

**Luminescent Lanthanide Helicates Self-Assembled from Ditopic Ligands
Bearing Phosphonic Acid or Phosphoester Units**

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SUPPLEMENTARY MATERIAL

10 pages

Table S1. Ligand-centered photophysical data for the ligands and for 2:3 Ln:L (Ln = La, Eu, Gd, Tb, Lu) solutions in Tris-HCl 0.1 M (pH 7.4).

Species	$E(^1\pi\pi^*) / \text{cm}^{-1}{}^a$	$E(^3\pi\pi^*) / \text{cm}^{-1}{}^b$
$\text{H}_2\text{L}^{\text{C}^3d}$	26600	20900, 22100
$[\text{La}_2(\text{L}^{\text{C}^3})_3]^d$	24300	20900, 22300
$[\text{Eu}_2(\text{L}^{\text{C}^3})_3]^d$	26750	20900, 22150
$[\text{Gd}_2(\text{L}^{\text{C}^3})_3]^d$	26450	19850, 22100
$[\text{Tb}_2(\text{L}^{\text{C}^3})_3]^d$	26650	21000, 22100
$[\text{Lu}_2(\text{L}^{\text{C}^3})_3]^d$	24050	20850, 22100
$\text{H}_4\text{L}^{\text{P}^3}$	26630	20865, 22015
$[\text{La}_2(\text{L}^{\text{P}^3})_3]$	24270	20865, 22075
$[\text{Eu}_2(\text{L}^{\text{P}^3})_3]$	26350	21020, 22210
$[\text{Gd}_2(\text{L}^{\text{P}^3})_3]$	26040	19745, 20410
$[\text{Tb}_2(\text{L}^{\text{P}^3})_3]$	26040	19715, 22285
$[\text{Lu}_2(\text{L}^{\text{P}^3})_3]$	23920	20790, 22270
$\text{H}_2\text{L}^{\text{P}^3\text{OEt}}$	29500	20000, 21000
$[\text{La}_2(\text{L}^{\text{P}^3\text{OEt}})_3]$	28500	19900, 21200
$[\text{Eu}_2(\text{L}^{\text{P}^3\text{OEt}})_3]$	28000	19950, 21250
$[\text{Gd}_2(\text{L}^{\text{P}^3\text{OEt}})_3]$	28500	20000, 21250
$[\text{Tb}_2(\text{L}^{\text{P}^3\text{OEt}})_3]$	28500	19950, 21050
$\text{H}_4\text{L}^{\text{P}}$	25445	n.d.
$[\text{La}_2(\text{L}^{\text{P}})_3]$	24690	20240, 22990
$[\text{Eu}_2(\text{L}^{\text{P}})_3]$	n.d.	21320
$[\text{Tb}_2(\text{L}^{\text{P}})_3]$	n.d.	n.d.
$[\text{Lu}_2(\text{L}^{\text{P}})_3]$	25000	21190, 22570
$\text{H}_2\text{L}^{\text{P}^{\text{OEt}}}$	25500	19250
$[\text{La}_2(\text{L}^{\text{P}^{\text{OEt}}})_3]$	24150	19900, 21400
$[\text{Eu}_2(\text{L}^{\text{P}^{\text{OEt}}})_3]$	25800 (weak)	ND
$[\text{Gd}_2(\text{L}^{\text{P}^{\text{OEt}}})_3]$	24250	19950, 21400
$[\text{Tb}_2(\text{L}^{\text{P}^{\text{OEt}}})_3]$	24600 (weak)	n.d.
$[\text{Lu}_2(\text{L}^{\text{P}^{\text{OEt}}})_3]$	23150	19100, 20400

^a Maximum of the fluorescence band at 295 K, $\lambda_{\text{ex}} = 388$ nm. ^b Maximum of the phosphorescence band at 77 K (time-delay 0.05 ms, $\lambda_{\text{ex}} = 388$ nm) and 0-phonon transition (italicized). ^c $\Delta E = E(^3\pi\pi^*, 0\text{-phonon}) - E(^5\text{D}_1)$ with $E(^5\text{D}_0) = 17\,250 \text{ cm}^{-1}$ and $E(^5\text{D}_4) = 20\,450 \text{ cm}^{-1}$. ^d taken from ref ²³.

