Supplementary Information

for

Lanthanide-mediated triangular cationic assemblies: structural and physico-chemical properties

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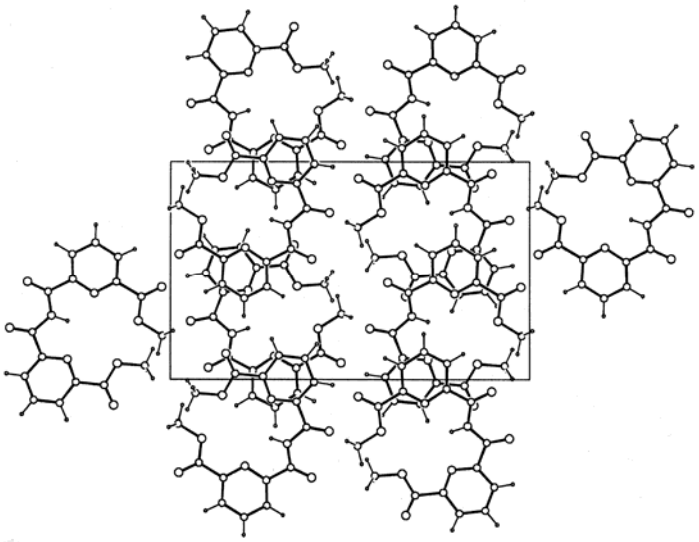
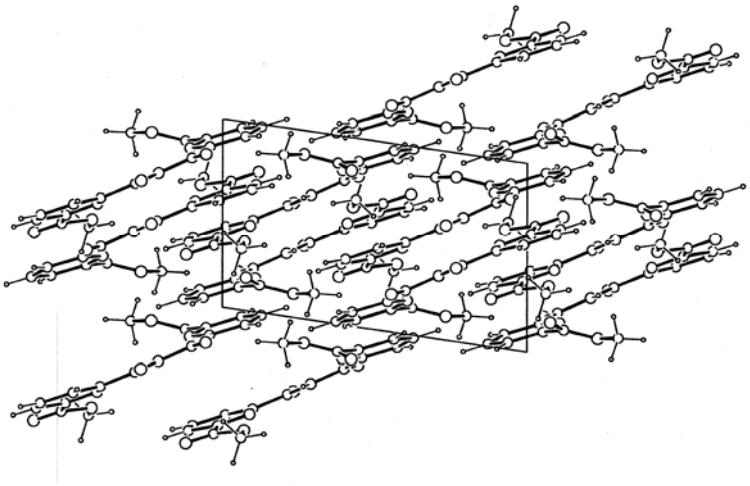
Table S1. Distances between lanthanide cations and coordinating atoms in the crystal structure of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$ and Tb_3(**L1**-H)$_3(CF_3SO_3)_6$.

