

Metal-Controlled Diastereoselective Self-Assembly and Circularly Polarized Luminescence of a Chiral Heptanuclear Europium Wheel

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S Supporting Information

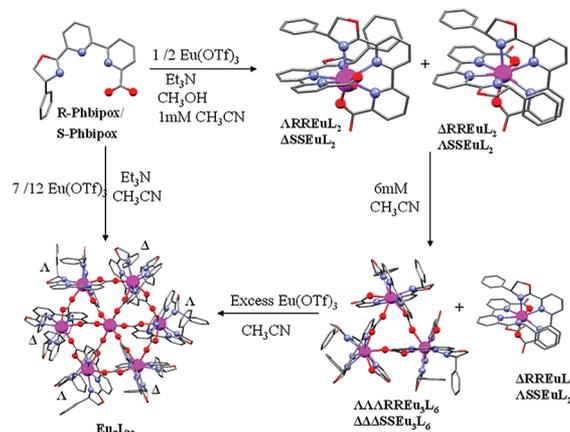
ABSTRACT: The chiral dissymmetric tetradentate ligand (*S*)-6'-(4-phenyloxazolin-2-yl)-2,2'-bipyridine-6-carboxylate (S-Phbipox) leads to the diastereoselective assembly of a homochiral Eu³⁺ triangle and a highly emissive (quantum yield = 27%) heptanuclear wheel that is the largest example of a chiral luminescent complex of Eu³⁺ reported to date. The nuclearity of the assembly is controlled by the solvent and the Eu³⁺ cation. All of the compounds show large circularly polarized luminescence with an activity that varies with the nature of the assembly (highest for the homochiral trimer).

Supramolecular chiral recognition processes play a key role in stereoselective catalytic and biological transformations. Chirality is also of high current interest in nanotechnology for the control of final architectures. The control of chirality around a metal center in molecular or supramolecular complexes is a key step in the development of enantioselective catalysts and chiroptical probes and sensors.^{1,2} In particular, the circularly polarized luminescence (CPL) observed in chiral lanthanide (Ln) complexes is of high current interest in biological probing and display technologies^{1,3–6} because of the attractive properties of Ln ions (large Stokes shift, long lifetimes, narrow emission bands, high quantum yields).⁷ However, enantiopure Ln complexes are mostly limited to few examples of mononuclear compounds^{1,3–5,8–11} and dinuclear helicates.¹² Although the supramolecular chemistry of Ln ions is less developed than that of d-block metal ions, reports of Ln-based polynuclear assemblies¹³ that have preprogrammed new original structures¹⁴ and of nanosized complexes with fascinating optical¹⁵ and magnetic properties¹⁶ are rapidly increasing. However, the high kinetic lability and lack of stereochemical preferences of Ln ions makes controlling their coordination spheres very difficult. Thus, very few enantiopure polynuclear Ln assemblies have been reported.^{17,18}

We recently reported the diastereoselective self-assembly of an enantiopure trinuclear Eu triangle, $\Delta\Delta\Delta$ -[Eu(S-Phbipox)₂]₃³⁺, promoted by the asymmetric ligand (*S*)-6'-(4-phenyloxazolin-2-yl)-2,2'-bipyridine-6-carboxylate (S-Phbipox).¹⁸ $\Delta\Delta\Delta$ -[Eu(S-Phbipox)₂]₃³⁺ self-assembles from con-

centrated acetonitrile solutions, while at lower concentrations, only the diastereomeric mononuclear complexes Δ -[Eu(S-Phbipox)₂]⁺ and Λ -[Eu(S-Phbipox)₂]⁺ form with partial stereoselectivity (Λ/Δ ratio \approx 1.8) (Scheme 1).

Scheme 1. Synthesis of the Enantiopure Wheels 1 and 2^a



^aExcess Eu(OTf)₃ ranged from 0.06 to 0.12 equiv per ligand.

