Chiral Nanoballs

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Lanthanitin: A Chiral Nanoball Encapsulating 18 Lanthanum Ions by Ferritin-Like Assembly**

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In self-assembly through metal–organic coordination chemistry, strong interaction between metal ions and polydentate ligands is the primary driving force. Contrary to processes 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 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*)-**1**H$_2$ and (*R*,*R*)-**1**H$_2$ (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°.

Colorless antiprismatic crystals of (*S*)-lanthanitin suitable for X-ray diffraction were grown from a mixture of (*S*,*S*)-**1**H$_2$ and $LaCl_3 \cdot 6\,H_2O$ in *N*,*N*′-diethylformamide (DEF) solution at 60 °C over two weeks (Figure 1 a). X-ray crystallographic studies revealed that the crystal belongs to the enantiomorphous space group $P4_122$. 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 $[La_{18}\{(S,S)\text{-}\mathbf{1}\}_{24}(CO_3)_2(H_2O)_{32}]^{2+}$ (Figure 1 b). 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

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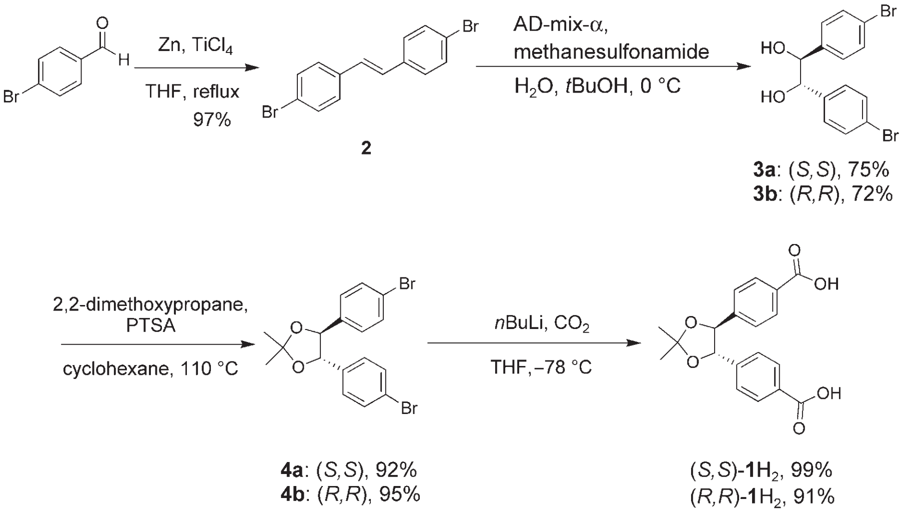

Scheme 1. Preparation of ligands (*S*,*S*)-**1**H$_2$ and (*R*,*R*)-**1**H$_2$. See the Supporting Information. PTSA = *para*-toluenesulfonic acid.

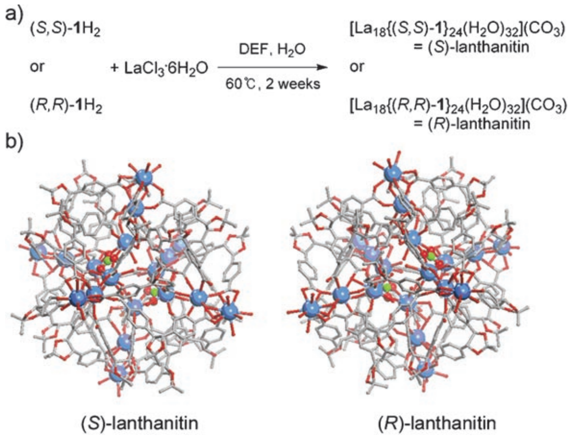

Figure 1. a) Preparation of lanthanitin enantiomers. b) Molecular structures of lanthanitins with octahedral arrangement of 18 La ions as large blue balls and the central carbonate carbon atoms as small green balls. Hydrogen atoms are omitted for clarity. Color code: C gray, O red.