Table S2. Lifetimes of the triplet states of the ligands and of their complexes with Ln = La, Gd, and Lu at 77 K, [L] = 10^{-4} M in Tris-HCl 0.1 M +10% glycerol.

	Ln	τ_1 / ms	%	τ_2 / ms	%
H_4L^{C3}	-	132 (15)	100	-	-
$[Ln_2(L^{C3})_3]$	La	104(2)	100	-	-
	Gd	96 (6)	100	-	-
	Lu	103 (18)	100	-	-
H_4L^{P3}	-	487 (15)	~65	123 (3)	~35
$[Ln_2(L^{P3})_3]$	La	539 (43)	~60	141 (13)	~40
	Gd	563 (23)	~95	49 (23)	~5
	Lu	452 (75)	~65	105 (9)	~35
H_2L^{P3OEt}	-	370 (100)	44	75 (20)	56
$[Ln_2(L^{P3OEt})_3]$	La	430 (40)	43	74 (17)	57
	Gd	160 (40)	71	60 (31)	29
	Lu	160 (30)	69	70 (27)	31
H_4L^P	-	565 (20)	44	96 (2)	56
$[Ln_2(L^P)_3]$	Lu	111 (8)	100	-	-
$[Ln_2(L^{POEt})_3]$	La	208 (4)	66	72 (4)	34
	Gd	32 (8)	90	5.63 (6)	10

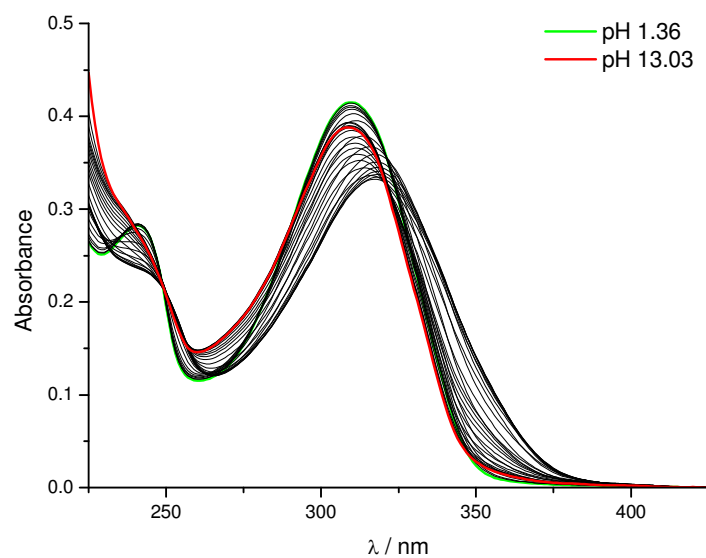


Figure S1. UV-Visible spectra of $\text{H}_4\text{L}^{\text{P}3}$ in the pH range 1.36 -13.03, $[\text{H}_4\text{L}^{\text{P}3}] = 8.98 \times 10^{-6}$ M, in KCl 0.1 M, 298 K.

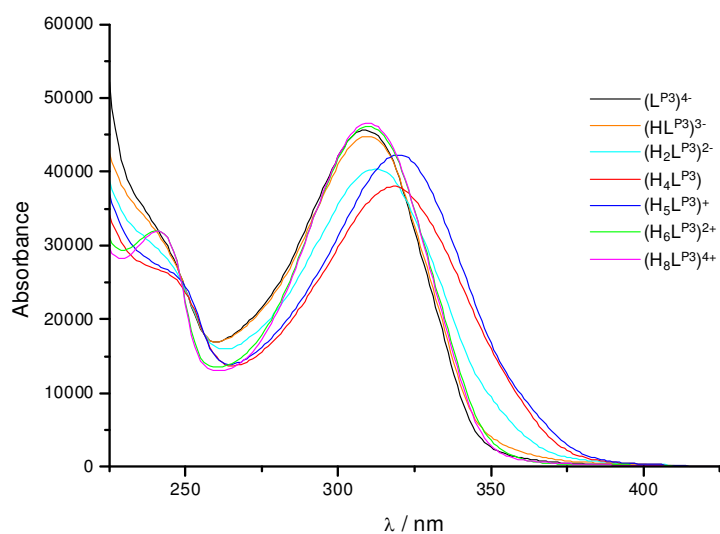


Figure S2. Re-calculated spectra of the different species, $[\text{H}_4\text{L}^{\text{P}3}]_{\text{t}} = 8.98 \times 10^{-6}$ M in KCl 0.1 M, 298 K.

