

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

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The segmental bidentate–tridentate–bidentate ligand L2 reacts with M^{II} (M = Cr, Zn) and Ln^{III} (Ln = La, Eu, Gd, Tb, Lu) to give the heterotrimetallic triple-stranded helicates [MLnM(L2)₃]⁷⁺. For M = Zn^{II}, the isolated complexes [ZnLnZn(L2)₃](CF₃SO₃)₇ (Ln = Eu, Tb) display only lanthanide-centred luminescence arising from the pseudo-tricapped trigonal prismatic LnN₉ coordination site. For M = Cr^{II}, rapid air oxidation provides Cr^{III} and leads to the isolation of inert [CrLnCr(L2)₃](CF₃SO₃)₉ (Ln = Eu, Tb) complexes, in which divergent intramolecular Ln → Cr energy transfers can be evidenced. Taking [ZnEuZn(L2)₃]⁷⁺ as a luminescent standard for Eu-centred emission, a quantitative treatment of the energy migration processes indicates that the rate constant characterizing the Eu → Cr energy transfer is more efficient in the trimetallic system, than in the analogous simple bimetallic edifice. Particular attention is focused on potential control of directional energy transfer processes in Cr–Ln pairs.

Introduction

Due to its high positive charge (+3), small ionic radius (61.5 pm) and considerable ligand-field stabilization energy,¹ trivalent chromium, Cr^{III}, mainly exists in coordination chemistry as kinetically inert pseudo-octahedral complexes displaying strong metal–ligand bonds.² Moreover, the peculiar orbitally non-degenerate quartet ground state, corresponding to the open shell (t_{2g})³ electronic configuration of octahedral Cr^{III} (⁴A_{2g} in O_h symmetry), prevents efficient associative pathways for ligand exchanges processes.^{1–3} Consequently, Cr^{III} complexes combine extreme kinetic inertness (the rate of water exchange in [Cr(H₂O)₆]³⁺ amounts to *k*_(298 K) = 2.4 × 10^{−6} s^{−1}),^{1,4} with predictable pseudo-octahedral geometries, which makes them ideal coordination models for the refinement of theoretical inorganic kinetic mechanisms^{3,5} and electronic spectroscopy.⁶ More recently, some interest has been focussed on the design of sophisticated polymetallic networks with predictable two-dimension and three-dimension organization based on inert negatively charged tris-oxalato [Cr(ox)₃]^{3−},⁷ or mixed oxalato-bipyridine [Cr(ox)₂(bipy)][−] building blocks.⁸ Interestingly, lanthanides have been used as counter-cations in

these infinite architectures,^{8,9} thus producing heterometallic Cr–Ln interactions, but only weak magnetic coupling results from the minute expansion of the 4f orbitals,⁹ which restricts the design of single molecular magnets (SMM) to extremely low temperatures.¹⁰ According to a functional point of view, the Cr–Ln association is more attractive for its optical properties because resonant intermetallic energy transfers depend on the spectral overlap integral Ω_{DA} between the absorption spectrum of the acceptor **A**, and the emission spectrum of the donor **D**. They can be thus operative over long distances, if the perturbation operator *H'* is of electrostatic origin (Fermi's golden rule, eqn (1), *W*_{DA} is the probability of the energy transfer).¹¹

$$W_{DA} = (2\pi/\hbar) |\langle DA^* | H' | D^*A \rangle|^2 \Omega_{DA} \quad (1)$$

Assuming the common approximation, which limits the electrostatic multipolar series to dipole–dipole interactions, Förster's theory predicts a (*R*^{DA})^{−6} dependence on the separation between the donor and the acceptor (eqn (19), *vide infra*).¹² Applying this treatment to Cr–Ln pairs gives critical distances for 50% energy transfer extending on the nanometric scale with *R*₀^{EuCr} = 11.5 Å,¹³ *R*₀^{TbCr} ≥ 20.1 Å,¹³ *R*₀^{CrNd} = 12.8 Å¹⁴ and *R*₀^{CrYb} = 9.1 Å at 10 K.¹⁴ When strong field α,α'-diimines are coordinated to Cr^{III} as in [Cr(2,2'-bipyridine)₃]³⁺ or [Cr(2-benzimidazol-pyridine)₃]³⁺, the integral overlap Ω_{LnCr} (or Ω_{CrLn}) mainly involves the low-lying excited Cr-centred excited states ²E and ²T₁,¹⁵ and some adequate Ln-centred levels.^{13,14} For Ln = Eu and Tb, which possess high-energy emitting levels in the visible range, Cr^{III} may act as an acceptor and Ln → Cr energy transfers, followed by Cr(²E) luminescence, are evidenced.^{13,16} Conversely, Ln = Nd, Ho, Er, Tm and Yb possess low-energy excited electronic states. Cr^{III} thus acts as a donor, and Cr → Ln energy transfers result in the sensitization of Ln-centred near infrared (NIR) emission.^{14,17} Although the significant spectral overlap between the transitions of the d-block donor (Cr(⁴T_{2g} → ⁴A_{2g}) and/or Cr(²E → ⁴A_{2g})) and specific

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† Electronic supplementary information (ESI) available: Tables of elemental analyses (Table S1), luminescence data for [ZnLnZn(L2)₃]⁷⁺ and [CrLnCr(L2)₃]⁹⁺ (Ln = Eu, Gd, Tb, Table S2), and longitudinal nuclear relaxation times for [ZnLnZn(L2)₃]⁷⁺ (Ln = Tb, Lu) (Table S3). Figures showing ESI-MS (Figure S1), spectrophotometric (Figures S2 and S3) and ¹H NMR (Figure S4) titrations. Figures showing ESI-MS (Figure S5), excitation (Figure S6) and emission (Figure S8) spectra of isolated [MLnM(L2)₃]^{7/9+} complexes. Figure S7 shows the temperature dependence of Eu(³D₀) lifetime in [ZnEuZn(L2)₃]⁷⁺. See DOI: 10.1039/b602392d

Ln-centred intra-configurational 4f $\rightarrow$ 4f absorption bands of NIR Ln-emitters has prompted the introduction of Cr^{III} in weak-field garnets (Al₂O₃) for sensitizing Ln^{III} (Ln = Nd, Er, Tm) *via* Cr $\rightarrow$ Ln energy transfers,¹⁸ only a few discrete heterometallic Cr–Ln pairs have been designed for unravelling the mechanism of intramolecular intermetallic optical communication. A first example [(acac)₂Cr(μ -ox)Ln(HBpz₃)₂] (Fig. 1a) has been shown by Kaizaki and co-workers to display intramolecular Ln $\rightarrow$ Cr (Ln = Eu, Tb) energy transfer processes, which completely quench Ln-centred emission,^{16b} or more interestingly Cr $\rightarrow$ Ln (Ln = Nd, Ho, Er, Tm, Yb) energy migrations responsible for the dual metal-centred emission of the sensitized Ln^{III} emitter, together with the residual phosphorescence of the Cr(³E) donor level.^{17c} According to a synthetic point of view, the latter heterobimetallic complexes are obtained by the simultaneous complexation of inert [Cr(acac)₂(ox)][–] and [HBpz₃][–] to Ln^{III}.¹⁷ An alternative strategy uses the labile Cr^{II} precursor (the rate of methanol exchange in [Cr(CH₃OH)₆]²⁺ amounts to $k_{(298\text{ K})} = 1.2 \times 10^8\text{ s}^{-1}$),¹⁹ for producing the self-assembled bimetallic helicate [CrLn(L1)₃]⁵⁺, which is further oxidized to give the inert Cr^{III}–Ln pair in [CrLn(L1)₃]⁶⁺ (Fig. 1b, see Fig. 3 for the structures of the ligands).¹³

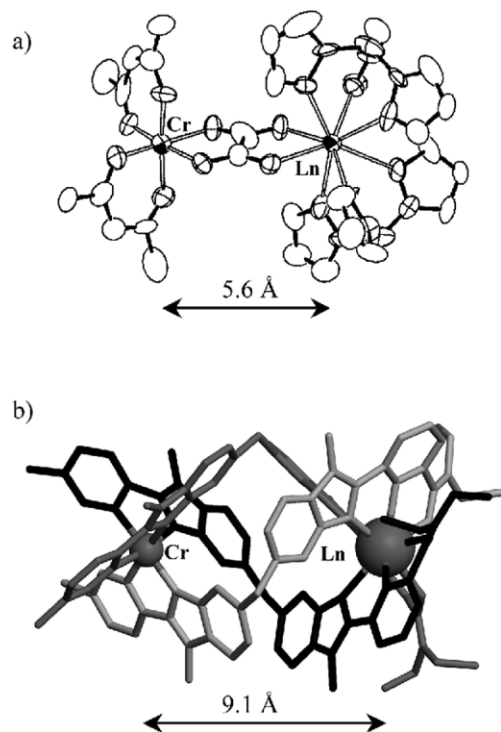


Fig. 1 Structures of discrete bimetallic CrLn complexes a) [(acac)₂Cr(ox)-Ln(HBpz₃)₂]^{16b,17} and b) [CrLn(L1)₃]⁶⁺,^{13,14} in which intramolecular intermetallic energy transfers have been evidenced.

Both intramolecular Ln $\rightarrow$ Cr (Ln = Eu, Tb)¹³ and Cr $\rightarrow$ Ln (Ln = Nd, Yb)¹⁴ energy transfers have been evidenced in [CrLn(L1)₃]⁶⁺, and a quantitative treatment of the energy migration processes according to the simple mechanism shown in Fig. 2 demonstrates that, except for Tb $\rightarrow$ Cr ($k_{\text{ET}}^{\text{Tb,Cr}} > 3.5 \times 10^4\text{ s}^{-1}$),¹³ the rate constants of energy transfers $k_{\text{ET}}^{\text{Ln,Cr}}$ or $k_{\text{ET}}^{\text{Cr,Ln}}$ are rather slow and fall within the range 10^2 – 10^3 s^{-1} for intermetallic Cr $\cdots$ Ln separations around 9.0–9.3 Å, taken as acceptable approximations for the donor–acceptor distances R^{DA} .^{13,14} Therefore, when Cr^{III} is

used as a donor for short-lived NIR lanthanide emitters ($k_{\text{Lum}}^{\text{Ln}} \approx 10^4$ – 10^5 s^{-1}) in these complexes, the combination of the long-lived Cr(³E) level ($k_{\text{Lum}}^{\text{Cr}} \approx 300\text{ s}^{-1}$) with the slow energy transfer process ($k_{\text{ET}}^{\text{Cr,Ln}} \approx 200\text{ s}^{-1}$) results in $k_{\text{Lum}}^{\text{Cr}} + k_{\text{ET}}^{\text{Cr,Ln}} \ll k_{\text{Lum}}^{\text{Ln}}$, and the de-excitation of the lanthanide emitter mirrors the long lifetime of the Cr donor (Fig. 2).¹⁴ The resulting extended NIR lifetime occurring within the millisecond range (instead of the usual microsecond regime) may greatly help in time-resolved analyses of NIR emitters involved in homogeneous fluoroimmunoassays.²⁰ However, this attractive property is obtained at the cost of the existence of poorly efficient energy transfer processes, and thus a poor sensitization of the NIR lanthanide probe. The only way for improving sensitivity of the NIR emission process without affecting the energy migration regime requires the connection of several [Cr(2-benzimidazol-pyridine)₃]³⁺ donors (similar to that found in [CrLn(L1)₃]⁶⁺, Fig. 1b) about a central Ln^{III} coordination site, with all Cr $\cdots$ Ln distances being fixed at 9.0–9.3 Å.

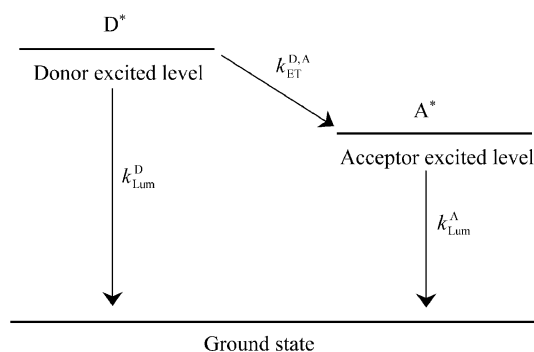


Fig. 2 Kinetic model for the deactivation and communication between d- and f-block-centred excited levels in [CrLn(L1)₃]⁶⁺ (Ln = Nd, Eu, Tb, Yb).^{13,14}

As a first step toward this goal, we report here on the encapsulation of the tricapped trigonal prismatic LnN₉ site between two inert facial [Cr(2-benzimidazol-pyridine)₃]³⁺ stoppers located at *ca.* 9 Å in the heterotrimetallic triple-stranded helicates [CrLnCr(L2)₃]⁹⁺ (Fig. 6). Moreover, the LnN₉ lanthanide coordination sphere produced in the latter trimetallic helicate is different from LnN₆O₃ found in [CrLn(L1)₃]⁶⁺, and we thus focus in this contribution on the thermodynamic, structural and photophysical consequences of this change in the highly charged helicate [CrLnCr(L2)₃]⁹⁺.

