Dinuclear Lanthanide Complexes supported by a hybrid Salicylaldiminato/Calix[4]arene-Ligand: Synthesis, Structure, Magnetic and Luminescence Properties of (HNEt$_3$)[Ln$_2$(HL)(L)] (Ln = Sm$^{III}$, Eu$^{III}$, Gd$^{III}$, Tb$^{III}$)

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Supporting Information

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1) ORTEP PLOT for HNEt₃[Sm₂(HL)(L)(MeCN)₂]·2.5MeCN (4·2.5MeCN).

Fig. S1. Single-crystal X-ray diffraction structure of the [Sm₂(HL)(L)(MeCN)₂]⁻ anion in crystals of (HNEt₃)[Sm₂(HL)(L)(MeCN)₂]·2.5MeCN (4·2.5MeCN). The HNEt₃⁺ ion and some MeCN solvate molecules are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

2. Analytical data for 2

Fig. S2. ¹H NMR spectrum of 2 in CD₂Cl₂ at ambient temperature.
Fig. S3. APT spectrum of 2 in CD$_2$Cl$_2$ at ambient temperature.

Fig. S4. ATR infrared spectrum of 2.
Fig. S5. ESI mass spectrum of 2.

3. Analytical data for 3

Fig. S6. $^1$H NMR spectrum of 3 in DMSO-d$_6$ at ambient temperature.
Fig. S7. APT spectrum of 3 in DMSO-d$_6$ at ambient temperature.

Fig. S8. $^1$H,$^1$H NOESY spectrum of 3 in DMSO-d$_6$ at ambient temperature.
Fig. S9. $^1$H,$^{13}$C HSQC spectrum of 3 in DMSO-d$_6$ at ambient temperature.

Fig. S10. $^1$H,$^{13}$C HMBC spectrum of 3 in DMSO-d$_6$ at ambient temperature.
Fig. S11. ATR infrared spectrum of 3.

Fig. S12. ESI mass spectrum of 3.
4. Analytical data for H₄L

Fig. S13. ¹H NMR spectrum of H₄L in CD₂Cl₂ at ambient temperature.

Fig. S14. APT spectrum of H₄L in CD₂Cl₂ at ambient temperature.
Fig. S15. ATR infrared spectrum of $\text{H}_4\text{L}$.

Fig. S16. ESI mass spectrum of $\text{H}_4\text{L}$.
Fig. S17. UV/vis spectrum of $\text{H}_4\text{L}$ in MeCN, $[\text{H}_4\text{L}] = 5 \cdot 10^{-5}$ M.

5. Analytical data for (NHEt$_3$)[Sm$_2$(L)(HL)] (4)

Fig. S18. ATR infrared spectrum of 4.
Fig. S19. ESI mass spectrum of 4.

Fig. S20. ESI mass spectrum of 4.

6. Analytical data for (NHEt$_3$)[Eu$_2$(L)(HL)] (5)
Fig. S21. ATR infrared spectrum of 5.

Fig. S22. ESI mass spectrum of 5.
Fig. S23. ESI mass spectrum of 5.

7. Analytical data for \((\text{HNEt}_3)[\text{Gd}_2(\text{L})(\text{HL})])\) (6)

Fig. S24. ATR infrared spectrum of 6.
Fig. S25. ESI mass spectrum of 6.

Fig. S26. ESI mass spectrum of 6.

8. Analytical data for (HNEt$_3$)$_2$[Tb$_2$(L)(HL)] (7)
Fig. S27. FT infrared spectrum of 7.

Fig. S28. ESI mass spectrum of 7.

9. Spectrophotometric titrations / Determination of Stability Constants
Batch data for (NHEt$_3$)[Sm$_2$(L)(HL)] (4)

**HypeSpec refinement output**

**Project title:** Titration of H$_4$L by Sm(NO$_3$)$_3$·6H$_2$O  
Converged in 1 iteration with sigma = 7.4369E-03

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Fig. S29. Titration isotherm extracted at 345 nm (left panel), spectrum corresponding to the 6th data point (right panel), and plot of residuals (bottom panels). Observed absorbance values are plotted as blue diamonds and the calculated ones as red crosses. The solid lines in the right panel show the calculated contribution of H$_4$L (red), Sm(NO$_3$)$_3$ (green) and the 1:1 complex (blue) to the total absorbance.

Batch data for (NHEt$_3$)[Eu$_2$(L)(HL)] (5)
Fig. S30. Spectrophotometric titration of $\text{H}_4\text{L}$ with Eu(NO$_3$)$_3$·6H$_2$O in CH$_3$CN (10$^{-5}$ M concentration) at constant ionic strength (10$^{-2}$ M N$^+$Bu$_4$PF$_6$, $T$ = 298 K) in the presence of 5·10$^{-4}$ M NEt$_3$. The green curve refers to a final molar ratio of M/$\text{H}_4\text{L}$ = 5.0. The inset shows the evolution of selected absorbance values versus the [Eu$^{III}$]/[$\text{H}_4\text{L}$] molar ratio.