Here we show that the controlled addition of Eu³⁺ to the mixture of diastereomeric complexes Δ - and Λ -[Eu(R-Phbipox)₂]⁺ leads to the diastereoselective self-assembly of the heptameric enantiopure Eu wheel [EuC(Λ -Eu(R-Phbipox)₂ Δ -Eu(R-Phbipox)₂)₃](OTf)₉ (**1**). Starting from a mixture of Eu³⁺ complexes of S-Phbipox, the isostructural complex [EuC(Δ -Eu(S-Phbipox)₂ Λ -Eu(S-Phbipox)₂)₃](OTf)₉ (**2**) was also isolated. These are very rare examples of large chiral enantiopure f-element assemblies and the first chiral luminescent wheels. We also show that the Δ -Eu and Λ -Eu monomers and the $\Lambda\Lambda\Lambda$ -Eu₃ and $\Delta\Delta\Delta$ -Eu₃ trinuclear and [EuC($\Lambda\Delta\Lambda\Delta\Delta\Delta$ -Eu₆)] heptanuclear assemblies give rise to Eu³⁺-centered CPL upon excitation of the Phbipox ligand, with the triangular complexes showing one of the highest efficiencies reported to date.

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Compounds **1** and **2** were prepared in 81% yield from the reactions of R- and S-Phbipox (formed from R- and S-PhbipoxH and NEt_3), respectively, with $\text{Eu}(\text{OTf})_3$ in a 12:7 ratio. X-ray diffraction (XRD) studies were carried out on crystals prepared by slow diffusion of hexane into a benzonitrile solution of **1**. The isostructural nature of **2** was confirmed by unit cell measurements on X-ray-quality crystals. In the cation $[\text{EuC}(\Lambda\text{-Eu}(\text{R-Phbipox})_2\Delta\text{-Eu}(\text{R-Phbipox})_2)_3]^{9+}$ (Figure 1),

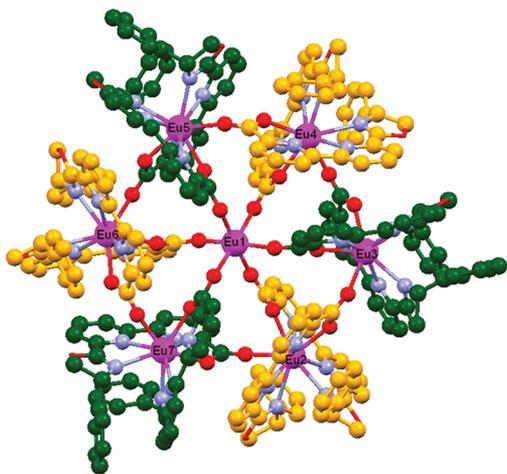


Figure 1. Crystal structure of the $[\text{EuC}(\Lambda\text{-Eu}(\text{R-Phbipox})_2\Delta\text{-Eu}(\text{R-Phbipox})_2)_3]^{9+}$ cation in **1**. O, red; Eu, pink; C in $[\Lambda\text{-Eu}(\text{R-Phbipox})_2]^+$, green; C in $[\Delta\text{-Eu}(\text{R-Phbipox})_2]^+$, orange.

three $[\Lambda\text{-Eu}(\text{R-Phbipox})_2]^+$ and three $[\Delta\text{-Eu}(\text{R-Phbipox})_2]^+$ complexes are connected in an alternating fashion through bridging carboxylate oxygens (one from an R-Phbipox ligand on each complex) to form the heterochiral cyclic structure. A seventh Eu^{3+} ion is encapsulated in the ring center and has a regular octahedral coordination sphere composed of six carboxylate oxygens from the coordinated Phbipox carboxylate ligands not involved in the ring formation. The overall structure is similar to that of the heptameric wheel $[\text{EuC}(\text{Eu}(\text{terpya})_2)_6](\text{OTf})_9$, obtained from the cation-promoted self-assembly of six Eu complexes of the achiral dissymmetric terpyridine monocarboxylate ligand (terpya).^{13d}