Results and discussion

Synthetic and thermodynamic aspects

Self-assembly of [ZnLnZn(L2)₃]⁷⁺, [CrLnCr(L2)₃]⁷⁺ and [CrLnCr(L2)₃]⁹⁺ in solution. The segmental bidentate–tridentate–bidentate ligand L2 is obtained by the simultaneous reductive cyclization of four *ortho*-nitroamide groups in the precursor **1** (Scheme 1).²¹ The ¹H NMR spectrum displays 15 signals, which reflect the dynamically average C_{2v}-symmetry of L2 on the NMR time scale (Fig. 4a and Table 1). Although paramagnetic low-spin Cr^{II} ($S = 1$) possesses a fast electronic relaxation time ($\tau_c \approx 10^{-12}\text{ s}$)²² combined with minor delocalization of the unpaired electrons,²³ the increased nuclear relaxation induced for ¹H nuclei

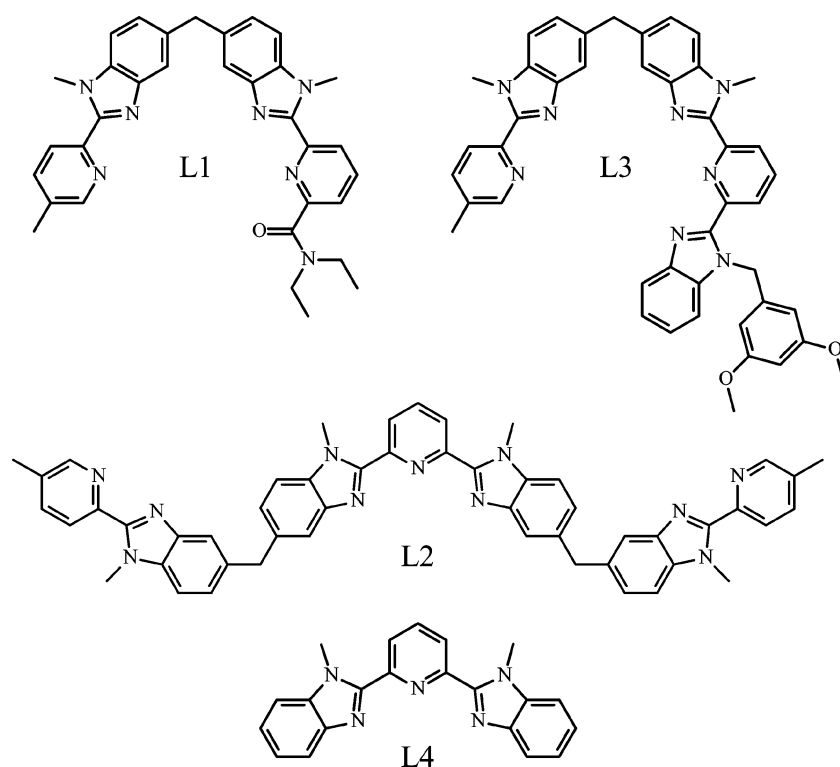


Fig. 3 Structures of the ligands L1–L4.

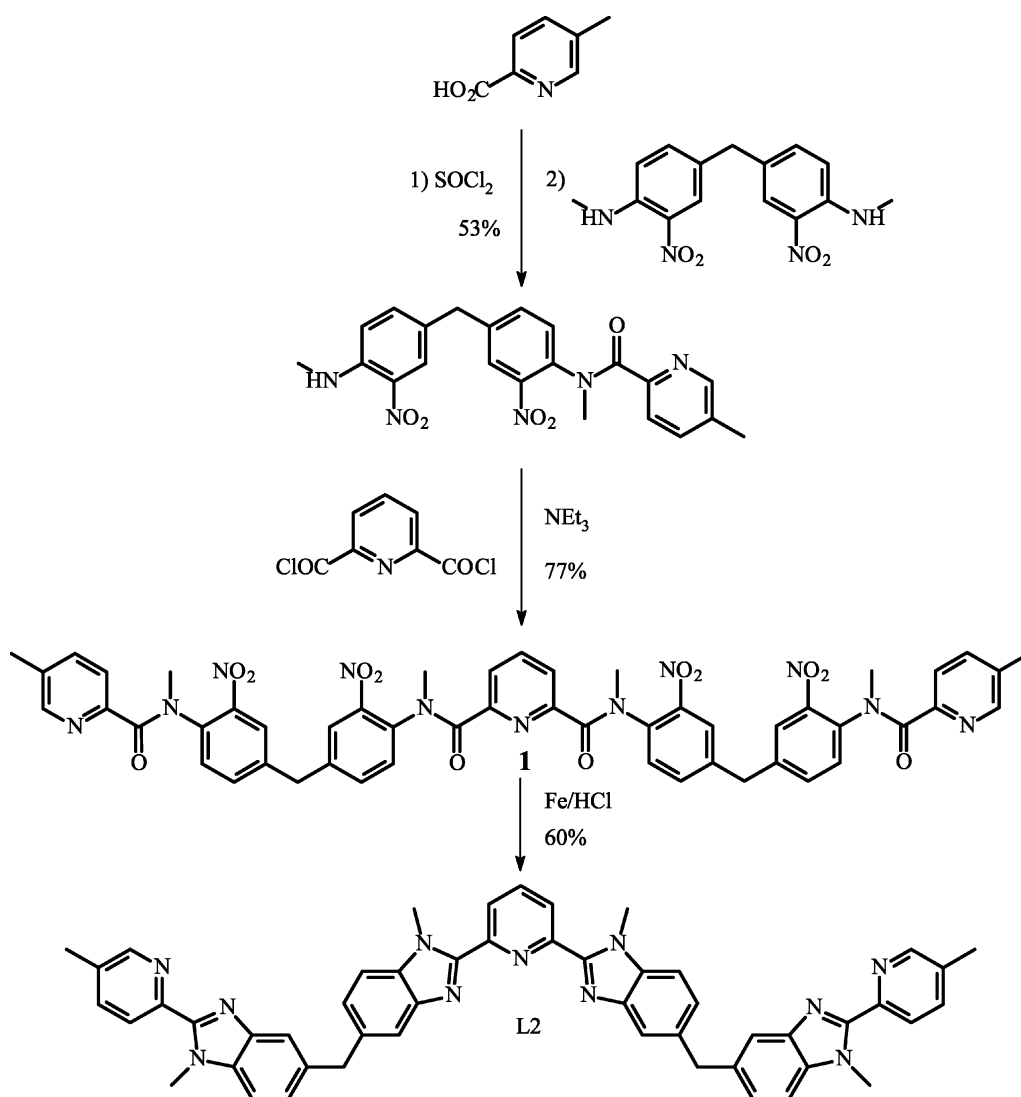
in $[\text{CrLn}(\text{L1})_3]^{5+}$ was shown to be large enough to significantly broaden and shift the signals of the bidentate units bound to Cr^{II} , thus preventing reliable assignment.¹³ The situation is more dramatic for $[\text{CrLnCr}(\text{L2})_3]^{7+}$, since each proton undergoes the effect of two paramagnetic Cr^{II} centres *via* through-bond (contact) and through-space (dipolar) mechanisms (Fig. S4a, ESI†).²⁴ We therefore decided to replace labile paramagnetic low-spin Cr^{II} with diamagnetic Zn^{II} in order to prepare $[\text{ZnLnZn}(\text{L2})_3]^{7+}$, which can be used as a structural model for NMR investigations. Moreover, ESI-MS can be reliably used as a guide for speciation in solution with Zn^{II} , but not with air-sensitive Cr^{II} complexes.

ESI-MS titrations of L2 (2×10^{-4} mol dm^{-3}) with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{CF}_3\text{SO}_3)_3 \cdot 3\text{H}_2\text{O}$ in $\text{CHCl}_3/\text{CH}_3\text{CN}$

(1 : 1) for various $\text{Zn} : \text{La} : \text{L2}$ ratios are dominated by the formation of homometallic complexes $[\text{Zn}(\text{L2})_2]^{2+}$, $[\text{Zn}_x(\text{L2})_x]^{2x+}$ ($x = 1, 2$) and $[\text{La}(\text{L2})(\text{CF}_3\text{SO}_3)_2]^+$, together with traces of the heterometallic complex $[\text{ZnLa}(\text{L2})(\text{CF}_3\text{SO}_3)_2]^{2+}$, but no peak corresponding to the target helicate $[\text{Zn}_x\text{La}(\text{L2})_3]^{(3+2x)+}$ could be detected (Fig. S1, ESI†). Increasing the total concentration of the ligand to millimolar concentration for the stoichiometric ratio $\text{La} : \text{Zn} : \text{L2} = 1 : 2 : 3$ shows the appearance of two weak peaks at $m/z = 599.5$ and $m/z = 786.8$ corresponding to $[\text{ZnLaZn}(\text{L2})_3(\text{CF}_3\text{SO}_3)_2]^{5+}$ and $[\text{ZnLaZn}(\text{L2})_3(\text{CF}_3\text{SO}_3)_3]^{4+}$. This behaviour suggests that the highly charged heterotrimetallic helicate is poorly stable in acetonitrile/chloroform mixtures. Parallel titrations at higher concentrations (total ligand concentration 10^{-2} mol dm^{-3}) have

Table 1 ^1H NMR shifts (in ppm with respect to TMS) for the ligand L2 in CDCl_3 and its complexes $[\text{ZnLnZn}(\text{L2})_3]^{7+}$ in CD_3CN at 293 K (Ln = La, Eu, Tb, Lu, Y)

	L2	$[\text{ZnLaZn}(\text{L2})_3]^{7+}$	$[\text{ZnLuZn}(\text{L2})_3]^{7+}$	$[\text{ZnYZn}(\text{L2})_3]^{7+}$	$[\text{ZnEuZn}(\text{L2})_3]^{7+}$	$[\text{ZnTbZn}(\text{L2})_3]^{7+}$
H1	8.48	7.88	7.85	7.88	8.44	3.62
H2	7.61	7.76	7.78	7.78	8.11	5.33
H3	8.19	8.06	8.10	8.09	8.57	3.22
H4	7.32	7.07	7.20	7.17	7.60	4.38
H5	7.21	6.86	6.91	6.90	7.13	0.42
H6	7.67	5.11	4.95	4.98	7.22	−12.55
H7,H7'	4.25	3.62, 3.22	3.55, 3.26	3.56, 3.26	4.15, 3.53	4.09, 7.44
H8	7.63	5.88	5.37	5.49	11.40	−49.0
H9	7.19	7.23	7.14	7.17	7.32	4.34
H10	7.30	7.61	7.54	7.56	5.93	8.63
H11	8.33	7.89	7.83	7.88	3.62	15.98
H12	7.98	8.07	7.83	7.88	5.49	15.43
H13	2.37	2.14	2.15	2.15	2.40	−0.14
H14	4.19	3.96	4.05	3.96	4.44	0.35
H15	4.17	3.88	3.98	4.03	2.55	16.30



Scheme 1 Synthesis of ligand L2.²¹

been followed by ^1H NMR spectroscopy (Fig. 4b–d). The addition of 0.33 eq. of La^{III} to a solution of L2 slightly affects the original spectrum of the free ligand, and new broad signals arise, which are diagnostic for the formation of flexible lanthanide complexes displaying intermediate exchange processes on the NMR time scale (Fig. 4b). The subsequent addition of 0.33 eq. of Zn^{II} to the mixture drastically reduces the intensity of the signals of the free ligands, which are replaced with novel signals associated with the formation of a symmetrical species (Fig. 4c). The latter complex is quantitatively formed when a total amount of 0.66 eq. of Zn^{II} has been added, which corresponds to the stoichiometry $\text{La} : \text{Zn} : \text{L2} = 1 : 2 : 3$ expected for entropically maximizing the formation of the target helicate $[\text{ZnLaZn}(\text{L2})_3]^{7+}$ in solution (Fig. 4d). We observe 16 signals characterizing one half of a ligand strand L2, which implies an average D_3 -symmetry. The transformation of the enantiotopic methylene protons H7–H7' in the free ligand (C_{2v} -symmetry, Fig. 4a) into diastereotopic protons in the final complex (Fig. 4d) confirms the wrapping of the ligand strands, and the removal of the symmetry planes. Finally, the detection of significant intrastrand H11–H15 and

H3–H14 NOE effects indicates that both the tridentate and the bidentate binding units adopt the cisoid conformation (*i.e.* the lone pairs of the nitrogen atoms of the adjacent pyridine and benzimidazole rings point in the same direction) compatible with their chelation to the metal ions. Concomitantly, the coordination of the tridentate and bidentate binding units results in the splitting of the ligand-centred $\pi \rightarrow \pi^*$ transitions, which allows the investigation of the complexation process by spectrophotometry.²⁵ Titrations of L2 ($2 \times 10^{-4} \text{ mol dm}^{-3}$) with $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Lu}$) for $\text{L2} : \text{La} = 0.1\text{--}2.5 : 1$ (Fig. S2a and S2b, ESI†), or with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ for $\text{L2} : \text{Zn} = 0.1\text{--}2.5 : 1$ (Fig. S2c and S2d, ESI†), or titrations of $[\text{Ln}(\text{L2})_3]^{3+}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Lu}$, total ligand concentration: $2 \times 10^{-4} \text{ mol dm}^{-3}$) with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ for $\text{L2} : \text{Zn} = 0.1\text{--}2.5 : 1$ (Fig. 5 and S3, ESI†) in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1 : 1) show complicated variations of the absorption spectra. Detailed mathematical analyses by using factor analysis²⁶ and evolving factor analysis²⁷ indicate the existence of a minimum of nine absorbing species (the free ligand and eight complexes) for rationalizing the spectrophotometric data (equilibria 2–9).

