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 MII (M = Cr, Zn) and LnIII (Ln = La, Eu, Tb, Lu) to give the heterotrimetallic triple-stranded helicates [MLnM(L2)3]7+. For M = ZnII, the isolated complexes [ZnLnZn(L2)](CF3SO3)7 (Ln = Eu, Tb) display only lanthanide-centred luminescence arising from the pseudo-tricapped trigonal prismatic LnN6 coordination site. For M = CrIII, rapid air oxidation provides CrIII and leads to the isolation of inert [CrLnCr(L2)](CF3SO3)9 (Ln = Eu, Tb) complexes, in which divergent intramolecular Ln → Cr energy transfers can be evidenced. Taking [ZnEuZn(L2)]+ 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, CrIII, 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 (t2g)3 electronic configuration of octahedral CrIII (A1g in Oh symmetry), prevents efficient associative pathways for ligand exchanges processes.3 Consequently, CrIII complexes combine extreme kinetic inertness (the rate of water exchange in [Cr(H2O)6]3− amounts to k(WH2O) = 2.4 × 10−6 s−1)4 with predictable pseudo-octahedral geometries, which makes them ideal coordination models for the refinement of theoretical inorganic kinetic mechanisms5,6 and electronic spectroscopy.6 More recently, some interest has been focused on the design of sophisticated polymeric networks with predictable two-dimension and three-dimension organization based on inert negatively charged tri-oxalato [Cr(ox)3]3− or mixed oxalato-bipyridine [Cr(ox)(bipy)]− building blocks.4 Interestingly, lanthanides have been used as counter-cations in these infinite architectures8 thus producing heterometallic Cr–Ln interactions, but only weak magnetic coupling results from the minute expansion of the 4f orbitals9 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 ΩDA 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)), WDA is the probability of the energy transfer).11

\[
W_{DA} = \frac{(2\pi/h)}{|DA^*|} |(DA^*)' |D'A' | Ω_{DA}
\]

Assuming the common approximation, which limits the electrostatic multipolar series to dipole–dipole interactions, Förster’s theory predicts a (RDA)−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 RDA > 11.5 Å, 11.5 Å > RDA > 20.1 Å, 13 RDA = 12.8 Å14 and RDA = 9.1 Å at 10 K.14 When strong field α,α’-diamines are coordinated to CrIII in [Cr(2,2’-bipyridine)] or [Cr(2-benzimidazol-pyridine)]11, the integral overlap ΩDA or ΩDA mainly involves the low-lying excited Cr-centred excited states E and T1,18 and some adequate Ln-centred levels.13,14 For Ln = Eu and Tb, which possess high-energy emitting levels in the visible range, CrIII may act as an acceptor and Ln → Cr energy transfers, followed by Cr(E) luminescence, are evidenced.13,16 Conversely, Ln = Nd, Ho, Er, Tm and Yb possess low-energy excited electronic states. CrIII 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(T3g − 4A2g)) and/or Cr(E → 4A2g)) and specific

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*Electronic supplementary information (ESI) available: Tables of elemental analyses (Table S1), luminescence data for [ZnLnZn(L2)]7+ and [CrLnCr(L2)]7+ (Ln = Eu, Tb) complexes. Figure S7 shows the temperature dependence of Eu(D1) lifetime in [ZnEuZn(L2)]. † 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 (Al$_2$O$_3$) for sensitizing Ln$^{III}$ (Ln = Nd, Er, Tm, Yb) energy migrations responsible for the dual field garnets (Al$_2$O$_3$) for sensitizing Ln$^{III}$ (Ln$^{III}$ = 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$^2E$ donor level.$^{15}$

According to a synthetic point of view, the latter heterobimetallic complexes are obtained by the simultaneous complexation of inert [Cr(acac)$_2$(ox)]$^{2+}$ and [HBpz$_3$]$^{-}$ to Ln$^{III}$. An alternative strategy uses the labile Cr$^{II}$ precursor (the rate of methanol exchange in further oxidized to give the inert Cr$^{III}$-Ln pair in [CrLn(L1)$_3$]$^{6+}$. 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)$_3$]$^{1+}$ donors (similar to that found in [CrLn(L1)]$^{n+}$, (Fig. 1b) about a central Ln$^{III}$ coordination site, with all Cr-..Ln distances being fixed at 9.0-9.3 Å.

![Fig. 1](image)

**Fig. 1** Structures of discrete bimetallic CrLn complexes a) [(acac)$_2$Cr(ox)-Ln(HBpz$_3$)]$^{18,17}$ and b) [CrLn(L1)]$^{12,14}$ 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)]$^{12}$, 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 ($k_{ET}^{Cr} > 3.5 \times 10^4$ s$^{-1}$), the rate constants of energy transfers $k_{ET}^{Ln}$ or $k_{ET}^{Cr}$ are rather slow and fall within the range $10^2-10^4$ s$^{-1}$ for intermetallic Cr $\cdots$ Ln separations around 9.0-9.3 Å, taken as acceptable approximations for the donor–acceptor distances $R_{DA}^{Cr,Ln}$. Therefore, when Cr$^{III}$ is used as a donor for short-lived NIR lanthanide emitters ($k_{ET}^{Ln} \approx 10^4$–$10^5$ s$^{-1}$) in these complexes, the combination of the long-lived Cr$^2E$ level ($k_{ET}^{Cr} \approx 300$ s$^{-1}$) with the slow energy transfer process ($k_{ET}^{Ln} \approx 200$ s$^{-1}$) results in $k_{ET}^{Cr} + k_{ET}^{Ln} > k_{ET}^{Ln}$, 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 fluorimunoassays.$^{26}$

Results and discussion

**Synthetic and thermodynamic aspects**

Self-assembly of [ZnLnZn(L2)]$^{16+}$, [CrLnCr(L2)]$^{16+}$ and [CrLnCr(L2)]$^{16+}$ 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 $^1$H NMR spectrum displays 15 signals, which reflect the dynamically average C$_{3v}$-symmetry of L2 on the NMR time scale (Fig. 4a and Table 1). Although paramagnetic low-spin Cr$^{III}$ ($S = 1$) possesses a fast electronic relaxation time ($\tau_e \approx 10^{-12}$ s)$^{22}$ combined with minor delocalization of the unpaired electrons,$^{23}$ the increased nuclear relaxation induced for $^1$H nuclei...
Fig. 3 Structures of the ligands L1–L4.

in [CrLn(L1)].14 was shown to be large enough to significantly broaden and shift the signals of the bidentate units bound to CrII, thus preventing reliable assignment.11 The situation is more dramatic for [CrLnCr(L2)].13, since each proton undergoes the effect of two paramagnetic CrII centres via through-bond (contact) and through-space (dipolar) mechanisms (Fig. S4a, ESI†).24 We therefore decided to replace labile paramagnetic low-spin CrII with diamagnetic ZnII in order to prepare [ZnLnZn(L2)].15, 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 ZnII, but not with air-sensitive CrII complexes.

