

Electronic Supplementary Information for Dalton Transactions

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Encapsulation of labile trivalent lanthanides into a homobimetallic chromium(III)-containing triple-stranded helicate. Synthesis, characterization and divergent intramolecular energy transfers

Martine Cantuel, Frédéric Gummy, Jean-Claude G. Bünzli,^{*} and Claude Piguet^{*}

Supporting Information

(12 pages)

Table S1 Elemental analyses (%C, %H, %N), synthetic yields (η) and molecular weights (MW) for $[\text{ZnLnZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_n$ (Ln = La, Eu, Gd, Tb, Lu) and $[\text{CrLnCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_n(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_p$.

Complexes	%C	%H	%N	η / %	MW / $\text{g}\cdot\text{mol}^{-1}$
$[\text{ZnLaZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_5$	50.09 (50.13)	3.91 (3.66)	12.01 (12.06)	70	3833.16
$[\text{ZnEuZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_7$	49.67 (49.50)	3.86 (3.71)	11.87 (11.91)	71	3882.25
$[\text{ZnGdZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_8$	49.21 (49.20)	3.87 (3.74)	11.78 (11.84)	74	3905.55
$[\text{ZnTbZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_6$	49.63 (49.64)	3.92 (3.67)	11.88 (11.94)	82	3871.19
$[\text{ZnLuZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_6$	49.48 (49.44)	3.84 (3.66)	11.90 (11.89)	73	3887.24
$[\text{CrLaCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_{12}(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.1}$	46.10 (46.18)	3.88 (3.71)	10.91 (10.90)	78	4254.86
$[\text{CrEuCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_8(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.1}$	46.67 (46.69)	3.66 (3.58)	11.02 (11.01)	88	4210.77
$[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_9(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.3}$	46.55 (46.54)	3.67 (3.69)	10.83 (10.82)	78	4312.38
$[\text{CrTbCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_7(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.3}$	46.86 (46.82)	3.65 (3.63)	10.99 (10.92)	86	4270.81
$[\text{CrLuCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_{10}(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.3}$	46.06 (46.15)	3.73 (3.70)	10.68 (10.73)	80	4348.11

Table S2 Lifetimes of $\text{Eu}({}^5\text{D}_0)$, $\text{Cr}({}^2\text{E})$ and $\text{Tb}({}^5\text{D}_4)$ excited levels (ms) in $[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_9(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.3}$, $[\text{CrGd}(\text{L}1)_3](\text{CF}_3\text{SO}_3)_5(\text{H}_2\text{O})_6$ ¹³ $[\text{ZnEuZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_7$, $[\text{ZnEu}(\text{L}3)_3](\text{ClO}_4)_5(\text{H}_2\text{O})_4$ ³² $[\text{ZnEu}(\text{L}1)_3](\text{CF}_3\text{SO}_3)_4(\text{ClO}_4)(\text{CH}_3\text{CN})_4$ ³³ $[\text{CrEuCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_8$ $(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.1}$, $[\text{CrEu}(\text{L}1)_3](\text{CF}_3\text{SO}_3)_5(\text{H}_2\text{O})_4$ ¹³ $[\text{ZnTbZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_6$ and $[\text{CrTbCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_7(^n\text{Bu}_4\text{NCF}_3\text{SO}_3)_{0.3}$ in the solid-state and in solution under various excitation conditions (analysing wavelengths set at the maximum of the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$, $\text{Tb}({}^5\text{D}_4 \rightarrow {}^7\text{F}_5)$ or $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ transitions).

T / K	Compd	$\bar{\nu}_{\text{exc}} / \text{cm}^{-1}$	$\bar{\nu}_{\text{an}} / \text{cm}^{-1}$	τ (ms)	Reference
10	$[\text{CrGdCr}(\text{L}2)_3]^{9+}$	21468	13245	2.27(1) $\text{Cr}({}^2\text{E})$	This work
295		21468	13316	0.031(1) $\text{Cr}({}^2\text{E})$	This work
10	$[\text{CrGd}(\text{L}1)_3]^{6+}$	21322	13301	3.62(1) $\text{Cr}({}^2\text{E})$	13
295		21322	13348	0.19(1) $\text{Cr}({}^2\text{E})$	13
10	$[\text{ZnEuZn}(\text{L}2)_3]^{7+}$	28169	16152	1.94(2) $\text{Eu}({}^5\text{D}_0)$	This work
		23810	16152	1.96(1) $\text{Eu}({}^5\text{D}_0)$	This work
		21468	16152	2.022(6) $\text{Eu}({}^5\text{D}_0)$	This work
		17218	16152	2.05(8) $\text{Eu}({}^5\text{D}_0)$	This work
^a		28169	16298	2.21(5) $\text{Eu}({}^5\text{D}_0)$	This work
295		23810	16152	0.69(4) $\text{Eu}({}^5\text{D}_0)$	This work
		21468	16152	0.683(2) $\text{Eu}({}^5\text{D}_0)$	This work
^a		28169	16298	1.48(1) $\text{Eu}({}^5\text{D}_0)$	This work
10	$[\text{ZnEu}(\text{L}3)_3]^{5+}$	25000	16152	1.96(7) $\text{Eu}({}^5\text{D}_0)$	32
10	$[\text{ZnEu}(\text{L}1)_3]^{5+}$	17235	16152	2.53(1) $\text{Eu}({}^5\text{D}_0)$	32
295		17241	16152	1.67(2) $\text{Eu}({}^5\text{D}_0)$	33
10	$[\text{CrEuCr}(\text{L}2)_3]^{9+}$	28169	13245	2.08(2) $\text{Cr}({}^2\text{E})$	This work

