

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

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Supporting Information

Synthetic Procedures

General considerations

The synthesis of the complexes and the sample preparation for NMR and spectroscopic studies were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 1 ppm. The solvents were purchased from Aldrich in their anhydrous form conditioned under argon and were vacuum distilled from K/benzophenone (diisopropylether) or CaH₂ (acetonitrile, methanol).

Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany. ¹H NMR spectra were recorded on Varian MERCURY 400 MHz and Bruker 500 MHz spectrometers. NMR chemical shifts are reported in ppm with solvent as internal reference.

Mass Spectroscopy

Mass spectra were acquired on a LXQ-linear ion trap (Thermo Scientific, San Jose, CA, USA), equipped with an electrospray source in a methanol and acetonitrile which was prepared and filtered on micro porous filters in the glove-box and maintained under argon until injection in the spectrometer. Electrospray full scan spectra, in the range of m/z 50 –3000 amu, were obtained by infusion through fused silica tubing at 2 – 10 μL min⁻¹.

The LXQ calibration (m/z 50-2000) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine/MRFA and Ultramark 1621). The LXQ calibration (m/z 2000-4000) was performed with ES tuning mix (Agilent). The temperature of the heated capillary of the LXQ was set to the range of 100– 120 °C, the ion spray voltage was in the range of 3 – 5 kV with an injection time of 1-10 ms. The experimental isotopic profile was compared in each case to the theoretical one.

Spherical hydrodynamic radius.

Pulsed-Field Gradient STimulated Echo (PFGSTE) diffusion NMR was used for measuring the diffusion coefficients (*D*) of the complexes in anhydrous acetonitrile¹. Diffusion

coefficient is a function of the molecular weight (M) and can be conveniently used for discriminating metallosupramolecular architectures in solution². The values of the measured coefficient diffusion can be used to estimate the solution molecular weight using the following equation^{1,2}:

$$\frac{D_A}{D_B} = \sqrt[3]{\frac{M_B}{M_A}}$$

$$\frac{M_{Eu7L12}}{M_{Eu3L6}} = \left(\frac{D_{Eu3L6}}{D_{Eu7L12}} \right)^3 = 2.2$$

The values measured in acetonitrile are in agreement with the presence of trinuclear and heptanuclear complexes as the ratio of the molecular weights is equal to the reciprocal cube of the ratio of diffusion coefficients measured.

The spherical hydrodynamic radius r_{sph} (called Stokes radius) of the molecule was calculated from the Stokes-Einstein equation and compared to the value obtained from the solid state structure and with a similar reference compound in the same solvent^{3,4}:

$$r_{\text{sph}} = \frac{k_B T}{6\pi\eta D}$$

η (Pa.s) = viscosity of the medium

k_B ($\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$) = Boltzmann constant.

T : absolute temperature (K)

D : diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)

Photophysical measurements

Luminescence measurements (spectra and lifetimes) were recorded by using a modular Fluorolog FL 3-22 spectrometer from Horiba-Jobin Yvon-Spex. It is equipped with a double grating excitation monochromator and a iHR320 imaging spectrometer coupled to a R928P Hamamatsu photomultiplier for visible measurement. For measurements in the NIR spectral range of the Phbipox complexes, the spectrometer was fitted with a second photomultiplier Hamamatsu R5509. The excitation source was a 450W Xe arc lamp and all spectra were

corrected for detection and optical spectral response (instrumental functions) of the spectrofluorimeter.

Phosphorescence lifetimes were measured in time-resolved mode. They are averages of three independent measurements that were taken by monitoring the decay at the maxima of the emission spectra. The exponential decays were analyzed by using the package Origin 7.0.

The quantum yields of the complexes formed with the Phbipox ligand were determined at room temperature through an absolute method⁵ using a home-modified integrating sphere coupled to the modular Fluorolog FL 3-22 spectrofluorimeter. The values reported are the average of three independent determinations for each sample. The absolute quantum yield was calculated using the following expressions:

$$\Phi = \frac{E_c}{L_a - L_c} = \frac{E_c}{L_a \cdot \alpha} \quad \alpha = \frac{L_a - L_c}{L_a}$$

Where E_c is the emission spectra in the emission range of the sample (ex: if the emission maximum is 600 nm, the range of this spectrum will be from 450 to 750 nm), L_c is the emission spectra of the excitation wavelength of the sample, L_a is the emission spectra of the excitation wavelength of the reference (quartz capillaries tube 4 mm in diameter filled with the solvent used).

The total quantum yield $\Phi_{\text{Eu}}^{\text{L}}$ is thus given by the equation below in which η_{ISC} is the $^1\pi\pi \rightarrow ^3\pi\pi^*$ conversion and η_{ET} the energy transfer from the ligand-centered to the metal-centered excited states ($^3\pi\pi^* \rightarrow \text{Ln}$).

$$\Phi_{\text{Eu}}^{\text{L}} = \eta_{\text{ISC}} \cdot \eta_{\text{ET}} \cdot \Phi_{\text{Eu}}^{\text{Eu}} = \eta_{\text{sens}} \cdot \Phi_{\text{Eu}}^{\text{Eu}}$$

The intrinsic quantum yields of Eu(III) $\Phi_{\text{Eu}}^{\text{Eu}}$ could not be determined experimentally upon direct f-f excitation because of very low absorption intensity. We have thus determined these values for our complexes by assuming that the dipole strength of the magnetic dipole $\text{Eu}(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ transition is constant. The radiative lifetime τ_{R} of the $\text{Eu}(^5\text{D}_0)$ level is given by

$$\text{the equation : } \tau_{\text{R}} = \frac{1}{A_{\text{MD},0} \cdot n^3} \cdot \left(\frac{I_{\text{MD}}}{I_{\text{tot}}} \right)$$

in which n is the refractive index ($n = 1.329$ for methanol, 1.344 for acetonitrile and 1.5 for solid state complexes), $A_{\text{MD},0} = 14.65 \text{ s}^{-1}$ is the spontaneous emission probability of the $\text{Eu}(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ transition, and $I_{\text{MD}}/I_{\text{tot}}$ is the ratio of the total integrated intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J = 0-6$) to the integrated intensity of the magnetic dipole $\text{Eu}(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ transition.

