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Enantiopure, Octadentate Ligands as Sensitizers for Europium and Terbium Circularly Polarized Luminescence in Aqueous Solution

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Abstract

Tb and Eu complexes of enantiopure ligands with a new modular design show strong overall luminescence and CPL activity in aqueous solution.

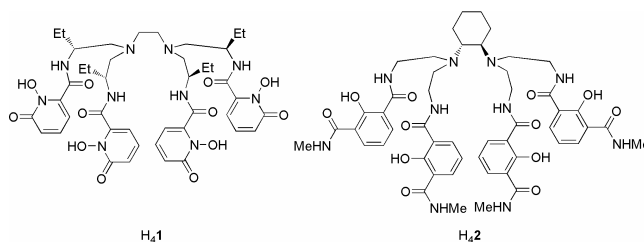
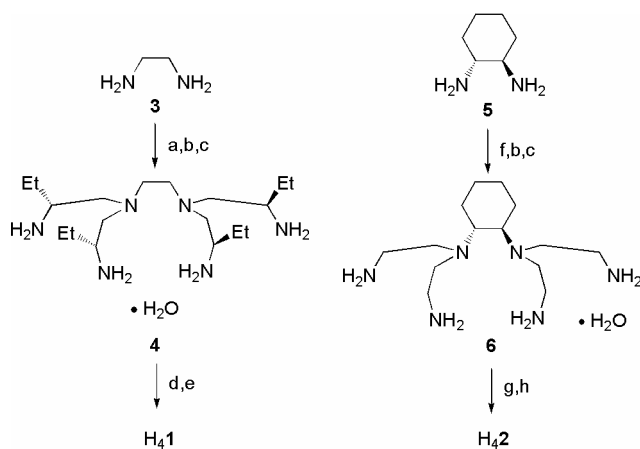


Figure 1. Enantiopure, octadentate ligands.



Scheme 1. Synthesis of ligands H₄1 and H₄2.

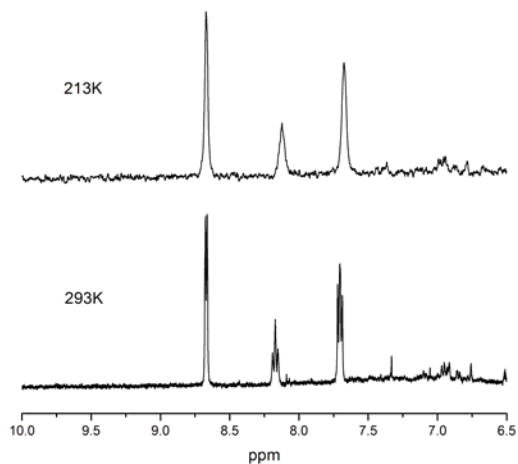


Figure 2. Aromatic region of the ^1H -NMR spectra (500 MHz) of a saturated solution of $[\text{Eu}(\text{H1})(\text{H}_2\text{O})]$ in CD_3OD at 293K (bottom) and 213K (top).

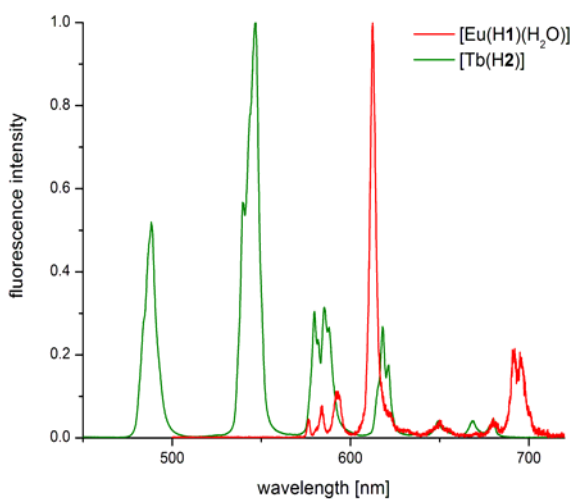


Figure 3. Normalized steady-state emission spectra ($\lambda_{\text{exc}} = 340 \text{ nm}$, ca. 10^{-5} M in 0.1 M Tris buffer, pH 7.4).

Table 1. Photophysical properties of the lanthanide complexes (ca. 10^{-5} M in 0.1 M Tris buffer, pH 7.4).

Complex	λ_{max} , [nm] (ϵ , [$\text{M}^{-1}\text{cm}^{-1}$])	λ_{exc} , [nm]	Quantum yield Φ^{a}	lifetime τ , [ms] ^b	q
$[\text{Eu}(\text{H1})(\text{H}_2\text{O})]$	341 (19 000 ^c)	340	0.077	0.48 (0.88)	0.84
$[\text{Tb}(\text{H2})]$	339 (28 200)	340	0.57	2.28 (2.59)	-0.04

^a Determined relative to quinine sulfate ($\Phi=0.546$) in 0.5 M sulfuric acid as standard; ^b in H_2O (in D_2O); ^c sat. solution, estimated ϵ .

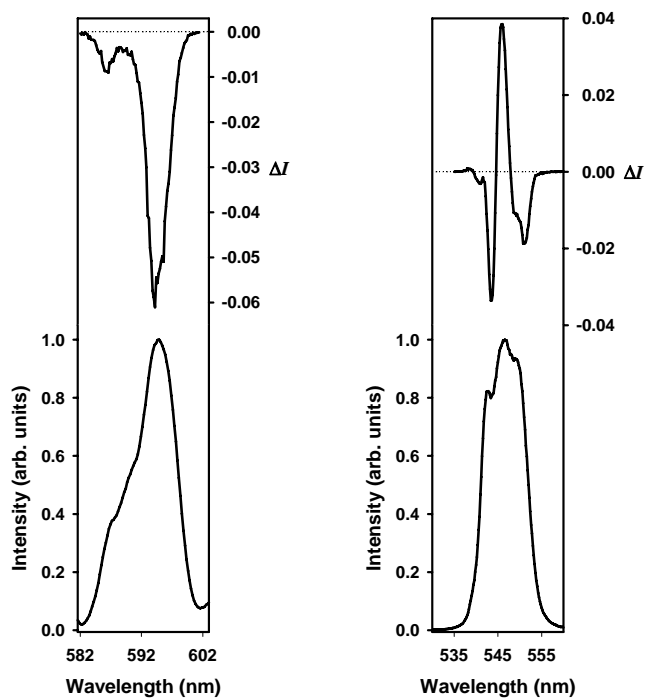


Figure 4. Circularly polarized luminescence (upper curves) and total luminescence (lower curves) spectra of the $^5D_0 \rightarrow ^7F_1$ transition of [Eu(H1)(H₂O)] (left) and $^5D_4 \rightarrow ^7F_5$ transition of [Tb(H2)] (right) in saturated aqueous solutions at pH 7.4 (0.1 M Tris buffer) and 295 K, upon excitation at 360 and 350 nm, respectively.

Table 2. CPL results for lanthanide complexes (saturated aqueous solutions in 0.1 M Tris buffer, pH 7.4).

Complex	Electronic transition	λ [nm]	g_{lum}
[Eu(H1)(H ₂ O)]	$^5D_0 \rightarrow ^7F_1$	586.6	-0.046
		594.2	-0.12
[Tb(H2)]	$^5D_4 \rightarrow ^7F_5$	543.6	-0.083
		545.8	+0.078
		551.0	-0.051