Optimizing Millisecond Time Scale Near-Infrared Emission in Polynuclear Chrome(III)–Lanthanide(III) Complexes

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ABSTRACT: This work illustrates a simple approach for optimizing long-lived near-infrared lanthanide-centered luminescence using trivalent chromium chromophores as sensitizers. Reactions of the segmental ligand \( L_2 \) with stoichiometric amounts of \( \text{M(CF}_3\text{SO}_3)\_2 \) (\( \text{M} = \text{Cr}, \text{Zn} \)) and \( \text{Ln(CF}_3\text{SO}_3)\_3 \) (\( \text{Ln} = \text{Nd}, \text{Er}, \text{Yb} \)) under aerobic conditions quantitatively yield the \( D_3\)-symmetrical trinuclear \( [\text{M}_2\text{Ln}\text{M(L}_2)_3]\text{CF}_3\text{SO}_3)_n \) complexes (\( n = 9 \)), in which the central lanthanide activator is sandwiched between the two transition metal cations. Visible or NIR irradiation of the peripheral Cr(III) chromophores in \( [\text{CrLnCr(L}_2)_3]\text{CF}_3\text{SO}_3)_n \) induces rate-limiting intramolecular intermetallic Cr\( \rightarrow \text{Ln} \) energy transfer processes (\( \text{Ln} = \text{Nd}, \text{Er}, \text{Yb} \)), which eventually produces lanthanide-centered near-infrared (NIR) or IR emission with apparent lifetimes within the millisecond range. As compared to the parent dinuclear complexes \( [\text{CrLn(L}_1)_3]\text{CF}_3\text{SO}_3)_n \), the connection of a second strong-field \( [\text{CrN}_3]^{\text{eff}} \) sensitizer in \( [\text{CrLnCr(L}_2)_3]\text{CF}_3\text{SO}_3)_n \) significantly enhances the emission intensity without perturbing the kinetic regime. This work opens novel exciting photophysical perspectives via the buildup of non-negligible population densities for the long-lived doubly excited state \( [\text{Cr}^*\text{LnCr}^*(L_2)_3]^{9n} \) under reasonable pumping powers.

INTRODUCTION

Formally, the near-infrared (NIR) spectral range starts at 750 nm (13 333 cm\(^{-1}\)), and many trivalent lanthanide ions, \( \text{Ln(III)} \) = \( \text{Pr}, \text{Nd}, \text{Sm}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb} \), display radiative f\( \rightarrow \)f transitions above this wavelength. Those with \( \text{Ln} = \text{Nd}, \text{Er}, \text{Yb} \) are often exploited for applications as optical amplifiers (for instance, in Er-doped silica fibers, which are transparent around 1550 nm, the wavelength of the Er\( ^{111/2} \rightarrow ^{15/2} \) emission), as laser materials (for instance, in Nd:YAG lasers based on the Nd\( ^{4\text{F}_1/2} \rightarrow ^{4\text{I}_{15/2}} \) transition at 1060–1090 nm), as NIR-sensitive light upconverting devices, and as luminescent probes for high-resolution analysis of deep living tissues (light transmission is maximized in the 850–1100 nm spectral range for biological material). In this context, hundreds of lanthanide-containing NIR emitters were synthesized and investigated during the past decade, with a special emphasis on the connection of sophisticated organic chromophores that are able to harvest near-UV or visible light for sensitizing NIR emission. Because energy transfer processes are optimized when the spectral overlap integral between the emission spectrum of the donor (i.e., that of the light-harvesting chromophore) and the absorption spectrum of the lanthanide activator is maximized, highly conjugated polyaromatic antennae emitting in the red part of the electromagnetic spectrum are actively investigated for improving the global sensitization process. However, the focus of many studies on practical applications has somewhat masked some of the less common photophysical properties of molecular lanthanide-centered NIR emissive complexes, which are currently underexploited. First, the estimated effective vibrational energies \( h\nu_{\text{eff}} \approx 2000 \text{ cm}^{-1} \) operative in molecular coordination complexes, combined with interactions of the metallic centers with solvent molecules possessing high-energy CH, OH, and NH oscillators, are particularly efficient for inducing nonradiative deexcitation pathways in lanthanide-centered NIR emitters. Consequently, the characteristic luminescence lifetimes of NIR-emitting \( \text{Ln(III)} \text{ ions}, \tau_{\text{em}} = 1/k_{\text{nr}} \), are on the (sub)microsecond time scale, which is far below their predicted millisecond radiative decays. Because biological materials