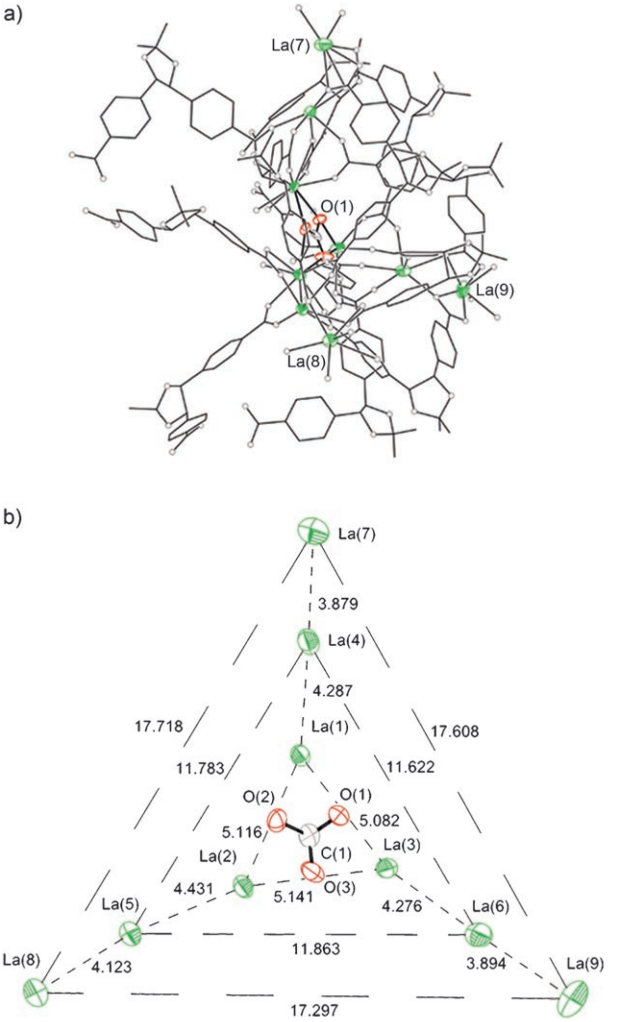

Figure 2. a) ORTEP drawing of the crystallographic asymmetric unit of (*S*)-lanthanitin, which is a half of the whole assembly as a result of crystallographic twofold symmetry. b) The arrangement of the nine La^{III} ions in the asymmetric unit around the central carbonate ion with interatomic distances in Å.

the asymmetric unit, {La(1),La(4),La(7)}, {La(2),La(5),La(8)}, and {La(3),La(6),La(9)} which together form a pyramidal shape with a small triangle {La(1),La(2),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 {La(7),La(8),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 La^{III} ions in the hemisphere have a coordination number of eight, except for La(8) and La(9), which are ten-coordinate (Figure 3). All three central lanthanum ions located on the first sphere, {La(1), La(2), and La(3)}, are coordinated by three kinds of ligands: two oxygen atoms of 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 La^{III} ions in the core of the molecule and their symmetry-related partners form hydrogen bonds among themselves and leave no void space. The La^{III} ions on the second sphere, {La(4), La(5), and La(6)}, have eight oxygen atoms as ligands, all of which are from carboxylates. The coordination between La^{III} and carboxylate exhibits three different modes: monodentate, bis-monodentate, and chelating, μ-O tridentate, except for one carboxylate group (Figure 3). For the 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.