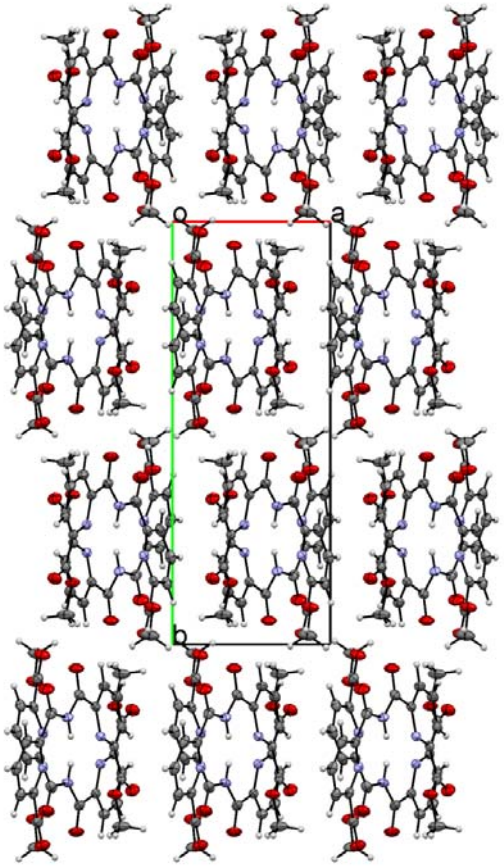
	Atomes	Distance 1	Distance 2	Distance 3
Eu_3(**L1**-H)$_3$	Eu—O (ester)	2.515 (4)	2.505 (4)	2.513 (4)
	Eu—O (ester)	2.498 (4)	2.478 (5)	2.461 (4)
	Eu—O (amide)	2.401 (4)	2.378 (4)	2.378 (3)
	Eu—O (amide)	2.416 (4)	2.401 (5)	2.403 (4)
	Eu—O ($CF_3SO_3^-$)	2.392 (4)	2.402 (4)	2.413 (4)
	Eu—O ($CF_3SO_3^-$)	2.420 (4)	2.498 (4)	2.417 (4)
	Eu—N (pyr.)	2.539 (4)	2.551 (5)	2.553 (4)
	Eu—N (pyr.)	2.551 (5)	2.543 (5)	2.577 (5)
	Eu—N (amide)	2.522 (5)	2.531 (4)	2.551 (5)
Tb_3(**L1**-H)$_3$	Tb—O (ester)	2.474 (9)	2.447 (8)	2.415 (9)
	Tb—O (ester)	2.495 (8)	2.465 (9)	2.487 (9)
	Tb—O (amide)	2.382 (8)	2.321 (7)	2.360 (6)
	Tb—O (amide)	2.375 (7)	2.387 (10)	2.368 (7)
	Tb1—O ($CF_3SO_3^-$)	2.362(8)	2.378 (8)	2.365(7)
	Tb1—O ($CF_3SO_3^-$)	2.414 (8)	2.491 (6)	2.413 (8)
	Tb1—N (pyr.)	2.492 (10)	2.537 (11)	2.521 (10)
	Tb1—N (pyr.)	2.485 (11)	2.467 (12)	2.505 (11)
	Tb1—N (amide)	2.487 (9)	2.500 (10)	2.511 (10)



a)



b)



c)

Figure S1. Stack interactions and the crystal packing in the crystal structure of **L1**. (a) view along *a* axis, (b) view along *b* axis, (c) view along *c* axis.

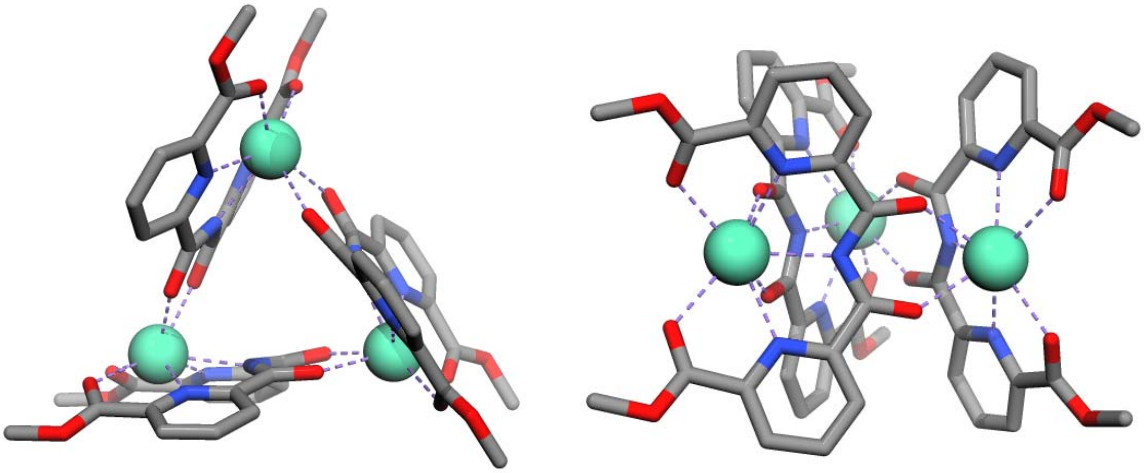


Figure S2. View of the crystal structure of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$. Coordinated triflate anions, hydrogen atoms and solvent molecules are omitted for the sake of clarity.