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irradiated in the visible do not produce strong background emission in the NIR range, time-gated amplification is not considered an important issue for short-term applications, and only few efforts have been focused on the lengthening of NIR lanthanide lifetimes in molecular systems. However, millisecond NIR lifetimes should offer remarkable opportunities (i) for security and identification systems that cannot be forged and (ii) for the quantification of trace targets in biological materials with time-gated detection. Second, broadband light-harvesting organic chromophores can be favorably replaced with d-block sensitizers possessing much narrower and tunable absorption bands to facilitate the design of more specific excitation/emission wavelength pairs.

For instance, cocrystallization of \([\text{Cr(CN)}_6]^{3-}\) with \(\text{Yb}^{3+}\) cations gives infinite \([\text{Cr(CN)}_6\mu-\text{CN}]^2\text{Ln}^{-}\) chains, in which the NIR emitting lanthanides could be indirectly sensitized by the blue excitation of the spin-allowed Cr(4T2 \rightarrow 4A2) transition. However, the efficient intermolecular Cr\(\rightarrow\)Ln energy transfer processes operating in these coordination polymers \((W_{\text{Cr}\rightarrow\text{Ln}} > 10^4 \text{ s}^{-1})\) did not offer a possibility for lengthening the Ln(III)-centered emission lifetimes.

To restrain Cr/Ln communication to an isolated pair of metals, for which the intermolecular energy transfer rate constant can be controlled, Kaizaki and Piguet designed two families of dinuclear Cr(III)/Ln(III) molecular complexes exhibiting Ln-centered NIR emission upon Cr(III) sensitization (Figure 1). The detection of residual Cr(2E \rightarrow 4A2) emission together with the target Yb(2F7/2 \rightarrow 2F5/2) fluorescence upon visible or NIR irradiation (Figure 1) confirmed that incomplete intramolecular Cr\(\rightarrow\)Yb energy transfers occur due to small \(W_{\text{Cr}\rightarrow\text{Yb}}\) rate constants, thus leading to long apparent Yb-centered NIR lifetimes mirroring the millisecond decay of the Cr(III) donor chromophore, but to small quantum yields. In this Article, we propose a simple and efficient strategy for optimizing lanthanide-centered emission intensity in such edifices by increasing their nuclearity and apply it to Ln = Nd, Er, and Yb.

### RESULTS AND DISCUSSION

#### Theoretical Background

The complete light-conversion processes in the dinuclear CrLn helicates can be modeled with the Jablonski diagram depicted in Figure 2a for Ln = Yb. The solutions of the associated kinetic differential equations, given in matrix form in eq 1, under continuous-wave irradiation of the Cr-centered transitions yield the variations of the steady-state population densities for the various levels (the 0.05 population density range is highlighted on the right) by using \(W_{\text{Cr} \rightarrow \text{Ln}} = 240 \text{ s}^{-1}\), \(k_{\text{CrGd}} = 270 \text{ s}^{-1}\), and \(k_{\text{Yb}^{*}} = 5 \times 10^4 \text{ s}^{-1}\) with increasing incident pump power \(P\).

\[
\begin{align*}
W_{\text{Cr} \rightarrow \text{Ln}} &= 240 \text{ s}^{-1} \\
k_{\text{CrGd}} &= 270 \text{ s}^{-1} \\
k_{\text{Yb}^{*}} &= 5 \times 10^4 \text{ s}^{-1}
\end{align*}
\]

The energy transfer rate constant measured in \([\text{CrGd}(\text{H}_2\text{O})_2(\text{dmf})_4]^{3+}\) is \(108 \text{ s}^{-1}\), while \(k_{\text{CrGd}}\) is the decay rate constant of Yb(2F5/2) in the absence of an acceptor and measured in \([\text{CrGd}(\text{H}_2\text{O})_2(\text{dmf})_4]^{3+}\).