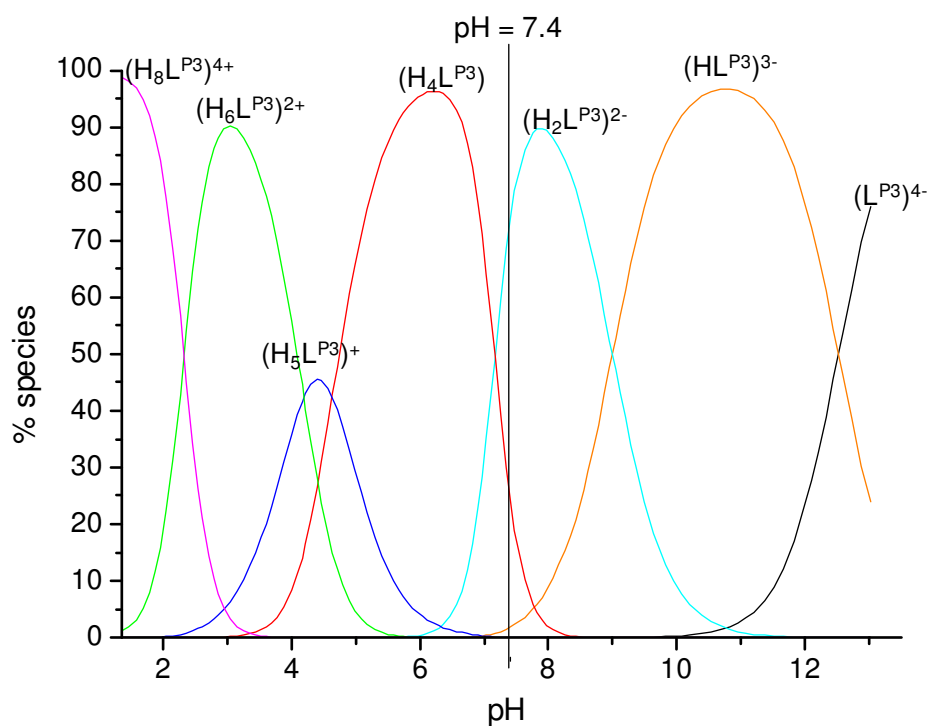


Figure S3. Distribution diagram of H_4L^{P3} as a function of pH, $[H_4L^{P3}]_t = 8.98 \times 10^{-6}$ M, 298 K, $I = 0.1$ M (KCl).