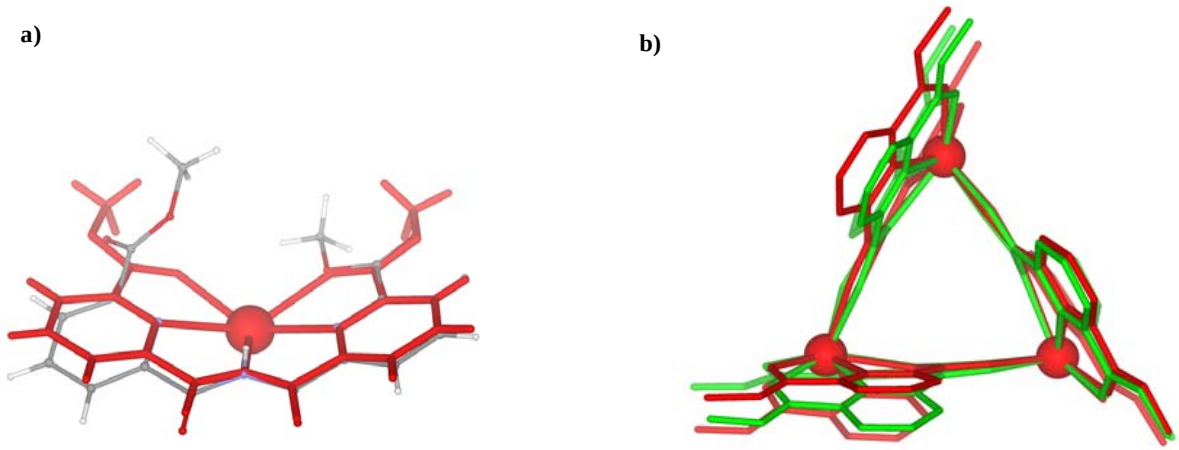


Figure S3. Superposition of crystal structures. a) Free **L1** and **L1** in the complex Eu_3(**L1**-H)$_3(CF_3SO_3)_6$. b) Eu_3(**L1**-H)$_3(CF_3SO_3)_6$ (in red) and Tb_3(**L1**-H)$_3(CF_3SO_3)_6$ (in green).