Circularly Polarized Luminescence

Circularly polarized luminescence and total luminescence spectra were recorded on an instrument described previously,^{6, 7} operating in a differential photon-counting mode. It is common to report the degree of CPL in terms of the luminescence dissymmetry factor, $g_{lum}(\lambda)$, which is defined as

$$g_{lum} = \frac{\Delta I}{\frac{1}{2}I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)}$$

where I_L and I_R refer, respectively to the intensity of left and right circularly polarized emissions. The standard deviation, σ_d , in the measurement of the luminescence dissymmetry factor, g_{lum} , is defined as

$$\sigma_d = \sqrt{\frac{2}{N}}$$

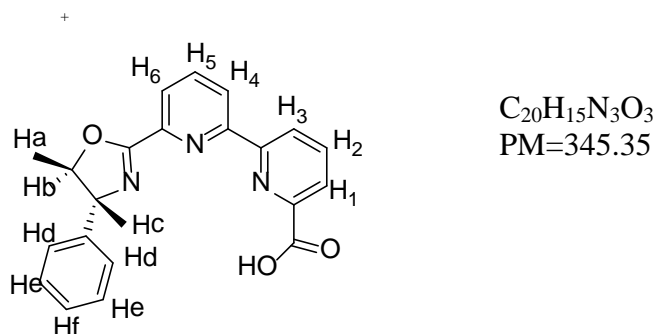
where N is the total number of photon-pulses counted. All the g_{lum} values reported in this study have been measured with a standard deviation, σ_d , of ± 0.01 and ± 0.001 for the CPL spectra of the ${}^5D_0 \rightarrow {}^7F_1$ and 7F_2 transitions, respectively.

The light source for indirect excitation was a continuous wave 1000 W xenon arc lamp from a Spex FluoroLog-2 spectrofluorometer, equipped with excitation and emission monochromators with dispersions of 4 nm/mm (SPEX, 1681B). All measurements were performed in quartz cuvettes with a path length of 0.4 or 1.0 cm.

Synthesis

The S-PhbipoxH ligand and R-PhbipoxH were prepared as previously described.⁸

(S) and (R)-6'-(4-phenyloxazolin-2-yl)-2,2'-bipyridine-6-carboxylic acid



¹H NMR (400MHz, DMSO-d₆, 308K) : δ = 4.31 (1H, t, J= 7.2Hz, Ha), 4.95 (1H, t, J= 7.2Hz, Hb), 5.51 (1H, t, J= 7.2Hz, Hc), 7.36 (5H, m, 2Hd, 2He, Hf), 8.16 (4H, m, H₁, H₂, H₅, H₆), 8.61 (1H, dd, J= 6.4Hz, J= 2.6Hz, H₄), 8.71 (1H, d, J= 6.6Hz, J= 2.4Hz, H₃)

¹³C NMR (400MHz, DMSO-d₆, 308K) : δ = 70.0 (CH₂), 75.4 (CH_{oxa}), 123.8 (CH_{py}), 124.3 (CH_{py}), 125.4 (CH_{py}), 125.8 (CH_{py}), 127.4 (5×CH_{Ph}), 127.1 (CH_{py}), 129.3 (CH_{py}), 139.2 (C_{Ph}), 139.6 (C_{py}), 142.99 (C_{py}), 146.8 (C_{py}), 155.2 (C_{py}), 163.6 (C_{oxa}), 166.6 (COOH)

ES-MS : m/z= 346.2 (MH⁺) and 363.2 (MNa⁺)

Elemental analysis :

S-Phbipox: (%) calculated for C₂₀H₁₅N₃O₃ (345.36 g/mol): C 69.56; H 4.38; N 12.17;
found: C 69.54; H 4.64; N 12.03

R-Phbipox: (%) calculated for C₂₀H₁₅N₃O₃ (345.36 g/mol): C 69.56; H 4.38; N 12.17;
found: C 69.37; H 4.70; N 12.39

[Eu(R-Phbipox)₂](OTf), [Eu(S-Phbipox)₂](OTf), [Nd(R-Phbipox)₂](OTf) were prepared according to the procedure previously described for [Eu(S-Phbipox)₂](OTf).⁸

[Eu(S-Phbipox)₂](OTf) and [Eu(R-Phbipox)₂](OTf)

Triethylamine (20.2 μl) was added to a solution of S-PhbipoxH or R-PhbipoxH (50 mg 0.145 mmol) in 2 mL anhydrous methanol. The resulting solution was stirred for 2 hours and a solution of Eu(OTf)₃ (0.0725 mmol) in methanol (1mL) 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 two weeks at 40 °C under vacuum (54- 66% yield).

Elemental analysis

[Eu(R-Phbipox)₂](OTf) :

(%) calcd. for C₄₁ H₂₈N₆O₉F₃SEu (989.72 g/mol) : C 49.76, H 2.85, N 8.49; found C 49.86, H 2.99, N 8.45.

¹H NMR (400MHz, CD₃OD, 298K):

(Δ)-[Eu(S-Phbipox)₂]⁺/ (Δ)-[Eu(R-Phbipox)₂]⁺ species : δ= 2.45 (4H, broad s, Hd), 3.55 (2H, broad t, Ha), 4.10 (2H, d, J = 7.8Hz, H6), 4.55 (4H, broad s, He), 5.37 (2H, t, J = 6.8Hz, Hf), 6.11 (2H, d, J = 7.8Hz, H4), 6.92 (2H, t, J = 7.8Hz, H5), 7.29 (2H, d, J = 7.8Hz, H1), 7.38 (2H, broad t, Hb), 7.53 (2H, d, J = 7.8Hz, H3), 8.75 (2H, t, J = 7.8Hz, H2), 11.70 (2H, broad t, Hc),

(Δ)-[Eu(S-Phbipox)₂]⁺/ (Δ)-[Eu(R-Phbipox)₂]⁺ species : δ= -13.38 (0.8H, broad t, Hc'), 0.41 (0.8H, broad t, Hb'), 1.58 (0.8H, broad s, H6'), 5.51 (0.8H, broad t, Ha'), 5.74 (1.6H, s, H4'), H5'), 6.95 (0.8H, m, H3'), 7.58 (0.8H, m, H1'), 8.86 (0.8H, t, J = 7.2Hz, H2'), 9.44 (0.8H, broad t, J = 7.2Hz, Hf'), 10.07 (1.6H, broad t, J = 7.2Hz, He'), 12.64 (1.6H, broad s, Hd')

¹H NMR (500MHz, CD₃CN, 263K) :

(Δ)-[Eu(S-Phbipox)₂]⁺/ (Δ)-[Eu(R-Phbipox)₂]⁺ species: δ= 0.45 (0.4H, broad t, Hc), 3.42 (0.4H, broad t, Ha), 2.71 (0.4H, broad t, Hb), 6.07 (0.4H, broad d, H6), 6.21 (0.8H, broad s,

H_d), 6.50 (0.4H, broad s, H₃), 7.21 (0.8H, broad s, H_e), 7.42 (0.4H, broad d, H₂), 7.50 (0.4H, broad t, H_f), 7.95 (0.4H, broad d, H₁), 8.50 (0.4H, d, J = 5.7Hz, H₄), 8.72 (0.4H, broad t, H₅)

($\Delta\Delta\Delta$)-[Eu(S-Phbipox)₂]₃⁺³ / ($\Lambda\Lambda\Lambda$)-[Eu(R-Phbipox)₂]₃⁺³ species:

● δ = -25.18 (1H, broad t, H_c), -7.83 (1H, broad d, H₆), -5.92 (1H, broad t, H_b), 1.53 (1H, broad t, H_a), 3.99 (1H, broad t, H₅), 6.34 (1H, d, J = 6.6Hz, H₃), 7.42 (1H, broad d, H₄), 9.54 (1H, broad t, H_f), 10.24 (2H, broad t, H_e), 11.12 (1H, broad t, H₂), 11.35 (1H, d, J = 6.1Hz, H₁), 13.57 (2H, broad s, H_d)

■ δ = -14.21 (1H, broad t, H_c), 0.33 (1H, broad t, H_b), 2.15 (1H, broad d, H₃), 3.28 (1H, broad t, H₂), 6.50 (1H, broad s H_a), 8.07 (1H, d, J = 7.9Hz, H₄), 9.54 (2H, broad t, H₅), 9.83 (3H, broad t, H₁, H_e), 10.37 (2H, broad s, H_d), 10.68 (1 H, broad t, H_f), 19.78 (1H, broad s, H₆)

ES-MS, CD₃OD: m/z = 841.1 {[Eu(S-Phbipox)₂]}⁺

ES-MS, CD₃CN: m/z = 841.3 {[Eu(S-Phbipox)₂]}⁺ m/z = 1335.0 [Eu₃(S-Phbipox)₆](OTf)²⁺

[Nd(R-Phbipox)₂](OTf)

The compound was prepared as described for the corresponding europium complex.

Yield 72%

¹H NMR (400 MHz, CD₃OD, 298K):

(Δ)-[Nd(R-Phbipox)₂]⁺ species:

δ = 27.56 (1H, m, H_c'), 17.40 (1H, s, H₃'), 13.29 (1H, s, H₆'), 11.93 (1H, s, H_a'), 11.09 (1H, s, H₂'), 8.25 (1H, s, H₅'), 7.56 (1H, s, H₁'), 6.37 (1H, s, H_f'), 5.13 (1H, s, H₄'), 4.39 (1H, s, H_e'), 3.95 (1H, d, J = 16.76 Hz, H_b'), 0.94 (1H, s, H_d')

(Λ)-[Nd(R-Phbipox)₂]⁺ species:

δ = 13.86 (1H, m, H_d), 9.77 (1H, s, H_e), 8.55 (1H, s, H_f), 7.95 (1H, s, H_a), 7.12 (1H, s, H₂), 5.73 (1H, s, H₁), 5.20 (1H, s, H₆), 3.95 (1H, d, J = 16.76 Hz, H₃), 3.50 (2H, d, J = 32.59 Hz, H_b, H₅), 1.30 (1H, t, J = 6.70, 6.70 Hz, H₄), -4.05 (1H, m, H_c)

¹H NMR (500 MHz, CD₃CN, 263K):

δ = 42.97-42.12 (1H, m, Hox), 28.43 (1H, s, Hox), 27.68 (1H, s, Hpy), 21.31 (1H, s, Hox), 12.45 (1H, s, Hox), 11.45 (1H, s, Hpy), 9.42 (1H, s, Hox), 6.36 (1H, s, Hpy), 4.63 (1H, s, Hpy), 3.88 (1H, m, Hph), 3.69 (1H, s, Hpy), 3.48 (2H, s, Hph), 3.41 (1H, s, Hph), 3.29 (1H, s, Hox), 2.91 (3H, s, Hpyr, Hph), 2.78 (1H, s, Hpy), 2.67 (2H, s, Hph), 1.71 (1H, s, Hpy), 1.36 (1H, s, Hpy), -0.69 (2H, s, Hph), -1.67 (1H, s, Hpy), -16.20 (1H, d, J = 3.77 Hz, Hpy)

Elemental analysis

{[Nd(R-Phbipox)₂](OTf)}·0.17Et₃NOTf : (%) calcd. for C_{42.19}H_{30.55}N_{6.17}O_{9.51}F_{3.51}S_{1.17}Nd (1024.54 g/mol) : C 49.46, H 3.00, N 8.43; found C 49.46, H 3.07, N 8.44.

ES-MS, CD₃OD: m/z= 832.4{[Nd(R-Phbipox)₂]}⁺

ES-MS, CD₃CN: m/z= 832.4 {[Nd(R-Phbipox)₂]}⁺ m/z = 1323.3 [Nd₃(R-Phbipox)₆](OTf)}²⁺

Eu⊂[(Λ-Eu(R-Phbipox)₂Δ-Eu(R-Phbipox)₂)₃](OTf)₉ and **Eu**⊂[(Λ-Eu(S-Phbipox)₂Δ-Eu(S-Phbipox)₂)₃](OTf)₉

Triethylamine (25μl) was added to a solution of S/R-Phbipox (55 mg, 0.155 mmol) in 2 mL anhydrous acetonitrile. The resulting solution was stirred for 2 hours and a solution of Eu(OTf)₃ (54.6mg, 0.090 mmol) in acetonitrile (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 two weeks at 40 °C under vacuum (81% yield). Crystals were prepared by slow diffusion of hexane on a benzonitrile solution of the complexes.

¹H NMR (400 MHz, CD₃OD, 298K) **Eu**⊂[(Λ-Eu(R-Phbipox)₂Δ-Eu(R-Phbipox)₂)₃](OTf)₉ and **Eu**⊂[(Λ-Eu(S-Phbipox)₂Δ-Eu(S-Phbipox)₂)₃](OTf)₉

δ= 18.06-17.68 (1H, m), 16.41-16.11 (1H, m), 13.49-13.02 (1H, m), 12.64-12.35 (1H, m), 11.97-11.67 (1H, m), 11.58-11.25 (1H, m), 10.66 (2H, s), 10.40 (2H, d, J = 6.99 Hz), 10.25 (2H, s), 10.13 (2H, s), 10.06-9.93 (1H, m), 9.80-9.66 (1H, m), 9.28-9.13 (1H, m), 9.10-8.90 (2H, m), 8.21 (1H, s), 8.10 (2H, s), 8.02 (1H, s), 7.72 (2H, dd, J = 24.78, 7.61 Hz), 7.68 (1H, t), 7.54 (4H, t, J = 7.54, 7.54 Hz), 7.36-7.25 (1H, m), 6.77-6.68 (1H, m), 6.61 (2H, s), 5.97-5.78 (1H, m), 5.09 (2H, s), 4.67-4.40 (2H, m), 4.40-4.25 (1H, m), 4.21 (3H, s), 3.80 (2H, s), 3.63 (1H, s), 2.52 (2H, s), 2.36-2.20 (1H, m), 2.20-2.05 (1H, m), 1.82-1.65 (2H, m), 1.65-1.52 (1H, m), 1.50-1.40 (1H, m), -0.34--0.54 (1H, m), -0.78--0.92 (1H, m), -3.94--4.18 (1H, m), -10.09--10.42 (1H, m)

ES-MS, CD₃CN: m/z= 1334.5{[Eu₆L₁₂]OTf₂}⁴⁺, 1829 {[Eu₆L₁₂]OTf₃}³⁺

Elemental analysis for

Eu₇ [(Λ-Eu(R-Phbipox)₂Δ-Eu(R-Phbipox)₂)₃](OTf)₉·Et₃NOTf

(%) calcd. for C₂₅₆H₁₈₃Eu₇F₃₀N₃₇O₆₆S₁₀(6787.73 g/mol) :C 45.30, H 2.72, N 7.63; found C 45.10, H 2.71, N 7.84.