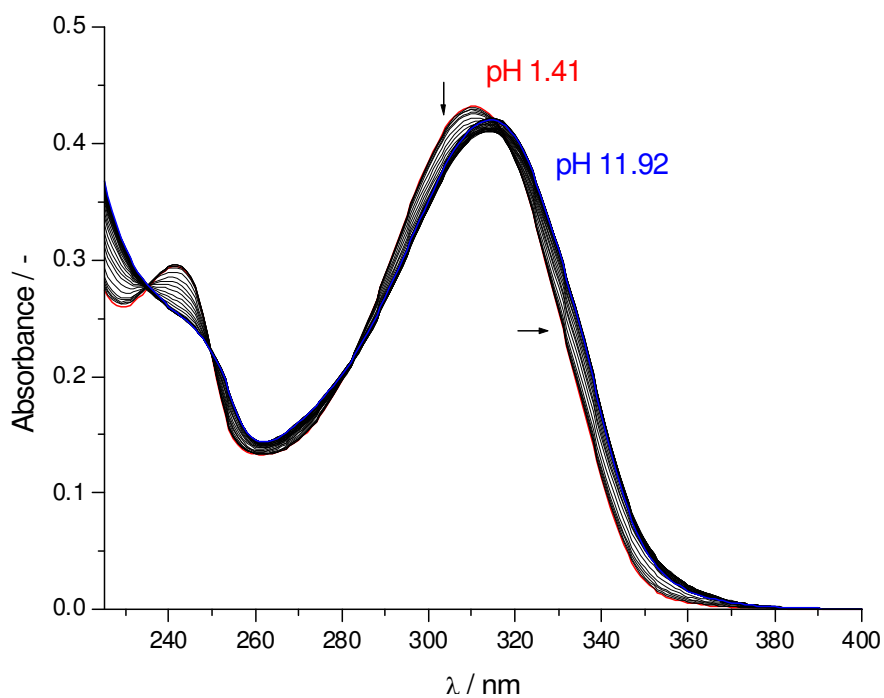


Figure S4. UV-Visible spectra of H_2L^{P3OEt} in the pH range 1.41 - 11.92, $[H_2L^{P3OEt}] = 1.31 \times 10^{-5}$ M, in KCl 0.1 M, 298 K.

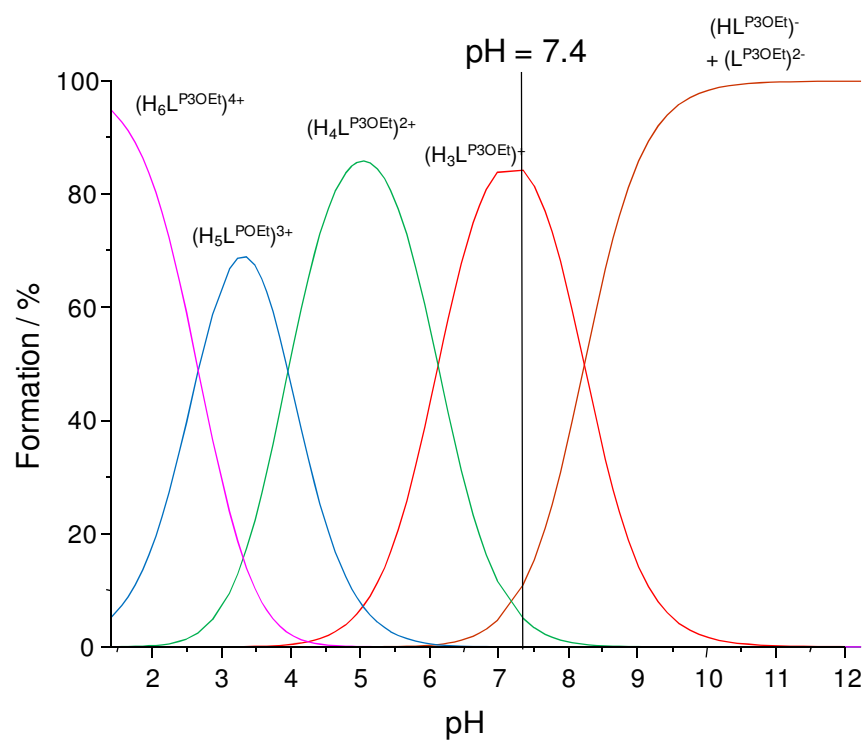


Figure S5. Distribution diagram of $\text{H}_2\text{L}^{\text{P3OEt}}$ as a function of pH, $[\text{H}_2\text{L}^{\text{P3OEt}}]_{\text{t}} = 1.31 \times 10^{-5} \text{ M}$, 298 K, $I = 0.1 \text{ M}$ (KCl).