ESI-MS titrations of L2 (2 × 10⁻⁴ mol dm⁻³) with Zn(CF₃SO₃)₂·6H₂O and La(CF₃SO₃)₃·3H₂O in CHCl₃/CH₃CN (1 : 1) for various Zn : La : L₂ ratios are dominated by the formation of homometallic complexes [Zn(L2)].13⁺, [Znₓ(L2)].13⁺ (x = 1, 2) and [La(L2)(CF₃SO₃)].13⁺, together with traces of the heterometallic complex [ZnLa(L2)(CF₃SO₃)].13⁺, but no peak corresponding to the target helicate [ZnₓLa(L2)].13₊ could be detected (Fig. S1, ESI†). Increasing the total concentration of the ligand to millimolar concentration for the stoichiometric ratio La : Zn : L₂ = 1 : 2 : 3 shows the appearance of two weak peaks at m/z = 599.5 and m/z = 786.8 corresponding to [ZnLaZn(L2)].13₊ and [ZnLaZn(L2)(CF₃SO₃)].13₊. 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

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been followed by $^1$H 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 La : Zn : L2 = 1 : 2 : 3 expected for entropically maximizing the formation of the target helicate [ZnLaZn(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 $\times 10^{-4}$ mol dm$^{-3}$) with Ln(CF$_3$SO$_3$)$_3$·nH$_2$O (Ln = La, Eu, Lu) for L2 : La = 0.1–2.5 : 1 (Fig. S2a and S2b, ESI†), or with Zn(CF$_3$SO$_3$)$_2$·6H$_2$O for L2 : Zn = 0.1–2.5 : 1 (Fig. S2c and S2d, ESI†), or titrations of [Ln(L2)$_3$]$^{3+}$ (Ln = La, Eu, Lu, total ligand concentration: 2 $\times 10^{-4}$ mol dm$^{-3}$) with Zn(CF$_3$SO$_3$)$_2$·6H$_2$O for L2 : Zn = 0.1–2.5 : 1 (Fig. 5 and S3, ESI†) in CHCl$_3$/CH$_3$CN (1 : 1) show complicated variations of the absorption spectra. Detailed mathematical analyses by using factor analysis$^{26}$ and evolving factor analysis$^{27}$ 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  $^1$H NMR titration of L2 with La$^{3+}$ and Zn$^{2+}$ in CDCl$\textsubscript{3}$/CD$_3$CN = 1 : 1 at 293 K (total ligand concentration = $10^{-2}$ 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 \([\text{La}(L_2)_3]^{3+}\) (total ligand concentration: \(2 \times 10^{-4}\) mol dm\(^{-3}\)) with \(\text{Zn(CF}_3\text{SO}_3)\cdot 6\text{H}_2\text{O}\) at 293 K in \(\text{CHCl}_3–\text{CH}_3\text{CN}=1:1\) (\(\text{Zn}:L_2=0.1–2.5:1\)). b) Corresponding variation of observed molar absorption at six different wavelengths.

\[\text{Zn}:L_2 \approx 0.3 \text{ and } \text{Zn}:L_2 \approx 0.7 \text{ for the titrations of } [\text{Ln}(L_2)_3]^{3+} (\text{Ln} = \text{La, Eu, Lu}) \text{ with } \text{Zn(CF}_3\text{SO}_3)\cdot 6\text{H}_2\text{O} \text{ (Fig. 5 and S3, ESI†), in agreement with the successive formation of } [\text{ZnLn}(L_2)_3]^{5+} \text{ and } [\text{ZnLnZn}(L_2)_3]^{7+} \text{ complexes as the main species in solution under these conditions.}

We conclude from the combination of ESI-MS, \(^1\text{H}\) NMR and spectrophotometric titrations that the target complexes \([\text{ZnLnZn}(L_2)_3]^{7+}\) can be formed in solution as the major species under a strict stoichiometric ratio \(\text{Zn}:\text{Ln}:L_2=2:1:3\) and millimolar concentrations of the ligand (Fig. 6).

As expected, the replacement of \(\text{Zn(CF}_3\text{SO}_3)\cdot 6\text{H}_2\text{O}\) with air-sensitive \(\text{Cr(CF}_3\text{SO}_3)\cdot \text{H}_2\text{O}\) produces broad \(^1\text{H}\) NMR signals for \([\text{CrLaCr}(L_2)_3]^{7+}\) under strict anaerobic conditions, which are typical of paramagnetic low-spin \(\text{Cr}^{II}\) 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 \(^1\text{H}\) NMR signals, compatible with the formation of slow-relaxing \(\text{Cr}^{III}\) (\(\tau \approx 10^{-9}\) s, Fig. S4b, ESI†). This \(\text{Cr}^{II} \rightarrow \text{Cr}^{III}\) oxidation is confirmed by the variation of the electronic absorption spectra recorded for \([\text{CrLnCr}(L_2)_3]^{7+}\) and \([\text{CrLnCr}(L_2)_3]^{9+}\) (\(\text{Ln} = \text{Eu, Lu, Fig. 7 and Table 2}\)). As previously discussed in detail for the absorption spectrum of \([\text{CrLn}(L_1)_3]^{5+}\), the \([\text{CrLnCr}(L_2)_3]^{7+}\) 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\(^{-1}\), \(\varepsilon = 3250\) M\(^{-1}\) cm\(^{-1}\) cm\(^{-1}\), \(\varepsilon = 1840\) M\(^{-1}\) cm\(^{-1}\), Table 2), which compare well with those found in \([\text{Cr}(2,2’\text{-bipyridine})_3]^{3+}\) (8700 cm\(^{-1}\), \(\varepsilon = 10000\) M\(^{-1}\) cm\(^{-1}\), 9900 cm\(^{-1}\), \(\varepsilon = 2900\) M\(^{-1}\) cm\(^{-1}\)),\(^{13}\) and in \([\text{CrLn}(L_1)_3]^{5+}\) (8300 cm\(^{-1}\), \(\varepsilon = 4300\) M\(^{-1}\) cm\(^{-1}\), 9090 cm\(^{-1}\), \(\varepsilon = 2900\) M\(^{-1}\) cm\(^{-1}\)).\(^{13}\) The series of poorly resolved bands in the range 11000–25000 cm\(^{-1}\) correspond to overlapping low-spin \(\text{Cr}^{III}\)-centred \(d-d\) transitions possessing significant CT character (a detailed assignment is given in Table 2).\(^{13}\)

