer. CD spectra were recorded on a Jasco J-810 spectropolarimeter.

Received: September 5, 2006
Published online: November 17, 2006

Keywords: carboxylate ligands · helical structures · lanthanum · nanostructures · self-assembly