X-Ray Crystallography

Diffraction measurements were done at the Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF) for complex **1**. A crystal of ~150 μm size has been selected and rapidly transferred to a 100 K nitrogen stream. Diffraction data were taken at 100 K using the MAR345 Image Plate detector, at the wavelength 0.70093 \AA and the crystal-to-detector distance of 250 mm. 250 frames with $\Delta\phi$ increments of 0.8° and 15 sec exposure time have been collected. All diffraction intensities could be indexed in a C-centered monoclinic lattice. The collected X-ray data were treated by the CrysAlisPro software⁹ and were subjected to a 2-cycle 3D integration, followed by the multi-scan absorption correction implemented in the integration software ($R_{\text{int}} = 0.0477$). 63575 diffraction intensities were integrated up to 1.3 \AA resolution. Mean $F^2/\sigma(F^2)$ for the data in the outer 1.35-1.30 \AA shell equals 5. The data were corrected for Lorentz and polarization effects. Absorption correction and scaling of frames for the decaying intensity of the synchrotron beam were performed using ABSPACK procedure implemented in CrysAlisPro.

The structure was solved by direct methods (SHELXS). Eu atoms and the primary coordination sphere, as well as the majority of the ligands could be partially located in the density maps. One ligand was idealized by applying bond and angle distance restraints and used for fitting onto the other partially resolved ligands using an algorithm implemented in PyMOL¹⁰. Dictionary restraints were sampled from the CSD database; the benzene rings were all refined as planar hexagons with C-C bonds of 1.39 \AA , and used in the next refinement cycles by conjugate-gradient least-squares method in SHELXL.

Some of the triflate, CF_3SO_3^- , anions could be assembled from the difference map peaks and the remaining anions were found by the ligand fitting procedure in COOT.¹¹ Finally, 14 out of 18 anions were located, with two of them refined at half occupancy. The anions were treated as rigid groups which were allowed to move with and rotate around the sulfur atom, the torsion angles were however restrained in the ideal staggered positions. 2 anions could not be confined to one positions and 2-fold positional disorder was applied to model the diffuse electron density. For the final cycles the structure was refined until the full convergence by full matrix least squares method using 2559 parameters and 2094 restraints for 29668 unique reflections in the 5-1.3 \AA resolution range. The complex as well as the located anions fit well into the electron density maps. There are large cavities present in the

crystal packing where the remaining 4 anions are thought to reside, although these are not likely to be restrained to a defined position. Only the 14 Eu atoms in the asymmetric unit were refined anisotropically, lighter atoms - isotropically, and hydrogens - in the riding mode.

Structure validation. Two independent 6+1 Eu rings of the same chirality are present in the structure. The two rings have very similar molecular geometry: when superposed, the RMS deviation of atomic positions is only 0.570 Å and the two complexes can be related by a pseudo 2-fold axis. However, an analysis for missing symmetry did not indicate higher lattice symmetry or additional symmetry elements.

The packing of the large supramolecular entities is not dense, as substantial unoccupied voids were detected in PLATON¹² even using a relatively large, 2.5 Å, probe. The largest voids are located at $x = 1/2, y = 0.054, z = 1/2$ and $x = 1/2, y = 0.392, z = 0$ (fractional coordinates), accounting for 12.5% of the volume.

Considering the similar values of the cell parameters a and c , a possibility of a merohedral twinning by a 2-fold rotation around the 101 direction has been verified and finally discarded.

The structure is validated by Checkcif tests. The alerts related to the short interatomic distances originate from the solvent disorder, and thus have to be discarded. Also, the use of long atom names, contested by Checkcif, is essential for the description of the structure containing 1102 independent atoms.

Crystal data. $\text{Eu}_7(\text{C}_{20}\text{H}_{14}\text{O}_3\text{N}_3)_{12}(\text{CF}_3\text{SO}_3)_9$, $M = 6537.52$ g/mol, monoclinic, space group $C2$, $a = 45.7446(11)$, $b = 31.0966(5)$, $c = 45.7325(11)$ Å, $\beta = 92.945(2)^\circ$, $V = 64969(3)$ Å³, $Z = 8$, $Z' = 2$, $\rho_c = 1.253$ g/cm³, $\mu = 1.447$ mm⁻¹, $T = 100$ K, $R_{\text{int}} = 0.0477$, $R_\sigma = 0.0684$. 2559 refined parameters were fitted to 29668 independent reflections (24620 with $I > 2\sigma(I)$) and 2094 restraints down to $R_1 = 0.0975$ for reflections with $I > 2\sigma(I)$ and $wR_2 = 0.2913$ for all independent reflections (Friedel pairs not merged), $\text{Goof} = 0.990$. Flack parameter equals 0.050(18) and 0.920(19) for the inverted configuration, $\Delta\rho_{\text{max/min}} = 1.13(13)/-0.80(13)$ e/Å³.

Measurement of the unit cell of **2** and diffraction measurements for **3** were performed using a Oxford Diffraction XCalibur S kappa geometry diffractometer (Mo-K α radiation, graphite monochromator, $\lambda = 0.71073$ Å). To prevent evaporation of co-crystallised solvent molecules the crystals were coated with light hydrocarbon oil. The cell parameters were obtained with intensities detected on three batches of 5 frames. The crystal-detector distance was 4.5 cm. The number of settings and frames has been

established taking in consideration the laue symmetry of the cell by CrysAlisPro Oxford-diffraction software. 86 images were collected at theta = 0 in 10s and 286 images were collected at theta = 45° in 40 s for 1° increments in ω . Unique intensities detected on all frames using the Oxford-diffraction Red program were used for refining the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the ABSPACK Oxford-diffraction program. For all structures space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure. The structures were solved by direct methods using the SHELXTL 6.14 package¹³ and for all atoms, including hydrogen atoms, were found by difference Fourier syntheses. Non-hydrogen atoms were anisotropically refined on F^2 . Hydrogen atoms were fixed in ideal position.