Upon air oxidation, the low-energy \(L_2 \rightarrow \text{Cr}^{III}\) LMCT and the spin-allowed \(\text{Cr}^{III}\)-centred transition responsible for the deep green colour of \([\text{CrLnCr}(L_2)_3]^{7+}\) 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 \(\text{Cr}^{III}\)-centred

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\(\text{[MLnM}(L_2)_3]\)^{7/9+}

(Fig. 6) Schematic representation of the complexation process leading to the triple-stranded helicate \([\text{MLnM}(L_2)_3]\)^{7/9+} (\(M = \text{Zn}^{II}, \text{Cr}^{II}\)). The structure of the complex corresponds to the optimized \(D_3\)-symmetrical geometry constructed for \([\text{Cr}^{III}\text{EuCr}^{III}(L2)_3]^{9+}\) by using the crystal structure of \([\text{Cr}^{III}\text{Eu}(L1)_3]^{6+}\) as model.

Fig. 7 Absorption spectra of a) \([\text{Cr}^{III}\text{LnCr}^{II}(L2)_3]^{7+}\) (black trace) and b) \([\text{Cr}^{III}\text{LnCr}^{III}(L2)_3]^{9+}\) (grey trace) in acetonitrile (2.1 \(\times 10^{-3}\) mol dm\(^{-3}\)).

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\(\varepsilon = 3250\) M\(^{-1}\) cm\(^{-1}\); 9460 cm\(^{-1}\), \(\varepsilon = 1840\) M\(^{-1}\) cm\(^{-1}\), Table 2), which compare well with those found in \([\text{Cr}(2,2’\text{-bipyridine})_3]^{3+}\) (8700 cm\(^{-1}\), \(\varepsilon = 10000\) M\(^{-1}\) cm\(^{-1}\), 9900 cm\(^{-1}\), \(\varepsilon = 2900\) M\(^{-1}\) cm\(^{-1}\))\(^{13}\) and in \([\text{CrLn}(L1)_3]^{5+}\) (8300 cm\(^{-1}\), \(\varepsilon = 4300\) M\(^{-1}\) cm\(^{-1}\), 9090 cm\(^{-1}\), \(\varepsilon = 2900\) M\(^{-1}\) cm\(^{-1}\)).\(^{13}\) The series of poorly resolved bands in the range 11000–25000 cm\(^{-1}\) correspond to overlapping low-spin \(\text{Cr}^{III}\)-centred \(d-d\) transitions possessing significant CT character (a detailed assignment is given in Table 2).\(^{13}\)

Upon air oxidation, the low-energy \(L_2 \rightarrow \text{Cr}^{III}\) LMCT and the spin-allowed \(\text{Cr}^{III}\)-centred transition responsible for the deep green colour of \([\text{CrLnCr}(L2)_3]^{7+}\) 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 \(\text{Cr}^{III}\)-centred
Table 2  Electronic spectral data for the heterometallic complexes [Cr\textsuperscript{III}LnCr\textsuperscript{III}(L\textsubscript{2})\textsuperscript{3}]\textsuperscript{9+} and [Cr\textsuperscript{III}LnCr\textsuperscript{III}(L\textsubscript{2})\textsuperscript{9+}] in acetonitrile at 293 K

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<th>Compound</th>
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<th>(d \rightarrow d + \text{CT})</th>
<th>Attribution</th>
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<td>3150 (107100 sh)</td>
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*Energies are given for the maximum of the band envelope in cm\(^{-1}\) and \(\varepsilon\) (in parentheses) in M\(^{-1}\) cm\(^{-1}\); sh = shoulder, CT = charge transfer, LMCT = ligand-to-metal charge transfer.

\(4A_2 \rightarrow 4T_2\) and \(4A_2 \rightarrow 4A_2\) transitions (in \(O_h\) symmetry), mixed with MLCT bands in the orange complex [CrLnCr\textsuperscript{II}\textsubscript{3}]\textsuperscript{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\textsuperscript{II}\textsubscript{3}]\textsuperscript{9+} characterized by a series of adducts [CrLnCr\textsuperscript{II}\textsubscript{3}(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{9}],\textsuperscript{9} (\(x = 0.7\), Fig. S5, ESI†).

Isolation and characterization of [ZnLnZn\textsubscript{2}][CF\textsubscript{3}SO\textsubscript{3}\textsubscript{3}] and [CrLnCr\textsubscript{2}][CF\textsubscript{3}SO\textsubscript{3}\textsubscript{3}], \((L_n = La, Eu, Gd, Tb, Lu)\). Stoichiometric mixing of L\textsubscript{2}, Ln(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{3}, \(\text{H}_2\text{O}\) \((L_n = La, Eu, Gd, Tb, Lu)\) and Zn(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{3}, \(\text{H}_2\text{O}\) \((L_n = La, n = 5; Ln = Eu, n = 7; Ln = Gd, n = 8; Ln = Tb, n = 6; Ln = Lu, n = 6, Table S1, ESI†)\). Replacement of Zn(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{3}, \(\text{H}_2\text{O}\) with Cr(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{3}, \(\text{H}_2\text{O}\) under nitrogen atmosphere provides deep green solutions of [CrLnCr\textsuperscript{II}\textsubscript{3}],\textsuperscript{9}. Air oxidation combined with the addition of \(\text{Bu}_4\text{N}(\text{CF}_3\text{SO}_3)\textsubscript{3}\text{H}_2\text{O}\) \((2.\text{eq})\) in acetonitrile followed by fractional crystallization with diethyl ether give 73–88% of yellow microcrystalline solids, whose elemental analyses correspond to [CrLnCr\textsuperscript{II}\textsubscript{3}(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{9}](CH\textsubscript{3}NO\textsubscript{2})\textsubscript{9}, in which the ligand L' is identical to L\textsubscript{2}, except for the replacement of the two terminal 5-methylpyridine groups with 6-(N,N'-diethylcarboxy)pyridine groups.