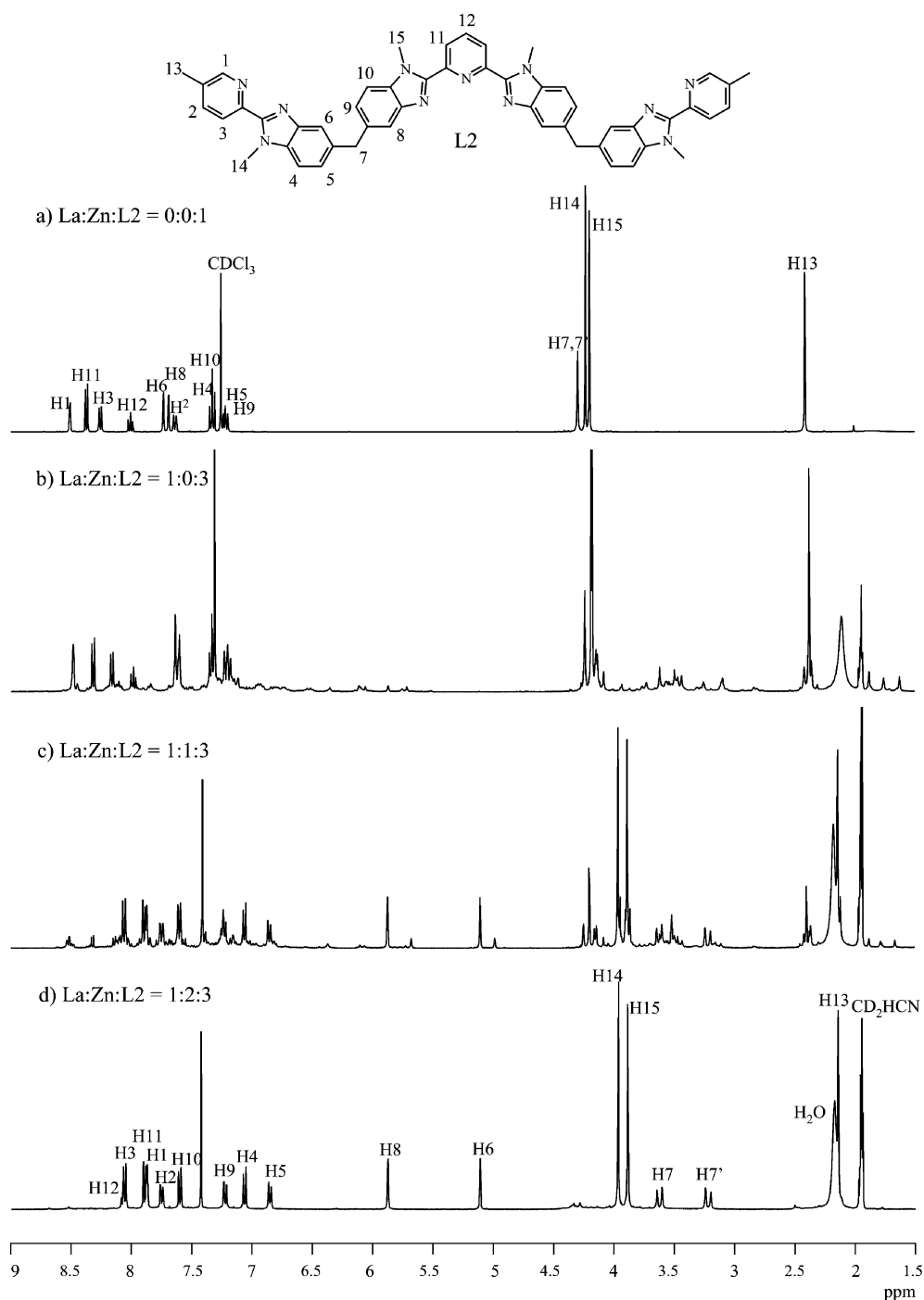
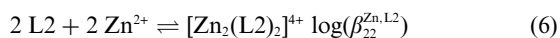
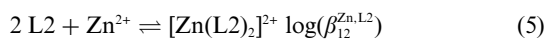
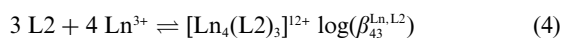
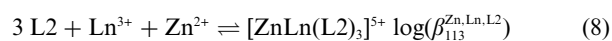
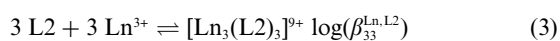
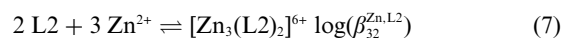
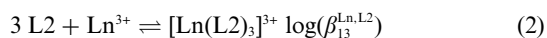


Fig. 4 ^1H NMR titration of L2 with La^{III} and Zn^{II} in $\text{CDCl}_3/\text{CD}_3\text{CN} = 1 : 1$ at 293 K (total ligand concentration = $10^{-2} \text{ mol dm}^{-3}$).



We were however unable to simultaneously and reliably fit the eight stability constants to the experimental data, because the non-linear least-squares procedure showed significant instability. Nevertheless, we systematically observed two end points at

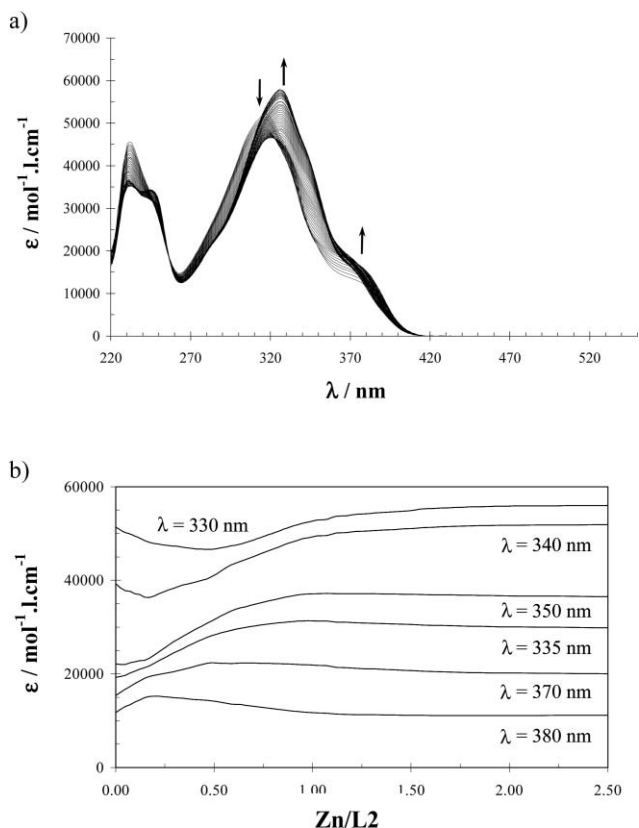


Fig. 5 a) Variation of absorption spectra observed for the spectrophotometric titration of $[\text{La}(\text{L}2)_3]^{3+}$ (total ligand concentration: $2 \times 10^{-4} \text{ mol dm}^{-3}$) with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 293 K in $\text{CHCl}_3\text{--CH}_3\text{CN} = 1:1$ ($\text{Zn} : \text{L}2 = 0.1\text{--}2.5 : 1$). b) Corresponding variation of observed molar absorption at six different wavelengths.

$\text{Zn} : \text{L}2 \approx 0.3$ and $\text{Zn} : \text{L}2 \approx 0.7$ for the titrations of $[\text{Ln}(\text{L}2)_3]^{3+}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Lu}$) with $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fig. 5 and S3, ESI†), in agreement with the successive formation of $[\text{ZnLn}(\text{L}2)_3]^{5+}$ and $[\text{ZnLnZn}(\text{L}2)_3]^{7+}$ complexes as the main species in solution under these conditions.

We conclude from the combination of ESI-MS, ^1H NMR and spectrophotometric titrations that the target complexes $[\text{ZnLnZn}(\text{L}2)_3]^{7+}$ can be formed in solution as the major species under a strict stoichiometric ratio $\text{Zn} : \text{Ln} : \text{L}2 = 2 : 1 : 3$ and millimolar concentrations of the ligand (Fig. 6).

As expected, the replacement of $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ with air-sensitive $\text{Cr}(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ produces broad ^1H NMR signals for $[\text{CrLaCr}(\text{L}2)_3]^{7+}$ under strict anaerobic conditions, which are typical of paramagnetic low-spin Cr^{II} cations (Fig. S4a, ESI†). We observe 16 signals spread over 70 ppm (-20 to 50 ppm, Fig. S4a, ESI†) compatible with D_3 -symmetry. Upon air oxidation, the fast colour change from deep green to orange is accompanied by a further drastic broadening of the ^1H NMR signals, compatible with the formation of slow-relaxing Cr^{III} ($\tau_c \approx 10^{-9}$ s, Fig. S4b, ESI†).⁴ This $\text{Cr}^{\text{II}} \rightarrow \text{Cr}^{\text{III}}$ oxidation is confirmed by the variation of the electronic absorption spectra recorded for $[\text{CrLnCr}(\text{L}2)_3]^{7+}$ and $[\text{CrLnCr}(\text{L}2)_3]^{9+}$ ($\text{Ln} = \text{Eu}, \text{Lu}$, Fig. 7 and Table 2). As previously discussed in detail for the absorption spectrum of $[\text{CrLn}(\text{L}1)_3]^{5+}$,¹³ the $[\text{CrLnCr}(\text{L}2)_3]^{7+}$ complexes show intense UV bands assigned to ligand-centred $\pi \rightarrow \pi^*$ transitions, together with less intense LMCT transitions occurring at low energy (8280 cm^{-1} ,

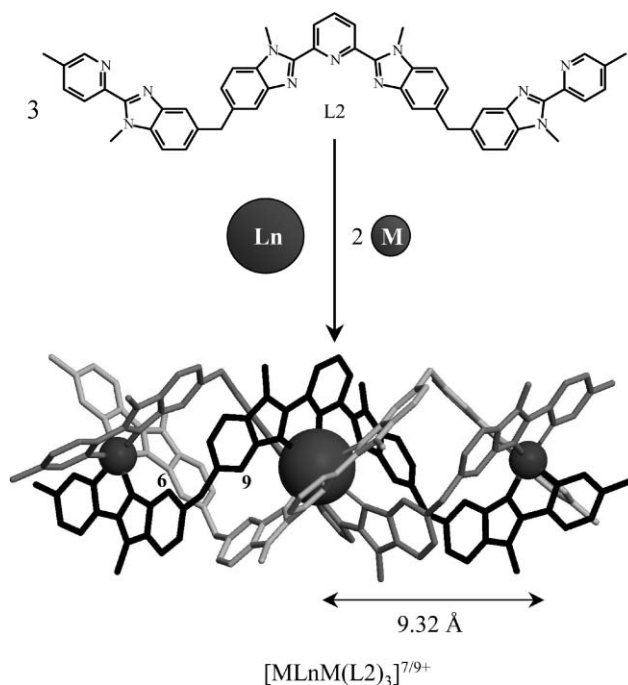


Fig. 6 Schematic representation of the complexation process leading to the triple-stranded helicate $[\text{MLnM}(\text{L}2)_3]^{7+}$ ($\text{M} = \text{Zn}^{\text{II}}, \text{Cr}^{\text{II}}$). The structure of the complex corresponds to the optimized D_3 -symmetrical geometry constructed for $[\text{Cr}^{\text{III}}\text{EuCr}^{\text{III}}(\text{L}2)_3]^{9+}$ by using the crystal structure of $[\text{Cr}^{\text{III}}\text{Eu}(\text{L}1)_3]^{6+}$ as model.