		28169	16155	0.196(1) Eu(⁵ D ₀)	This work
		24390	13228	2.10(1) Cr(² E)	This work
		24390	16152	0.20(1) Eu(⁵ D ₀)	This work
^a		28169	13228	3.1(1) Cr(² E)	This work
^a		28169	16155	0.24(1) Eu(⁵ D ₀)	This work
295		28169	13316	0.033(1) Cr(² E)	This work
		28169	16155	0.095(2) Eu(⁵ D ₀)	This work
		24390	13245	0.030(1) Cr(² E)	This work
		24390	16152	0.101(5) Eu(⁵ D ₀)	This work
^a		28169	13228	0.012(1) Cr(² E)	This work
^a		28169	16155	0.076(1) Eu(⁵ D ₀)	This work
10	[CrEu(L1) ₃] ⁶⁺	28329	13301	3.46(1) Cr(² E)	13
		28329	16218	0.55(4) Eu(⁵ D ₀)	13
295		28329	13348	0.09(1) Cr(² E)	13
		28329	16218	0.59(1) Eu(⁵ D ₀)	13
10	[ZnTbZn(L2) ₃] ⁷⁺	28169	18375	1.3(1) Tb(⁵ D ₄)	This work
		23810	18375	1.67(6) Tb(⁵ D ₄)	This work
		20492	18375	1.54(4) Tb(⁵ D ₄)	This work
10	[CrTbCr(L2) ₃] ⁹⁺	28169	13228	1.8(2) Cr(² E)	This work
		28169	18375	0.00175(4) Tb(⁵ D ₄)	This work
295		28169	13228	0.106(3) Cr(² E)	This work
		28169	18375	^b	This work

^a 10⁻³ mol·dm⁻³ in acetonitrile. ^b Not detected.

Table S3 Longitudinal ^1H nuclear relaxation times for the aromatic protons H1-H12 in $[\text{ZnTbZn}(\text{L}2)_3]^{7+}$ (T_{li}^{exp}) and in $[\text{ZnLuZn}(\text{L}2)_3]^{7+}$ (T_{li}^{dia}), and computed paramagnetic relaxation times (T_{li}^{para} , eq 11) and Tb...H distances ($r_i^{\text{ZnTbZn,solution}}$, eq 13) in CD_3CN at 293 K.

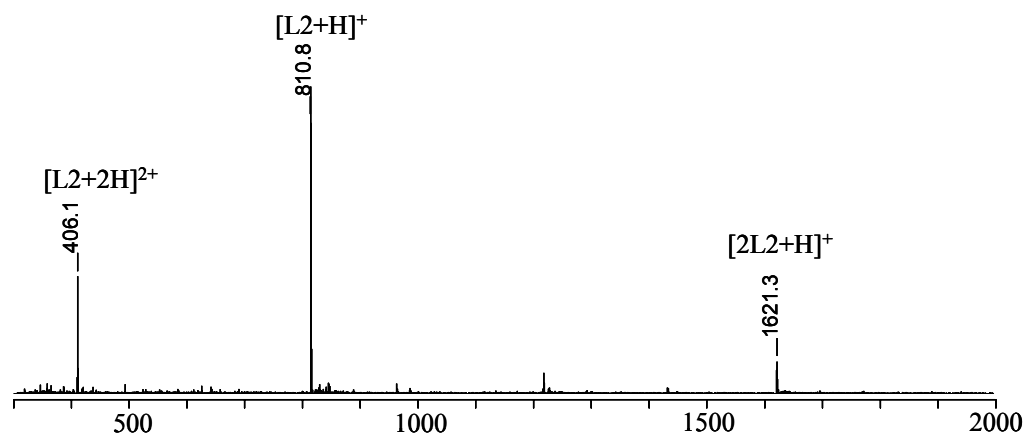
Proton ^a	$\delta_{\text{Hi}}^{\text{exp}}$ /ppm ^b	T_{li}^{exp} /ms	T_{li}^{dia} /ms	T_{li}^{para} /ms	$r_i^{\text{ZnEu,solid}}$ /Å ^c	$r_i^{\text{ZnTbZn,solution}}$ /Å ^d
H1	3.62	2.72E+02	1.62E+03	3.26E+02	11.8	11.8
H2	5.33	3.68E+02	9.62E+02	5.95E+02	12.4	13.0
H3	3.22	1.38E+02	1.01E+03	1.60E+02	10.7	10.4
H4	4.38	1.36E+02	1.04E+03	1.56E+02	8.7	10.4
H5	0.42	2.80E+01	8.20E+02	3.08E+01	7.6	7.9
H6	-12.55	1.13E+01	2.09E+03	1.13E+01	6.7	6.7
H7	7.44	1.82E+01	3.07E+02	1.86E+01	7.5	7.3
H7'	4.09	1.00E+01	3.07E+02	1.04E+01	6.3	6.6
H8	-49.0	3.64E-01	2.05E+03	3.64E-01	3.8	3.8
H9	4.34	1.63E+01	8.78E+02	1.65E+01	7.4	7.2
H10	8.63	1.22E+01	1.05E+03	1.23E+01	7.0	6.8
H11	15.98	3.49E+00	9.62E+02	3.51E+00	5.5	5.5
H12	15.43	7.45E+00	9.62E+02	7.51E+00	6.3	6.3