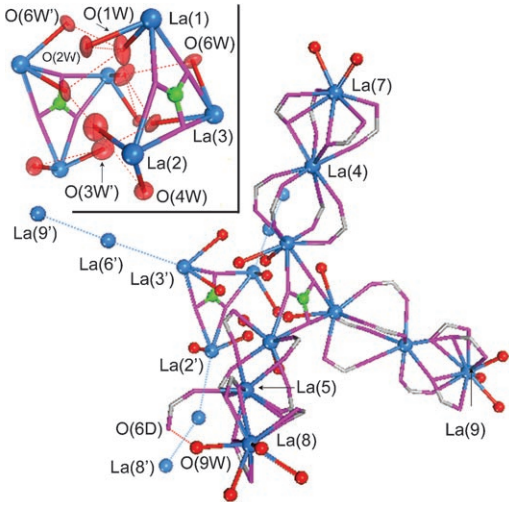

Figure 3. Coordination environment of the La^{III} atoms (blue) with partial atomic numbering scheme is shown with only carboxylate moieties (gray and pink), carbonate ions (green and pink), and coordinating water molecules (red) for simplicity. The primed numbers denote twofold-symmetry-related atoms. The 12 coordinating water molecules attached to the central 6 La atoms, O(1W)–O(6W) and O(1W')–O(6W') are drawn with thermal ellipsoids in the inset. Possible hydrogen bonds are indicated as dotted red lines. One of the carboxylate oxygen atoms, O(6D), is not bound to an La atom and instead forms a hydrogen bond with O(9W).

To grasp the framework structure, the molecule can be disassembled schematically into six $La_3[(S,S)\text{-}\mathbf{1}]_4$ 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 lanthanitin with a close structural resemblance to ferritin.[9] The arrangement of the organic linkers in lanthanitin is the same as that of the protein subunits in ferritin (Figure 4b and c).

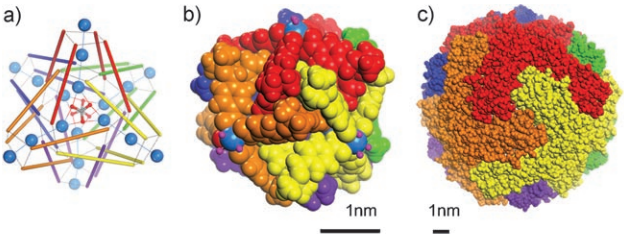

Figure 4. a) Schematic representation of lanthanitin which shows that six sets of $La_3(\mathbf{1})_4$ moieties come together around the central carbonate ions to form the whole molecule. The 24 ligands are grouped into six sets, drawn with different colors. b) Space-filling model of lanthanitin. Colors match those of (a). c) Structure of bacterioferritin (PDB code: 1BFR). Twenty four subunits are grouped as six sets for comparison with the arrangement of ligands in lanthanitin.

Neglecting the minor distortions around the La^{III} 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*)-lanthanitin 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.

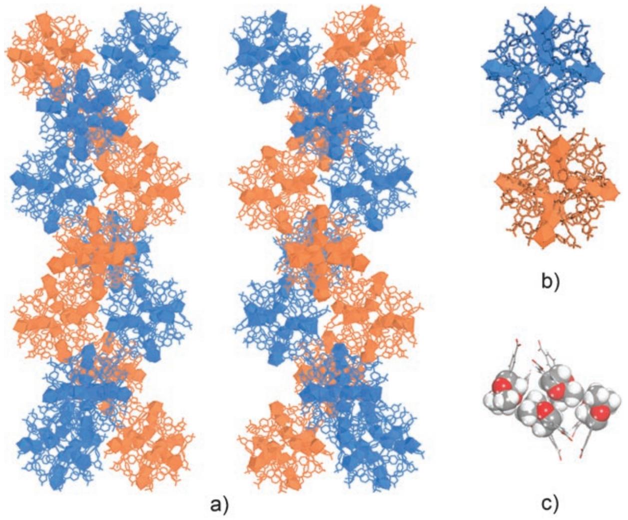

Figure 5. a) Double helices formed by the lanthanitins with 1.5 helical turns. The two single helices are distinguished by blue and light brown colors. (*S*)-Lanthanitin (left) forms a right-handed double helix, and (*R*)-lanthanitin a left-handed one (right). b) Two lanthanitin molecules in contact showing the boundary region. c) Two ligands from each lanthanitin unit participate in the contact; the acetonide moieties including the DMM groups of the ligands are drawn as space-filling models.