Structural aspects

X-Ray diffraction study of CrEuCr. Despite numerous attempts for re-crystallizing ZnEuZn 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\textsuperscript{II}\textsubscript{3}],\textsuperscript{9} provides prisms, for which a monoclinic unit cell with \(a = 28.79\) Å, \(b = 16.63\) Å, \(c = 43.86\) Å, \(\beta = 104.8^\circ\) and \(V = 20300\) Å\(^3\) can be determined. The volume of the unit cell compares well with \(V = 25888\) Å\(^3\) (monoclinic, \(P2_1/c, Z = 4\) found for a closely related heterotrimetallic triple-stranded helical complex [EuLaEu\textsubscript{2}][CF\textsubscript{3}SO\textsubscript{3}\textsubscript{3}](CH\textsubscript{3}NO\textsubscript{2})\textsubscript{9}, in which the ligand L' is identical to L\textsubscript{2}, except for the replacement of the two terminal 5-methylpyridine groups with 6-(N,N'-diethylcarboxy)pyridine groups.

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\textsuperscript{II} as a structural probe and high-resolution emission spectroscopy.\textsuperscript{29} The excitation spectrum of ZnEuZn recorded upon monitoring the Eu\textsuperscript{II}\textsubscript{2}(\(D_0 \rightarrow \tilde{T}_2\)) transition displays ligand-centred \(\pi \rightarrow \pi^*\) absorptions, together with specific narrow peaks typical for Eu-centred intra-configurational 4\(f\) \(\rightarrow\) 4\(f\) absorptions (Fig. S6a, ESI†). The high-resolution excitation profile of the Eu\textsuperscript{II}\textsubscript{2}(\(D_0 \rightarrow \tilde{T}_2\)) transition in ZnEuZn at 10 K shows a single and symmetrical band (full width at half height, \(\text{fwhh} = 19.8\) cm\(^{-1}\)) indicating the existence of a single Eu\textsuperscript{II} coordination site in a polycrystalline material (Fig. 8a).

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\[ \tilde{V} = V_0 + C_{CN} \sum_n n_i \cdot \delta_i \]
Fig. 8  a) Excitation spectrum of ZnEuZn recorded upon monitoring Eu(5D0 $\rightarrow$ 7F0) 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$_{\text{CN}}$ is an empirical parameter depending on the coordination number of Eu$^{\text{III}}$. C$_{\text{CN}}$ = 1 for nine-coordinate sites, $n_i$ is the number of i-type atoms in the coordination sphere, $\delta_i$ is the ability of atom i to accept electronic delocalization from the metal with $\delta_i = -15.3$ cm$^{-1}$ for heterocyclic nitrogen atoms, and $v_0 = 17374$ cm$^{-1}$ is the energy of Eu(F$_0$ $\rightarrow$ 1D$_{0}$) for the free ion). For the pseudo-tricapped trigonal EuN$_6$ site proposed in the model of ZnEuZn (Fig. 6), we calculate $\tilde{v} = 17236$ cm$^{-1}$ at 295 K, which translates into $\tilde{v} = 17224$ cm$^{-1}$ at 10 K (assuming the accepted 1 cm$^{-1}$/24 K dependence of the energy of the Eu(5D$_0$ $\leftrightarrow$ 7F$_0$) transition with temperature). This prediction matches fairly well the experimental value found for ZnEuZn ($\tilde{v}$ = 17221 cm$^{-1}$ at 10 K, Table 3), and those previously reported for [ZnEu(L3)$_3$]$^{1+}$, (1724 cm$^{-1}$ at 10 K, Table 3) and [Eu(L4)$_3$]$^{1+}$ (17223 cm$^{-1}$ at 10 K, Table 3), in which the existence of the pseudo-tricapped trigonal prismatic EuN$_6$ site has been unambiguously evidenced in the associated X-ray crystal structures.