^a For the numbering scheme, see Figure 4. ^b Chemical shifts with respect to TMS for $[\text{ZnTbZn}(\text{L}2)_3]^{7+}$. ^c Eu...H distances measured in the crystal structure of $[\text{ZnEu}(\text{L}1)_3](\text{CF}_3\text{SO}_3)_4(\text{ClO}_4)(\text{CH}_3\text{CN})_4$.³³ ^d Computed with eq. 13 by using $r_{\text{H}6}^{\text{ZnEu,solid}} = 6.7 \text{ \AA}$ as reference.

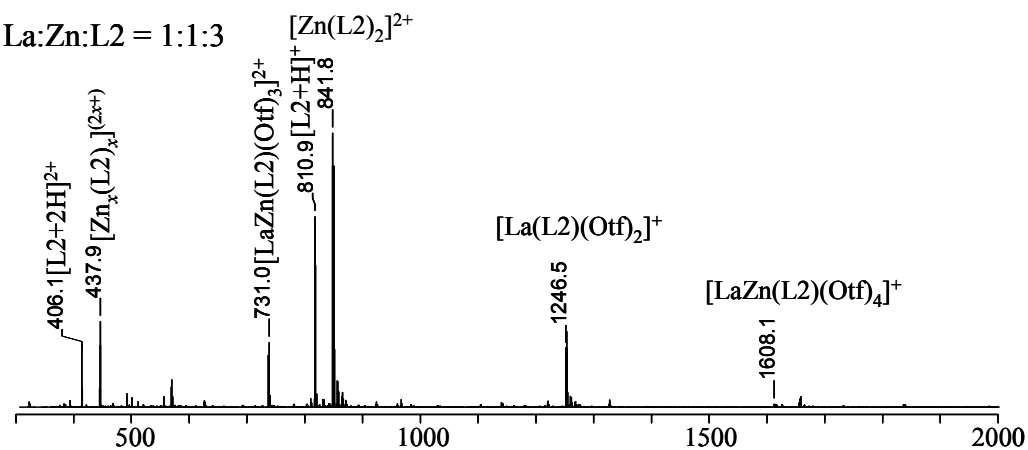
Table S4 Lifetimes of the ligand-centred $^3\pi\pi^*$ excited levels in $[\text{ZnGdZn}(\text{L}2)_3]^{7+}$ and $[\text{CrGdCr}(\text{L}2)_3]^{9+}$.

Complex	T / K	$\lambda_{\text{exc}} / \text{nm}$	$\lambda_{\text{an}} / \text{nm}$	τ_1 / ms	τ_2 / ms
ZnGdZn	10	355	530	2.45 (86 %)	0.49 (14 %)
	295	355	610	0.042 (64 %)	0.006 (36 %)
CrGdCr	77	274	475	1.58 (63 %)	0.12 (37 %)
			538	1.59 (49 %)	0.12 (51 %)
	295	365	416	0.18 (29 %)	0.011 (71 %)
			437	0.23 (22 %)	0.012 (78 %)
			470	0.012 (78 %)	0.011 (84 %)