(*R*)-Lanthanitin, the chiral counterpart of (*S*)-lanthanitin, was prepared by employing $(R,R)\text{-}\mathbf{1}H_2$ in place of $(S,S)\text{-}\mathbf{1}H_2$. As we expected, (*R*)-lanthanitin belongs to space group $P4_322$, which forms an enantiomorphous pair with $P4_122$ 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

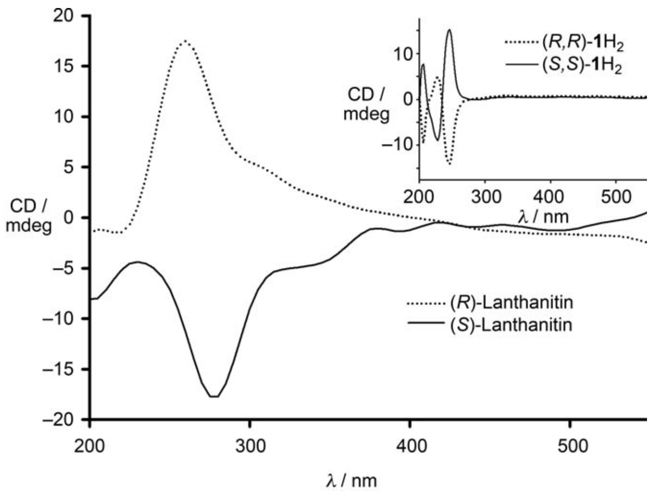

Figure 6. CD data obtained from a transparent disk with a radius of 5 mm made from a mixture of crystalline lanthanitin (3 mg) and KBr (100 mg). The inset shows the CD spectra of the ligands in methanol.

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 (*S*,*S*)-**1**H$_2$ and (*R*,*R*)-**1**H$_2$ were prepared according to the methods described in the Supporting Information. A mixture of $LaCl_3{\cdot}6H_2O$ (0.010 g, 0.10 mmol) and (*S*,*S*)-**1**H$_2$ or (*R*,*R*)-**1**H$_2$ (0.010 g, 0.10 mmol) in DEF (3 mL) and H_2O (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 (%) calcd for (*S*)-lanthanitin $[La_{18}(CO_3)_2(C_{19}H_{16}O_6)_{24}(H_2O)_{32}]CO_3{\cdot}20.5H_2O{\cdot}1.5DEF$: 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, $0.50 \times 0.30 \times 0.30$ mm^3, $C_{466.5}H_{505.5}N_{1.5}O_{207}La_{18}$, $M = 11945.6$, tetragonal, space group $P4_122$ (No. 91), $T = 243(2)$ K, $a = 27.5037(10)$, $c = 80.460(3)$ Å, $V = 60864(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.304$ g m^{-3}, $\mu(Mo_{K\alpha}) = 1.312$ mm^{-1}. A crystal was attached to a glass capillary, which was positioned in a $N_{2(g)}$ 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 ($\lambda = 0.71073$ 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 211 188 reflections were collected in the range $1.05 \leq \theta \leq 20.84°$, of which 32 002 were independent and 22 331 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least-squares refinement were conducted on F_o^2 data and converged to give $R1 = 0.0835$ ($I > 2\sigma(I)$), $wR2 = 0.2268$ (all data), and GOF = 1.029. Most non-hydrogen atoms were refined anisotropically, except for six atoms with nonpositive-definite problems. Hydrogen atoms were generated with the ideal geometry. The absolute configuration was confirmed by the Flack *x* parameter of 0.060(19).

X-ray structural analysis of (*R*)-lanthanitin: prismatic colorless crystal, $0.35 \times 0.30 \times 0.25$ mm^3, $C_{466.5}H_{505.5}N_{1.5}O_{207}La_{18}$, $M = 11945.6$, tetragonal, space group $P4_322$ (No. 95), $T = 130(2)$ K, $a = 27.2922(6)$, $c = 79.728(3)$ Å, $V = 59386(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.336$ g m^{-3}, $\mu(Mo_{K\alpha}) = 1.345$ mm^{-1}. Final refinement converged to $R1 = 0.0921$ ($I > 2\sigma(I)$), $wR2 = 0.2341$ (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 sphere in the optical path of the instrument. This J-810 was specifically modified to allow simultaneous detection of LD (linear dichroism) as a simple way to verify potential artifacts.

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