The external Eu^{3+} ions in **1** are ninefold-coordinated by six nitrogens and two oxygens from the two Phbipox ligands and the bridging oxygen from a Phbipox ligand of an adjacent mononuclear complex. The Eu^{3+} coordination sphere is best described as a distorted tricapped trigonal prism (Figure S1 in the Supporting Information). The six crystallographically inequivalent Eu^{3+} ions of the noncentrosymmetric $[\text{EuC}(\Lambda\text{-Eu}(\text{R-Phbipox})_2\Delta\text{-Eu}(\text{R-Phbipox})_2)_3]^{9+}$ cation are located at the corners of a pseudo-hexagon with a diameter (defined as the distance between two opposite Eu^{3+} ions) of 12.6 Å (Figure S2). In each $[\text{Eu}(\text{R-Phbipox})_2]^+$ unit of **1**, strong $\pi\text{-}\pi$ interactions are found between the oxazoline phenyl ring of each Phbipox ligand and one pyridine ring of the other ligand (Table S1).

The crystal structure of **1** shows that the Δ and Λ complexes alternate to yield the final chiral assembly. Mercury models of the possible alternative diastereoisomers (all involving the proximity of complexes with the same chirality) suggest the presence of important steric constraints arising from the orientation of the phenyl substituents on the oxazoline rings when complexes of the same Δ or Λ chirality are brought

together. Similar steric constraints were shown to be the origin of the diastereoselective assembly of the $\Delta\Delta\Delta\text{-}[\text{Eu}(\text{S-Phbipox})_2]_3^{3+}$ trimer.¹⁸ The fact that such steric constraints play an important role in the diastereoselectivity of the self-assembly process was confirmed by NMR studies. The ^1H NMR spectrum of an acetonitrile solution of $[\text{Eu}(\text{R-Phbipox})_2]^+$ and $\text{Eu}(\text{OTf})_3$ in a 6:1 ratio (Figure 2c) shows

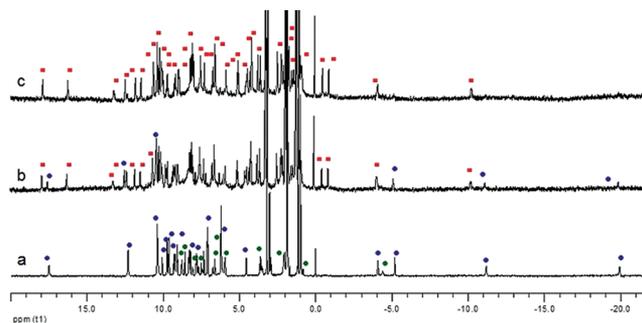


Figure 2. ^1H NMR titration by addition of (b) $1/3$ and (c) $1/6$ equiv of $\text{Eu}(\text{OTf})_3$ to (a) a 6 mM solution of $[\text{Eu}(\text{R-Phbipox})_2](\text{OTf})$ in anhydrous acetonitrile at 298 K and 500 MHz. Blue ●, green ●, and red ■ denote signals from the trinuclear, mononuclear, and heptanuclear (**1**) complexes, respectively.

the presence of one major set of 48 signals assigned to the protons of the four different R-Phbipox ligands from two different (Δ and Λ) mononuclear complexes present in **1**, in agreement with the pseudo- C_3 symmetry of the solid-state structure of **1**. The same ^1H NMR spectrum was obtained for an acetonitrile solution of R-PhbipoxH and $\text{Eu}(\text{OTf})_3$ in a 12:7 ratio in the presence of 12 equiv of NEt_3 , suggesting that self-assembly can also occur directly from the mixture of ligand and metal in the correct stoichiometric ratio. Again, the same ^1H NMR spectrum was observed for isolated **1** in anhydrous acetonitrile (Figure S4). This indicates that the chiral assembly is stable in acetonitrile solution. In contrast, ^1H NMR studies showed that dissolution of **1** (1 mM) in methanol or pyridine slowly (over a day) disrupts the cyclic structure, affording the corresponding mononuclear complex, as indicated by the presence of the 24 signals assigned to the two mononuclear Λ and Δ species. This probably results from the displacement of the bridging carboxylate O atoms by solvent molecules, as was observed previously for the trinuclear complex $(\Delta\Delta\Delta)\text{-}[\text{Eu}(\text{S-Phbipox})_2]_3^{3+}$.¹⁸