The X-ray diffraction analysis of **3** revealed the presence of two distinct co-crystallized cations $\Delta\Delta\Delta$ -[Eu(S-Phbipox)₂]₃³⁺ and (Λ) [Eu(S-Phbipox)₂]⁺. **3** crystallizes in the crystallises in the chiral orthorhombic space group P2₁2₁2₁ and is isostructural with the previously reported $\{(\Delta\Delta\Delta)$ -[Eu(S-Phbipox)₂]₃ (Λ) [Eu(S-Phbipox)₂]\}OTf₄ enantiomer.⁸

Structure Description of **1**

The six crystallographically inequivalent lanthanide ions of the non-centrosymmetric cation [Eu \subset (Λ -Eu(R-Phbipox)₂ Δ -Eu(R-Phbipox)₂)]₃⁹⁺ are located in the corners of a pseudo-hexagon. The diameter of hexagon, defined as the distance of the two opposite europium ions, is (12.6 Å) (Figure S2). The pseudo-hexagon deviates only slightly from planarity with three europium (Eu2, Eu4, Eu6) situated above and three europium ions (Eu1, Eu3, Eu5) situated below (\pm 0.47(2) Å) the mean plane passing through the central Eu1 ion. The six carboxylate oxygen atoms are also located in the corners of a pseudo-hexagon with a smaller deviation from planarity.

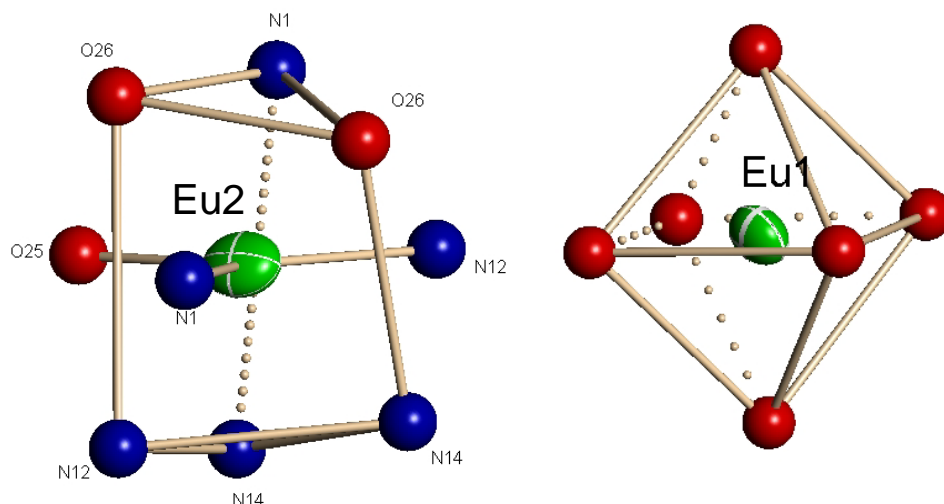


Figure S1: Coordination polyhedrons of the europium ions in $[\text{Eu}_1 \subset (\text{Eu}_2(\text{R-Phbipox})_2)_6](\text{OTf})_9$

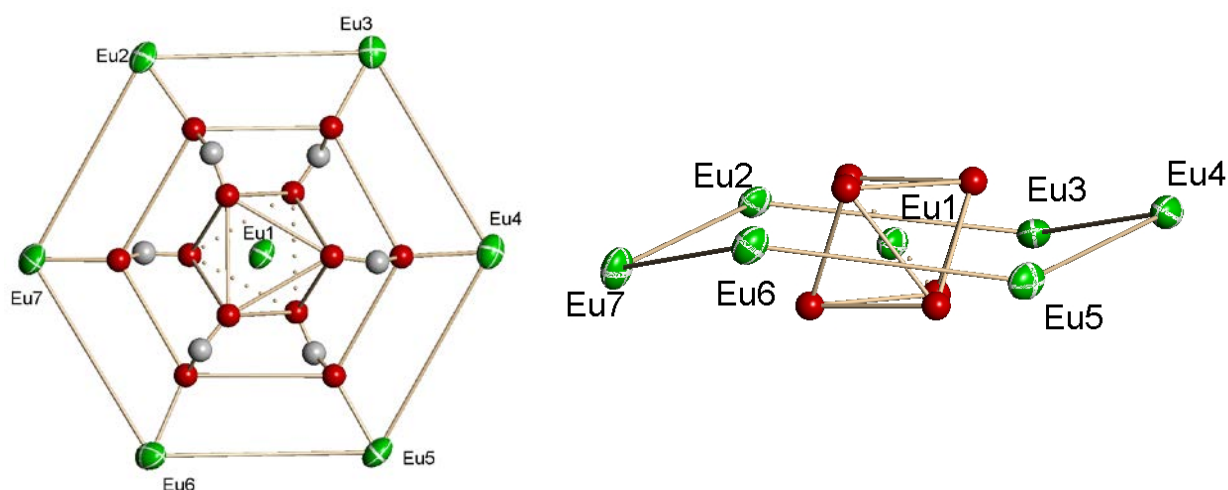


Figure S2: Top and side view of the coordination polyhedron of Eu1 and of the hexagon formed by the carboxylate oxygens and the six Eu ions.

The angles between the two ligands mean planes for $[\Delta\text{-Eu}(\text{R-Phbipox})_2]^+$ ($74.9(9)^\circ$) and for $[\Lambda\text{-Eu}(\text{R-Phbipox})_2]^+$ ($71.1(9)^\circ$) in the heptanuclear complex **1** are smaller than for the mononuclear $[\text{Eu}(\text{terpya})_2]^+$ complexes (77.8°) in the previously reported $[\text{Eu} \subset (\text{Eu}(\text{terpya})_2)_6](\text{OTf})_9$ heptanuclear wheel.¹⁴ The mean Eu-O distance ($2.37(6) \text{ \AA}$) is similar to the mean Eu-O distance found in the previously reported trinuclear complex $(\Delta\Delta\Delta)\text{-}[\text{Eu}(\text{S-Phbipox})_2]_3^{+3}$ ($2.39(2) \text{ \AA}$).⁸ The mean value of the Eu-N ($2.58(6) \text{ \AA}$) is similar to the one found in $[\text{Eu} \subset (\text{Eu}(\text{terpya})_2)_6](\text{OTf})_9$ where Eu-N = $2.57(5) \text{ \AA}$.¹⁴ The mean Eu1-O distance for the octahedral coordinated central europium ion in **1** is $2.33(3) \text{ \AA}$ is similar to that

of $[\text{Eu}(\text{terpya})_2]_6(\text{OTf})_9$ (2.31(1) Å).¹⁴ The Eu-Eu distances (Eu-Eu1 = 6.29 Å and Eu-Eu = 6.34 Å) are slightly longer than the ones measured in $[\text{Eu}(\text{terpya})_2]_6(\text{OTf})_9$ (6.24 Å and 6.29 Å).¹⁴

In each $[\text{Eu}(\text{Phbipox})_2]^+$ complex of **1** strong π - π interactions are found between the oxazoline phenyl rings of each tetradentate ligand and one pyridine ring of the other ligand (Table S1).