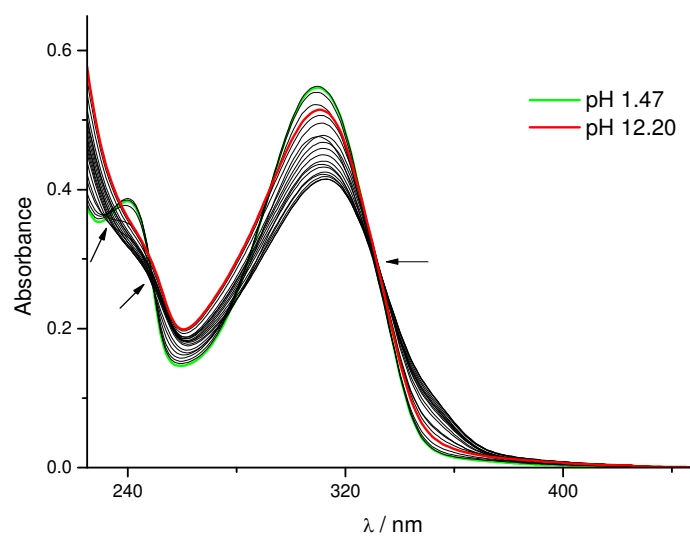


Figure S6. UV-Visible spectra of $\text{H}_2\text{L}^{\text{POEt}}$ in the pH range 1.47 -12.20, $[\text{H}_2\text{L}^{\text{POEt}}] = 1.56 \times 10^{-5} \text{ M}$, in KCl 0.1 M, 298 K.

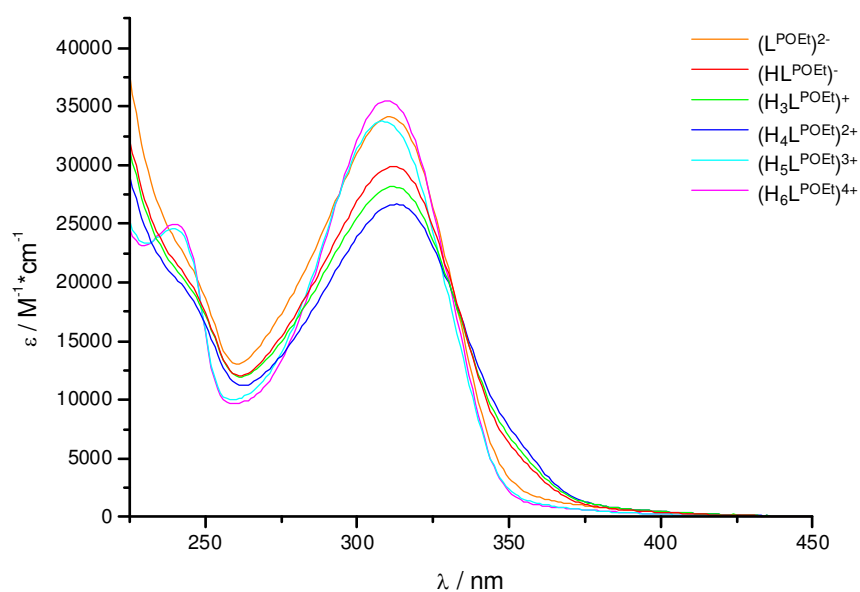


Figure S7. Re -calculated spectra of the different species, $[\text{H}_2\text{L}^{\text{POEt}}]_{\text{t}} = 1.56 \times 10^{-5} \text{ M}$, 298 K.