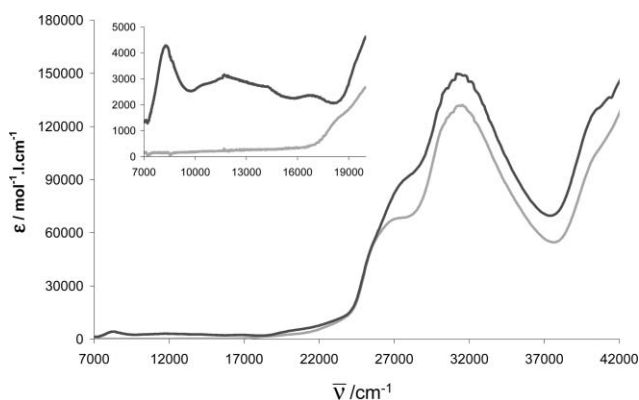


Fig. 7 Absorption spectra of a) $[\text{Cr}^{\text{II}}\text{LnCr}^{\text{II}}(\text{L}2)_3]^{7+}$ (black trace) and b) $[\text{Cr}^{\text{III}}\text{LnCr}^{\text{III}}(\text{L}2)_3]^{9+}$ (grey trace) in acetonitrile ($2.1 \times 10^{-3} \text{ mol dm}^{-3}$).

$\varepsilon = 3250 \text{ M}^{-1} \text{ cm}^{-1}$; 9460 cm^{-1} , $\varepsilon = 1840 \text{ M}^{-1} \text{ cm}^{-1}$, Table 2), which compare well with those found in $[\text{Cr}(2,2'\text{-bipyridine})_3]^{2+}$ (8700 cm^{-1} , $\varepsilon = 10000 \text{ M}^{-1} \text{ cm}^{-1}$; 9900 cm^{-1} , $\varepsilon = 2900 \text{ M}^{-1} \text{ cm}^{-1}$)²⁸ and in $[\text{CrLn}(\text{L}1)_3]^{5+}$ (8300 cm^{-1} , $\varepsilon = 4300 \text{ M}^{-1} \text{ cm}^{-1}$; 9090 cm^{-1} , $\varepsilon = 2900 \text{ M}^{-1} \text{ cm}^{-1}$).¹³ The series of poorly resolved bands in the range $11000\text{--}25000 \text{ cm}^{-1}$ correspond to overlapping low-spin Cr^{II} -centred d–d transitions possessing significant CT character (a detailed assignment is given in Table 2).¹³

Upon air oxidation, the low-energy $\text{L}2 \rightarrow \text{Cr}^{\text{II}}$ LMCT and the spin-allowed Cr^{II} -centred transition responsible for the deep green colour of $[\text{CrLnCr}(\text{L}2)_3]^{7+}$ are replaced by a shoulder on the low-energy side of the ligand-centred $\pi \rightarrow \pi^*$ transitions (Fig. 7), which is assigned to the novel spin-allowed Cr^{III} -centred

Table 2 Electronic spectral data for the heterometallic complexes [Cr^{II}LnCr^{II}(L2)₃]⁷⁺ and [Cr^{III}LnCr^{III}(L2)₃]⁹⁺ in acetonitrile at 293 K^a

Compound	$\pi \rightarrow \pi^*$	$d \rightarrow d + CT$	Attribution
L2	31150 (85800)		
[CrEuCr(L2) ₃] ⁷⁺	40490 (107100 sh)	25550 (29550 sh)	³ T ₁ → ³ T ₂ (b) + CT
	31150 (121490)	20000 (3100 sh)	³ T ₁ → ³ E(b) + CT
	27550 (94150 sh)	16640 (1720)	³ T ₁ → ³ A ₁ + ³ A ₂ + CT
		14184 (1460)	³ T ₁ → ³ T ₁ (a) + ³ T ₂ (a) + CT
		11450 (1530)	³ T ₁ → ³ E(a) + CT
[CrLuCr(L2) ₃] ⁷⁺		9460 (1840 sh)	LMCT
		8280 (3250)	LMCT
	40650 (130500 sh)	25400 (49500 sh)	³ T ₁ → ³ T ₂ (b) + CT
	31150 (149800)	20000 (4630 sh)	³ T ₁ → ³ E(b) + CT
	27300 (86700 sh)	16690 (2370)	³ T ₁ → ³ A ₁ + ³ A ₂ + CT
		14200 (2700)	³ T ₁ → ³ T ₁ (a) + ³ T ₂ (a) + CT
		11765 (3140)	³ T ₁ → ³ E(a) + CT
		10225 (2700)	LMCT
[CrEuCr(L2) ₃] ⁹⁺	40160 (109400 sh)	27250 (85740)	⁴ A ₂ → ⁴ T ₁ + CT
	31350 (136550)	20000 (1460)	⁴ A ₂ → ⁴ T ₂ + CT
	27250 (85740)		
[CrLuCr(L2) ₃] ⁹⁺	40160 (100630 sh)	27100 (68000)	⁴ A ₂ → ⁴ T ₁ + CT
	31350 (131900)	20000 (2680 sh)	⁴ A ₂ → ⁴ T ₂ + CT
	27100 (68000)		

^a Energies are given for the maximum of the band envelope in cm⁻¹ and ϵ (in parentheses) in M⁻¹ cm⁻¹; sh = shoulder, CT = charge transfer, LMCT = ligand-to-metal charge transfer.

⁴A₂ → ⁴T₂ and ⁴A₂ → ⁴T₁ transitions (in *O_h* symmetry), mixed with MLCT bands in the orange complex [CrLnCr(L2)₃]⁹⁺. Obviously, the oxidized CrLnCr complexes are stable enough to be analyzed with ESI-MS, and the resulting spectra show the exclusive formation of [CrLnCr(L2)₃]⁹⁺ characterized by a series of adducts [CrLnCr(L2)₃(CF₃SO₃)_x]^{(9-x)+} (*x* = 0–7, Fig. S5, ESI†).

Isolation and characterization of [ZnLnZn(L2)₃](CF₃SO₃)₇ and [CrLnCr(L2)₃](CF₃SO₃)₉ (Ln = La, Eu, Gd, Tb, Lu). Stoichiometric mixing of L2, Ln(CF₃SO₃)₃·*n*H₂O (Ln = La, Eu, Gd, Tb, Lu) and Zn(CF₃SO₃)₂·6H₂O (3 : 1 : 2) in dichloromethane/acetonitrile (1 : 1) followed by slow diffusion of diethyl ether yields 70–82% of microcrystalline needles of [ZnLnZn(L2)₃](CF₃SO₃)₇·*n*H₂O (Ln = La, *n* = 5; Ln = Eu, *n* = 7; Ln = Gd, *n* = 8; Ln = Tb, *n* = 6; Ln = Lu, *n* = 6, Table S1, ESI†). Replacement of Zn(CF₃SO₃)₂·6H₂O with Cr(CF₃SO₃)₂·H₂O¹³ under nitrogen atmosphere provides deep green solutions of [CrLnCr(L2)₃]⁷⁺. Air oxidation combined with the addition of ⁿBu₄N(CF₃SO₃) (2 eq.) in acetonitrile followed by fractional crystallization with diethyl ether give 73–88% of yellow microcrystalline solids, whose elemental analyses correspond to [CrLnCr(L2)₃](CF₃SO₃)₉·*n*H₂O·*p*ⁿBu₄N(CF₃SO₃) (Ln = La, *n* = 12, *p* = 0.1; Ln = Eu, *n* = 8, *p* = 0.1; Ln = Gd, *n* = 9, *p* = 0.3; Ln = Tb, *n* = 7, *p* = 0.3; Ln = Lu, *n* = 10, *p* = 0.3, Table S1, ESI†). The presence of small amounts of co-crystallized ⁿBu₄N(CF₃SO₃) in the final CrLnCr complexes has been confirmed by ¹H NMR spectroscopy. Re-dissolution of all complexes in CH₃CN at millimolar concentrations provides ¹H NMR, ESI-MS and electronic absorption spectra identical to those obtained during the investigation of the self-assembly process occurring in solution. For simplifying the rest of the discussions, the solid [ZnLnZn(L2)₃](CF₃SO₃)₇·*n*H₂O and [CrLnCr(L2)₃](CF₃SO₃)₉·*n*H₂O·*p*ⁿBu₄N(CF₃SO₃) complexes will be termed ZnLnZn and CrLnCr, respectively.

Structural aspects

X-Ray diffraction study of CrEuCr. Despite numerous attempts for re-crystallizing ZnLnZn or CrLnCr complexes, we were unable to obtain single crystals of sufficient quality for high-resolution X-ray diffraction studies. However, diffusion of di-isopropylether into a nitromethane solution of [CrEuCr(L2)₃]⁹⁺ provides prisms, for which a monoclinic unit cell with *a* = 28.79 Å, *b* = 16.63 Å, *c* = 43.86 Å, β = 104.8° and *V* = 20300 Å³ can be determined. The volume of the unit cell compares well with *V* = 25888 Å³ (monoclinic, *P*2₁/*c*, *Z* = 4) found for a closely related heterotrimetallic triple-stranded helical complex [EuLaEu(L')₃](CF₃SO₃)₉(CH₃NO₂)₉, in which the ligand L' is identical to L2, except for the replacement of the two terminal 5-methylpyridine groups with 6-(*N,N'*-diethylcarboxy)pyridine groups.²⁹

High-resolution emission spectroscopy of ZnEuZn and CrEuCr. In the absence of X-ray crystal structure data, the nature and geometry of the lanthanide coordination site in ZnLnZn and CrLnCr have been addressed by using Eu^{III} as a structural probe and high-resolution emission spectroscopy.³⁰ The excitation spectrum of ZnEuZn recorded upon monitoring the Eu(⁵D₀ → ⁷F₂) transition displays ligand-centred $\pi \rightarrow \pi^*$ absorptions, together with specific narrow peaks typical for Eu-centred intra-configurational 4f → 4f absorptions (Fig. S6a, ESI†). The high-resolution excitation profile of the Eu(⁵D₀ ← ⁷F₀) transition in ZnEuZn at 10 K shows a single and symmetrical band (full width at half height, fwhh = 19.8 cm⁻¹) indicating the existence of a single Eu^{III} coordination site in a polycrystalline material (Fig. 8a).³⁰ The energy of the Eu(⁵D₀ ← ⁷F₀) transition at 295 K ($\tilde{\nu}$ in cm⁻¹) can be correlated with the ability of the coordinated atoms to produce a nephelauxetic effect according to eqn (10)³¹

$$\tilde{\nu} = \tilde{\nu}_0 + C_{CN} \cdot \sum_i n_i \cdot \delta_i \quad (10)$$