Figure 2. (a) Kinetic scheme for modeling the light-conversion process occurring in \([\text{CrYb}(\text{L}1)_3]^{3+}\) upon irradiation into the Cr-centered absorption bands and (b) computed steady-state population densities for the various levels (the 0.05 population density range is highlighted on the right) by using \(W_{\text{Cr} \rightarrow \text{Ln}} = 240 \text{ s}^{-1}\), \(k_{\text{CrGd}} = 270 \text{ s}^{-1}\), and \(k_{\text{Yb}^{*}} = 5 \times 10^4 \text{ s}^{-1}\) with increasing incident pump power \(P\).

The pump rate constant, \(k_{\text{CrGd}}\), is given by eq 2 in which \(\alpha_{\text{Cr}}\) is the absorption cross section of the Cr-centered transition and \(\sigma_P\) is the pump wavelength, \(\omega_P\) is the pump radius, \(P\) is the incident pump power, \(h\) is the Planck constant, and \(c\) is the vacuum speed of light.
Because \( k_{Cr}^{*} \approx k_{Yb}^{*} \), the population densities of the Yb-centered excited levels \( |\beta⟩ \) and \( |\gamma⟩ \) remain negligible for all incident pump powers, and as the intrinsic luminescence quantum efficiency of the Yb luminescence, \( \eta_{Yb}^{*} \), is low, the intensity of the NIR emission remains marginal \( (I \propto \eta_{Yb}^{*} (N_{Yb}^{0} + N_{Yb}^{\gamma})) \), Figure S2, Supporting Information. However, its apparent exponential decay \( \tau_{Yb}^{*} = 1/k_{Yb}^{*} \) = 1.96 ms in \([CrYbCr(L2)]^{3+}\) mirrors the long Cr(III) donor lifetime.16

With this in mind, the only available option for improving emission intensity in molecular edifices without affecting the apparent millisecond dynamics of the Yb-centered NIR emission observed in dinuclear helicates requires the connection of additional Cr(III) sensitizers with identical photophysical properties. A first step toward this goal is to extend the polynuclear axis by addition of a second terminal Cr(III) ion. The trinuclear dimeric complex \([CrYbCr(L2)]^{3+}\) is expected to meet the above-mentioned criterion (Figure 3a):23 introduction of the rate constants obtained for \([CrYbCr(L1)]^{3+}\) into a kinetic scheme adapted to \([CrYbCr(L2)]^{3+}\) (Figure 3b, Supporting Information). It is worth noting here that the Yb-centered NIR luminescence in \([CrYbCr(L2)]^{3+}\) is expected to mainly originate from the singly excited state \( CrYb*Cr \) \( (|\beta⟩ \) in Figure 3b) at low incident pump power, as found for \([CrYbCr(L1)]^{3+}\), whereas the doubly excited state \( Cr*Yb*Cr \) \( (|\gamma⟩ \) in Figure 3b) becomes the main contributor at higher incident pump power (Figure S3b, Supporting Information), a characteristic inherent to the trinuclear molecular complex.

In the following sections, the accuracy of these predictions for the complete molecular light- conversion process leading to NIR emission in the trinuclear complexes is demonstrated for \([CrLnCr(L2)]^{3+}\) \( (Ln = Nd, Er, Yb) \) in which the twin d-block metal ions act as sensitizers, as well as for the reference helicates \([ZnLnZn(L2)]^{2+}\) for which no d-block sensitization is present.