a) La:Zn:L2 = 1:0:3



b) La:Zn:L2 = 1:1:3



c) La:Zn:L2 = 1:2:3

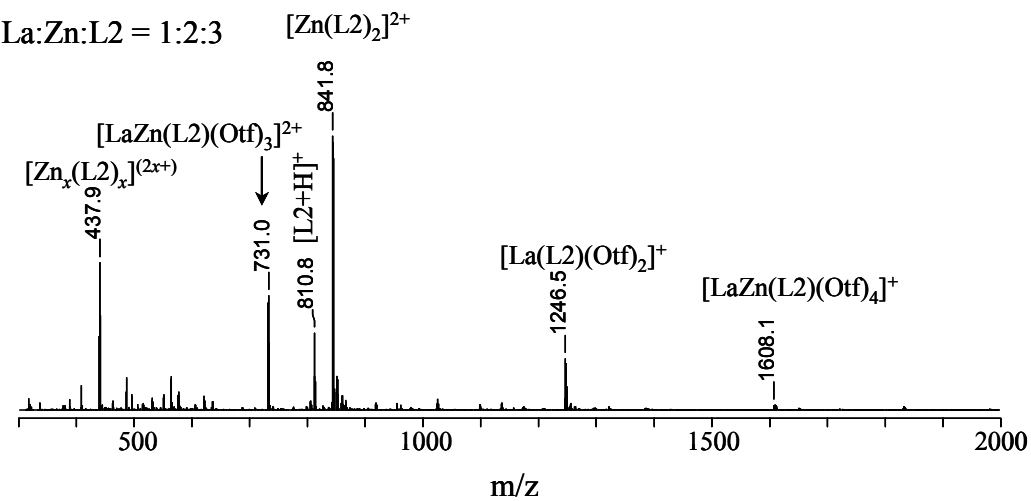


Figure S1 ESI-MS titration of L2 with $La(CF_3SO_3)_3 \cdot 3H_2O$ and $Zn(CF_3SO_3)_2 \cdot 6H_2O$ in $CHCl_3:CH_3CN = 1:1$ (total ligand concentration $2 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$).