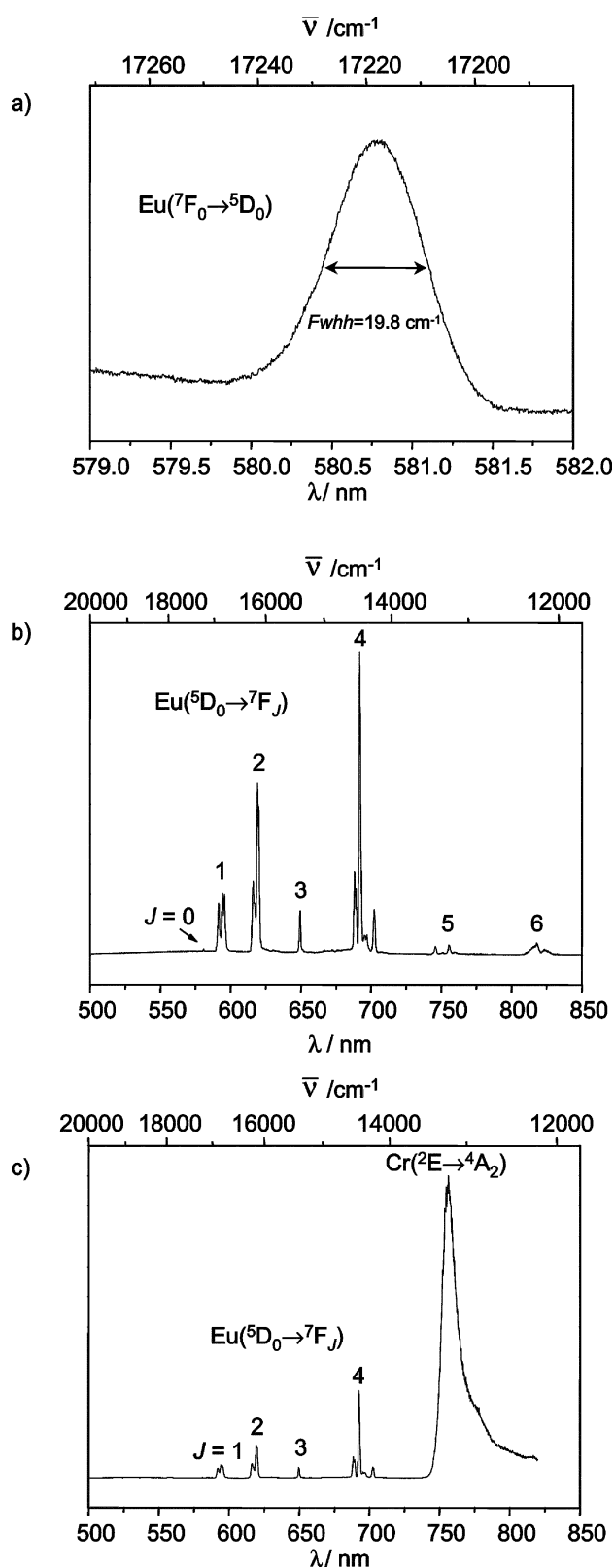


Fig. 8 a) Excitation spectrum of ZnEuZn recorded upon monitoring $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ at 10 K. b) Emission spectrum of ZnEuZn at 10 K ($\lambda_{\text{exc}} = 466$ nm). c) Emission spectrum of CrEuCr at 10 K ($\lambda_{\text{exc}} = 355$ nm).

(C_{CN} is an empirical parameter depending on the coordination number of Eu^{III} , $C_{\text{CN}} = 1$ for nine-coordinate sites, n_i is the

number of i -type atoms in the coordination sphere, δ_i is the ability of atom i to accept electronic delocalization from the metal with $\delta_i = -15.3$ cm^{-1} for heterocyclic nitrogen atoms,^{32,33} and $\tilde{\nu}_0 = 17374$ cm^{-1} is the energy of $\text{Eu}({}^7\text{F}_0 \rightarrow {}^5\text{D}_0)$ for the free ion). For the pseudo-tricapped trigonal EuN_9 site proposed in the model of ZnEuZn (Fig. 6), we calculate $\tilde{\nu} = 17236$ cm^{-1} at 295 K, which translates into $\tilde{\nu} = 17224$ cm^{-1} at 10 K (assuming the accepted 1 $\text{cm}^{-1}/24$ K dependence of the energy of the $\text{Eu}({}^5\text{D}_0 \leftarrow {}^7\text{F}_0)$ transition with temperature).³⁰ This prediction matches fairly well the experimental value found for ZnEuZn (17221 cm^{-1} at 10 K, Table 3), and those previously reported for $[\text{ZnEu}(\text{L}3)_3]^{5+}$ (17224 cm^{-1} at 10 K, Table 3)³² and $[\text{Eu}(\text{L}4)_3]^{3+}$ (17223 cm^{-1} at 10 K, Table 3),³⁴ in which the existence of the pseudo-tricapped trigonal prismatic EuN_9 site has been unambiguously evidenced in the associated X-ray crystal structures.

The detailed analysis of the crystal-field splitting of the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_J)$ ($J = 0-6$, Table 3) in the emission spectrum of ZnEuZn (Fig. 8b) is diagnostic for a distorted trigonal symmetry around Eu^{III} . The $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_0)$, which is forbidden in D_3 by symmetry-related selection rules, but allowed in C_3 point group, is extremely weak. The magnetically-allowed $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ transition is split into one singlet ($A_1 \rightarrow A_2$, 312 cm^{-1} above ${}^7\text{F}_0$, Table 3) and one doublet ($A_1 \rightarrow E$, barycentre 410 cm^{-1} above ${}^7\text{F}_0$, Table 3), with $\Delta E_{A-E} = 98$ cm^{-1} ; further splitting of the $A_1 \rightarrow E$ component ($\Delta E_{E-E} = 32$ cm^{-1}) is assigned to deviation from ideal trigonal symmetry.³⁴ Interestingly, a point charge electrostatic model predicts that the energetic separation ΔE_{A-E} between the ${}^7\text{F}_1(A)$ and ${}^7\text{F}_1(E)$ sublevels is proportional to the absolute magnitude of the second-rank crystal-field parameter $|B_0^2|$, while deviation from trigonal symmetry involves the additional second-rank crystal-field parameter $|B_2^2|$, which is proportional to the splitting of the ${}^7\text{F}_1(E)$ sublevel (ΔE_{E-E}).³⁵ We thus deduce that the symmetry of the EuN_9 site is very similar in ZnEuZn ($\Delta E_{A-E} = 98$ cm^{-1} , $\Delta E_{E-E} = 32$ cm^{-1} , Table 3), and in the analogous heterobimetallic complex $[\text{ZnEu}(\text{L}3)_3]^{5+}$ ($\Delta E_{A-E} = 94$ cm^{-1} , $\Delta E_{E-E} = 43$ cm^{-1} , Table 3),³² but slightly more distorted than in the less constrained monometallic complex $[\text{Eu}(\text{L}4)_3]^{3+}$ ($\Delta E_{A-E} = 119$ cm^{-1} , $\Delta E_{E-E} = 17$ cm^{-1} , Table 3).³⁴ The forced electric dipole $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ transition comprises two main bands, assigned to the allowed $A_1 \rightarrow E$ components in D_3 symmetry, which are further split into two components each ($\Delta E_{E-E} = 21-24$ cm^{-1} , Table 3). We could not unambiguously detect the $A_1 \rightarrow A_1$ transition, which is forbidden in D_3 -symmetry, but allowed in C_3 -symmetry, thus confirming a minor distortion from tricapped trigonal prismatic microsymmetry around Eu^{III} . Again close similarity of the crystal field splitting of the $\text{Eu}({}^7\text{F}_J)$ levels ($J = 0-6$, Table 3) observed in ZnEuZn, with those reported for $[\text{ZnEu}(\text{L}3)_3]^{5+}$ ³² and $[\text{Eu}(\text{L}4)_3]^{3+}$ ³⁴ indicates very similar EuN_9 sites in the three complexes. The long $\text{Eu}({}^5\text{D}_0)$ lifetime determined for ZnEuZn at 10 K (1.94–2.05 ms, Table 4 and Table S2, ESI†) also agrees with similar measurements performed for $[\text{ZnEu}(\text{L}3)_3]^{5+}$ (1.96(7) ms)³² and $[\text{Eu}(\text{L}4)_3]^{3+}$ (1.87(4) ms).³⁴ Moreover, the typical fast decrease of the $\text{Eu}({}^5\text{D}_0)$ lifetime with increasing temperature (Fig. S7, ESI†) is the signature of the existence of a low-lying LMCT state, which efficiently quenches $\text{Eu}({}^5\text{D}_0)$ emission at room temperature.³⁶ This effect has been investigated in details for $[\text{Eu}(\text{L}4)_3]^{3+}$,³⁶ and it arises from the coordination of nine heterocyclic nitrogen atoms to Eu^{III} , which favours the $\text{Eu}^{\text{III}} \rightarrow \text{Eu}^{\text{II}}$ reduction process.

Table 3 Energy (cm^{-1}) of the identified crystal-field sublevels of the $\text{Eu}({}^7\text{F}_J)$ manifold ($J = 1-4$) and $\text{Eu}({}^5\text{D}_0)$ in $[\text{ZnEuZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7(\text{H}_2\text{O})_7$, $[\text{ZnEu}(\text{L}3)_3](\text{ClO}_4)_3(\text{H}_2\text{O})_4$,³² $[\text{Eu}(\text{L}4)_3](\text{ClO}_4)_3$,³⁴ $[\text{ZnEu}(\text{L}1)_3](\text{CF}_3\text{SO}_3)_4(\text{ClO}_4)(\text{CH}_3\text{CN})_4$,³³ $[\text{CrEuCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{H}_2\text{O})_8$ ("Bu₄NCF₃SO₃)_{0.1} and $[\text{CrEu}(\text{L}1)_3](\text{CF}_3\text{SO}_3)_5(\text{H}_2\text{O})_4$ ¹³ as determined from excitation and emission spectra in the solid state at 10 K; ${}^7\text{F}_0$ is taken as the origin

Compound	$[\text{ZnEuZn}(\text{L}2)_3]^{7+}$	$[\text{ZnEu}(\text{L}3)_3]^{5+}$	$[\text{Eu}(\text{L}4)_3]^{3+}$	$[\text{ZnEu}(\text{L}1)_3]^{5+}$	$[\text{CrEuCr}(\text{L}2)_3]^{9+}$	$[\text{CrEu}(\text{L}1)_3]^{6+}$
Site	EuN_9	EuN_9	EuN_9	EuN_6O_3	EuN_9	EuN_6O_3
Ref.	This work	32	34	33	This work	13
${}^7\text{F}_0$	0	0	0	0	0	0
${}^7\text{F}_1$	312	315	300	294	326	320
	394	387	410	411	389	368
	426	430	427	432	423	444
${}^7\text{F}_2$	990	987	986	984	989	980
	1011	1027	1009	1002	1015	997
	1071	1067	1077	1043	1068	1053
	1095	1097	1089	1085	1083	1113
${}^7\text{F}_3$	1825	1825	1819	1824	1824	1829
${}^7\text{F}_4$	2692	2694	2693	2706	2692	2697
	2714	2717	2715	2717	2713	2724
	2772	2774	2754	2799	2780	2806
	2841	2843	2785	2860	2838	2846
	2872	2874	2876	2888	2869	2894
	2980	2981	2981	2990	2981	2983
${}^5\text{D}_0$	17221	17224	17223	17220	17218	17216

Table 4 Emission $\text{Eu}({}^5\text{D}_0)$ lifetimes and associated rate constants for the complexes $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$, $[\text{CrEuCr}(\text{L}2)_3]^{9+}$, $[\text{ZnEu}(\text{L}1)_3]^{5+}$,³³ and $[\text{CrEu}(\text{L}1)_3]^{6+}$ ¹³

Compound	T/K	$\tau_{\text{obs}}^{\text{MEuM}}/\text{ms}$	$k_{\text{obs}}^{\text{MEuM}}/\text{ms}^{-1}$	$\eta_{\text{global}}^{\text{CrEuCr}^a}$ (%)	$k_{\text{ET}}^{\text{Eu,Cr}^b}/\text{ms}^{-1}$	$R_0^{\text{EuCr}^c}/\text{\AA}$	Reference
$[\text{ZnEuZn}(\text{L}2)_3]^{7+}$	10	1.96(1)	0.510(3)				This work
	295	0.69(4)	1.45(9)				This work
	10^d	2.21(5)	0.45(1)				This work
	295^d	1.48(1)	0.680(5)				This work
$[\text{CrEuCr}(\text{L}2)_3]^{9+}$	10	0.20(1)	5.0(3)	90(4)	2.2(1)	11.9(2)	This work
	295	0.10(1)	10(1)	86(8)	4.3(4)	11.2(4)	This work
	10^d	0.24(1)	4.2(2)	89(6)	1.9(1)	11.8(2)	This work
	295^d	0.076(1)	13.2(2)	95(8)	6.2(5)	13.5(3)	This work
Compound	T/K	$\tau_{\text{obs}}^{\text{EuM}}/\text{ms}$	$k_{\text{obs}}^{\text{EuM}}/\text{ms}^{-1}$	η^{EuCr} (%)	$k_{\text{ET}}^{\text{Eu,Cr}^b}/\text{ms}^{-1}$	$R_0^{\text{EuCr}^c}/\text{\AA}$	Reference
$[\text{EuZn}(\text{L}1)_3]^{5+}$	10	2.53(1)	0.400(2)				33
	295	1.67(2)	0.60(2)				33
$[\text{CrEu}(\text{L}1)_3]^{6+}$	10	0.55(4)	1.8(1)	78(5)	1.42(9)	11.5(1)	13
	295	0.59(1)	1.69(3)	65(4)	1.10(7)	10.3(1)	13

^a Calculated with eqn (14). ^b Calculated with eqn (17). ^c Calculated with eqn (19). ^d $10^{-3} \text{ mol dm}^{-3}$ in acetonitrile solution.