The detailed analysis of the crystal-field splitting of the Eu(5D$_0$ $\rightarrow$ 7F$_0$) $(J = 0$–$6$, Table 3) in the emission spectrum of ZnEuZn (Fig. 8b) is diagnostic for a distorted trigonal symmetry around Eu$^{\text{III}}$. The Eu(5D$_0$ $\rightarrow$ 7F$_0$) transition is forbidden in D$_3$ by symmetry-related selection rules, but allowed in C$_3$ point group, is extremely weak. The magnetically-allowed Eu(5D$_0$ $\rightarrow$ 7F$_0$) transition is split into one singlet (A$_1$ $\rightarrow$ A$_2$, 312 cm$^{-1}$ above $7F_0$, Table 3) and one doublet (A$_1$ $\rightarrow$ E, barycentre 410 cm$^{-1}$ above $7F_0$, Table 3), with $\Delta E_{A,E} = 98$ cm$^{-1}$; further splitting of the A$_1$ $\rightarrow$ E component ($\Delta E_{A,E} = 32$ cm$^{-1}$) is assigned to deviation from ideal trigonal symmetry. Interestingly, a point charge electrostatic model predicts that the energetic separation $\Delta E_{A,E}$ between the 7F$_1$(A) and 7F$_1$(E) sublevels is proportional to the absolute magnitude of the second-rank crystal-field parameter $|B_{2g}|$, while deviation from trigonal symmetry involves the additional second-rank crystal-field parameter $|B_{2g}|$, which is proportional to the splitting of the 7F$_1$(E) sublevel ($\Delta E_{E,E}$). We thus deduce that the symmetry of the EuN$_6$ 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 [ZnEu(L3)$_3$]$^{1+}$ ($\Delta E_{A,E} = 94$ cm$^{-1}$, $\Delta E_{E,E} = 43$ cm$^{-1}$, Table 3), but slightly more distorted than in the less constrained mononuclear complex [Eu(L4)$_3$]$^{1+}$ ($\Delta E_{A,E} = 119$ cm$^{-1}$, $\Delta E_{E,E} = 17$ cm$^{-1}$, Table 3). The forced electric dipole Eu(5D$_0$ $\rightarrow$ 7F$_0$) 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$_2$ 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$^{\text{III}}$. Again close similarity of the crystals field splitting of the Eu(7F$_1$) levels $(J = 0$–$6$, Table 3) observed in ZnEuZn, with those reported for [ZnEu(L3)$_3$]$^{1+}$ and [Eu(L4)$_3$]$^{1+}$, indicates very similar EuN$_6$ sites in the three complexes. The long Eu(5D$_0$) 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 [ZnEu(L3)$_3$]$^{1+}$ (1.96(7) ms)$^{12}$ and [Eu(L4)$_3$]$^{1+}$ (1.87(4) ms). Moreover, the typical fast decrease of the Eu(5D$_0$) lifetime with increasing temperature (Fig. S7, ESI†) is the signature of the existence of a low-lying LMCT state, which efficiently quenches Eu(5D$_0$) emission at room temperature. This effect has been investigated in details for [Eu(L4)$_3$]$^{1+}$ and it arises from the coordination of nine heterocyclic nitrogen atoms to Eu$^{\text{III}}$, which favours the Eu$^{\text{III}}$ $\rightarrow$ Eu$^{\text{II}}$ reduction process.
For CrEuCr, the excitation spectrum recorded upon monitoring the Eu(\(^{1}D_{0} \rightarrow \ ^{7}F_{j}\)) 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 Cr(\(^{2}E \rightarrow \ ^{4}A_2\)) transition, the excitation profile is completed by direct sensitization (Fig. S6c). Both the energy (13245 cm\(^{-1}\)) and the Cr(\(^{2}E \rightarrow \ ^{4}A_2\)) lifetime (0.24 ms) (Table S2, ESI†) are comparable with those reported for \([\text{CrEu(L1)}]^{3+}\) (13301 cm\(^{-1}\) at 10 K, \(\tau = 3.46\) ms),\(^{2}i\) in agreement with the existence of similar terminal trigonally distorted \([\text{Cr(2-benzimidazol-pyridine)}]^{3+}\) 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 Eu(\(^{1}D_{0} \rightarrow \ ^{7}F_{j}\)) transition, we calculate \(\Delta E_{A_{E-E}} = 80\) cm\(^{-1}\), \(\Delta E_{E-E} = 34\) cm\(^{-1}\), Table 3). It is worth noting that Cr-centred excitation at 21470 cm\(^{-1}\) (Cr(\(^{4}A_2 \rightarrow \ ^{4}T_2\))) results in the exclusive detection of the Cr(\(^{2}E \rightarrow \ ^{4}A_2\)) emission, in line with the absence of intramolecular Cr → Eu energy transfer processes. However, the reverse situation is found upon Eu-centred excitation (i.e. observation of the luminescence in both Eu-centred and Cr-centred emission), which implies the existence of a partial Eu → Cr energy transfer (Fig. 10, vide infra) responsible for the reduced Eu(\(^{1}D_{0}\)) lifetime measured in CrEuCr (\(\tau = 0.20-0.24\) 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

<table>
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<th>Compound</th>
<th>([\text{ZnEuZn(L2)}]^{3+})</th>
<th>([\text{ZnEu(L3)}]^{3+})</th>
<th>([\text{ZnEu(L4)}]^{3+})</th>
<th>([\text{ZnEuZn(L2)}]^{3+})</th>
<th>([\text{CrEuCr(L2)}]^{3+})</th>
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<td>EuN(_9)</td>
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* Calculated with eqn (14). ∗ Calculated with eqn (17). ∗ Calculated with eqn (19). ∗ 10\(^{-7}\) mol dm\(^{-3}\) in acetonitrile solution.

Table 3 Energy (cm\(^{-1}\)) of the identified crystal-field sublevels of the Eu(\(^{7}F_{j}\)) manifold (\(J = 1-4\)) and Eu(\(^{1}D_{0}\)) in [ZnEuZn(L2)]\(^{(3+)}\)(CF\(_3\)SO\(_3\))\(_5\)(H\(_2\)O)\(_4\), [ZnEu(L3)]\(^{(3+)}\)(CF\(_3\)SO\(_3\))\(_5\)(H\(_2\)O)\(_4\), [ZnEu(L4)]\(^{(3+)}\)(CF\(_3\)SO\(_3\))\(_5\)(CH\(_3\)CN)\(_3\), [CrEuCr(L2)]\(^{(3+)}\)(CF\(_3\)SO\(_3\))\(_5\)(H\(_2\)O)\(_4\) and [CrEu(L1)]\(^{(3+)}\)(CF\(_3\)SO\(_3\))\(_5\)(H\(_2\)O)\(_4\) as determined from excitation and emission spectra in the solid state at 10 K; \(^{3}F_{0}\) is taken as the origin.

Table 4 Emission Eu(\(^{1}D_{0}\)) lifetimes and associated rate constants for the complexes [ZnEuZn(L2)]\(^{(3+)}\), [CrEuCr(L2)]\(^{(3+)}\), [ZnEu(L1)]\(^{(3+)}\), and [CrEu(L1)]\(^{(3+)}\)\(^{13}\).
tridentate 2,6-bis(benzimidazol-2-yl)pyridine units, as found in the
D3-symmetrical complex [Eu(L4)]+ . 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(L1)]+ (H6 is used as a reference, see text).