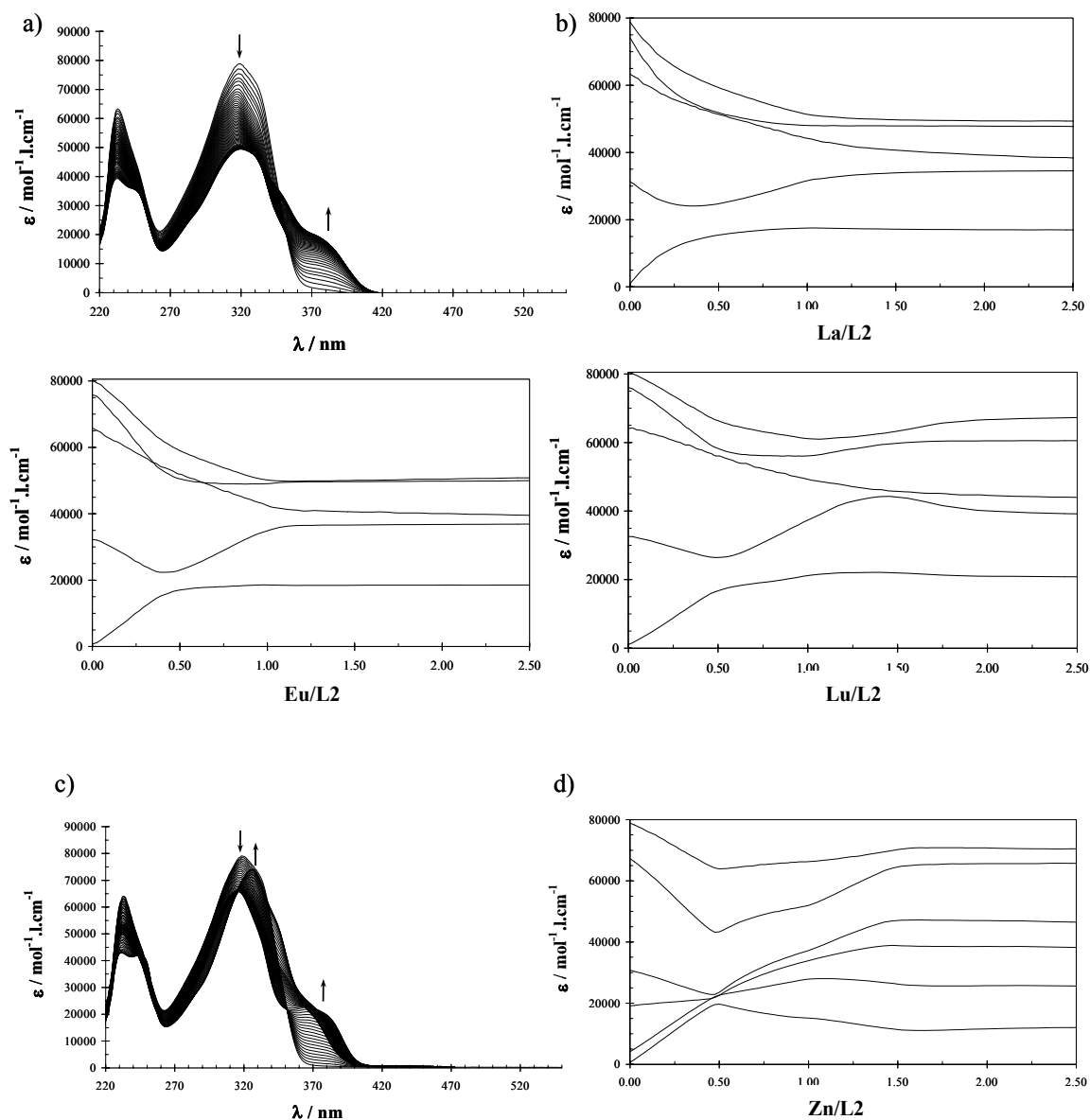


Figure S2 a) Variation of absorption spectra observed for the spectrophotometric titration of L2 (total ligand concentration: $2 \cdot 10^{-4}$ mol·dm⁻³) with Ln(CF₃SO₃)₃·*n*H₂O at 293 K in CHCl₃:CH₃CN = 1:1 (*n* = 2-3, Ln = La, Eu, Lu, Ln:L2 = 0.1-2.5). b) Corresponding variation of observed molar extinctions at five different wavelengths. c) Variation of absorption spectra observed for the spectrophotometric titration of L2 (total ligand concentration: $2 \cdot 10^{-4}$ mol·dm⁻³) with Zn(CF₃SO₃)₂·6H₂O at 293 K in CHCl₃:CH₃CN = 1:1 (Zn:L2 = 0.1-2.5). b) Corresponding variation of observed molar extinctions at six different wavelengths.

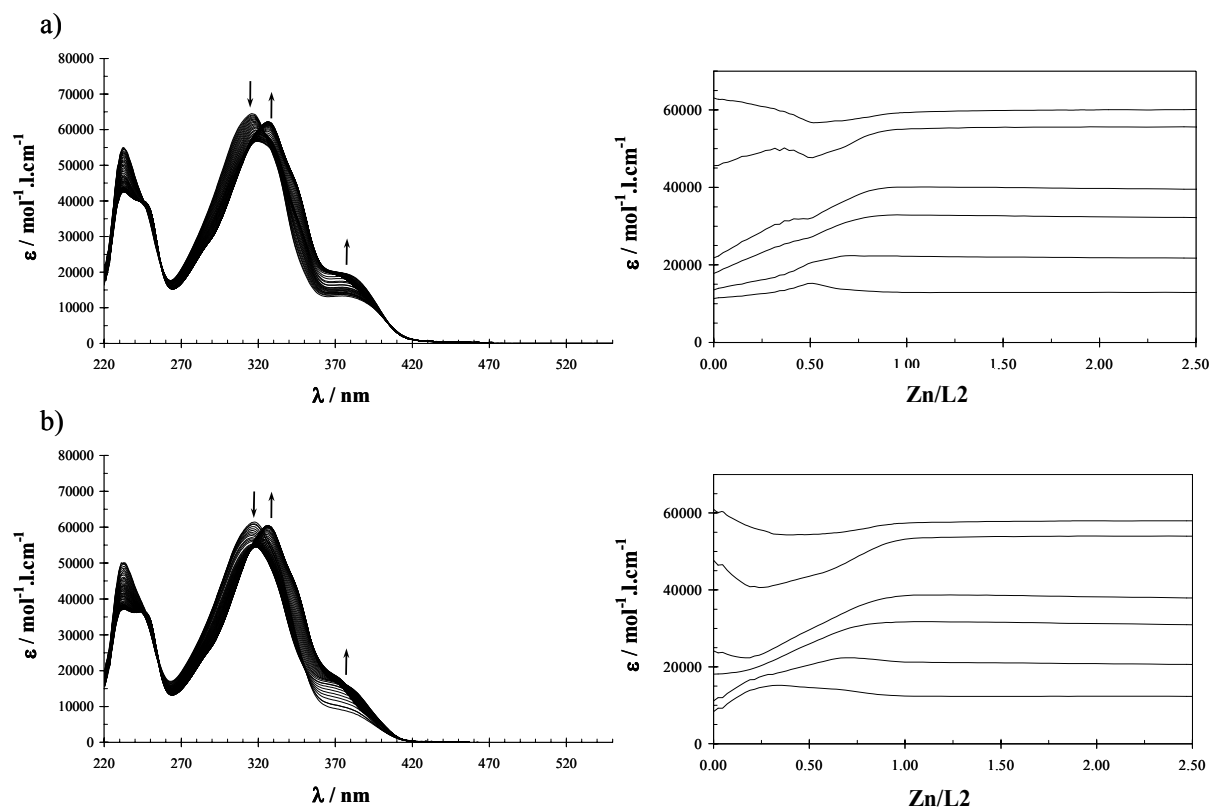


Figure S3 a) Variation of absorption spectra observed for the spectrophotometric titration of $[\text{Eu}(\text{L}2)_3]^{3+}$ (total ligand concentration: $2 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 293 K in $\text{CHCl}_3:\text{CH}_3\text{CN} = 1:1$ ($\text{Zn}:\text{L}2 = 0.1\text{-}2.5$) and corresponding variation of observed molar extinctions at six different wavelengths. b) Variation of absorption spectra observed for the spectrophotometric titration of $[\text{Lu}(\text{L}2)_3]^{3+}$ (total ligand concentration: $2 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 293 K in $\text{CHCl}_3:\text{CH}_3\text{CN} = 1:1$ ($\text{Zn}:\text{L}2 = 0.1\text{-}2.5$) and corresponding variation of observed molar extinctions at six different wavelengths.