For CrEuCr, the excitation spectrum recorded upon monitoring the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ transition mainly shows the ligand-centred $\pi \rightarrow \pi^*$ absorption as previously described for ZnEuZn (Fig. S6b, ESI†). When the analysis wavelength is set on the $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ transition, the excitation profile is completed by direct sensitization of the spin-allowed Cr-centred ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition at $21\,500 \text{ cm}^{-1}$ (Fig. S6b, ESI†). Upon excitation of the $\pi \rightarrow \pi^*$ transitions, the emission spectrum displays the narrow $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_J)$ transitions ($J = 0-4$), together with $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ transitions, the latter masking the weaker $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_J)$ ($J = 5-6$) emission bands (Fig. 8c). Both the energy (13245 cm^{-1} at 10 K, Table S2, ESI†) of the $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ transition and the associated $\text{Cr}({}^2\text{E})$ lifetime (2.08–2.10 ms, Table S2, ESI†) are comparable with those reported for $[\text{CrEu}(\text{L}1)_3]^{6+}$ (13301 cm^{-1} at 10 K, $\tau = 3.46 \text{ ms}$),¹³ in agreement with the existence of similar terminal trigonally distorted $[\text{Cr}(\text{2-benzimidazol-pyridine})_3]^{3+}$ chromophores in the bi- and trimetallic complexes. The crystal-field splitting of the Eu-centred transitions in CrEuCr is almost identical to that obtained for ZnEuZn

(Table 3), thus pointing to very similar EuN_9 coordination sites in both trimetallic complexes (from the splitting of the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ transition, we calculate $\Delta E_{\text{A-E}} = 80 \text{ cm}^{-1}$, $\Delta E_{\text{E-E}} = 34 \text{ cm}^{-1}$, Table 3). It is worth noting that Cr-centred excitation at 21470 cm^{-1} ($\text{Cr}({}^4\text{A}_2 \rightarrow {}^4\text{T}_2)$) results in the exclusive detection of the $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ emission, in line with the absence of intramolecular $\text{Cr} \rightarrow \text{Eu}$ energy transfer processes. However, the reverse situation is found upon Eu-centred excitation (*i.e.* observation of the luminescence of both Eu-centred and Cr-centred emission), which implies the existence of a partial $\text{Eu} \rightarrow \text{Cr}$ energy transfer (Fig. 10, *vide infra*) responsible for the reduced $\text{Eu}({}^5\text{D}_0)$ lifetime measured in CrEuCr ($\tau = 0.20\text{--}0.24 \text{ ms}$ at 10 K, Tables 4 and S2, ESI†). We can therefore safely conclude from the X-ray diffraction and high-resolution emission studies that (i) ZnEuZn and CrEuCr exhibit very similar structures, (ii) the terminal d-block ions are pseudo-octahedrally coordinated by three bidentate 2-benzimidazolpyridine units and (iii) europium is encapsulated within a slightly distorted tricapped trigonal prismatic EuN_9 site provided by the three wrapped central

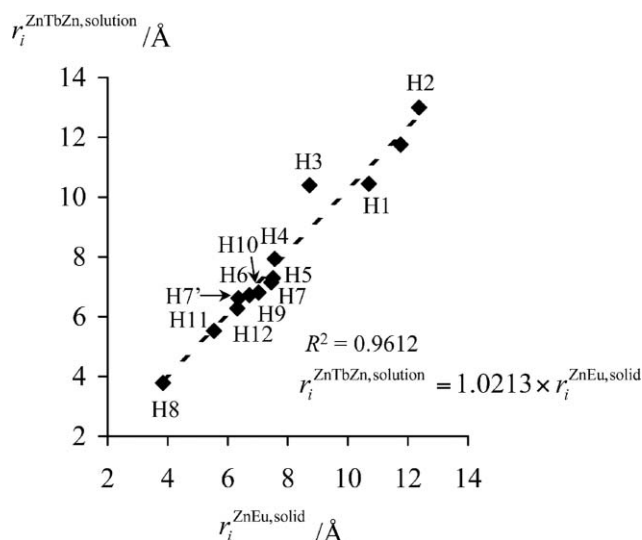


Fig. 9 Correlation between Ln...Hi distances observed in the crystal structure of [ZnEu(L1)₃]⁵⁺,³³ and those determined by paramagnetic ¹H NMR in acetonitrile with eqn (13) for [ZnTbZn(L2)₃]⁷⁺ (H6 is used as a reference, see text).

tridentate 2,6-bis(benzimidazol-2-yl)pyridine units, as found in the *D*₃-symmetrical complex [Eu(L4)₃]³⁺. All these characteristics are compatible with the structural model shown in Fig. 6.

¹H NMR spectroscopy of ZnLnZn in solution (Ln = La, Eu, Tb, Lu, Y). Although the emission spectra become broader in solution, the conservation of both crystal-field splitting patterns and lifetimes for Eu- and Cr-centred luminescence, observed when dissolving microcrystals of ZnEuZn in acetonitrile (10^{−3} mol dm^{−3}, Table S2, ESI†), demonstrates that the solid-state structure is maintained in solution, as previously established for [ZnEu(L3)₃]⁵⁺³² and [ZnEu(L1)₃]⁵⁺³³. The ¹H NMR spectra of [ZnLnZn(L2)₃]⁷⁺ (Ln = La, Eu, Tb, Lu, Y) systematically show eleven aromatic C–Hi signals (*i* = 1–6 and 8–12, numbering in Fig. 4), together with AB spin systems for the diastereotopic methylene protons H7, H7', which implies dynamically averaged *D*₃-symmetry for the trimetallic complexes in solution (Table 1 and Fig. 4d). The unusual shielding of H6 and H8 in the diamagnetic complexes [ZnLnZn(L2)₃]⁷⁺ (Ln = La, Lu, Y, Table 1) is diagnostic for the wrapping of the three strands about the metal ions, which puts these protons in the shielding region of the benzimidazole ring of an adjacent strand (Fig. 6), as previously established for

the analogous bimetallic triple-helical complexes [ZnEu(L3)₃]⁵⁺ ($\delta_{\text{H6}} = 5.02$ ppm, $\delta_{\text{H8}} = 5.42$ ppm),³² and [ZnEu(L1)₃]⁵⁺ ($\delta_{\text{H6}} = 5.34$ ppm, $\delta_{\text{H8}} = 5.44$ ppm).³³ In order to obtain intramolecular Ln...Hi distances in [ZnLnZn(L2)₃]⁷⁺, we have resorted to the extra nuclear relaxation induced by the lanthanide electronic spin. For fast-relaxing paramagnetic lanthanides (Ln = Ce–Yb, except Gd), the increase of the longitudinal nuclear relaxation rate for a proton Hi

$$1/T_{\text{li}}^{\text{para}} = 1/T_{\text{li}}^{\text{exp}} - 1/T_{\text{li}}^{\text{dia}} \quad (11)$$

is dominated by dipolar electron–nucleus interactions modelled with eqn (12), whereby the constants have their usual meaning, μ_{eff} is the electronic effective magnetic moment, H_0 is the magnetic field, τ_r and τ_e are the rotational and electronic correlation times, and r_i is the Ln...Hi distance.²⁴

$$\begin{aligned} \frac{1}{T_{\text{li}}^{\text{para}}} &= \frac{1}{T_{\text{li}}^{\text{transient}}} + \frac{1}{T_{\text{li}}^{\text{static}}} \\ &= \frac{4}{3} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_i \mu_{\text{eff}}^2 \beta^2}{r_i^6} \tau_e + \frac{6}{5} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_i^2 \mu_{\text{eff}}^4 \beta^4 H_0^2}{r_i^6 (3kT)^2} \left(\frac{\tau_r}{1 + \omega_i^2 \tau_r^2} \right) \\ &= E_i \left(\frac{1}{r_i^6} \right) \end{aligned} \quad (12)$$

Since both transient and static (*i.e.* Curie spin) dipolar contributions depend on r_i^{-6} for a given complex at fixed temperature, we deduce that $1/T_{\text{li}}^{\text{para}}$ is simply proportional to r_i^{-6} with a scaling factor E_i , which is maximum for lanthanide cations possessing a large magnetic momentum (μ_{eff} is maximum) at high magnetic fields (H_0 is maximum). When a reference Ln...Hi distance, r_{ref} , is accessible in a lanthanide paramagnetic complex, all the remaining Ln...Hi distances can be easily determined from the measurement of the paramagnetic longitudinal relaxation rates with eqn (13).²⁴

$$r_i = r_{\text{ref}} \cdot \sqrt[6]{T_{\text{li}}^{\text{para}}/T_{\text{ref}}^{\text{para}}} \quad (13)$$

Because Tb^{III} complexes possess large electronic magnetic momenta,²⁴ we have focused on [ZnTbZn(L2)₃]⁷⁺, for which the experimental characteristic longitudinal relaxation times $T_{\text{li}}^{\text{exp}}$ have been determined by ¹H NMR spectroscopy (Table S3, ESI†). After correcting for the diamagnetic contribution $T_{\text{li}}^{\text{dia}}$ measured in [ZnLuZn(L2)₃]⁷⁺ (eqn (11) and Table S3, ESI†), the resulting paramagnetic contributions $T_{\text{li}}^{\text{para}}$ have been used to compute r_i with eqn (13). Since the diamagnetic shifts of H6 are almost identical in [ZnLu(L1)₃]⁵⁺, [ZnLu(L3)₃]⁵⁺ and in [ZnLuZn(L2)₃]⁷⁺ despite their extreme sensitivity to the exact wrapping of the strands, we

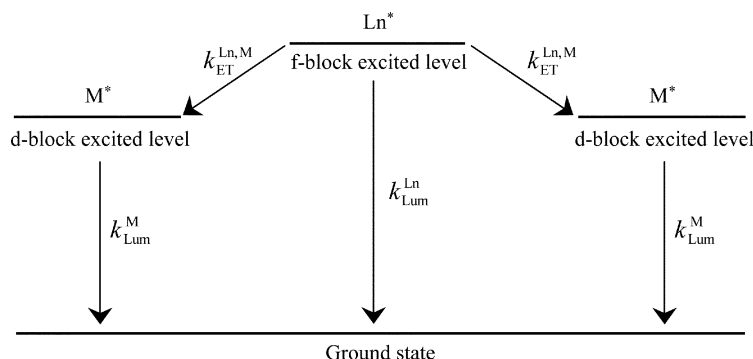


Fig. 10 Kinetic model for the deactivation and communication of f-block and d-block-centred excited levels in [MLnM(L2)₃]⁹⁺ (M = Cr, Ln = Eu, Tb).

can safely conclude that H6 occupy very similar positions in the three complexes, and the $\text{Eu} \cdots \text{H6}$ distance observed in the crystal structure of $[\text{ZnEu}(\text{L1})_3](\text{CF}_3\text{SO}_3)_4(\text{ClO}_4)(\text{CH}_3\text{CN})_4$ has been used as reference ($r_{\text{ref}} = 6.7 \text{ \AA}$).³³ The $\text{Tb} \cdots \text{Hi}$ distances calculated for $[\text{ZnTbZn}(\text{L2})_3]^{7+}$ with eqn (13) are collected in Table S3 ($i = 1\text{--}5$ and $8\text{--}2$, ESI†), and they closely match those found in the crystal structure of $[\text{ZnEu}(\text{L1})_3]^{5+}$ (Fig. 9). We conclude that the triple-helical organization of the strands about the $\text{Zn} \cdots \text{Ln}$ axis is very similar in $[\text{ZnEu}(\text{L1})_3]^{5+}$ and in $[\text{ZnTbZn}(\text{L2})_3]^{7+}$, which further justifies the model proposed in Fig. 6 for the heterotrimetallic complexes $[\text{MLnM}(\text{L2})_3]^{7/9+}$ ($\text{M} = \text{Cr}, \text{Ln}$). Moreover, the crystal structure of $[\text{ZnEu}(\text{L1})_3]^{5+}$,³³ which is almost superimposable with that of $[\text{CrEu}(\text{L1})_3]^{6+}$,¹³ can be used as a reliable structural model for the ‘asymmetric unit’ of the D_3 -symmetrical trimetallic complexes $[\text{MLnM}(\text{L2})_3]^{7/9+}$ ($\text{M} = \text{Cr}, \text{Ln}$).