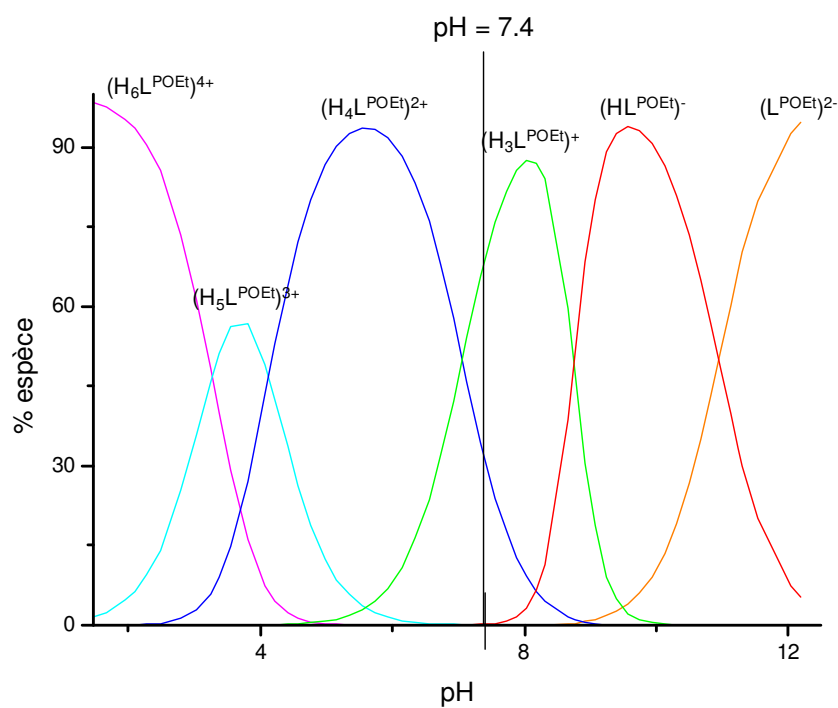


Figure S8. Distribution diagram of $\text{H}_2\text{L}^{\text{POEt}}$ as a function of pH, $[\text{H}_2\text{L}^{\text{POEt}}]_{\text{t}} = 1.56 \times 10^{-5} \text{ M}$, 298 K, $I = 0.1 \text{ M}$ (KCl).

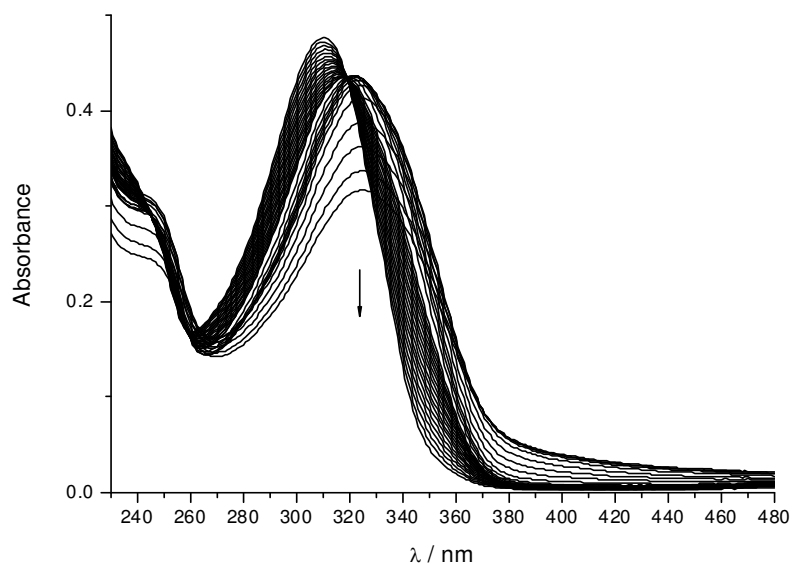


Figure S9. UV-Vis titration of $\text{H}_4\text{L}^{\text{P3}}$ $9 \times 10^{-6} \text{ M}$ with $\text{Eu}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ at $\text{pH} = 7.4$ (Tris-HCl 0.1 M), 298 K ; $R = [\text{Eu}]_t / [\text{H}_4\text{L}^{\text{P3}}]_t$.