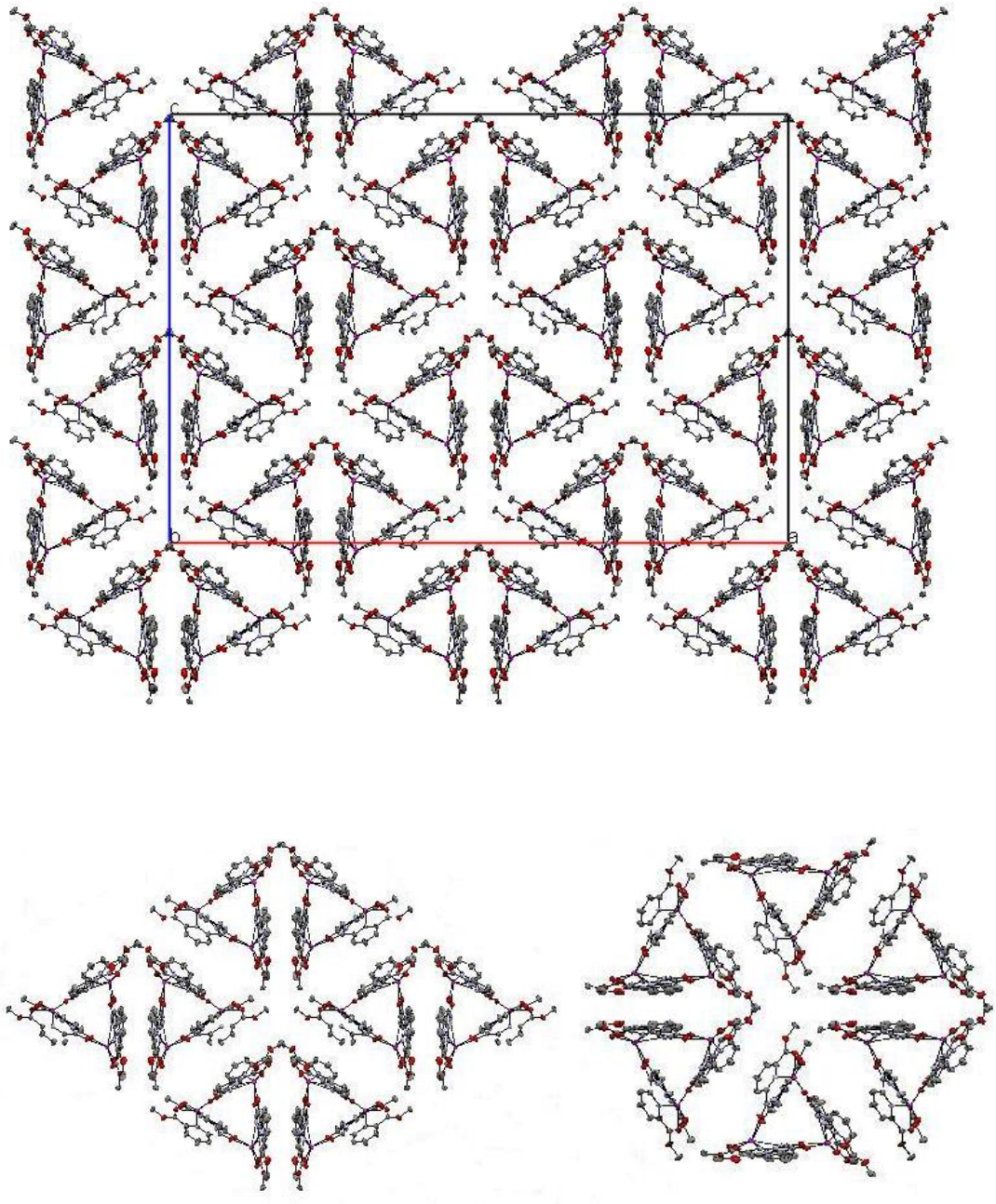


Figure S4a. Crystal packing mode of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$. View along the *b* axis.

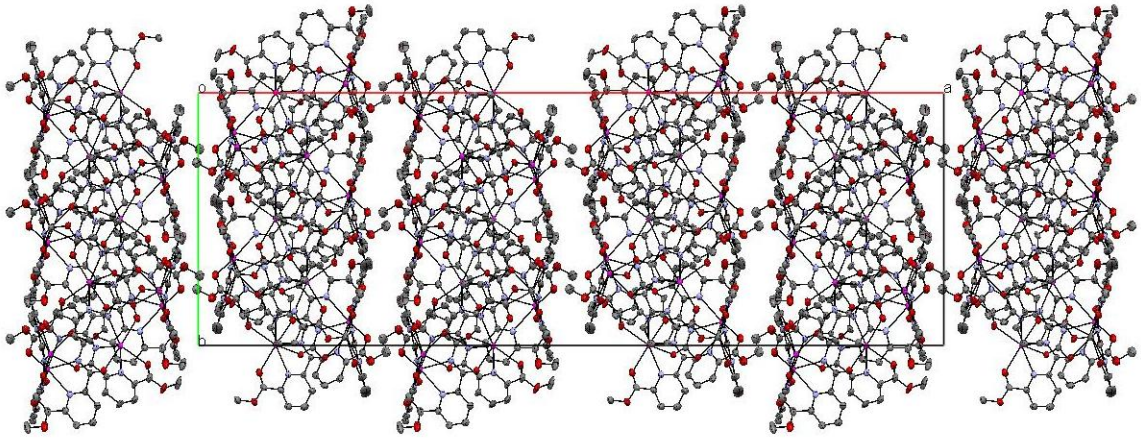


Figure S4b. Crystal packing mode of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$. View along the *c* axis.