Functional aspects

Indirect sensitization processes involving ligand-to-metal energy transfer processes in ZnLnZn and CrLnCr ($\text{Ln} = \text{Eu}, \text{Gd}$). In the absence of $\text{L2} \rightarrow \text{metal}$ transfer in ZnGdZn (*i.e.* neither Zn^{II} nor Gd^{III} possess accessible excited states for accepting energy from $\text{L}(\pi\pi^*)$), the coordinated tritopic ligand L2 shows a broad and poorly structured emission band in the $20\,800\text{--}16\,000 \text{ cm}^{-1}$ range ($\tilde{\nu}_{\text{max}} = 18\,900 \text{ cm}^{-1}$). Its associated lifetime is bi-exponential with $\tau_1 = 2.45 \text{ ms}$ (86%) and $\tau_2 = 0.49 \text{ ms}$ (14%), which is typical for emissions arising from the $\text{L2}({}^3\pi\pi^*)$ excited states located on different parts of the ligand, due to the isolating effects of the methylene spacers.^{32,33} At 295 K, efficient thermally-activated non-radiative processes reduce $\text{L2}({}^3\pi\pi^*)$ lifetimes to $\tau_1 = 42 \text{ }\mu\text{s}$ (64%) and $\tau_2 = 6 \text{ }\mu\text{s}$ (36%). Upon replacement of Zn^{II} with Cr^{III} in CrGdCr , the $\text{L2}({}^3\pi\pi^*)$ band is shifted by approximately 5500 cm^{-1} toward higher energy ($26\,000\text{--}20\,000 \text{ cm}^{-1}$ range, $\tilde{\nu}_{\text{max}} = 24\,450 \text{ cm}^{-1}$ at 10 K), while its lifetimes are only marginally reduced with respect to those measured in ZnGdZn (Table S4, ESI†). This suggests that (i) the bidentate binding units co-ordinated to the d-block ion strongly contributes to the ligand-centred ${}^3\pi\pi^*$ emission and (ii) the $\text{L2}({}^3\pi\pi^*) \rightarrow \text{Cr}^{\text{III}}$ transfer is poorly efficient. Conversely, only a faint residual ligand-centred ${}^3\pi\pi^*$ emission is detected in the emission spectra of ZnEuZn and CrEuCr , which points to an efficient $\text{L2}({}^3\pi\pi^*) \rightarrow \text{Eu}^{\text{III}}$ sensitization process, as similarly reported for $[\text{ZnEu}(\text{L3})_3]^{5+}$,³² $[\text{ZnEu}(\text{L1})_3]^{5+}$ ³³ and $[\text{CrEu}(\text{L1})_3]^{6+}$.¹³ We conclude that the energy of $\text{L2}({}^3\pi\pi^*)$ in the complexes MLnM is more adequate for resonant energy transfer processes with Eu^{III} than with Cr^{III} .

Cr-centred luminescence in $[\text{CrLnCr}(\text{L2})_3](\text{CF}_3\text{SO}_3)_9$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$). Excitation through the ligand-centred $\pi\pi^*$ ($\tilde{\nu}_{\text{exc}} = 28170 \text{ cm}^{-1}$) or *via* Cr^{III} -centred ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ ($\tilde{\nu}_{\text{exc}} = 20492 \text{ cm}^{-1}$, Fig. S6d†) in CrGdCr produces identical emission spectra displaying the characteristic $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ transition at $13\,245 \text{ cm}^{-1}$, combined with weak Stokes phonon side bands ($13\,100\text{--}12\,900 \text{ cm}^{-1}$, Fig. S8, ESI†), in good agreement with a similar behaviour reported for $[\text{CrGd}(\text{L3})_3]^{6+}$ ($13\,301 \text{ cm}^{-1}$).³³ The $\text{Cr}({}^2\text{E})$ lifetime at 10 K is long ($2.27(1) \text{ ms}$, Table S2, ESI†) and points to only minor non-radiative processes affecting the Cr^{III} -centred emission. However, both intensity (Fig. S8, ESI†) and lifetime of the $\text{Cr}({}^2\text{E})$ emission in CrGdCr dramatically decrease at higher temperature ($\tau_{295 \text{ K}} = 0.031 \text{ ms}$, Table S2, ESI†), which is tentatively attributed to thermally-activated energy migration processes, as previously

discussed for $[\text{CrGd}(\text{L1})_3]^{6+}$.^{13,37} Moreover, the maximum of the $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ emission band shifts from $13\,245 \text{ cm}^{-1}$ at 10 K to $13\,316 \text{ cm}^{-1}$ at 295 K ($\Delta E = 71 \text{ cm}^{-1}$, Fig. S8, ESI†), a change in energy much larger than $\Delta E = 15 \text{ cm}^{-1}$ expected for the splitting of the $\text{Cr}({}^2\text{E})$ level by trigonal symmetry, which accounts for the hot band emission in the model complex $[\text{Cr}(2,2'\text{-bipyridine})_3]^{3+}$.^{37b} We thus suspect that the long-lived luminescence observed at 10 K indeed originates from pseudo-octahedral CrN_6 chromophores found in CrGdCr . At room temperature, fast energy migration processes combined with the existence of small amounts of killer sites provided by minor crystal defects and/or photochemical degradations are responsible for the short shifted $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ emission. For CrEuCr and CrTbCr , the long-lived Cr^{III} -centred emission is strictly maintained at 10 K, whatever the origin of the sensitization process, *i.e.* *via* ligand-centred or Ln -centred excited states (Fig. 8b, Table S2, ESI†), consistent with no $\text{Cr} \rightarrow \text{Eu}$ energy transfer.

Intramolecular $\text{Ln} \rightarrow \text{Cr}$ communication in CrLnCr ($\text{Ln} = \text{Eu}, \text{Tb}$). Upon irradiation of the ligand-centred $\pi\pi^*$ excited states at $28\,170 \text{ cm}^{-1}$ in CrEuCr , we observe the dual metal-centred emission of $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_J)$ ($J = 0\text{--}4$) and $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ (Fig. 8c). At 10 K, the deep red Cr-centred emission dominates (89% of the total luminescence), but reduces to 68% at 295 K. Compared with ZnEuZn , the $\text{Eu}({}^5\text{D}_0)$ lifetime in CrEuCr is dramatically shortened (Table 4) as a result of the occurrence of $\text{Eu} \rightarrow \text{Cr}$ energy transfer processes. The intramolecular origin of the latter energy transfers is demonstrated by related dynamic measurements obtained for $[\text{CrEuCr}(\text{L2})_3]^{9+}$ in acetonitrile, which closely mirror those obtained in the solid state (Table 4). We can therefore analyse the $\text{Eu} \rightarrow \text{Cr}$ intermetallic communication according to the simple scheme shown in Fig. 10, and for which the global efficiency of the energy transfer processes in CrEuCr is given in eqn (14).

$$\eta_{\text{global}}^{\text{CrLnCr}} = \frac{2k_{\text{ET}}^{\text{Ln,Cr}}}{k_{\text{Lum}}^{\text{Ln}} + 2k_{\text{ET}}^{\text{Ln,Cr}}} \quad (14)$$

Assuming that $k_{\text{Lum}}^{\text{Eu}}$ is identical in ZnEuZn and CrEuCr , we can write

$$k_{\text{Lum}}^{\text{Eu}} = k_{\text{Lum}}^{\text{ZnEuZn}} = (\tau_{\text{obs}}^{\text{ZnEuZn}})^{-1} \quad (15)$$

$$k_{\text{Lum}}^{\text{Eu}} + 2k_{\text{ET}}^{\text{Eu,Cr}} = k_{\text{obs}}^{\text{CrEuCr}} = (\tau_{\text{obs}}^{\text{CrEuCr}})^{-1} \quad (16)$$

Substituting eqn (15) into eqn (16) allows the calculation of the rate of intermetallic energy transfer (eqn (17)), while parallel substitution of eqn (15) and (16) into eqn (14) gives the well-known eqn (18), which is commonly used for estimating the efficiency of energy transfer processes.³⁰

$$k_{\text{ET}}^{\text{Eu,Cr}} = \frac{k_{\text{obs}}^{\text{CrEuCr}} - k_{\text{obs}}^{\text{ZnEuZn}}}{2} = \frac{(\tau_{\text{obs}}^{\text{CrEuCr}})^{-1} - (\tau_{\text{obs}}^{\text{ZnEuZn}})^{-1}}{2} \quad (17)$$

$$\eta_{\text{global}}^{\text{CrEuCr}} = 1 - \frac{\tau_{\text{obs}}^{\text{CrEuCr}}}{\tau_{\text{obs}}^{\text{ZnEuZn}}} \quad (18)$$

From the experimental lifetimes measured for ZnEuZn and CrEuCr , we calculate with eqn (18) that $\eta_{\text{global}}^{\text{CrEuCr}} \approx 90\%$ at 10 and 295 K, in the solid state and in solution (Table 4). As expected from the existence of two Cr^{III} acceptors in CrEuCr , the contribution of the intramolecular $\text{Eu} \rightarrow \text{Cr}$ energy transfers to the quenching of $\text{Eu}({}^5\text{D}_0)$ luminescence is larger than that previously reported for $[\text{CrEu}(\text{L1})_3]^{6+}$ ($\eta^{\text{CrEu}} = 65\text{--}78\%$, Table 4).¹³ The individual

rate constants $k_{\text{ET}}^{\text{Eu,Cr}}$ in CrEuCr and in $[\text{CrEu}(\text{L}1)_3]^{6+}$ can be directly compared in order to quantify the relative efficiency of the $\text{Eu} \rightarrow \text{Cr}$ communication in the two complexes. From eqn (17), we calculate $k_{\text{ET}}^{\text{Eu,Cr}}(\text{CrEuCr}) > k_{\text{ET}}^{\text{Eu,Cr}}(\text{CrEu})$,¹³ thus leading to the ratios $k_{\text{ET}}^{\text{Eu,Cr}}(\text{CrEuCr})/k_{\text{ET}}^{\text{Eu,Cr}}(\text{CrEu}) = 1.6(2)$ at 10 K and $k_{\text{ET}}^{\text{Eu,Cr}}(\text{CrEuCr})/k_{\text{ET}}^{\text{Eu,Cr}}(\text{CrEu}) = 3.9(6)$ at 295 K (Table 4). Modelling the $\text{Eu} \rightarrow \text{Cr}$ energy transfer with a simple dipole–dipole mechanism (eqn 19)¹² is reasonable according to (i) the large $\text{Eu} \cdots \text{Cr}$ intermetallic separation measured in the crystal structure of $[\text{CrEu}(\text{L}1)_3]^{6+}$ ($R^{\text{EuCr}} = 9.32 \text{ \AA}$),¹³ which is expected to be very similar in CrEuCr, and (ii) the minute expansion of the 4f orbitals.³⁰

$$\eta_{\text{single}}^{\text{CrEuCr}} = \frac{k_{\text{ET}}^{\text{Eu,Cr}}}{k_{\text{Lum}}^{\text{Eu}} + k_{\text{ET}}^{\text{Eu,Cr}}} = \frac{1}{1 + (R^{\text{EuCr}}/R_0^{\text{EuCr}})^6} \quad (19)$$

Taking the rate constants collected in Table 4, we calculate with eqn (19) the critical distances for 50% energy transfer $R_0^{\text{EuCr}} = 11.2\text{--}13.5 \text{ \AA}$, which are in the nanometric range (Table 4). Theoretically, R_0^{EuCr} can be estimated with eqn (20), in which κ^2 is an orientation factor having an isotropic limit of $2/3$, ϕ_{F} is the quantum yield of the donor luminescence in the absence of acceptor (*i.e.* the europium quantum yield measured in ZnEuZn), n is the refractive index of the intermetallic medium and J is the overlap integral between the emission spectrum of the donor (Eu^{III}) and the absorption spectrum of the acceptor (Cr^{III}) in $\text{cm}^6 \text{ mol}^{-1}$.³⁰

$$(R_0^{\text{EuCr}})^6 = 8.75 \times 10^{-25} \times \kappa^2 \times \phi_{\text{L}} \times n^{-4} \times J [\text{cm}^6] \quad (20)$$

