

Diastereoselective Self-Assembly of a Homochiral Europium Triangle from a Bipyoxazoline–Carboxylate Ligand

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Self-assembly plays a crucial role in the formation of many chiral structures in nature. The control of the chirality of self-assembled architectures is very important for the application of these systems in catalysis, molecular recognition and sensing of biological substrates.^[1,2] Lanthanide-based chiral supramolecular architectures are particularly attractive because of the spectroscopic and catalytic properties of these ions.^[3–5] However, their kinetic lability and weak stereochemical preferences cause the design of enantiopure molecular and supramolecular architectures to be particularly difficult. A few mononuclear complexes of lanthanides with chiral pre-determination have been obtained by using enantiopure ligands and have been used as chiral luminescent probes or chiral catalysts.^[1,4–10] Fewer examples of chiral polynuclear assemblies have been described for lanthanides.^[3,11–16] Some original examples of chiral assemblies were obtained from the controlled hydrolysis^[11–13] or CO₂ fixation reactions^[15,16] of lanthanide salts in the presence of chiral ligands. In these synthetic methods the hydroxo and the carbonate groups play an important role in the formation of the heteroleptic assemblies causing the rational design of the final assembly to be difficult. Dimetallic triple-stranded helicates are to date the only reported example of pre-programmed,^[17,18] enantiomerically pure polynuclear lanthanide assemblies.^[3,16] We have previously demonstrated that large polynuclear wheel-shaped lanthanide compounds can be selectively assembled by using a metal-directed synthesis in the presence of a dissymmetric terpyridine–carboxylate ligand.^[19] This ligand promotes the assembly of oligo-

nuclear lanthanide complexes rather than polymeric structures through the formation of carboxylate bridges. This work has now been successfully extended to the synthesis of a chiral polynuclear assembly through a careful ligand design. Here we describe the use of the chiral carboxylate-derivatised bipyoxazoline ligand (*S*)-Phbipox (6'-(4-phenyloxazolin-2-yl)-2,2'-bipyridine-6-carboxylic acid; Figure 1) to promote the diastereoselective self-assembly of the novel homochiral trinuclear europium complex ($\Delta\Delta\Delta$)-[Eu((*S*)-Phbipox)₂]₃⁺³ (**1**).

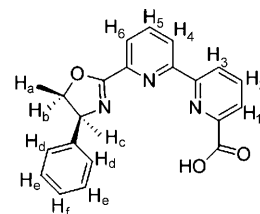


Figure 1. Structure and numbering scheme for NMR spectral assignments of the ligand (*S*)-PhbipoxH.

We demonstrate that the chirality of the ligand is transferred in a concentration-dependent formation of the trinuclear assembly to give the enantiopure $\Delta\Delta\Delta$ isomer. At low concentration the diastereomeric complexes (Δ)-[Eu((*S*)-Phbipox)₂]⁺ (**2**) and (Λ)-[Eu((*S*)-Phbipox)₂]⁺ (**3**) form with partial stereoselectivity (Λ/Δ ratio of ≈ 1.8). At higher concentration the homochiral trinuclear complex **1** self-assembles selectively in solution from the mononuclear bis-ligand **2** complex through the formation of carboxylate bridges.

The enantiomerically pure ligand (*S*)-Phbipox has been prepared in seven steps from commercial dimethylbipyridine in 13% total yield. The synthetic procedure is outlined in Scheme S1 in the Supporting Information and involves the reaction of the ethyl 6'-(chlorocarbonyl)-2,2'-bipyridine-6-carboxylic acid with (*S*)-2-phenylglycinol followed by the simultaneous intramolecular ring closure and saponification in an aqueous ethanolic potassium hydroxide solution to afford the desired (*S*)-Phbipox product.