The 1H NMR spectra of [ZnLnZn(L2)]+ (Ln = La, Eu, Tb, Lu, Y) systematically show eleven aromatic C−H 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 D3-symmetry for the trimetallic complexes in solution (Table 1 and Fig. 4d). The unusual shielding of H6 and H8 in the diamagnetic complexes [ZnLuZn(L2)]+ (eqn (11) and Table S3, ESI†), the resulting para signals (H6, 5.02 ppm, H8, 5.42 ppm) in [ZnLuZn(L2)]+ despite the analogous bimetallic triple-helical complexes [ZnEu(L3)]+ (δH6 = 5.34 ppm, δH8 = 5.44 ppm). In order to obtain intramolecular Ln⋯Hi distances in [ZnLuZn(L2)]+, 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

\[
\frac{1}{T_{1\text{exp}}} = \frac{1}{T_{1\text{trans}}} + \frac{1}{T_{1\text{st}}}
\]

(11)
dominated by dipolar electron–nucleus interactions modelled with eqn (12), whereby the constants have their usual meaning, \(\mu_{\text{eff}}\) is the electronic effective magnetic moment, \(H_0\) is the magnetic field, \(\tau_i\) and \(\tau_s\) are the rotational and electronic correlation times, and \(r_i\) is the Ln⋯Hi distance:\n
\[
\frac{1}{T_{1\text{exp}}} = \frac{1}{T_{1\text{trans}}} + \frac{1}{T_{1\text{st}}} = \frac{4}{3} \frac{\mu_{\text{eff}}^2}{4\pi} \frac{\gamma^2 H_0^2 r_i^6}{\tau_i} + \frac{6}{5} \frac{\mu_{\text{L}}^2}{4\pi} \frac{\gamma^2 H_0^2 r_i^6}{r_i^4} \left(\frac{T_{1\text{exp}}}{T_{1\text{trans}}} - 1\right)
\]

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 \(1/T_{1\text{trans}}\) is simply proportional to \(r_i^6\) with a scaling factor \(E_\text{p}\), which is maximum for lanthanide cations possessing a large magnetic momentum (\(\mu_{\text{eff}}\) is maximum) at high magnetic fields (\(H_0\) is maximum). When a reference Ln⋯Hi distance, \(r_{\text{ref}}\), 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)\n
\[
r_i = r_{\text{ref}} \cdot \sqrt{\frac{T_{1\text{trans}}}{T_{1\text{exp}}}}
\]

Because TbIII complexes possess large electronic magnetic moments, we have focused on [ZnTbZn(L2)]+, for which the experimental characteristic longitudinal relaxation times \(T_{1\text{trans}}\) have been determined by 1H NMR spectroscopy (Table S3, ESI†). After correcting for the diamagnetic contribution \(T_{1\text{st}}\) measured in [ZnLuZn(L2)]+ (eqn (11) and Table S3, ESI†), the resulting paramagnetic contributions \(T_{1\text{trans}}\) have been used to compute \(r_i\). Since the diamagnetic shifts of H6 are almost identical in [ZnLu(L1)]+, [ZnLu(L3)]+ and in [ZnLuZn(L2)]+, 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)]+ (M = Cr, Ln = Eu, Tb).
can safely conclude that H6 occupy very similar positions in the three complexes, and the Eu···H6 distance observed in the crystal structure of [ZnEu(L1)](CF3SO3)(ClO4)(CH3CN), has been used as reference (rref = 6.7 Å). The Tb···H distances calculated for [ZnTbZn(L2)]+ with eqn (13) are collected in Table S3 (i = 1–5 and 8–2, ESI†), and they closely match those found in the crystal structure of [ZnEu(L1)]+ (Fig. 9). We conclude that the triple-helical organization of the strands about the Zn···Ln axis is very similar in [ZnEu(L1)]+ and in [ZnTbZn(L2)]+, which further justifies the model proposed in Fig. 6 for the heterotrimetallic complexes [MLnM(L2)3]7/9+ (M = Cr, Ln). Moreover, the crystal structure of [ZnEu(L1)]+, which is almost superimposable with that of [CrEu(L1)]+,13 can be used as a reliable structural model for the ‘asymmetric unit’ of the D3-symmetrical trimetallic complexes [MLnM(L2)3]7/9+ (M = Cr, Ln).

Functional aspects

Indirect sensitization processes involving ligand-to-metal energy transfer processes in ZnLuZn and CrLuCr (Lu = Eu, Gd). In the absence of L2 → metal transfer in ZnGdZn (i.e. neither ZnIII nor GdIII possess accessible excited states for accepting energy from L(π*)), the coordinated tritopic ligand L2 shows a broad and poorly structured emission band in the 20800–16000 cm−1 range (τmax = 18 900 cm−1). Its associated lifetime is bi-exponential with τ1 = 2.45 ms (86%) and τ2 = 0.49 ms (14%), which is typical for emissions arising from the L2(π*) excited states located on different parts of the ligand, due to the isolating effects of the methylene spacers.12,13 At 295 K, efficient thermally-activated non-radiative processes reduce L2(π*) lifetimes to τ1 = 42 μs (64%) and τ2 = 6 μs (36%). Upon replacement of ZnII with CrIII in CrGdCr, the L2(π*) band is shifted by approximately 5500 cm−1 toward higher energy (26000–20 000 cm−1 range, τmax = 24 450 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 π* emission and (ii) the L2(π*) → CrIII transfer is poorly efficient. Conversely, only a faint residual ligand-centred π* emission is detected in the emission spectra of ZnEuZn and CrEuCr, which points to an efficient L2(π*) → EuIII sensitization process, as similarly reported for [ZnEu(L3)]+1,13 [ZnEu(L1)]+1,13 and [CrEu(L1)]+.11 We conclude that the energy of L2(π*) in the complexes MLnM is more adequate for resonant energy transfer processes with EuIII than with CrIII.