Surprisingly, the critical distances R_0^{EuCr} measured in the trimetallic CrEuCr complex are marginally larger than those found in the bimetallic analogue $[\text{CrEu}(\text{L}1)_3]^{6+}$ (Table 4), despite the considerable decrease of the donor quantum yield when going from a EuN_6O_3 site in $[\text{ZnEu}(\text{L}1)_3]^{5+}$ ($\phi_{\text{L}} = 0.34\%$, $10^{-4} \text{ mol dm}^{-3}$ in acetonitrile at 293 K)¹³ to the less luminescent EuN_9 site in $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$ ($\phi_{\text{L}} = 0.002\%$, $10^{-4} \text{ mol dm}^{-3}$ in acetonitrile at 293 K). This ratio $\phi_{\text{L}}^{\text{Eu}}(\text{EuZnEu})/\phi_{\text{L}}^{\text{Eu}}(\text{EuZn}) = 0.0059$ translates into $R_0^{\text{EuCr}}(\text{CrEuCr})/R_0^{\text{EuCr}}(\text{CrEu}) = 0.42$ by using eqn (20). The experimental data $R_0^{\text{EuCr}}(\text{CrEuCr})/R_0^{\text{EuCr}}(\text{CrEu}) = 1.03(2)$ at 10 K and 1.08(3) at 295 K (Table 4) imply that $\kappa^2 \times n^{-4} \times J(\text{CrEuCr})/\kappa^2 \times n^{-4} \times J(\text{CrEu}) \approx 2.5$. Since both the orientation factor κ^2 and the local refractive index separating Eu^{III} and Cr^{III} can be reasonably assumed to be similar in the two analogous triple-stranded helicates, we tentatively assign this compensation effect to an increase of the overlap integral J in CrEuCr. To understand this, one has to realize that the Eu^{III} emission intensity is quite small in both bimetallic and trimetallic helicates, so that minute changes in the crystal-field splitting or in the transition probabilities associated with the various sub-levels, may generate large changes in J .

When Tb^{III} is used as the donor in CrTbCr , we calculate $\eta_{\text{global}}^{\text{CrTbCr}} \geq 99.9\%$ with eqn (18) at 10 K (lifetimes taken from Table S2, ESI†), which points to a quantitative $\text{Tb} \rightarrow \text{Cr}$ energy transfer process, as previously reported for $[\text{CrTb}(\text{L}1)_3]^{6+}$.¹³ An efficient thermally-activated $\text{Tb}({}^4\text{D}_4) \rightarrow {}^3\pi\pi^*$ energy back transfer operates in CrTbCr and ZnTbZn, as previously described for $[\text{ZnTb}(\text{L}3)_3]^{5+}$,³² $[\text{ZnTb}(\text{L}1)_3]^{5+}$,³³ and $[\text{Tb}(\text{L}4)_3]^{3+}$,³⁴ which prevents the detection of residual Tb^{III} -centred emissions at room temperature.

Conclusion

The idea of exploiting the chiral macrobicyclic cavity produced by the wrapping of the three ligand strands about two terminal pseudo-octahedral d-block cations in a triple helicate was suggested in 1997,³⁸ and experimentally demonstrated by Albrecht and co-workers for Ti^{IV} and Ga^{III} metallocryptates, in which negatively charged oxygen atoms can bind alkali cations in the internal cavity.³⁹ In parallel work, Chaudhuri and collaborators introduced the concept of using inert pseudo-octahedral Cr^{III} stoppers for producing kinetically stable macrobicyclic cavities, in which labile alkaline earth and 3d-block cations in different oxidation states can be encapsulated.⁴⁰ However, to the best of our knowledge, the complexes $[\text{CrLnCr}(\text{L}2)_3]^{9+}$ represent the first examples, in which both aspects are combined to produce a triple-helical nine-coordinate macrobicyclic cavity adapted for the complexation of labile trivalent lanthanides. Interestingly, the seminal contributions of Albrecht³⁹ and Chaudhuri⁴⁰ focused on negatively charged ligand strands, which limit short-distance intermetallic repulsion thanks to charge compensation. In $[\text{ZnLnZn}(\text{L}2)_3]^{7+}$ and $[\text{CrLnCr}(\text{L}2)_3]^{9+}$, the intermetallic separation is large enough to allow the quantitative formation of the highly charged complexes in solution at millimolar concentrations, that is we are able to kinetically control the incorporation of Ln^{III} ions in self-assembled macrobicyclic cavities. Moreover, the replacement of the terminal N_2O tridentate binding site in L1 with a central N_3 binding unit in L2 for complexing Ln^{III} was initially thought to be deleterious for both stability constants⁴¹ and Ln^{III} -centred luminescence ($\text{Ln} = \text{Eu}, \text{Tb}$).³⁶ We indeed detect a considerable decrease of the Eu-centred luminescent quantum yield in $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$ compared with $[\text{ZnEu}(\text{L}1)_3]^{5+}$, but an unexpected compensation effect assigned to an increase of the spectral overlap integral leads to sizeable intramolecular intermetallic communication and light-conversion. In future work, we will address the potential use of convergent $\text{Cr} \rightarrow \text{Ln}$ transfers for efficiently sensitizing NIR emitters ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$) while simultaneously lengthening their apparent lifetime.

Experimental

Solvents and starting materials

These were purchased from Fluka AG (Buchs, Switzerland) and used without further purification unless otherwise stated. The segmental ligand L2²¹ and the chromium(II) salt $\text{Cr}(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ ¹³ were obtained according to literature procedures. The triflate salts $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Lu}, \text{Y}$) were prepared from the corresponding oxides (Rhodia, 99.99%) and dried according to published procedures.⁴² The Ln content of the solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.⁴³

Preparation of the complexes $[\text{ZnLnZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, n = 5$; $\text{Ln} = \text{Eu}, n = 7$; $\text{Ln} = \text{Gd}, n = 8$; $\text{Ln} = \text{Tb}, n = 6$; $\text{Ln} = \text{Lu}, n = 6$)

A solution of $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Lu}$; 0.017 mmol) in acetonitrile (2 cm^3) was added to a solution of L2 (41.3 mg, 0.051 mmol) in acetonitrile–dichloromethane

(12 cm³ : 12 cm³). After stirring for 2 h at rt, a solution of Zn(CF₃SO₃)₂·6H₂O (12.3 mg, 0.034 mmol) was added in acetonitrile (2 cm³). After stirring for 1 h at rt, the solvent was evaporated and the pale yellow residue was dissolved in a minimum of acetonitrile. Slow diffusion of diethyl ether (3 days) provided 70–82% of microcrystalline needles of [ZnLnZn(L2)₃](CF₃SO₃)₉·nH₂O (Ln = La, n = 5; Ln = Eu, n = 7; Ln = Gd, n = 8; Ln = Tb, n = 6; Ln = Lu, n = 6). All the complexes were characterized by their IR spectra and gave satisfactory elemental analyses (Table S1, ESI†).

Preparation of the complexes [CrLnCr(L2)₃](CF₃SO₃)₉·nH₂O·pⁿBu₄N(CF₃SO₃) (Ln = La, n = 12, p = 0.1; Ln = Eu, n = 8, p = 0.1; Ln = Gd, n = 9, p = 0.3; Ln = Tb, n = 7, p = 0.3; Ln = Lu, n = 10, p = 0.3)

A solution of Ln(CF₃SO₃)₃·nH₂O (Ln = La, Eu, Gd, Tb, Lu; 0.017 mmol) in acetonitrile (2 cm³) was added to a solution of L2 (41.3 mg, 0.051 mmol) in acetonitrile/dichloromethane (12 cm³ : 12 cm³). After stirring for 2 h at rt, the solvent was removed under vacuum and the residue transferred into a glove box under an inert atmosphere. Dissolution into degassed acetonitrile (25 cm³), followed by the addition of a deep blue solution of Cr(CF₃SO₃)₂·H₂O (12.6 mg, 0.034 mmol) in acetonitrile (1 cm³) produced a deep green mixture, which was stirred for one night under an inert atmosphere. ⁿBu₄N(CF₃SO₃) (13.3 mg, 0.034 mmol) was added, followed by slow bubbling of air for two hours. The solution turned orange, the solvent was removed, and the solid residue dissolved in acetonitrile. Fractional crystallization by using slow diffusion of diethyl ether provided 73–88% of orange microcrystalline powders of [CrLnCr(L2)₃](CF₃SO₃)₉·nH₂O·pⁿBu₄N(CF₃SO₃) (Ln = La, n = 12, p = 0.1; Ln = Eu, n = 8, p = 0.1; Ln = Gd, n = 9, p = 0.3; Ln = Tb, n = 7, p = 0.3; Ln = Lu, n = 10, p = 0.3, Table S1, ESI†). All the complexes were characterized by their IR spectra and gave satisfactory elemental analyses (Table S1, ESI†).

Spectroscopic and analytical measurements

Electronic spectra in the UV-Vis region were recorded at 293 K from solutions in MeCN with a Perkin-Elmer Lambda 900 spectrometer using quartz cells of 0.1 and 1 mm path length. Spectrophotometric titrations were performed with a J & M diode array spectrometer (Tidas series) connected to an external computer. In a typical experiment, 50 cm³ of L2 in acetonitrile/chloroform (1 : 1; 2 × 10^{−4} mol dm^{−3}) were titrated at 20 °C with an equimolar solution of Ln(CF₃SO₃)₃·nH₂O (10^{−3} mol dm^{−3}) or Zn(CF₃SO₃)₂·nH₂O (10^{−3} mol dm^{−3}) in acetonitrile/chloroform (1 : 1) under an inert atmosphere. After each addition of 0.20 ml, the absorbance was recorded using Hellma optrodes (optical path length 0.1 cm) immersed in the thermostated titration vessel and connected to the spectrometer. Mathematical treatment of the spectrophotometric titrations was performed with factor analysis²⁶ and with the SPECFIT program.²⁷ IR spectra were obtained from KBr pellets with a FT-IR Perkin-Elmer Spectrum One. ¹H NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer. Chemical shifts are given in ppm with respect to TMS. The determination of longitudinal relaxation times (T₁) used the inversion–recovery technique. Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded on a Finnigan SSQ7000 instrument. The equipment and experimental proce-

dures for luminescence measurements in the visible range were published previously.⁴⁴ Excitation of the finely powdered samples was achieved by a 450 W xenon high-pressure lamp coupled with a monochromator or a Coherent Innova Argon laser. The emitted light was analyzed at 90° with a Spex 1404 double monochromator with holographic gratings (band-path used 0.01–0.2 nm). Light intensity was measured by a RCA 31034 photomultiplier with a cooled S-20 photocathode (−20 °C), coupled to a Lecroy linear amplifier (500 MHz) and a Stanford Research SR-400 double photon counter. The emission spectra were corrected for the instrumental function. The excitation spectra were corrected for the emission of the Xenon lamp. Luminescent lifetimes were measured using excitation provided by a Quantum Brilliant Nd:YAG laser equipped with frequency doubler, tripler and quadrupler as well as with an OPOTEK MagicPrism™ OPO crystal. The output signal of the photomultiplier was fed into a Stanford Research SR-430 multichannel scaler and transferred to a PC. Lifetimes are averages of 3 independent determinations. Quantum yields were determined using a Perkin Elmer LS50B fluorimeter. The quantum yields were calculated using the equation $\phi_x/\phi_r = [A_r(\tilde{\nu}) \times I_r(\tilde{\nu}) \times n_r^2 \times D_x]/[A_x(\tilde{\nu}) \times I_x(\tilde{\nu}) \times n_x^2 \times D_r]$, where x refers to the sample and r to the reference; *A* is the absorbance, $\tilde{\nu}$ the excitation wavenumber used, *I* the intensity of the excitation light at this energy, *n* the refractive index (*n* = 1.341 for acetonitrile solution and *n* = 1.330 for 0.1 mol dm^{−3} aqueous Tris-buffer solution) and *D* the integrated emitted intensity. Cs₃[Eu(2,6-pyridinedicarboxylic acid)₃] (ϕ = 9.5% in 0.1 mol dm^{−3} aqueous Tris-buffer solution) was used as reference.⁴⁵ Elemental analyses were performed by Dr H. Eder from the Microchemical Laboratory of the University of Geneva.

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