**HypeSpec refinement output**

Project title: Titration of H$_4$L by Eu(NO$_3$)$_3$·6H$_2$O
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Fig. S31. Titration isotherm extracted at 345 nm (left panel), spectrum corresponding to the 10th data point (right panel), and plot of residuals (bottom panels). Observed absorbance values are plotted as blue diamonds and the calculated ones as red crosses. The solid lines in the right panel show the calculated contribution of \( \text{H}_4\text{L} \) (red), \( \text{Eu(NO}_3)_3 \) (green) and the 1:1 complex (blue) to the total absorbance.

Batch data for \((\text{NHEt}_3)[\text{Gd}_2(\text{L})(\text{HL})])\) (6)

Fig. S32. Spectrophotometric titration of \( \text{H}_4\text{L} \) with \( \text{Gd(NO}_3)_3 \cdot \text{6H}_2\text{O} \) in \( \text{CH}_3\text{CN} \) (10\(^{-5}\) M concentration) at constant ionic strength (10\(^{-2}\) M \( \text{N}^+\text{Bu}_4\text{PF}_6 \), \( T = 298 \text{ K} \)) in the presence of
5·10^{-4} \text{ M NEt}_3. \text{ The green curve refers to a final molar ratio of } M/H_4L = 5.0. \text{ The inset shows the evolution of selected absorbance values versus the } [\text{Gd}^{III}]/[H_4L] \text{ molar ratio.}

**HypeSpec refinement output**

Project title: Titration of $H_4L$ by Gd(NO$_3$)$_3$·6H$_2$O
Converged in 1 iteration with sigma = 9.3291E-03

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Fig. S33. Titration isotherm extracted at 345 nm (left panel), spectrum corresponding to the 10th data point (right panel), and plot of residuals (bottom panels). Observed absorbance values are plotted as blue diamonds and the calculated ones as red crosses. The solid lines in the right panel show the calculated contribution of $H_4L$ (red), Gd(NO$_3$)$_3$ (green) and the 1:1 complex (blue) to the total absorbance.
Batch data for (NHEt$_3$)$_3$[Tb$_2$(L)(HL)] (7)

Fig. S34. Spectrophotometric titration of H$_4$L with Tb(NO$_3$)$_3$·6H$_2$O in CH$_3$CN (10$^{-5}$ M concentration) at constant ionic strength (10$^{-2}$ M N$^o$Bu$_4$PF$_6$, $T = 298$ K) in the presence of 5·10$^{-4}$ M NEt$_3$. The green curve refers to a final molar ratio of M/H$_4$L = 5.0. The inset shows the evolution of selected absorbance values versus the [Tb$^{III}$]/[H$_4$L] molar ratio.

**HypeSpec refinement output**

Project title: Titration of H$_4$L by Tb(NO$_3$)$_3$·6H$_2$O
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Fig. S35. Titration isotherm extracted at 345 nm (left panel), spectrum corresponding to the 6th data point (right panel), and plot of residuals (bottom panels). Observed absorbance values are plotted as blue diamonds and the calculated ones as red crosses. The solid lines in the right panel show the calculated contribution of H₄L (red), Tb(NO₃)₃ (green) and the 1:1 complex (blue) to the total absorbance.

Eq. S1. Expression used for analysis of the temperature dependence of $\chi_M T$ for the dinuclear Sm compound 4.¹

$$\chi_M T = \frac{N_e \mu_B^2}{3k_B \chi} (2.143 + 7.347 + (42.92x + 1.64) e^{-7x/2} + (283.7x - 0.6571)e^{-8x} + (620.6x - 1.94)e^{-27x/2} + (1122x - 2.835)e^{-20x} + (1813x - 3.556)e^{-55x/2}) / (3 + 4e^{-7x/2} + 5e^{-8x} + 6e^{-27x/2} + 7e^{-20x} + 8e^{-55x/2})$$ (S1)

$$x = 1/k_B T$$

Eq. S2: Expression used for analysis of the temperature dependence of $\chi_M T$ for the dinuclear Eu compound 5.

$$\chi_M T = \frac{N_e \mu_B^2}{3k_B \chi} (24 + (27x/2 - 3/2)e^{-x} + (135x/2 - 5/2)e^{-3x} + (189x - 7/2)e^{-6x} + (405x - 9/2)e^{-10x} + (1485x/2 - 11/2)e^{-15x} + (2457x/2 - 13/2)e^{-21x}) / (1 + 3e^{-x} + 5e^{-3x} + 7e^{-6x} + 9e^{-10x} + 11e^{-15x} + 13e^{-21x})$$ (S2)
Fig. S36. Temperature dependence of the inverse molar susceptibility (Curie-Weiss plot) of 6. The solid line corresponds to the best fit of the experimental data.

Fig. S37. Temperature dependence of the inverse molar susceptibility (Curie-Weiss plot) of 7. The solid line corresponds to the best fit of the experimental data.
Fig. S38. Emission profile for 4%wt (HNET$_3$)$_2$$\text{Gd}_2(\text{HL})(\text{L})$] in polycarbonate matrix at 77 K. Pink: 100 $\mu$s delay, dark cyan: 650 $\mu$s delay. The excitation wavelength is 285 nm.