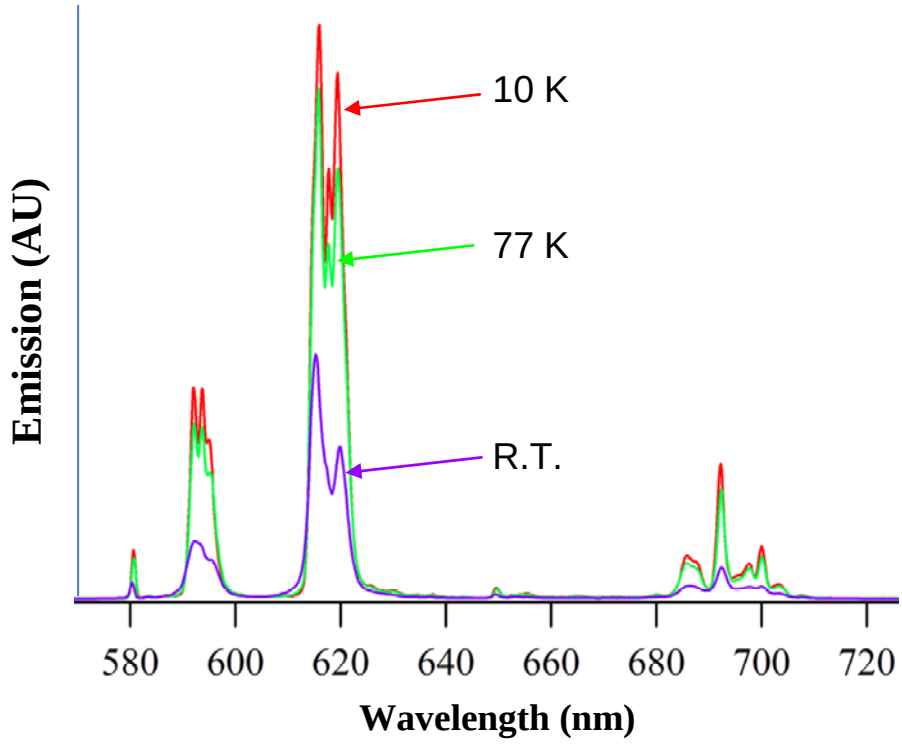


Figure S5. Comparison of emission spectra of Eu_3(**L1**-H)$_3$$(CF_3SO_3)_6$ at different temperatures (λ_{ex} = 280 nm).

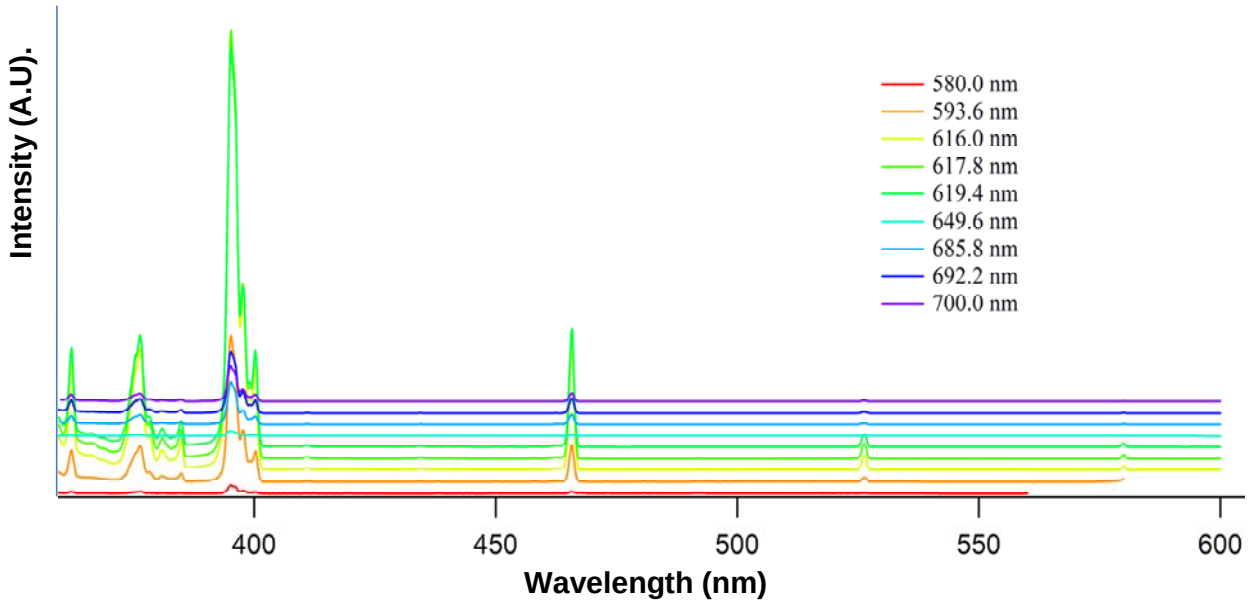


Figure S6. Excitation spectra of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$ at 10 K for different emission wavelengths.