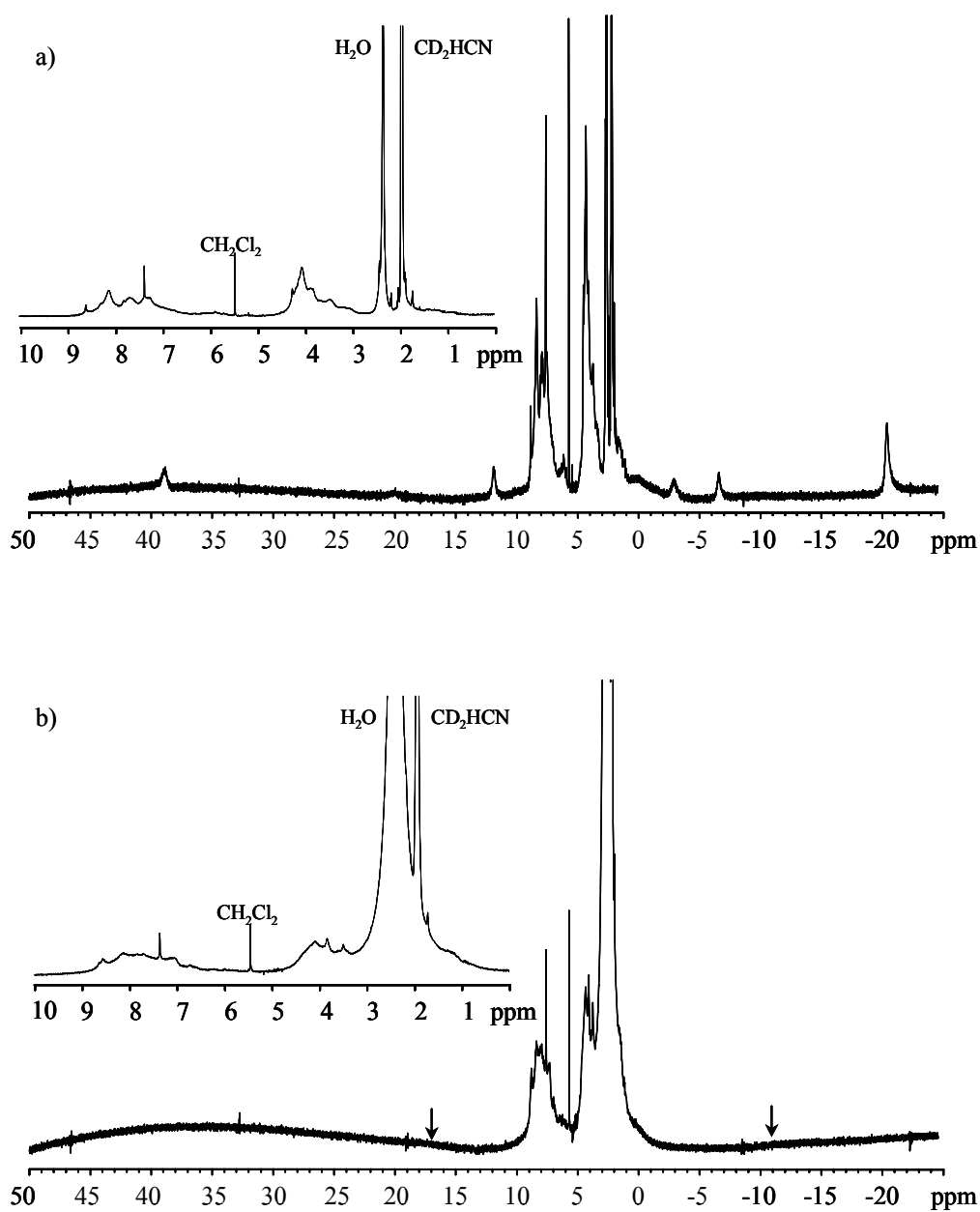


Figure S4 ^1H NMR spectra of a) $[\text{Cr}^{\text{II}}\text{LaCr}^{\text{II}}(\text{L}2)_3]^{7+}$ and b) $[\text{Cr}^{\text{III}}\text{LaCr}^{\text{III}}(\text{L}2)_3]^{9+}$ in CD_3CN at 243 K (total ligand concentration: $2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$).