Proton NMR studies show that the reaction of Eu(OTf)₃ with two equivalents of (*S*)-Phbipox in anhydrous methanol in the presence of triethylamine affords a mixture of the two diastereoisomeric bis-ligand complexes **2** and **3**, which

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correspond to the two different helical arrangements (left and right, respectively) that the two ligands can adopt when they bind the metal. Chiral induction from the (*S*)-Phbipox ligand occurs during metal coordination leading to a Λ/Δ ratio determined by NMR spectroscopy to be approximately 1.8 in a 7 mM solution of anhydrous methanol at room temperature. Two distinct sets of 12 NMR signals are observed for the 14 protons of the two C_2 symmetric diastereoisomers (Figure 2). The 2D EXSY (exchange spectroscopy) NMR

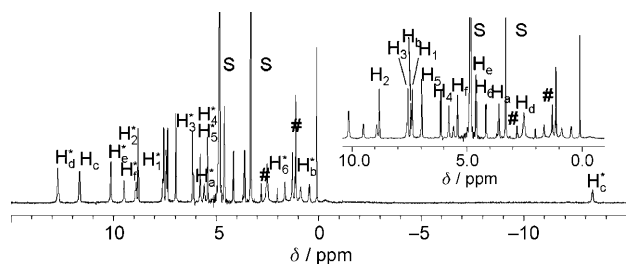


Figure 2. ^1H NMR spectra of (Δ) - $[\text{Eu}((S)\text{-Phbipox})_2]^+$ (H_x^*) and (Λ) - $[\text{Eu}((S)\text{-Phbipox})_2]^+$ (H_x ; Mercury 400 MHz, 298 K, 7 mM). S = CD_3OD , # = triethylammonium.

study shows the presence of a slow exchange between the two complexes in solution. At higher concentrations (from 14 mM) the NMR spectra show an additional set of 24 signals suggesting the formation of an additional species (Figure S1 in the Supporting Information). These signals were assigned to the trinuclear complex $[(\Delta\Delta\Delta)\text{-}[\text{Eu}((S)\text{-Phbipox})_2]_3]^{+3}$ in which the two independent ligands give rise to two different sets of 12 signals. No signals from heterochiral species were observed. The addition of a small amount of water ($<0.03\%$) does not significantly affect the oligomerisation process.

This assignment is in agreement with the solid-state crystal structure determined by X-ray diffraction on single crystals of the $[\text{Eu}((S)\text{-Phbipox})_2]\text{OTf}$ complex isolated from 24 mM methanol solutions. Notably, X-ray diffraction analysis revealed the presence of two distinct co-crystallised molecules in the compound $[(\Delta\Delta\Delta)\text{-}[\text{Eu}((S)\text{-Phbipox})_2]_3\text{-}(\Lambda)\text{-}[\text{Eu}((S)\text{-Phbipox})_2]]\text{OTf}_4$ (**4**). The proton NMR spectra of the bulk isolated complex (see the Experimental Section and Figure S2 in the Supporting Information) in deuterated acetonitrile shows the presence of the trinuclear complex from 6 mM, probably as a result of the lower polarity and lower coordinating ability of this solvent. Moreover, the

NMR spectrum shows a Λ/Δ ratio of approximately 0.6 indicating that the crystallisation process leads to an increase of the Δ monomer with respect to the Λ complex. Pulsed-field gradient stimulated echo (PFGSTE) diffusion NMR spectroscopy was used to measure the diffusion coefficient (D) of **1**, **2** and **3** in 6 mM acetonitrile and methanol solutions.^[20] The diffusion coefficient is a function of the molecular weight (M) and can be conveniently used to discriminate metallosupramolecular architectures in solution.^[21] Because the trimeric and monomeric complexes have both globular shape and similar microscopic densities, which can be anticipated from their crystal structure, the Stokes–Einstein equation can be used to estimate the relative molecular size of the solution species.^[21] The values measured in acetonitrile $[M\Delta\Delta\Delta/M\Delta = (D\Delta/D\Delta\Delta\Delta)^3 = 2.8(6)]$ are in agreement with the presence of one trinuclear complex and two mononuclear species. In 6 mM methanol solution only the monomeric complexes are present. The calculated values of the spherical hydrodynamic radius (8.2 Å for the trimeric species and 5.8 Å for the monomeric ones) compare very well with the value estimated from the crystal structure (7.7 and 5.1 Å, respectively). The intensity of the NMR signals assigned to the trimeric complex increases in methanol and acetonitrile with increasing concentration. This increase is associated with an intensity decrease of only one of the two set of signals corresponding to the two diastereoisomeric bis-ligand complexes. This shows that only one diastereoisomer, which has been identified as the Δ isomer on the basis of the X-ray crystal structure, undergoes the oligomerisation process. Only the presence of the trimeric species and of the residual Λ monomer can be detected in 30 mM acetonitrile solutions of the $[\text{Eu}((S)\text{-Phbipox})_2]^+$ complex (Figure 3).