Table S1: Distances and angles between rings centroids showing π - π interactions in **1**.

	Pyridine /Ligand	Phenyl	Distance	Angle
Eu2	N1/ L2	L1	3.557	6.04
Eu2	N12 / L1	L2	3.761	1.49
Eu3	N12 / L4	L3	3.690	6.07
Eu3	N12 / L3	L4	3.947	3.78
Eu4	N12 / L6	L5	3.851	1.27
Eu4	N1 / L5	L6	3.520	4.07
Eu5	N12/ L7	L8	3.881	11.59
Eu5	N1 / L8	L7	3.931	8.79
Eu6	N12 / L9	L10	3.728	9.03
Eu6	N1 / L10	L9	3.476	4.11
Eu7	N12 / L11	L12	3.737	6.58
Eu7	N12 / L12	L11	3.905	12.08

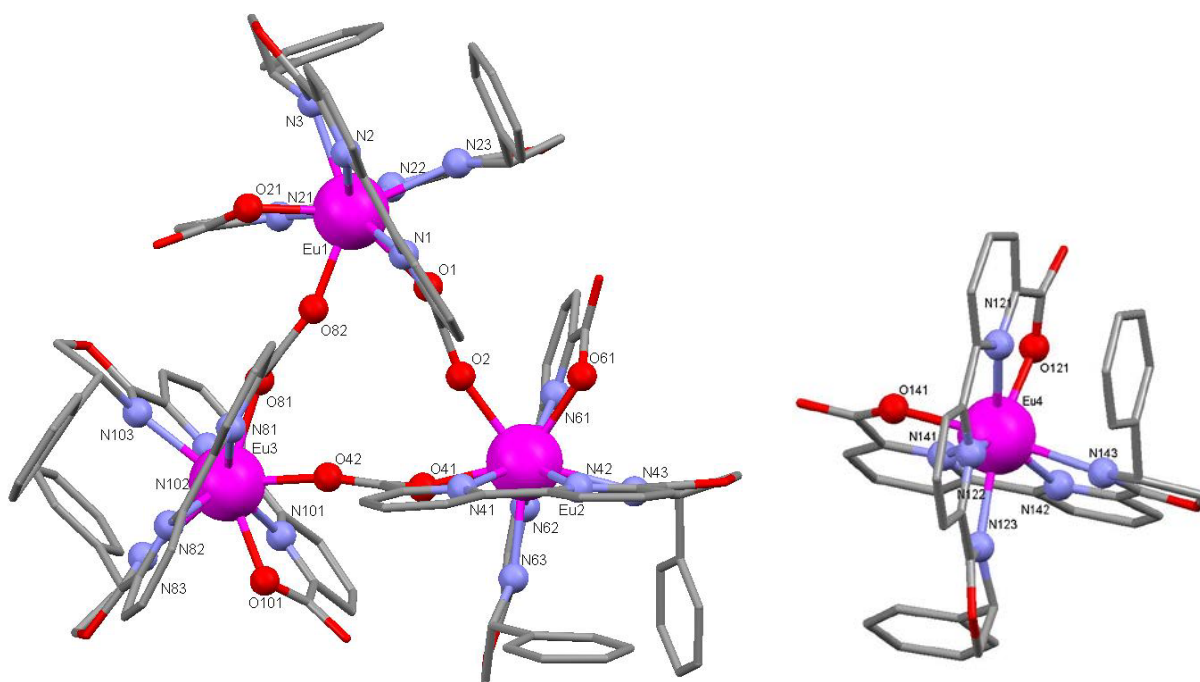


Figure S3: Mercury diagram of the structure of $[\Lambda\Lambda\Lambda\text{-}\{\text{Eu}(\text{R-Phbipox})_2\}_3\cdot\Delta\text{-}\{\text{Eu}(\text{R-Phbipox})_2\}]^{4+}$ in **3**.

NMR Studies

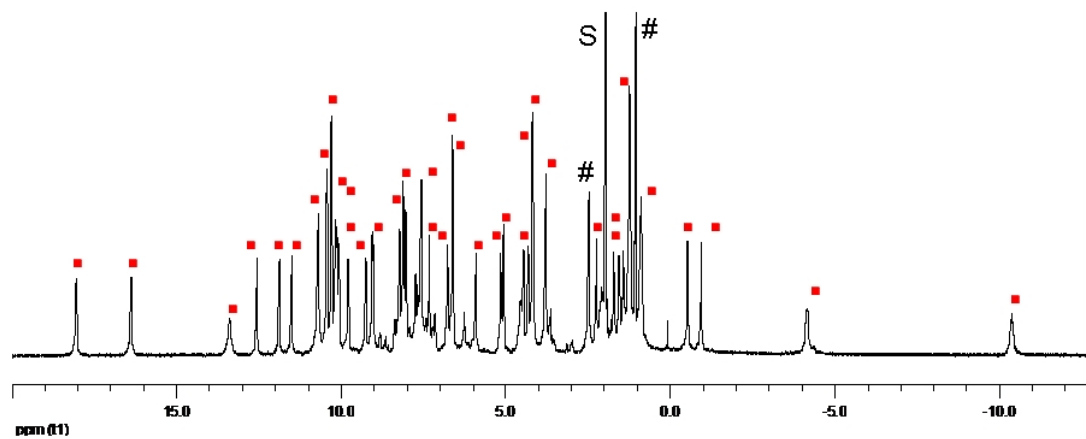


Figure S4. ^1H NMR spectrum of a 6 mM solution of **1** in anhydrous acetonitrile at 298 K and 500 MHz.