**Synthesis and Structural Characterization of \([ZnLnZn(L2)]^{2+}\)** and \([CrLnCr(L2)]^{3+}\) \( (Ln = Nd, Er, Yb) \). Stoichiometric mixing of \( M(CF_{3}SO_{3})_{2} \cdot xH_{2}O \) \( (M = Cr(II), Zn(II); 2 equiv) and Ln(CF_{3}SO_{3})_{3} \cdot nH_{2}O \) \( (Ln = Nd, Er, Yb; 1 equiv) \) with the segmental tridentate ligand \( L_{2} \) (3 equiv) in acetonitrile quantitatively yields the targeted self-assembled triple-stranded complexes \([MLnM(L2)]^{2+}\) as previously established for \( Ln = La, Eu, Gd, Tb, \) and \( Lu \) (Figure 3a).23a

Whereas the air-sensitive dinuclear chromium(II) complexes are not isolated, slow diffusion of diethyl ether into concentrated acetonitrile solutions containing an excess of Bu_{4}N(CF_{3}SO_{3}) (=TBAf, Table S1) after slow diethyl ether into concentrated acetonitrile solutions containing an excess of Bu_{4}N(CF_{3}SO_{3}) (=TBAf, Table S1). Because of the slow electronic relaxation rate of the nondegenerate Cr(III) ground state,23b 1H NMR spectra of these complexes are too broad for any reliable characterization of these complexes (Figure S6), but ESI-MS data strongly support the exclusive formation of \([CrLnCr(L2)]^{3+}\) in acetonitrile (Table S2 and Figure S4b). Recrystallization by slow diffusion of diethyl ether into propionitrile solutions yields fragile orange needles of \([CrLnCr(L2)]^{3+}\) in acetonitrile (Table S2) and Figure S4b).
analyses, and their crystal structures indeed confirm the existence of almost superimposable pseudo-D₃ symmetrical triple-stranded helical cations (Figures S7–S9), together with disordered noncoordinated trilate anions and propionitrile molecules (Figure 4b). DFT-optimized Zn–N and Eu–N bond lengths in \([\text{ZnEuZn}(L_2)_3]^{7+}\) and observed Cr–N and Ln–N bond lengths in \([\text{CrLnCr}(L_2)_3]^{9+}\) have standard values. The d-block atoms (Zn or Cr) occupy axially compressed pseudo-octahedral sites produced by the three bound terminal chelating didentate benzimidazole-pyridine units, while trivalent lanthanides lie in the central pseudotricapped trigonal prismatic cavities provided by the nine heterocyclic nitrogen atoms of the three wrapped tridentate units, while trivalent lanthanides lie in the central pseudo-octahedral sites produced by the three bound terminal chelating didentate benzimidazole-pyridine units, while trivalent lanthanides lie in the central pseudotricapped trigonal prismatic cavities provided by the nine heterocyclic nitrogen atoms of the three wrapped tridentate units. The replacement of the terminal diamagnetic Zn(II) with open-shell Cr(III) in \([\text{CrGdCr}(L_2)_3]^{9+}\) enhances the paramagnetic coupling mechanism responsible for the increasing intensity of the spin-forbidden \(\pi^*\rightleftharpoons\pi^*\) phosphorescence arising at 24 510 cm⁻¹ (dissociative unit, \(\tau = 5.19(1)\) ms) and 21 050 cm⁻¹ (tridentate unit, \(\tau = 1.58(1)\) ms, Figure 5).

These spectroscopic levels are summarized in the associated Jablonski diagram (Figure 6, center), which can be completed with the Cr(2E) excited state evidenced by intramolecular L₂→Cr energy transfer processes sensitizing the famous long-lived Cr(2E→4A₂) luminescence at 13 240 cm⁻¹ in \([\text{CrGdCr}(L_2)_3]^{9+}\left(\frac{\Delta_{\text{Cr}}}{k_{\text{Cr}}} = 2.27(2)\right)\) ms at 10 K, Table 1, column 2, Figure 5, and Figure S10).