These results highlight the diastereoselectivity of the self-assembly process, which only involves (Δ) - $[\text{Eu}((S)\text{-Phbipox})_2]$ species whereas the formation of the other possible chiral assemblies $\Delta\Delta\Lambda$, $\Lambda\Lambda\Lambda$ and $\Delta\Lambda\Lambda$ is not observed.

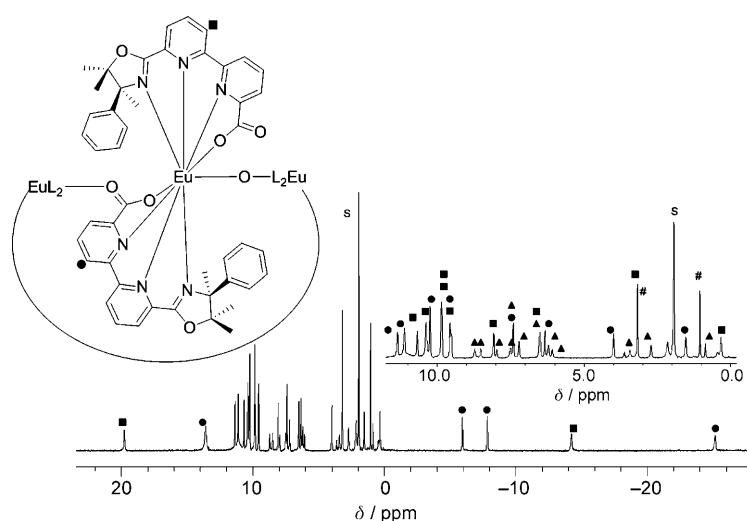


Figure 3. ^1H NMR spectra of $(\Delta\Delta\Delta)\text{-}[\text{Eu}((S)\text{-Phbipox})_2]_3^{+3}$ (■ and ●) and $(\Lambda)\text{-}[\text{Eu}((S)\text{-Phbipox})_2]^+$ (▲; Bruker 500 MHz, 263 K, 30 mM). S = CD_3CN , # = triethylammonium.

This result also suggests that in anhydrous acetonitrile the ligand (*S*)-Phbipox[−] remains bound to the metal ion preventing the rearrangement of the Δ isomer into the Λ one.

Compound **4** crystallises in the chiral orthorhombic space group $P2_12_12_1$. Isomorphous crystals were obtained from a concentrated acetonitrile solution. The structure of the monomeric (Λ)-[Eu(*S*)-Phbipox]₂⁺ cation in **4** is shown in Figure 4. The structure of the trinuclear cation [($\Delta\Delta\Delta$)-

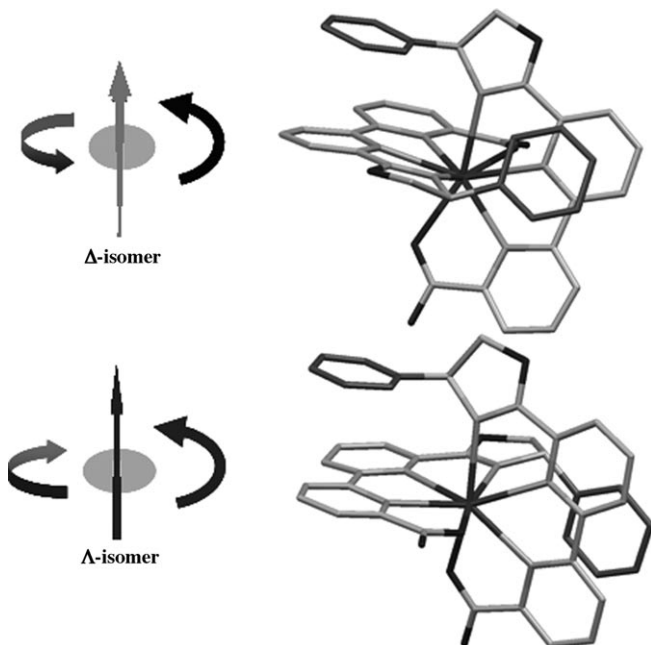


Figure 4. The structure of the monomeric (Λ)-[EuL₂]⁺ and (Δ)-[EuL₂]⁺ isomers. The arrow starts from the carboxylic group and ends at the phenyl group of the ligand.