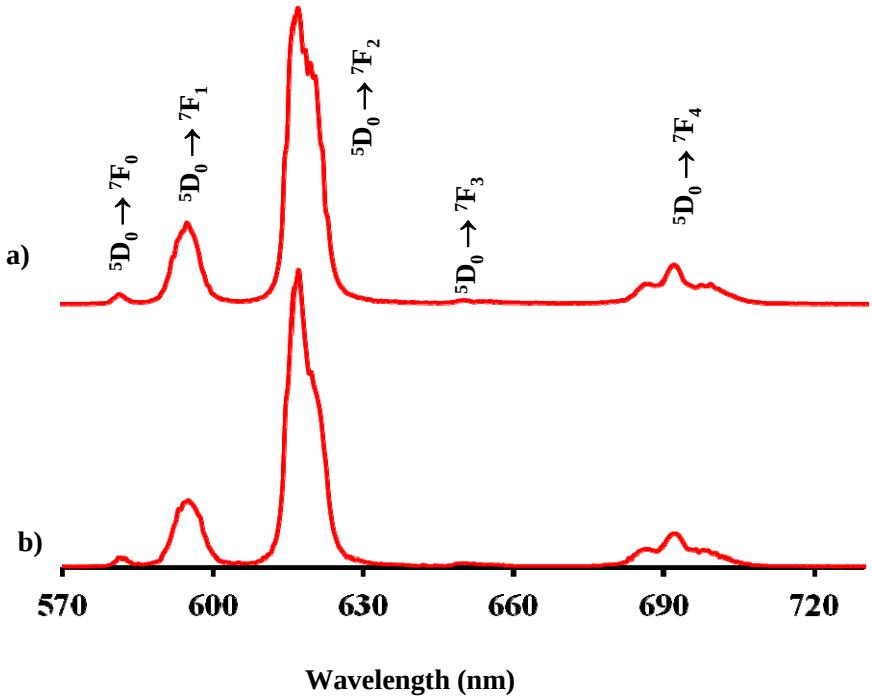


Figure S7. a) Emission spectrum of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$ prepared *in-situ* in dry CH_3CN (298 K, λ_{ex} = 280 nm). b) Emission spectrum of Eu_3(**L1**-H)$_3(CF_3SO_3)_6$ isolated in the solid state and dissolved in dry CH_3CN (298 K, λ_{ex} = 280 nm).