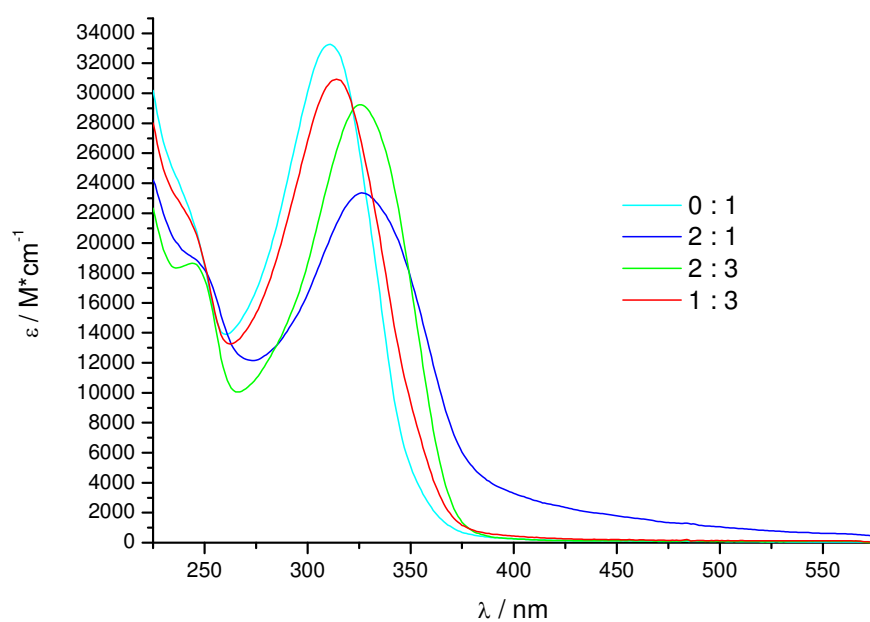


Figure S10. Re-calculated spectra for the UV-Vis titration of $\text{H}_4\text{L}^{\text{P3}}$ with Eu^{III} , $[\text{H}_4\text{L}^{\text{P3}}] = 9 \times 10^{-6} \text{ M}$, in Tris-HCl 0.1 M at 298 K .

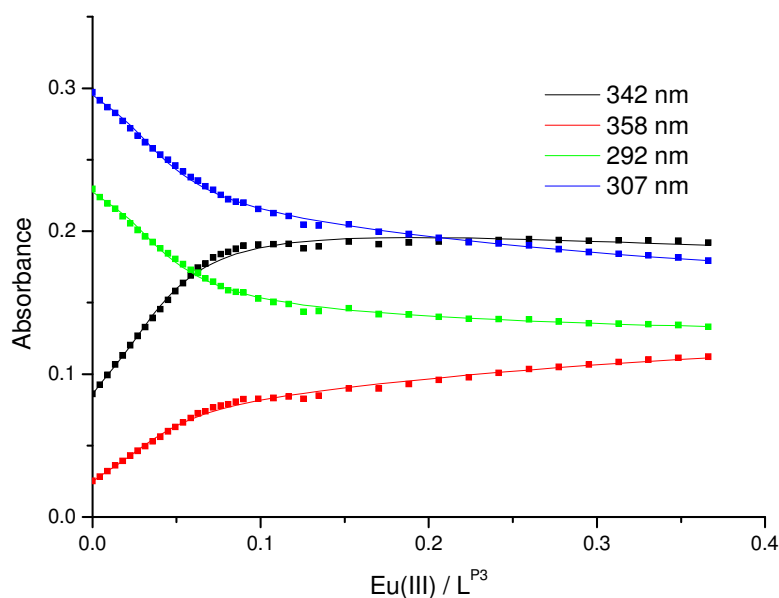


Figure S11. Absorbance at four wavelengths during the UV-Vis titration of H_4L^{P3} with Eu^{III} , $[H_4L^{P3}] = 9 \times 10^{-6} M$, in Tris HCl 0.1 M.

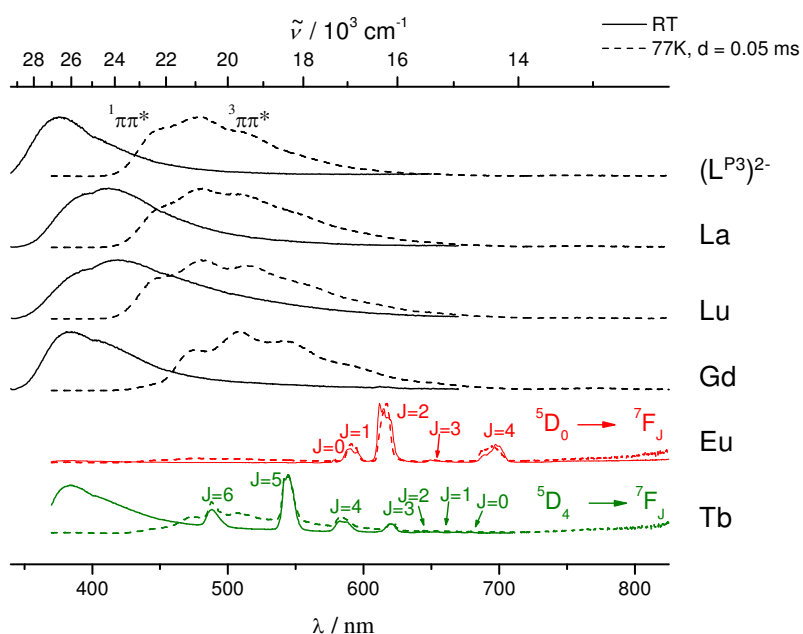


Figure S12. Luminescence spectra of H_4L^{P3} and its 2:3 complexes at room temperature (solid lines, $[H_4L^{P3}] = 10^{-4} M$, Tris-HCl 0.1 M, pH = 7.4, at 295 K, no delay) and at 77 K (dotted lines, 0.05 ms delay, Tris-HCl 0.1 M containing 10% glycerol); $\lambda_{ex} = 338 nm$.