[Eu(*S*)-Phbipox]₂]₃³⁺ in **4** is presented in Figure 5 whereas detail of the (Δ)-[Eu(*S*)-Phbipox]₂⁺ fragments is shown in Figure 4.

In the (Λ)-[Eu(*S*)-Phbipox]₂⁺ cation the Eu ion is eight-coordinated by the six nitrogen atoms and the two oxygen atoms from the (*S*)-Phbipox[−] ligand with a distorted dodecahedron geometry (Figure S6 in the Supporting Information). The two *S* ligands wrap around the metal with a Λ stereochemistry. The two ligand mean planes form an angle of approximately 90°. Strong π - π interactions (see Table S3 in the Supporting Information) are found between the oxazoline phenyl rings of each tetradentate ligand and one pyridine ring of the other ligand. The presence of π - π interactions between the two ligands should play an important role in the observed rigidity of complexes **2** and **3** in acetonitrile solution. The mean values of the Eu-N (2.57 Å (2) and 2.54 Å (3)) and Eu-O bond lengths (2.39 Å (2) and 2.30 Å (3)) are similar to those found in the eight-coordinate complex [Eu(L)₂] isolated from methanol in the presence of the dissymmetric ligand 2,2':6',2''-terpyridine-2-carboxylic acid (mean Eu-O = 2.31(1) and Eu-N = 2.53(5) Å).

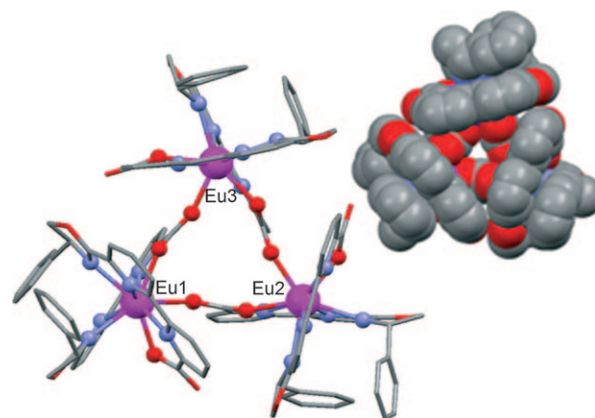


Figure 5. Diagram of the structure [($\Delta\Delta\Delta$)-[Eu(*S*)-Phbipox]₂]₃³⁺ in **4** and the spacefill diagram (created by using the MERCURY 2.2 program).

In the [($\Delta\Delta\Delta$)-[Eu(*S*)-Phbipox]₂]₃³⁺ cation three crystallographically inequivalent (Δ)-[Eu(*S*)-Phbipox]₂⁺ complexes are connected through a carboxylate oxygen from one of the (*S*)-Phbipox[−] ligands to form an equilateral triangle with the Eu-Eu distances ranging from 6.685 to 6.780 Å. Each Eu ion is nine-coordinate with distorted tricapped trigonal prism geometry by the six nitrogen and the two oxygen atoms from the two (*S*)-Phbipox[−] ligands and by the carboxylate oxygen from a neighbour complex.

In each monomeric unit of the trinuclear complex the two (*S*)-Phbipox[−] ligands wrap around the metal ion with a Δ stereochemistry. The angle between the two ligand mean planes is approximately 107°. Strong π - π interactions (see Table S3 in the Supporting Information) are found between the oxazoline phenyl rings of each tetradentate ligand and one pyridine ring of the other ligand. The crystal structure of **4** shows that the (*S*)-Phbipox[−] ligands can wrap around the metal with the two different Δ and Λ stereochemistries. However, only the Δ complexes self-assemble to form a homochiral trinuclear structure. The molecular model (made by using the MERCURY 2.2 program)^[22] of a trinuclear structure built from mononuclear (Λ)-[Eu(*S*)-Phbipox]₂⁺ entities (Figure 6) suggests that important steric constraints resulting from the orientation of the phenyl substituents on the oxazoline ring are present when mononuclear complexes with Λ conformation are brought in close proximity. Similar constraints are observed for $\Lambda\Delta\Delta$ and $\Lambda\Lambda\Delta$ isomers (see Figure S7 in the Supporting Information). Such steric constraints should play an important role in the diastereoselectivity of the self-assembly process.