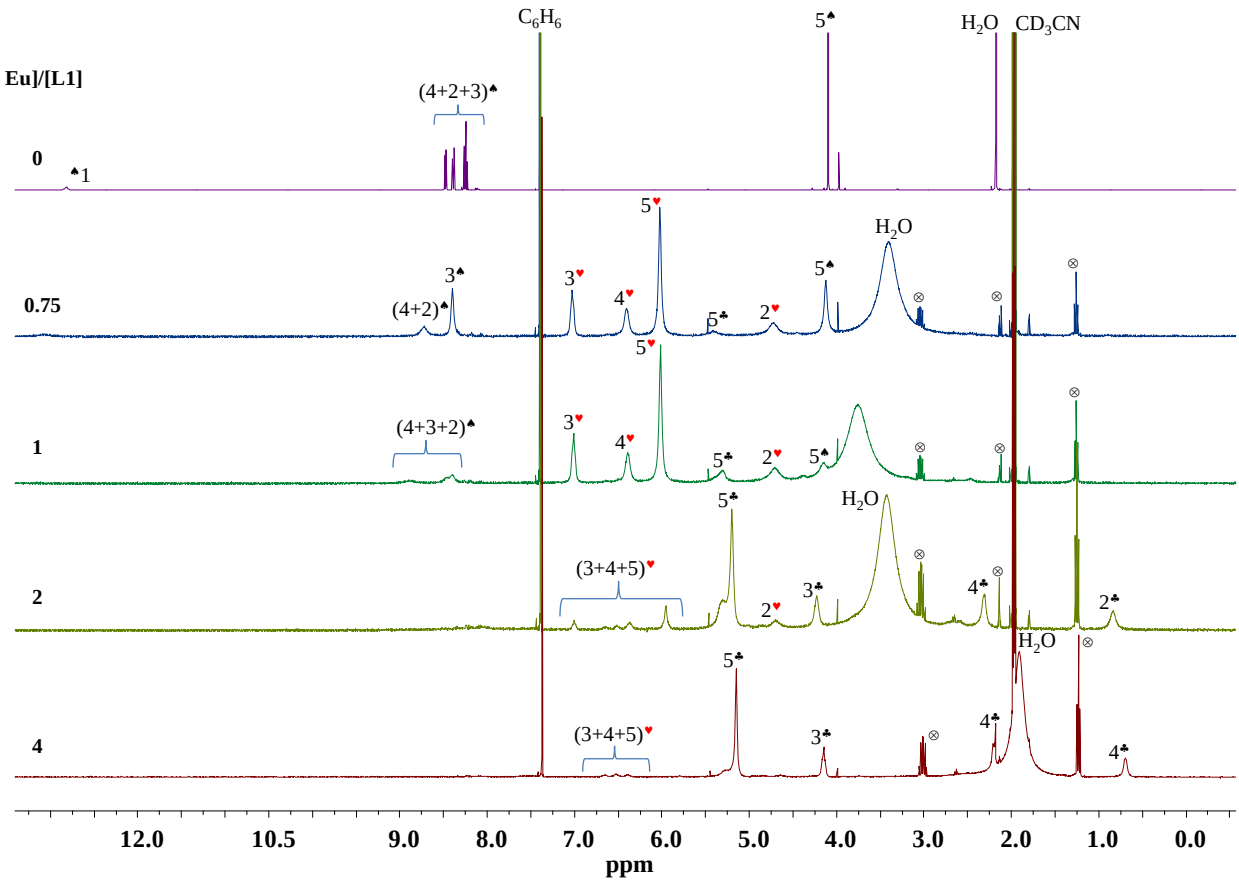


Figure S8. Variation of 1H NMR spectra with the addition of Eu(III) to **L1**. The symbols indicate the signals of the following species: ♠ = **L1**, ♥ = $[Eu_3(\mathbf{L1}\text{-}H)_3]^{6+}$, ♣ = $[Eu_2(\mathbf{L1}\text{-}H)]^{5+}$, ⊗ = impurities coming with the metal salt.

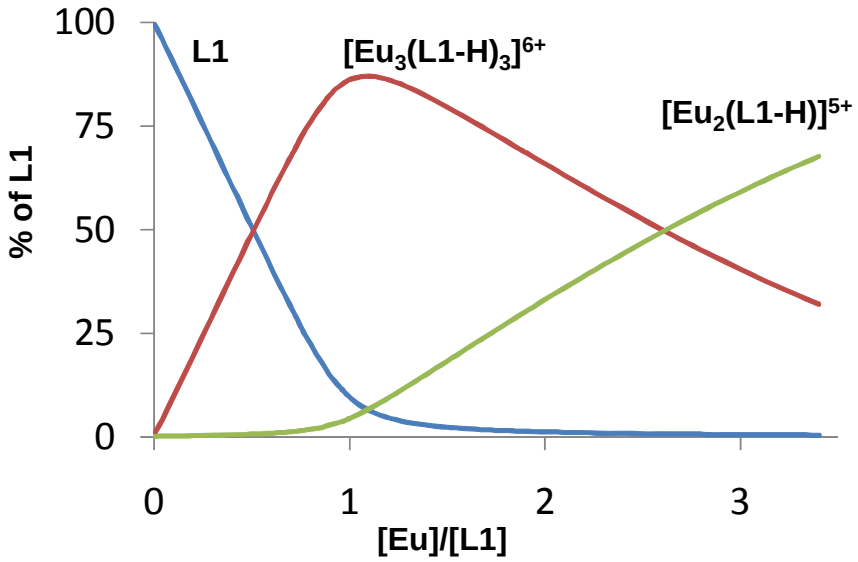


Figure S9. Distribution curves calculated from the fit of the spectrophotometric titration with the Specfit program ($[\mathbf{L1}]_{tot} = 10^{-3}$ M).