The associated excitation profile recorded for \([\text{CrGdCr}(L_2)_3]^{9+}\) upon monitoring the Cr(2E→4A₂) transition unravels that both Cr-centered \(\pi^*\rightleftharpoons\pi^*\) phosphorescence at 13 330 cm⁻¹; Cr(2T₁ e⁻A₂) at 19 970/21 780 cm⁻¹ and ligand-centered (>24 500 cm⁻¹) excitation processes (Figure S11) contribute to NIR phosphorescence centered at 13 240 cm⁻¹ (Figure 6). Because of the pseudo-D₃ symmetry in \([\text{CrGdCr}(L_2)_3]^{9+}\), the Cr(2T₂) and Cr(2T₁) excited levels are split into A + E components. From the barycenter of these transitions, we can estimate the Cr(III) pseudo-octahedral ligand-field strength \(\Lambda = 20 880 \text{ cm}^{-1}\) and the Racah parameter \(B = 750 \text{ cm}^{-1}\), that is reduced to 72% of its free ion value by the nephelauxetic effect; see eq 3 with \(C \approx 4B\) for N-donor atoms bound to Cr(III).
Distances for 50% Energy Transfer (\(\text{ZnLnZn(CF}_3\text{SO}_3)_9\) (Ln = Nd, Er, Yb). The Cr(2T2) levels are omitted for molecular complexes with reasonably protected coordination emissions are within the microsecond range as expected for individual components summarizing the excitation processes (straight upward arrows), resonant energy transfer processes (horizontal dashed arrows), phonon-assisted energy transfer processes (diagonal dashed arrows), nonradiative multiphonon relaxation (undulating arrows), and observed radiative emission processes (straight downward arrows) occurring in [ZnLnZn(L2)_3](CF3SO3)_9 and [CrLnCr(L2)_3](CF3SO3)_9 (Ln = Nd, Er, Yb). The Cr(2T2) levels are omitted for clarity, although they can act as a relay for energy transfer processes.

\[
\Delta E = E[\text{Cr}^2\text{E})] - E[\text{Cr}^2\text{A}_2]) = (9B + 3C - 90B^2/\Delta) = 13330\text{cm}^{-1} \tag{3}
\]

The energies of the Ln-centered excited levels are deduced from excitation of the ligand-centered \(1\pi^*\) singlet states in [ZnLnZn(L2)_3](CF3SO3)_9 (Ln = Nd, Er, Yb), which produces residual ligand-centered emission because of incomplete singlet states in [CrLnCr(L2)_3](CF3SO3)_9 (Ln = Nd, Er, Yb). The Cr(2E) excited state can be sensitized in [CrLnCr(L2)_3](CF3SO3)_9 by selective laser excitation of the Cr(2E)/Nd(4F3/2) transition at \(13330\text{cm}^{-1}\) (Figure S15a), and at \(\approx 6500\text{cm}^{-1}\) for Er\(1\text{I}_{13/2} \rightarrow 1\text{I}_{15/2}\) (Figure S15b).

**Table 1. Rate Constants (k/s\(^{-1}\)), Efficiencies (\(\eta\), eq 5), Intramolecular Intermetallic Ln-Cr Distances (\(R_{\text{CrLa}}/\AA\), and Critical Distances for 50% Energy Transfer (\(R_{\text{ZnZn}}/\AA\), eq 6) in [LnCr(L1)_3](CF3SO3)_9 and [CrLnCr(L2)_3](CF3SO3)_9 (Ln = Nd, Er, Yb; 10 K)\(^a\)**