The formation of **1** was followed by an ^1H NMR titration of a 6 mM solution of $[\text{Eu}(\text{R-Phbipox})_2]^+$ in acetonitrile with 0.12–0.25 equiv of $\text{Eu}(\text{OTf})_3$. The ^1H NMR spectrum of the 6 mM solution of $[\text{Eu}(\text{R-Phbipox})_2]\text{OTf}$ in acetonitrile (Figure 2a) shows the presence of trinuclear $\Lambda\Lambda\Lambda\text{-}[\text{Eu}(\text{R-Phbipox})_2]_3^{3+}$, as reported previously for the S-Phbipox enantiomer.¹⁸ The structure of this assembly was confirmed by XRD analysis of crystals isolated from a concentrated acetonitrile solution of $[\text{Eu}(\text{R-Phbipox})_2]\text{OTf}$, which revealed the presence of two distinct cocrystallized molecules in the compound $\{\Lambda\Lambda\Lambda\text{-}[\text{Eu}(\text{R-Phbipox})_2]_3\cdot\Delta\text{-}[\text{Eu}(\text{R-Phbipox})_2]\}(\text{OTf})_4$ (**3**) (Figure S3). Addition of 0.12–0.17 equiv of $\text{Eu}(\text{OTf})_3$ to the 6 mM solution of $[\text{Eu}(\text{R-Phbipox})_2]\text{OTf}$ in acetonitrile resulted in the progressive disappearance of the NMR signals assigned to the monomeric and trimeric complexes and to the appearance of the signals assigned to **1** (Figure 2b). The addition of 0.25 equiv of $\text{Eu}(\text{OTf})_3$ did not lead to the formation of additional species, suggesting that the heptanuclear

clear wheel is the only thermodynamically favored assembly in solution. These results confirm the diastereoselectivity of the cation-promoted assembly of the **1** from three Δ and three Λ diastereomers. Moreover, they show that the excess cation promotes the transformation of the trinuclear assembly into the heptanuclear assembly.

To confirm the nuclearity of the oligomeric assembly in solution, pulsed-field-gradient stimulated-echo diffusion NMR spectroscopy¹⁹ was used to measure the diffusion coefficients (D) of a mixture of trinuclear $\Lambda\Lambda\Lambda$ -[Eu(R-Phbipox)₂]₃³⁺ and heptanuclear [EuC(Λ -Eu(R-Phbipox)₂ Δ -Eu(R-Phbipox)₂)₃](OTf)₉ complexes in anhydrous deuterated acetonitrile. D is a function of the molecular weight and can be conveniently used to discriminate metallosupramolecular architectures in solution.²⁰ The values measured in acetonitrile [$M_1/M_{\Lambda\Lambda\Lambda} = (D_{\Lambda\Lambda\Lambda}/D_1)^3 = 2.2$] are in agreement with the presence of trinuclear and heptanuclear complexes. The Stokes–Einstein equation was applied to calculate the spherical hydrodynamic radii of the complexes, as they have both globular shapes. The calculated values of 8.0 Å for the trimeric species and 10.3 Å for the heptanuclear ones in acetonitrile (Table S2) compare very well with the values estimated from the crystal structures (7.7¹⁸ and 10.1 Å, respectively).

Preliminary studies (Figure S5) showed that the analogous heptanuclear assembly [NdC(Λ -Nd(R-Phbipox)₂ Δ -Nd(R-Phbipox)₂)₃](OTf)₉ can be obtained following the procedure shown in Scheme 1. The obtained crystals were not of sufficient quality to obtain a high-quality XRD structure, but the unit cell parameters confirmed that the isolated complex is isostructural to **1**. Preliminary NMR studies also showed that in contrast to the Eu and Nd wheels, a well-defined heptanuclear species does not form when excess Yb³⁺ is added to a solution of the [Yb(R-Phpybox)₂]⁺ complexes, suggesting that the diastereoselective assembly of **1** and **2** is controlled by the size of the central cation.