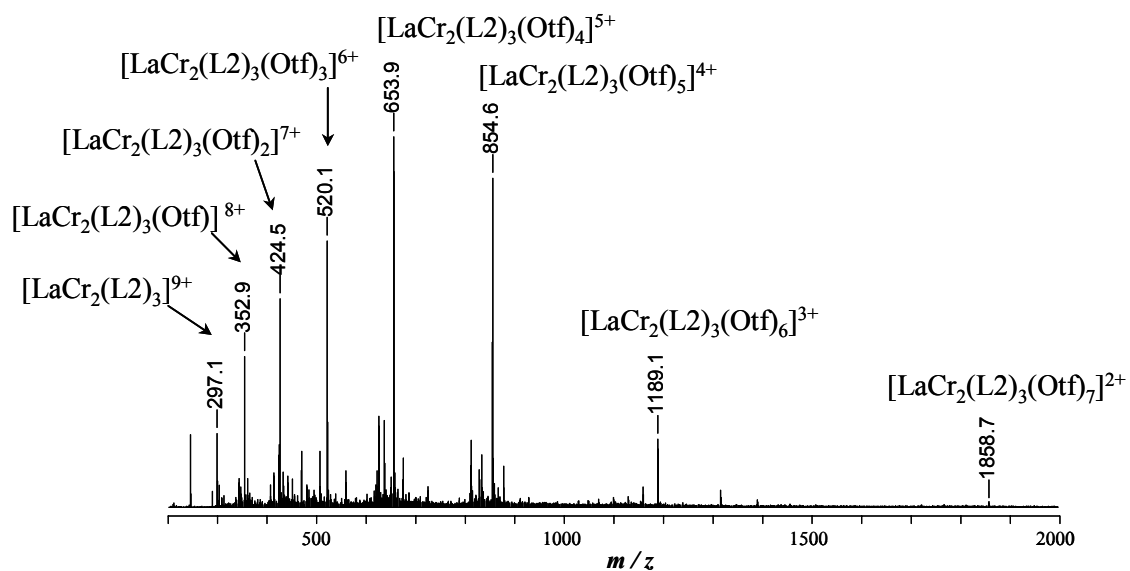


Figure S5 ESI-MS spectrum of $[CrLaCr(L_2)_3]^{9+}$ in acetonitrile (total ligand concentration: $3 \cdot 10^{-4}$ mol·dm⁻³).