Cr-centred luminescence in [CrLnCr(L2)](CF3SO3)2 (Ln = Eu, Gd, Tb). Excitation through the ligand-centred π* (τexc = 28170 cm−1) or via CrIII-centred 4A2 → 2T2 (τexc = 20492 cm−1, Fig. S6f) in CrGdCr produces identical emission spectra displacing the characteristic Cr(4E → 4A2) transition at 13 245 cm−1, combined with weak Stokes phonon side bands (13 100–12 900 cm−1, Fig. S8, ESI†), in good agreement with a similar behaviour reported for [CrGd(L3)]+ (13 301 cm−1).13 The Cr(4E) lifetime at 10 K is long (2.27(1) ms, Table S2, ESI†) and points to only minor non-radiative processes affecting the CrIII-centred emission. However, both intensity (Fig. S8, ESI†) and lifetime of the Cr(4E) emission in CrGdCr dramatically decrease at higher temperature (τ295K = 0.031 ms, Table S2, ESI†), which is tentatively attributed to thermally-activated energy migration processes, as previously discussed for [CrGd(L1)]+.15,37 Moreover, the maximum of the Cr(4E → 4A2) emission band shifts from 13 245 cm−1 at 10 K to 13 316 cm−1 at 295 K (ΔE = 71 cm−1, Fig. S8, ESI†), a change in energy much larger than ΔE = 15 cm−1 expected for the splitting of the Cr(4E) level by trigonal symmetry, which accounts for the hot band emission in the model complex [Cr(2,2-bipyridine)]+1,19 We thus suspect that the long-lived luminescence observed at 10 K indeed originates from pseudo-octahedral CrN6 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 Cr(4E → 4A2) emission. For CrEuCr and CrTbCr, the long-lived CrIII-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 Cr → Eu energy transfer.

Intramolecular Ln → Cr communication in CrLnCr (Ln = Eu, Tb). Upon irradiation of the ligand-centred ππ* excited states at 28 170 cm−1 in CrEuCr, we observe the dual metal-centred emission of Eu(5D0 → 7F2) (J = 0–4) and Cr(4E → 4A2) (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 Eu(5D0) lifetime in CrEuCr is dramatically shortened (Table 4) as a result of the occurrence of Eu → Cr energy transfer processes. The intramolecular origin of the latter energy transfers is demonstrated by related dynamic measurements obtained for [CrEuCr(L2)]+ in acetonitrile, which closely mirror those obtained in the solid state (Table 4). We can therefore analyse the Eu → 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 by eqn (14).

\[
\eta_{\text{global}}^{\text{CrEuCr}} = \frac{2k_{\text{Lum}}^{\text{Cr}}}{k_{\text{Lum}}^{\text{Cr}} + 2k_{\text{ET}}^{\text{Cr}}}
\]

(14)

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

\[
k_{\text{Lum}}^{\text{Eu}} = k_{\text{ZnEuZn}}^{\text{Eu}} = \left(\frac{\tau_{\text{obs}}^{\text{Eu}}}{\tau_{\text{exc}}^{\text{Eu}}}\right)^{-1}
\]

(15)

\[
k_{\text{ET}}^{\text{Cr}} = k_{\text{CrEuCr}}^{\text{ET}} = \left(\frac{\tau_{\text{obs}}^{\text{Cr}}}{\tau_{\text{exc}}^{\text{Cr}}}\right)^{-1}
\]

(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.40

\[
k_{\text{ET}}^{\text{Cr}} = \frac{k_{\text{CrEuCr}}^{\text{ET}} - k_{\text{ZnEuZn}}^{\text{Eu}}}{2} = \left(\frac{\tau_{\text{obs}}^{\text{Cr}}}{\tau_{\text{exc}}^{\text{Cr}}}\right)^{-1} - \left(\frac{\tau_{\text{obs}}^{\text{Eu}}}{\tau_{\text{exc}}^{\text{Eu}}}\right)^{-1}
\]

(17)

\[
\eta_{\text{global}}^{\text{CrEuCr}} = 1 - \frac{\tau_{\text{obs}}^{\text{Cr}}}{\tau_{\text{obs}}^{\text{Eu}}}
\]

(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 K and 295 K, in the solid state and in solution (Table 4). As expected from the existence of two CrIII acceptors in CrEuCr, the contribution of the intramolecular Eu → Cr energy transfers to the quenching of Eu(D0) luminescence is larger than that previously reported for [CrEu(L1)]+ (\( \eta_{\text{CrEu}} = 65–78\% \), Table 4).19 The individual
rate constants $k_{CrEu}^{ET}$ in CrEuCr and in [CrEu(L1)]$^{9+}$ can be directly compared in order to quantify the relative efficiency of the Eu → Cr communication in the two complexes. From eqn (17), we calculate $k_{ET}^{CrEu}$, $k_{CrEu}^{ET}$ (CrEu),

Thus leading to the ratios $k_{CrEu}^{ET}$ (CrEuCr)/$k_{CrEu}^{ET}$ (CrEu) = 1.6(2) at 10 K and $k_{CrEu}^{ET}$ (CrEuCr)/$k_{CrEu}^{ET}$ (CrEu) = 3.9(6) at 295 K (Table 4). Modelling the Eu → Cr energy transfer with a simple dipole-dipole mechanism (eqn 19)$^{11}$ is reasonable according to (i) the large Eu → Cr intermetallic separation measured in the crystal structure of [CrEu(L1)]$^{9+}$ ($R_{EuCr} = 9.32 Å$),

which is expected to be very similar in CrEuCr, and (ii) the minute expansion of the 4f orbitals.$^{10}$

$$k_{CrEu}^{ET} = \frac{k_{CrEu}^{ET}}{k_{CrEu}^{ET} + k_{CrEu}^{ET}} = \frac{1}{1 + (R_{EuCr}^{ET}/R_{CrCr}^{ET})^4} \quad (19)$$

Taking the rate constants collected in Table 4, we calculate with eqn (19) the critical distances for 50% energy transfer $R_{et}^{EuCr}$ = 11.2–13.5 Å, which are in the nanometric range (Table 4). Theoretically, $R_{et}^{EuCr}$ can be estimated with eqn (20), in which $\kappa$ is an orientation factor having an isotropic limit of 2/3, $\phi_e$ 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 cm$^3$ mol$^{-1}$.10

$$R_{et}^{EuCr}(\% ) = 8.75 \times 10^{-25} \times \kappa^2 \times \phi_e \times n^4 \times J [\text{cm}^3]$$