The luminescence emission spectrum of the [Eu(*S*)-Phbipox]₂⁺ complex carried out in anhydrous methanol (7 mm) also show the presence of europium species of different symmetry with respect to those found in acetonitrile solutions (7–26 mm). This is in agreement with the different metal environment observed for the trinuclear assembly (present in acetonitrile) compared with the mononuclear complex (the only species present in 7 mm methanol solution, Figure 7). The luminescence quantum yield measured

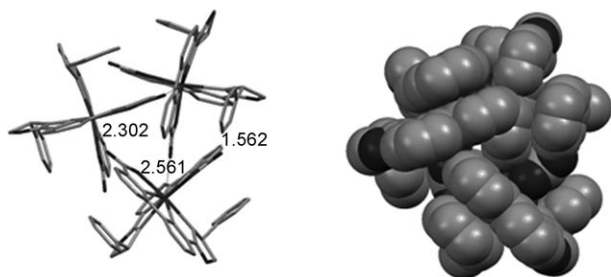


Figure 6. Molecular models built from the structures of the Δ and Λ in **4** showing the sterical constraints preventing the formation of the heterochiral trinuclear complexes $[(\Lambda\Lambda\Lambda)\text{-[Eu}((S)\text{-Phbipox)}_2\text{]}_3]^+{}^{3+}$ (created by using the MERCURY 2.2 program).

in methanol with excitation at 279 and 340 nm varied between 20(2) and 28(1)% depending of the concentration used (6–7 mm). Circularly polarised luminescence studies

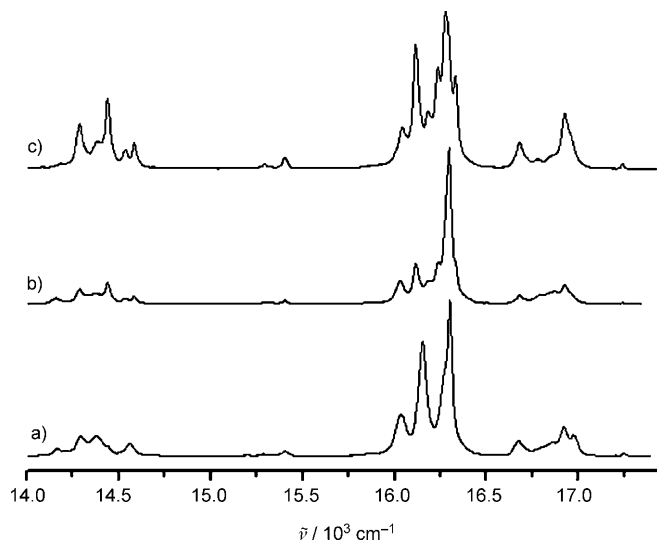


Figure 7. Normalised emission spectra of $[\text{Eu}((S)\text{-Phbipox)}_2]\text{OTf}$ at a) 7 mm in CD_3OD , b) 7 mm in CH_3CN , c) 26 mm in CH_3CN .

will be carried out in future work to investigate the influence of the concentration and of chirality on the photophysical properties.^[23]

In summary, we have reported a rare enantiopure trinuclear europium complex obtained in a novel concentration-dependent self-assembly process promoted by a new (*S*)-Phbipox[−] ligand. We have shown that selective homochiral recognition occurs, probably as a result of sterical interaction, during the self-assembly of the bis-ligand monomeric complexes to yield the final trinuclear species. Some selectivity was also found in the self-assembly of the two ligands around the europium centre to afford the Λ and Δ monomeric isomers.

Future studies will be directed to tune the ligand bulk and cation size with the objective of increasing the stereoselectivity of the self-assembly of the monomeric complex. This

system is also particularly well suited for the self-assembly of larger cluster structures by using template cations,^[19] and work in this direction is in progress.