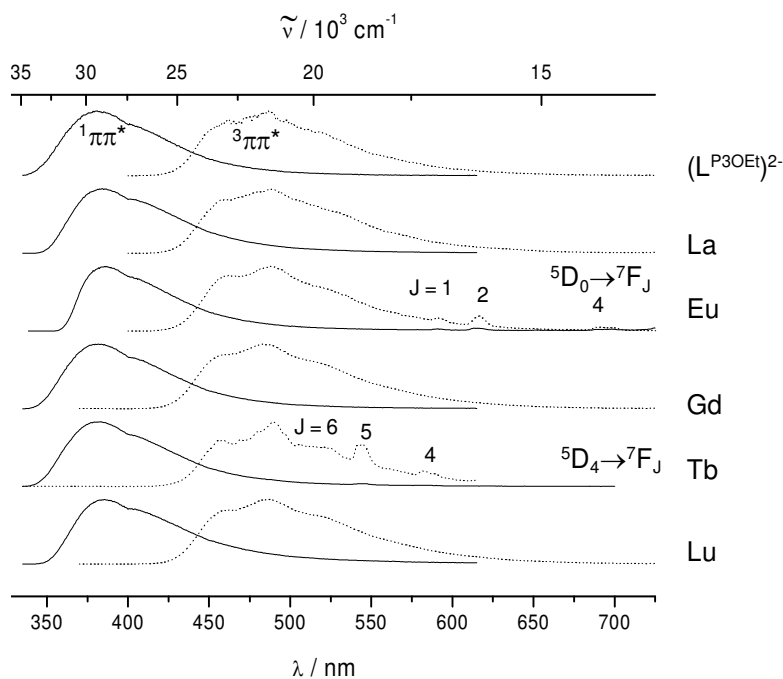


Figure S13. Luminescence spectra of $\text{H}_2\text{L}^{\text{P3OEt}}$ and its 2:3 complexes at room temperature (solid lines, $[\text{H}_2\text{L}^{\text{P3OEt}}] = 10^{-4}$ M, Tris-HCl 0.1M, pH = 7.4, at 295 K, no delay) and at 77 K (dotted lines, 0.05 ms delay, Tris-HCl 0.1M containing 10% glycerol); $\lambda_{\text{ex}} = 315$ nm.

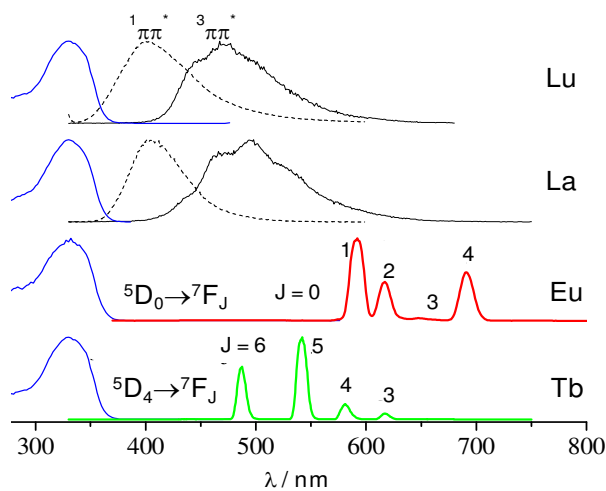


Figure S14. Luminescence spectra of $\text{H}_4\text{L}^{\text{P}}$ and its 2:3 complexes at room temperature (dotted lines, $[\text{H}_4\text{L}^{\text{P}}] = 10^{-4}$ M, Tris-HCl 0.1M, pH = 7.4, at 295 K, no delay) and at 77 K (solid lines, 0.05 ms delay, Tris-HCl 0.1 M containing 10% glycerol); $\lambda_{\text{ex}} = 315$ nm.