

Antenna effect in Ln^{III} nitrates: the role of N-containing aromatic ligands in luminescence enhancement

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S1. Experimental section, general remarks.

All chemicals and solvents were used as purchased without further purification. The lanthanide nitrates with two bpy ligands Ln(NO₃)₃bpy₂ **1** (Ln = Eu), **3** (Ln = Tb) and [Eu(NO₃)bpy₂]⁺·bpy **2** were obtained according to published procedures.^{S1,S2} Elemental analyses were performed with a PerkinElmer 2400 Series II elemental CHNS/O analyzer.

S2. Optical measurements.

Luminescent measurements in the visible region were performed with a Horiba-Jobin-Yvon-Spex Fluorolog FL 3-22 spectrometer, which has a 450 W xenon arc lamp as the excitation source for steady state measurements and 150W xenon pulse lamp for kinetic experiments. The technique involved the use of specially designed, cylindrical sealed quartz cuvettes for manipulation with air-sensitive compounds. Time-resolved experiments, namely, luminescence lanthanide lifetimes (τ), were measured with initial delay = 0.05 ms, step size = 0.02 ms, and final window = 10 ms at least three times by monitoring the decay at the maxima of the emission spectra. For phosphorescence spectrum initial delay = 0.1 ms. The quantum yield measurements were carried out on solid samples with a Spectralone-covered G8 integration sphere (GMP SA, Switzerland) under ligand excitation, according to the absolute method of Wrighton.^{S3-S5} Each sample was measured several times under slightly different experimental conditions. The estimated error for quantum yields was ± 10%. All complexes studied were powdered.

The intrinsic quantum yield of the europium-centered emission (Q_{Eu}^{Eu}) was calculated using Werts' formula:^{S6}

$$Q_{Eu}^{Eu} = \frac{\tau_{obs}}{\tau_R} = \tau_{obs} \cdot A_{MD,0} \cdot n^3 \cdot \left(\frac{I_{tot}}{I_{MD,0}} \right),$$

where $A_{MD,0}$ is a constant spontaneous emission probability (14.65 s^{-1} for Eu^{III}), n is the refractive index, I_{tot} is the total area of the emission spectrum ($^5\text{D}_0 \rightarrow ^7\text{F}_J$, $J = 0-6$), and $I_{MD,0}$ is the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ band area. The refractive index was taken as 1.5 for all cases.

The overall quantum yield of photoluminescence can be calculated as $Q_{Ln}^L = \eta_{sens} \cdot Q_{Ln}^{Ln}$, where η_{sens} is the efficacy with which electromagnetic energy is transferred from the ligands to the Eu^{III} ion.

S3. Synthesis of complexes.

The compounds were obtained by mixing of ethanol solutions of europium nitrate $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and 2,2'-bipyridine (Aldrich).

***Eu(NO₃)₃bpy₂* 1.** A solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.089 g, 0.2 mmol) in 8 mL of ethanol was added dropwise to a solution of 2,2'-bipyridine (0.063 g, 0.4 mmol) in 10 mL of ethanol. The reaction mixture was stirred around 1 h at $T = 40^\circ\text{C}$ up to the formation of the precipitation. Colorless crystals were obtained after 1-2 days by slow evaporation method. The crystals were dried under dynamic vacuum for 2 h. Yield: 97%. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_7\text{O}_9\text{Eu}_1$ (650.35): C, 36.94%; H, 2.48%; N, 15.08%. Found: C, 36.62%; H, 2.42%; N, 14.96%.

***Eu(NO₃)₃bpy₃* 2.** A solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.089 g, 0.2 mmol) in 8 mL of ethanol was added dropwise to a solution of 2,2'-bipyridine (0.0937 g, 0.6 mmol) in 15 mL of ethanol. The reaction mixture was stirred around 2 h at $T = 40^\circ\text{C}$ up to the formation of the precipitation. Colorless crystals were obtained after 1-2 days by slow evaporation method. The crystals were dried under dynamic vacuum for 2 h. Yield: 74%. Calcd. for $\text{C}_{30}\text{H}_{24}\text{N}_9\text{O}_9\text{Eu}_1$ (806.5): C, 44.68%; H, 3.00%; N, 15.63 %. Found: C, 44.33%; H, 2.94%; N, 15.72%.

***Tb(NO₃)₃bpy₂* 3.** Following the procedure described above for complex **1**, $\text{Tb}(\text{NO}_3)_3\text{bpy}_2$ complex were obtained. Yield: 94%. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_7\text{O}_9\text{Tb}_1$ (657.31): C, 36.55%; H, 2.45%; N, 14.92%. Found: C, 36.33%; H, 2.44%; N, 14.72%.