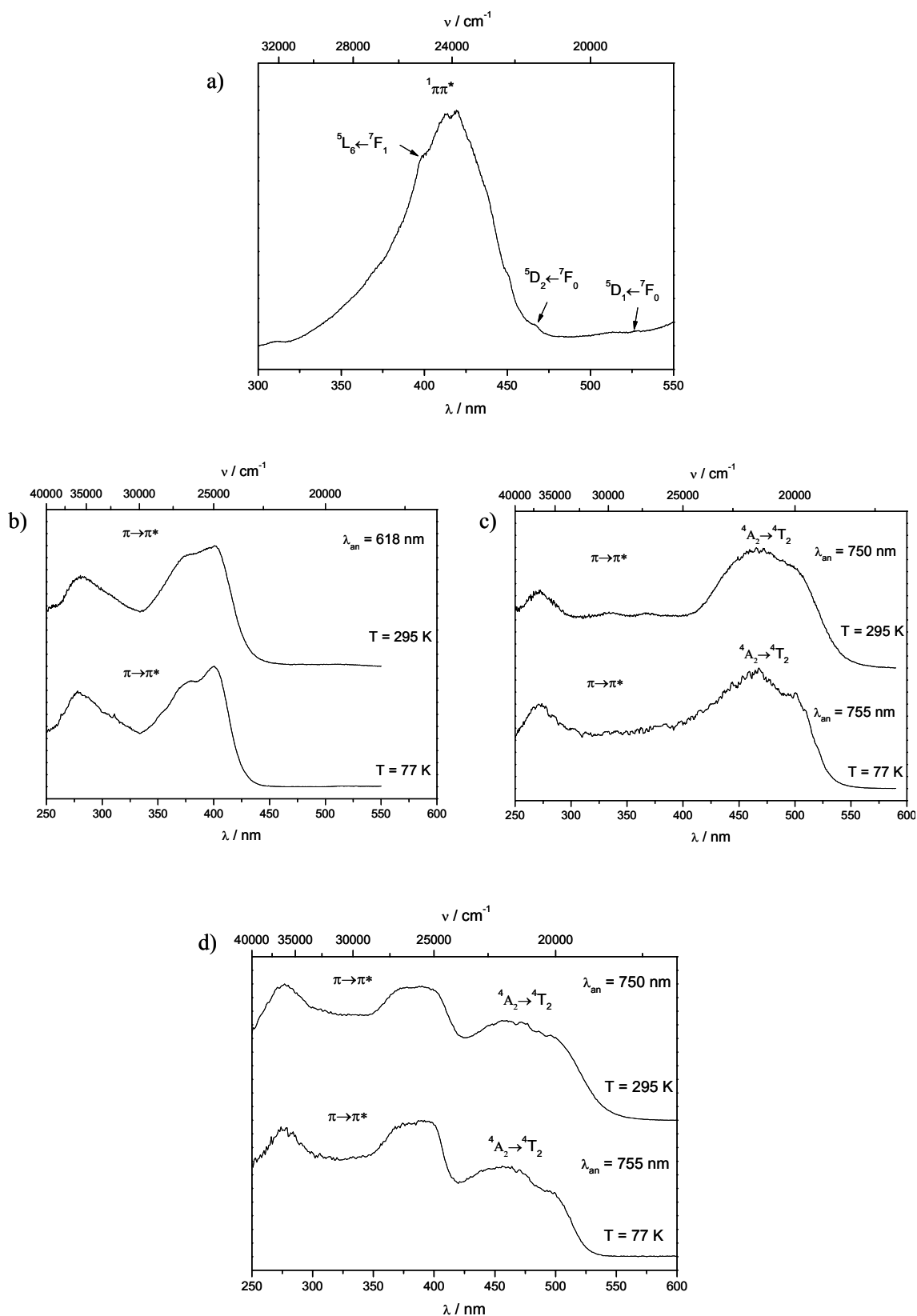


Figure S6 Excitation spectra of a) $[\text{ZnEuZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7$ upon monitoring $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ at 10K, b) $[\text{CrEuCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ upon monitoring $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ at 77K and 295K, c) $[\text{CrEuCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ upon monitoring $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ at 77K and 295K and d) $[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ upon monitoring $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ at 77K and 295K.

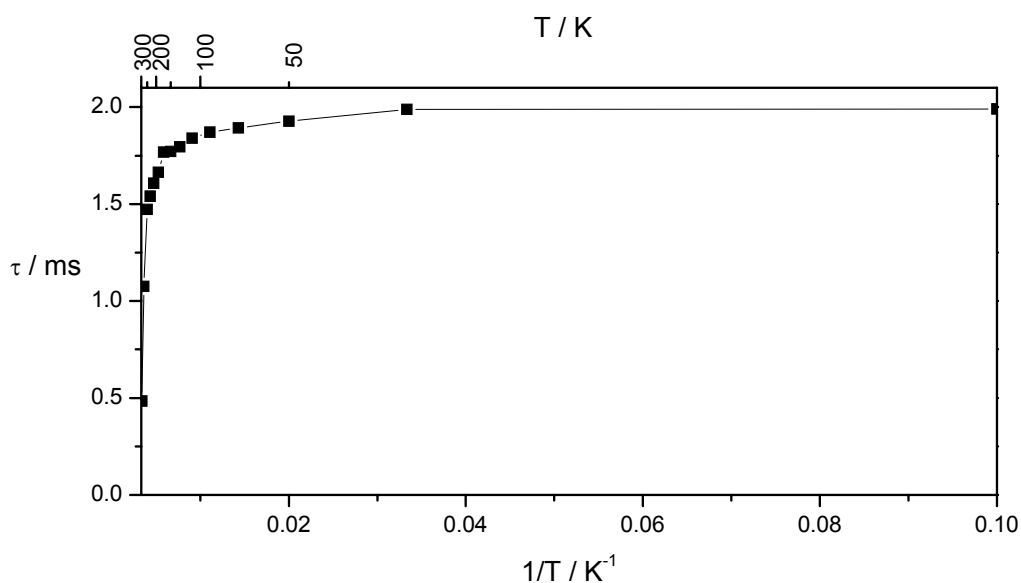


Figure S7 Variation of $\text{Eu}(^5\text{D}_0)$ lifetime with respect to the temperature for $[\text{ZnEuZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7$ ($\bar{\nu}_{\text{exc}} = 24390 \text{ cm}^{-1}$).

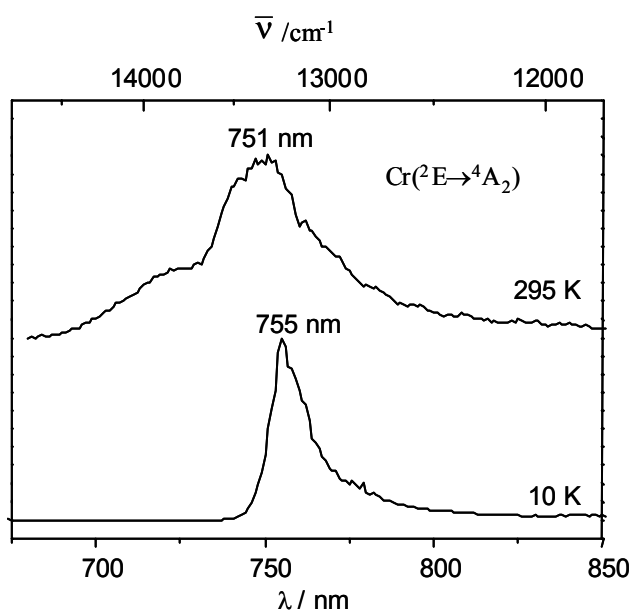


Figure S8 Emission spectra of $[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ at 10 and 295 K ($\bar{\nu}_{\text{exc}} = 28170 \text{ cm}^{-1}$).