The luminescence emission spectra of **2** at room temperature upon broadband excitation in acetonitrile and in the solid state are given in Figure S6, and the luminescence quantum yields of **2** and the mononuclear analogue [Eu(R-Phbipox)₂](OTf) in acetonitrile solution are given in Table 1. The analysis of the crystal-field splittings in the emission spectra of the two complexes is consistent with their X-ray structures. They are highly luminescent, with the quantum yield of the metal-

Table 1. Absolute Quantum Yields ($\Phi_{\text{Eu}}^{\text{L}}$) and Luminescence Dissymmetry Factors (g_{lum}) of the Eu ⁵D₀ Excited Level in [Eu(R-Phbipox)₂]⁺, [Eu(S-Phbipox)₂]⁺, and [EuC(Eu(S-Phbipox)₂)₆]⁹⁺ in Acetonitrile (298 K, $\lambda_{\text{ex}} = 339$ –340 nm)

cation (conc.)	$\Phi_{\text{Eu}}^{\text{L}}$ (%)	g_{lum}^a	
		⁵ D ₀ → ⁷ F ₁	⁵ D ₀ → ⁷ F ₂
[Eu(R-Phbipox) ₂] ⁺ (6 mM)	25 (1)	-0.45	+0.020
[Eu(S-Phbipox) ₂] ⁺ (6 mM)		+0.45	
[Eu(S-Phbipox) ₂] ⁺ (2 mM)		+0.15	-0.005
[Eu(R-Phbipox) ₂] ⁺ (1 mM)		-0.04	+0.007
[Eu(S-Phbipox) ₂] ⁺ (1 mM)		+0.06	-0.003
[EuC(Eu(S-Phbipox) ₂) ₆] ⁹⁺ (1 mM)	27 (1)	+0.10	-0.010

^aObtained from CPL measurements using the ⁵D₀ → ⁷F₁ (magnetic dipole, $\lambda = 590.6$ –592.8 nm) and ⁵D₀ → ⁷F₂ (electric dipole, $\lambda = 613$ –614 nm) transitions. The g_{lum} values reported here were measured with standard deviations of ± 0.01 and ± 0.001 for the CPL spectra of the ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ transitions, respectively.

centered luminescence being slightly higher for the heptanuclear complex (27%) than for the mononuclear one (25%). This suggests that the cyclic arrangement of six Eu components does not lead to intramolecular quenching effects as observed in the trimetallic helicates,²¹ despite the shorter distance between the neighboring EuL₂ units (6.34 Å) relative to the intermetallic distance in the trimetallic helicates (9–9.3 Å). Indeed, the sensitization efficiencies of the mononuclear and heptanuclear complexes are in the same range with relatively small variations (average of 55%) as a result of their similar coordination environments. In view of the strong luminescence emission of these Eu³⁺ complexes, we decided to use CPL, a technique allying the sensitivity and specificity of the signal for chiral environments, to monitor the assembly of the trinuclear and heptanuclear assemblies from the mononuclear Eu–Phbipox complexes.

A strong CPL signal was measured upon UV excitation of the mononuclear complexes [Eu(S-Phbipox)₂](OTf) and [Eu(R-Phbipox)₂](OTf) in 1 and 6 mM solutions in anhydrous acetonitrile. The complexes ([Eu(S-Phbipox)₂](OTf) and [Eu(R-Phbipox)₂](OTf) give rise to mirror-image CPL spectra for the ⁵D₀ → ⁷F₁ transition at 6 mM (Figure 3a). The CPL