Table S2: Diffusion coefficient values of $[\text{Eu} \subset (\Lambda\text{-Eu}(\text{R-Phbipox})_2\Delta\text{-Eu}(\text{R-Phbipox})_2)_3]^{9+}$ and $\Lambda\Lambda\Lambda\text{-}[\text{Eu}(\text{R-Phbipox})_2]_3^{3+}$, and estimated spherical radii

Solvent	Compound	D [$\text{m}^2\cdot\text{s}^{-1}$]	r_{sph} [\AA] _{exp}
CD_3CN	$\Lambda\Lambda\Lambda\text{-}[\text{Eu}(\text{R-Phbipox})_2]_3^{3+}$	$7.90(5) \cdot 10^{-10}$	8.0
$\eta=0.345$ mPa.s (298 K)	$[\text{Eu} \subset (\Lambda\text{-Eu}(\text{R-Phbipox})_2\Delta\text{-Eu}(\text{R-Phbipox})_2)_3]^{9+}$	$6.08(6) \cdot 10^{-10}$	10.3

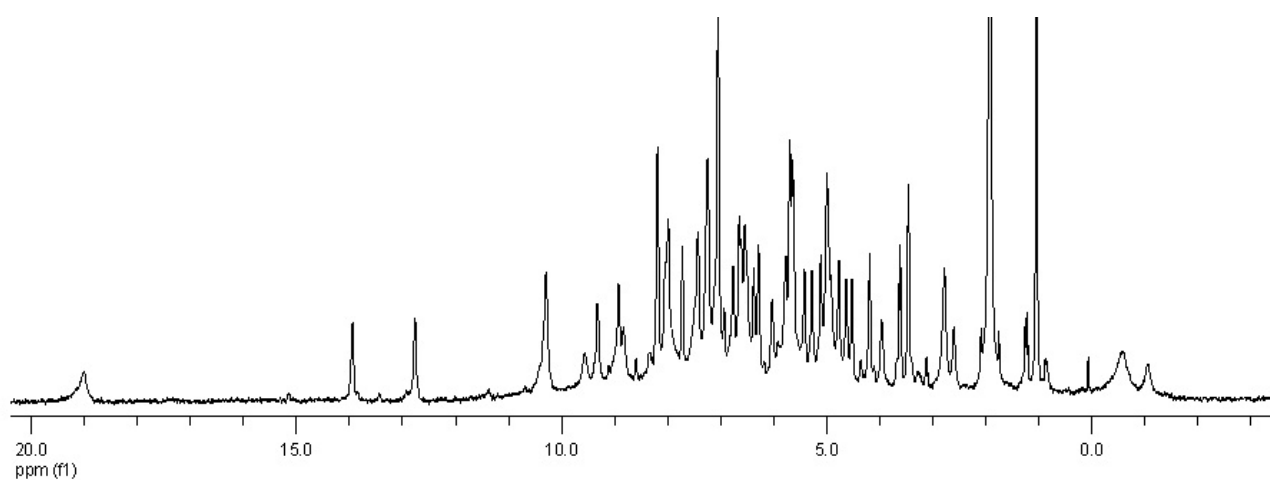


Figure S5: ^1H NMR spectrum of a solution of $[\text{Nd} \subset (\Lambda\text{-Nd}(\text{R-Phbipox})_2\Delta\text{-Nd}(\text{R-Phbipox})_2)_3](\text{OTf})_9$ in anhydrous acetonitrile at 298 K and 500 MHz

Photophysical Measurements

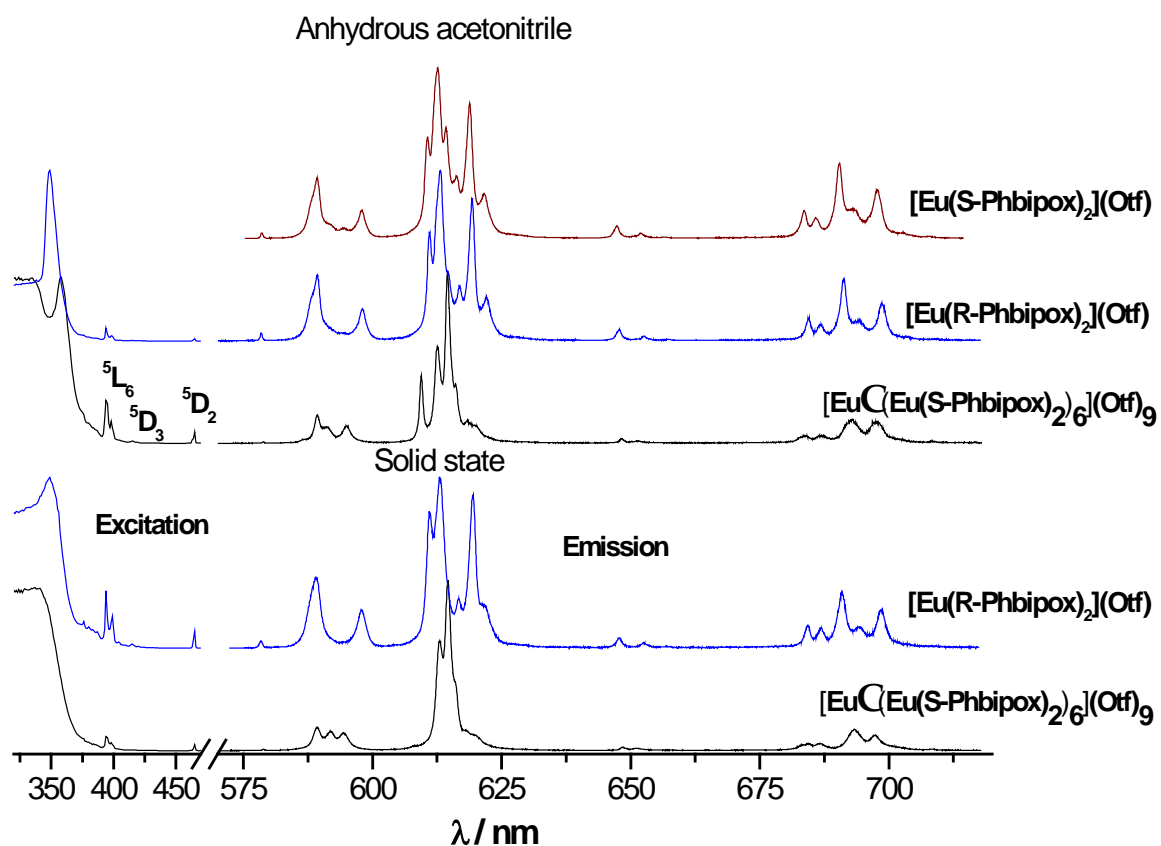


Figure S6: Normalized emission ($\lambda_{\text{ex}} = 339\text{-}340\text{ nm}$) and excitation (upon monitoring the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ transition) spectra of $[\text{Eu}(\text{R-Phbipox})_2](\text{OTf})$, $[\text{Eu}(\text{S-Phbipox})_2](\text{OTf})$ and $[\text{Eu}^{\subset}(\Lambda\text{-Eu}(\text{S-Phbipox})_2\Delta\text{-Eu}(\text{S-Phbipox})_2)_3](\text{OTf})_9$ in solid state and in 6 mM CH_3CN at room temperature.