Experimental Section

Synthesis of $[\text{Eu}((S)\text{-Phbipox)}_2]\text{OTf}$: Triethylamine (20.2 μL) was added to a solution of (*S*)-Phbipox (50 mg 0.145 mmol) in anhydrous methanol (2 mL). The resulting solution was stirred for 2 h and a solution of $\text{Eu}(\text{OTf})_3$ (0.0725 mmol) in methanol (1 mL) was then added. The resulting solution was stirred at room temperature for an hour. Diisopropylether was then added to afford a white microcrystalline solid precipitate that was filtered and dried for two weeks at 40 °C under vacuum (87% yield). ¹H NMR for the $(\Lambda)\text{-[Eu}((S)\text{-Phbipox)}_2]^+$ species (500 MHz, CD_3CN , −10 °C): δ = 0.45 (0.4H, brt; H_c), 3.42 (0.4H, brt; H_d), 2.71 (0.4H, brt; H_b), 6.07 (0.4H, brd; H_e), 6.21 (0.8H, brs; H_d), 6.50 (0.4H, brs; H_3), 7.21 (0.8H, brs; H_c), 7.42 (0.4H, brd; H_2), 7.50 (0.4H, brt; H_1), 7.95 (0.4H, brd; H_1), 8.72 (0.4H, brt; H_3), 8.50 (0.4H, d, J = 5.7 Hz; H_4); ¹H NMR for the $(\Delta\Delta\Delta)\text{-[Eu}((S)\text{-Phbipox)}_2]^+{}^{3+}$ species (500 MHz, CD_3CN , −10 °C): ●: −25.18 (1H, brt; H_c), −7.83 (1H, brd; H_e), −5.92 (1H, brt; H_b), 1.53 (1H, brt; H_a), 3.99 (1H, brt; H_5), 6.34 (1H, d, J = 6.6 Hz; H_3), 7.42 (1H, brd; H_4), 9.54 (1H, brt; H_1), 10.24 (2H, brt; H_2), 11.12 (1H, brt; H_2), 11.35 (1H, d, J = 6.1 Hz; H_2), 13.57 (2H, brs; H_4); ■: −14.21 (1H, brt; H_c), 0.33 (1H, brt; H_b), 2.15 (1H, brd; H_3), 3.28 (1H, brt; H_2), 6.50 (1H, brs; H_a), 8.07 (1H, d, J = 7.9 Hz; H_4), 89.54 (2H, brt; H_5), 9.83 (3H, brt, H_1 ; H_c), 10.37 (2H, brs; H_4), 10.68 (1H, brt; H_1), 19.78 (1H, brs; H_e); MS (ES⁺) CD_3OD : m/z = 841.1 $[\text{Eu}((S)\text{-Phbipox)}_2]^+$; MS (ES⁺) CD_3CN : m/z = 841.3 $[\text{Eu}((S)\text{-Phbipox)}_2]^+$, 335 $[\text{Eu}_3((S)\text{-Phbipox)}_6](\text{OTf})_2^{3+}$; elemental analysis calcd (%) for $[\text{Eu}((S)\text{-Phbipox)}_2]\text{OTf}\cdot 1.26\text{Et}_3\text{NOTf}_3$ ($\text{C}_{49.82}\text{H}_{46.9}\text{N}_{7.26}\text{O}_{12.78}\text{F}_{6.78}\text{S}_{2.26}\text{Eu}$, M_w = 1305.23): C 45.85, H 3.32, N 7.89; found: C 45.85, H 3.62, N 7.79;

Crystal data for **4:** $\text{C}_{172.50}\text{H}_{148}\text{Eu}_4\text{F}_{12}\text{N}_{24}\text{O}_{45.50}\text{S}_4$; M_r = 4249.23; crystal size = $0.20 \times 0.15 \times 0.15 \text{ mm}^3$; orthorhombic; space group $P2_12_12_1$; a = 17.3481(10), b = 32.1765(15), c = 32.4386(12) Å; $\alpha = \beta = \gamma = 90^\circ$; V = 18107.3(15) Å³; Z = 4; ρ_{calcd} = 1.559 mgm^{-3} ; μ = 1.510 mm^{-1} ; λ = 0.71073 Å; T = 150 (2) K; $3.02^\circ < 2\theta_{\text{max}} < 23.25^\circ$; 42715 reflections collected; 25589 unique reflections (R_{int} = 0.0459); R_1 = 0.05031, wR_2 = 0.1001 [$I > 2\sigma(I)$]; R_1 = 0.0806, wR_2 = 0.1058 (all data); residual electron density = 1.515 $\text{e}\text{Å}^{-3}$.

CCDC-763804 contains 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.

The figure graphics were generated by using the MERCURY 2.2 program supplied with the Cambridge Structural Database.^[22] Further experimental details, including ligand synthesis, X-ray crystallography and mass spectroscopy are given in the Supporting Information.

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Keywords: chirality • cluster compounds • lanthanides • luminescence • N,O ligands • self-assembly

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