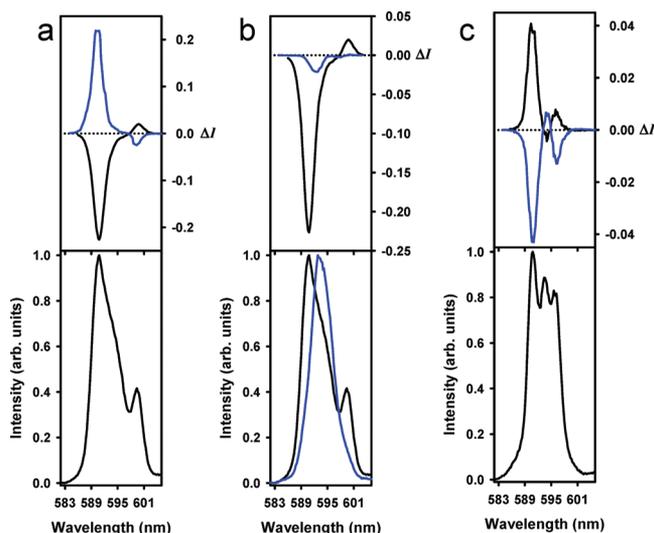


Figure 3. (top) CPL and (bottom) total luminescence spectra of the ⁵D₀ → ⁷F₁ transition at 295 K in anhydrous CH₃CN solutions of (a) [Eu(S-Phbipox)₂](OTf) (blue) and [Eu(R-Phbipox)₂](OTf) (black) (6 mM, $\lambda_{\text{ex}} = 335$ –338 nm), (b) [Eu(R-Phbipox)₂](OTf) at 1 mM (blue) and 6 mM (black) ($\lambda_{\text{ex}} = 331$ –335 nm), and (c) [EuC(Eu(S-Phbipox)₂)₆](OTf)₉ (black) and [EuC(Eu(R-Phbipox)₂)₆](OTf)₉ (blue) (2 mM, $\lambda_{\text{ex}} = 347$ –348 nm).

spectra of the complex [Eu(R-Phbipox)₂](OTf) in CH₃CN show important differences in the magnitude, sign, and shape of the signals depending on the concentration (Figure 3b). Similarly, the luminescence dissymmetry factor g_{lum} (Table 1 and Tables S4 and S5) increases with concentration, reaching maximum values of -0.45 for [Eu(R-Phbipox)₂](OTf) and +0.45 for [Eu(S-Phbipox)₂](OTf) for the Eu ⁵D₀ → ⁷F₁ transition at 6 mM, which are among the highest reported for chiral complexes of europium.^{3,9,22} This increase parallels the formation of the homochiral trinuclear assemblies $\Lambda\Lambda\Lambda$ -[Eu(R-Phbipox)₂]₃³⁺ and $\Delta\Delta\Delta$ -[Eu(S-Phbipox)₂]₃³⁺ at high concentrations of the [Eu(R-Phbipox)₂](OTf) and [Eu(S-Phbipox)₂](OTf) complexes in acetonitrile.¹⁸ In 1 mM acetonitrile solutions, where only the monomeric complexes

are present, $|g_{lum}|$ values of less than 0.10 were measured. CPL spectra of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions of the heptanuclear wheels **1** and **2** were also recorded at a concentration of 2 mM in anhydrous acetonitrile and gave rise to mirror images (Figure 3c and Figure S7).

The CPL activity measured for heptanuclear wheel **2** ($g_{lum} \approx 0.10$ at $\lambda = 590.6$ nm) is similar to that for the mononuclear complex ($g_{lum} \approx 0.06$). This is in agreement with the heterochiral nature of **2**, which retains the same mixture of Λ and Δ isomers found in solutions of the mononuclear complexes $[Eu(S\text{-Phbipox})_2](OTf)$.

In conclusion, we have shown that a chiral dissymmetric tetradentate ligand can be used to promote the selective assembly of new chiral heptanuclear wheels that are the largest examples of chiral complexes of Eu^{3+} reported to date. The nuclearity of the assembly of polynuclear Eu complexes promoted by the chiral Phbipox ligand can be controlled by the Eu^{3+} cation. The cation-controlled self-assembly of the wheel from mono and trinuclear species is diastereoselective, and only one of the 13 possible isomers forms. The formation of the different species can be followed by CPL; while the CPL activity of the mononuclear species is retained in the heptanuclear wheel, the trimeric complex shows one of the highest CPL activities reported to date. The cation-directed assembly presented here is also well-adapted for the synthesis of chiral heteropolymetallic species, and work in this direction is in progress.

■ ASSOCIATED CONTENT

Supporting Information

Complete synthetic and experimental details, selected 1H NMR and fluorescence spectra, D values and CPL data, and X-ray crystallographic data (CIF). 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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