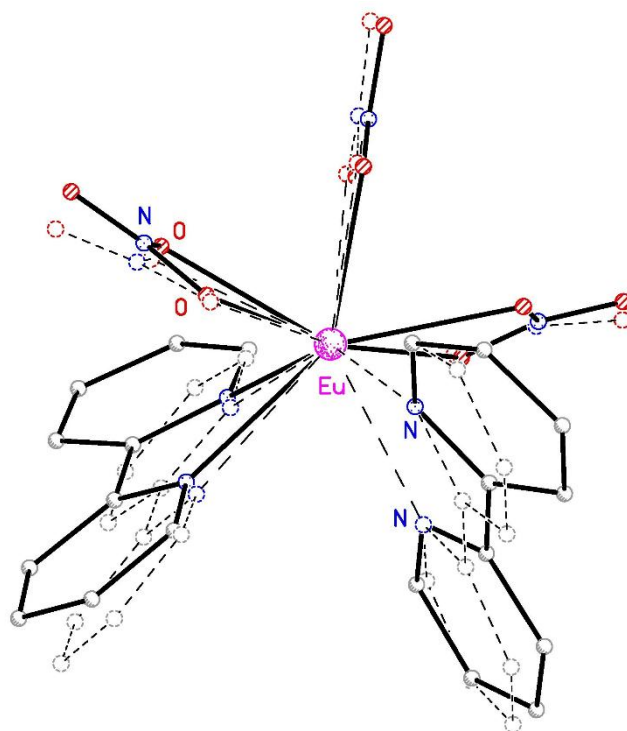


Figure S1 The best fitting of coordination polyhedrons of complexes **1** and **2**. Ligands of complex **1** are shown by dashed lines.

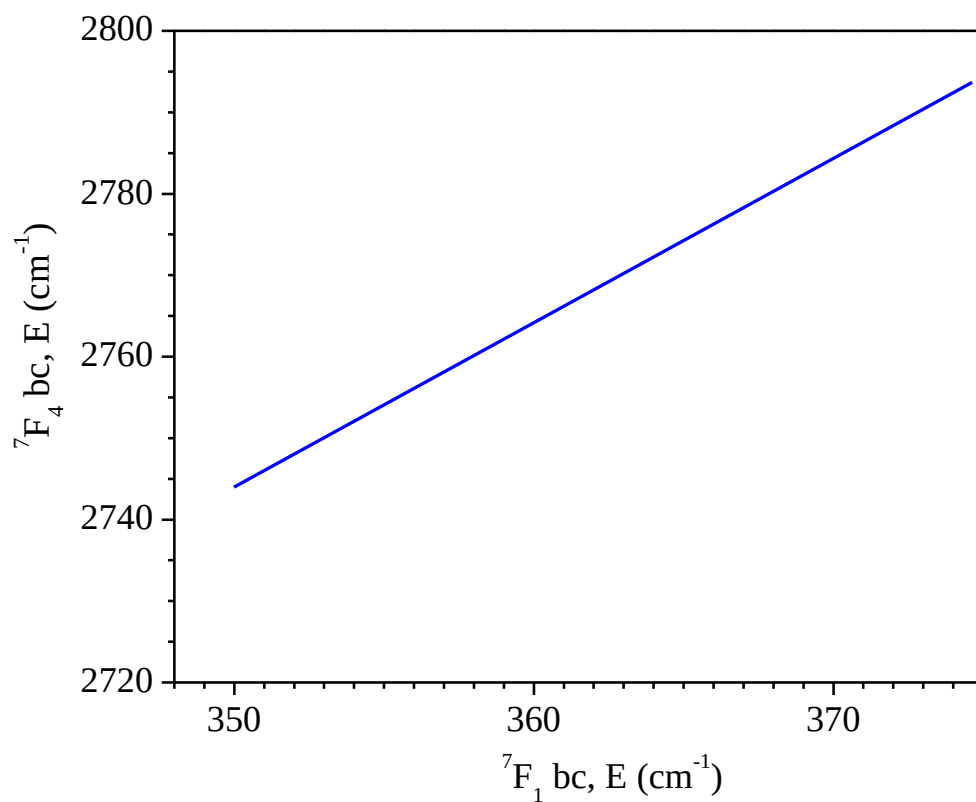


Figure S2 Correlation curve for barycenters of the 7F_4 multiplet as a function of barycenters of the 7F_1 multiplet obtained for Eu nitrates with 1,10-phenanthroline derivatives.^{S7}

S4. Multipole refinement and topology analysis

The multipole refinement was carried out within the Hansen-Coppens formalism^{S8} using the XD program package with the core and valence electron density derived from wave functions fitted to a relativistic Dirac-Fock solution.^{S9} Before the refinement, the C–H bond distances were normalised to 1.082 Å. The level of multipole expansion was hexadecapole for Eu and octapole for all other atoms. The refinement was carried out against F. The multipole refinement converged to R = 0.0174, wR = 0.0156 and GOF = 0.788 for 15831 merged reflections with $F > 3\sigma(F)$. Analysis of the topology of $\rho(r)$ functions was carried out using the WINXPRO program package.^{S10}

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