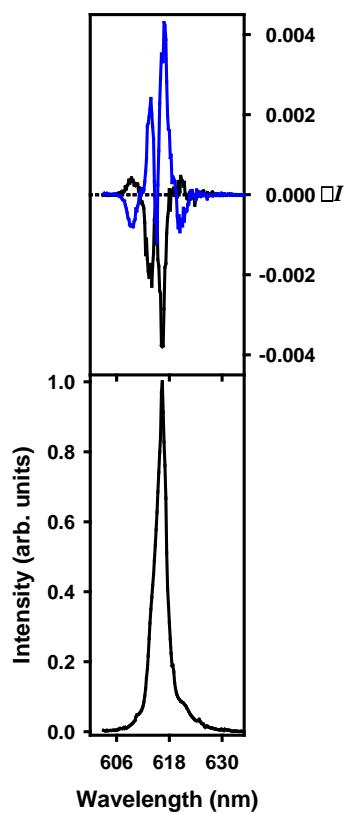


Figure S7: Circularly polarized luminescence (upper curves) and total luminescence (lower curve) spectra of the ${}^5D_0 \rightarrow {}^7F_2$ transitions of $[\text{Eu} \subset (\text{Eu}(\text{S-Phbipox})_2)_6](\text{OTf})_9$ (black) and $[\text{Eu} \subset (\text{Eu}(\text{R-Phbipox})_2)_6](\text{OTf})_9$ (blue) at 2 mM in anhydrous CH_3CN solutions at 295 K, upon excitation at 347-348 nm respectively.

Table S3 Absolute Quantum Yields, Lifetimes and Dissymmetry Factors of the Eu (5D_0) Excited Level in $[\text{Eu}(\text{R-Phbipox})_2](\text{OTf})$, $[\text{Eu}(\text{S-Phbipox})_2](\text{OTf})$ and $[\text{Eu}\subset(\text{Eu}(\text{S-Phbipox})_2)_6](\text{OTf})_9$ complexes in solid state and acetonitrile solutions at 298K with $\lambda_{\text{ex}} = 339\text{-}340$ nm.

Complex	$\Phi_{\text{Eu}}^{\text{L}}$ (%)	$\Phi_{\text{Eu}}^{\text{Eu}}$ (%) ^[a]	τ_{rad} (ms) ^[a]	η_{sens} ^[a]	g_{lum} (λ/nm) ^[b]		τ_{obs} (ms) ^[c]
					$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	
CH ₃ CN (6 mM)							
[Eu(R-Phbipox)₂]⁺	25(1)	31	4.6	81	-0.45 (590.8)	+0.02(612.4)	1.41(1)
[Eu(S-Phbipox)₂]⁺					+0.45 (590.8)		
CH ₃ CN (2 mM)							
[Eu(S-Phbipox)₂]⁺					+0.15(590.6)	-	
						0.005(613.8)	
CH ₃ CN (1 mM)							
[Eu(R-Phbipox)₂]⁺					-0.04(592.8)	+0.007(613)	
[Eu(S-Phbipox)₂]⁺					+0.06(590.6)	-0.003(614)	
[Eu \subset (Eu(S-	27(1)	48	3.6	57	+0.1 (590.6)	-0.01(614)	1.75(1)
Phbipox)₂]⁹⁺							
solid							
[Eu(R-Phbipox)₂]⁺	24(1)	59	3.4	44			1.87(2)
[Eu \subset (Eu(S-	37(1)	69	3.0	54			2.05(1)
Phbipox)₂]⁹⁺							

[a] See above for calculation. [b] Obtained by the CPL measurements at the $^5D_0 \rightarrow ^7F_1$ (magnetic dipole) and $^5D_0 \rightarrow ^7F_2$ (electric dipole) transitions. [c] Analyzing wavelength set on the maximum of the $^5D_0 \rightarrow ^7F_2$ transition.

Table S4: Dissymmetry factors obtained by the CPL measurements of the Eu(III) complexes. at the $^5D_0 \rightarrow ^7F_1$ (magnetic dipole) and $^5D_0 \rightarrow ^7F_2$ (electric dipole) transitions

Complex	Electronic transition	Λ [nm]	g_{lum}	Solvent
[Eu(R-Phbipox) ₂](OTf) ($\lambda_{exc} = 331\text{nm}$)	$^5D_0 \rightarrow ^7F_1$	592.8	-0.04	1 mM CH ₃ CN
		597.2	-0.01	
	$^5D_0 \rightarrow ^7F_2$	613.0	+0.007	
		619.4	+0.04	
[Eu(R-Phbipox) ₂](OTf) ($\lambda_{exc} = 335\text{ nm}$)	$^5D_0 \rightarrow ^7F_1$	590.8	-0.45	6 mM CH ₃ CN
		599.8	+0.10	
	$^5D_0 \rightarrow ^7F_2$	612.4	+0.02	
		620.2	+0.11	
[Eu(S-Phbipox) ₂](OTf) ($\lambda_{exc} = 334\text{ nm}$)	$^5D_0 \rightarrow ^7F_1$	593.0	+0.06	1 mM CH ₃ CN
		598.8	-0.02	
	$^5D_0 \rightarrow ^7F_2$	614.0	-0.003	
		620.8	-0.02	
[Eu(S-Phbipox) ₂](OTf) ($\lambda_{exc} = 338\text{ nm}$)	$^5D_0 \rightarrow ^7F_1$	590.8	+0.45	6 mM CH ₃ CN
		599.8	-0.10	

Table S5: Dissymmetry factors obtained by the CPL measurements of the heptanuclear Eu(III) wheel at the $^5D_0 \rightarrow ^7F_1$ (magnetic dipole) and $^5D_0 \rightarrow ^7F_2$ (electric dipole) transitions

Complex	Electronic transition	λ [nm]	g_{lum}	Solvent
[Eu ₇ (Eu(S-Phbipox) ₂) ₆](OTf) ₉ (λ_{exc} =344 nm)	$^5D_0 \rightarrow ^7F_1$	590.6	+0.10	1 mM CH ₃ CN
		595.6	+0.01	
	$^5D_0 \rightarrow ^7F_2$	614.0	-0.01	
		616.4	-0.006	
[Eu ₇ (Eu(S-Phbipox) ₂) ₆](OTf) ₉ (λ_{exc} =348 nm)	$^5D_0 \rightarrow ^7F_1$	590.6	+0.09	2 mM CH ₃ CN
		595.6-596.0	+0.02	
	$^5D_0 \rightarrow ^7F_2$	614.0	-0.01	
		616.4	-0.006	
[Eu(S-Phbipox) ₂] ₂ OTf (λ_{exc} =334 nm)	$^5D_0 \rightarrow ^7F_1$	593.0	+0.06	1 mM CH ₃ CN
		598.8	-0.02	
	$^5D_0 \rightarrow ^7F_2$	614.0	-0.003	
		620.8	-0.02	
[Eu(S-Phbipox) ₂] ₂ OTf (λ_{exc} =335 nm)	$^5D_0 \rightarrow ^7F_1$	590.6	+0.15	2 mM CH ₃ CN
		598.8	-0.02	
	$^5D_0 \rightarrow ^7F_2$	613.8	-0.005	
		620.8	-0.04	

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