Surprisingly, the critical distances $R_{et}^{EuCr}$ measured in the trimetallc CrEuCr complex are marginally larger than those found in the bimetallic analogue [CrEu(L1)]$^{9+}$ (Table 4), despite the considerable decrease of the donor quantum yield when going from a Eu$^3+$ site in [ZnEu(ZnL2)]$^{7+}$ ($\phi_e$ = 0.34%, 10$^{-4}$ mol dm$^{-3}$ in acetonitrile at 293 K)$^{13}$ to the less luminescent Eu$^3+$ site in [ZnEu(ZnL2)]$^{5+}$ ($\phi_e$ = 0.002%, 10$^{-4}$ mol dm$^{-3}$ in acetonitrile at 293 K). This ratio $\phi_e^{ZnEu}/\phi_e^{ZnZn}$ = 0.0059 translates into $R_{et}^{EuCr}$ (CrEuCr)/$R_{et}^{EuCr}$ (CrEu) = 0.42 by using eqn (20). The experimental data $R_{et}^{EuCr}$ (CrEuCr)/$R_{et}^{EuCr}$ (CrEu) = 1.03(2) at 10 K and 1.08(3) at 295 K (Table 4) imply that $\kappa^2 \times n^4 \times J$ (CrEuCr)/$\kappa^2 \times n^4 \times J$ (CrEuCr) ≈ 2.5. Since both the orientation factor $\kappa$ 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 $\eta_{glob}^{TbCr} \geq 99.9\%$ with eqn (18) at 10 K (lifetimes taken from Table S2, ESI†), which points to a quantitative Tb → Cr energy transfer process, as previously reported for [CrTb(L1)]$^{9+}$.13 An efficient thermally-activated Tb$^{(D)} \rightarrow \lambda\pi^*\pi^*$ energy back transfer operates in CrTbCr and ZnTbZn, as previously described for [ZnTb(L3)]$^{9+}$,12 [ZnTb(L1)]$^{9+}$ and [Tb(L4)]$^{9+}$,14 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 1997,18 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$^{III}$ stops for producing kinetically stable macrocyclic 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 [CrLnCr(L2)]$^{7+}$ represent the first examples, in which both aspects are combined to produce a triple-helical nine-coordinate macrocyclic cavity adapted for the complexation of labile trivalent lanthanides. Interestingly, the seminal contributions of Albrecht18 and Chaudhuri40 focused on negatively charged ligand strands, which limit short-distance intermetallic repulsion thanks to charge compensation. In [ZnEuLZn(L2)]$^{7+}$ and [CrLnCr(L2)]$^{7+}$, 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 macrocyclic cavities. Moreover, the replacement of the terminal N$_2$O tridentate bidenting site in L1 with a central N$_2$ binding unit in L2 for complexing Ln$^{III}$ was initially thought to be deleterious for both stability constants41 and Ln$^{III}$-centred luminescence (Ln = Eu, Tb).38 We indeed detect a considerable decrease of the Eu-centred luminescent quantum yield in [ZnEuZnL2)$^{7+}$ compared with [ZnEuL1)$^{7+}$, 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 Cr → Ln transfers for efficiently sensitizing NIR emitters (Ln = Nd, Er, 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 terminal ligand L2$^9$ and the chromium(II) salt Cr(CF$_3$SO$_3$)$_2$.H$_2$O$^{11}$ were obtained according to literature procedures. The triflate salts Ln(CF$_3$SO$_3$)$_2$.nH$_2$O (Ln = La, Eu, Gd, Tb, Lu, 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 Titroplex III (Merck) in the presence of urotropine and xylene orange.$^{43}$

Preparation of the complexes [ZnLnZn(L2)](CF$_3$SO$_3$)$_2$.nH$_2$O (Ln = La, n = 5; Ln = Eu, n = 7; Ln = Gd, n = 8; Ln = Tb, n = 6; Ln = Lu, n = 6)

A solution of Ln(CF$_3$SO$_3$)$_2$.nH$_2$O (Ln = La, Eu, Gd, Tb, 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.
A typical experiment, 50 cm$^3$ of L$_2$ in acetonitrile/chloroform (2:1) was added to a solution of Ln(CF$_3$SO$_3$)$_3$·nBu$_4$N(CF$_3$SO$_3$) (Ln = La, n = 12, p = 0.1; Ln = Eu, n = 8, p = 0.1; 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†). A solution of Ln(CF$_3$SO$_3$)$_3$·nH$_2$O (Ln = La, n = 12, p = 0.1; Ln = Eu, n = 8, p = 0.1; Ln = Gd, n = 8; Ln = Tb, n = 7, p = 0.3; Ln = Lu, n = 10, p = 0.3) was added to a solution of Ln(CF$_3$SO$_3$)$_3$·nBu$_4$N(CF$_3$SO$_3$) (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) in acetonitrile (2 cm$^3$) was added to a solution of L$_2$ (41.3 mg, 0.051 mmol) in acetonitrile/dichloromethane (12 cm$^3$ : 12 cm$^3$). 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. A solution of Ln(CF$_3$SO$_3$)$_3$·nH$_2$O (12.6 mg, 0.034 mmol) in acetonitrile (1 cm$^3$) produced a deep green mixture, which was stirred for one night under an inert atmosphere. This was 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 and the pale yellow residue was dissolved in a minimum of acetonitrile (2 cm$^3$). After stirring for 1 h at rt, the solvent was evaporated with the SPECFIT program. All the complexes were characterized by their IR spectra and gave satisfactory elemental analyses (Table S1, ESI†).

**Preparation of the complexes [CrLnCr(L2)][(CF$_3$SO$_3$)$_2$·nH$_2$O·pBu$_4$N(CF$_3$SO$_3$)]**

Electronic spectra in the UV-Vis region were recorded at 293 K and with the SPECFIT program. 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 using 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 quadrapler 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 $\phi = [I(\tilde{r}) \times I(\tilde{r})] / [I(\tilde{r}) \times I(\tilde{r}) \times I(\tilde{r}) \times I(\tilde{r})]$, where $\tilde{r}$ r refers to the sample, and $\tilde{r}$ r to the reference; $A$ is the absorbance, $I$ 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. Cs$_2$[Eu(2,6-pyridinedicarboxylic acid)]$_3$ was used as reference. Elemental analyses were performed by Dr H. Eder from the Microchemical Laboratory of the University of Geneva.

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