<table>
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<th>compd</th>
<th>(k_{\text{CrGd}}^{\text{Zn}})</th>
<th>(k_{\text{CrGd}}^{\text{La}})</th>
<th>(k_{\text{ZnGd}}^{\text{Zn}})</th>
<th>(k_{\text{ZnGd}}^{\text{La}})</th>
<th>(W_{\text{Gd-In}})</th>
<th>(\eta_{\text{Gd-In}})</th>
<th>(R_{\text{CrLa}})</th>
<th>(R_{\text{ZnZn}})</th>
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<td>6.85x10^5</td>
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<td>0.87x10^3</td>
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<td>4.5x10^3</td>
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</tr>
<tr>
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<td>5.0x10^5</td>
<td>2.1x10^3</td>
<td>1.1x10^3</td>
<td>0.5x10^3</td>
<td>0.3x10^3</td>
<td>8.9x10^3</td>
<td>3.3x10^3</td>
<td>16</td>
</tr>
<tr>
<td>[YbZn(L1)_3]</td>
<td>4.40x10^3</td>
<td>5.0x10^5</td>
<td>2.1x10^3</td>
<td>1.2x10^3</td>
<td>0.6x10^3</td>
<td>0.4x10^3</td>
<td>8.9x10^3</td>
<td>2.2x10^3</td>
<td>16</td>
</tr>
<tr>
<td>[CrGdCr(L1)_3]</td>
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<td>3.2x10^4</td>
<td>2.0x10^6</td>
<td>7.6x10^3</td>
<td>0.3x10^3</td>
<td>0.9x10^3</td>
<td>0.5x10^3</td>
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<td>this work</td>
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<td>6.9x10^2</td>
<td>9.3x10^3</td>
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<td>4.9x10^3</td>
<td>0.8x10^3</td>
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<td>0.5x10^3</td>
<td>9.8x10^3</td>
<td>this work</td>
</tr>
</tbody>
</table>

\(a\) \(R_{\text{CrLa}} = R_{\text{CrLn}} + R_{\text{LnLa}}\), and \(R_{\text{ZnZn}}\) are reported with their experimental standard deviations. All other uncertainties are calculated by using standard mathematical propagations.
produces a non-negligible transient population only for the lowest excited Cr*LnCr state (\( \ell \alpha \) level in Figure 3b), which relaxes (i) via radiative and nonradiative pathways (\( k^{-1}_{\text{CrLaCr}} \)) toward the CrLnCr ground state (0 level in Figure 3b) and (ii) via energy transfer \( W_{\text{CrLaCr}}^{\text{CrLnCr}} \) toward the CrLn*Cr state (\( \ell \beta \) level in Figure 3b). This simple kinetic scheme allows straightforward estimates of energy transfer rate constants (1,000 < \( k_{\text{CrLaCr}} \) < 0.1 eq 4) and efficiencies (\( \eta_{\text{CrLaCr}} \)) by using the experimental characteristic lifetimes of the Cr(2E) excited state measured for the isostructural [CrGdCr(L2)\(_3\)]\(^{19+} \) (\( \tau_{\text{CrGdCr(E)}} \)) and [CrLnCr(L2)\(_3\)]\(^{19+} \) (\( \tau_{\text{CrLnCr(E)}} \)) complexes (Ln = Nd, Er, Yb, Table 1).\(^{12} \)

\[
\begin{align*}
W_{\text{CrLaCr} \rightarrow \text{Ln}} &= \frac{k_{\text{CrLaCr}}}{k_{\text{CrLnCr}}} = \left( \frac{\tau_{\text{CrLnCr(E)}}}{\tau_{\text{CrGdCr(E)}}} \right)^{1} \left( \frac{\tau_{\text{CrLnCr(E)}}}{\tau_{\text{CrGdCr(E)}}} \right)^{-1} \\
\eta_{\text{CrLaCr} \rightarrow \text{Ln}} &= \frac{W_{\text{CrLaCr} \rightarrow \text{Ln}}}{W_{\text{CrLaCr} \rightarrow \text{Ln}} + k_{\text{CrLnCr}}} = 1 - \frac{k_{\text{CrLnCr}}}{k_{\text{CrLaCr}}} = 1 - \frac{\tau_{\text{CrLnCr(E)}}}{\tau_{\text{CrGdCr(E)}}} \\
\end{align*}
\]

(5)

The calculated rate constants for the intramolecular Cr-Ln energy transfer processes are similar for the dinuclear [CrLn(L1)\(_3\)]\(^{6+} \) and trinuclear [CrLnCr(L2)\(_3\)]\(^{19+} \) complexes (Ln = Nd, Yb, Table 1, column 6), in line with the starting hypothesis. This leads to slightly less efficient energy transfer for the latter complexes because of the shorter intrinsic Cr(2E) lifetime in [CrGdCr(L2)\(_3\)]\(^{19+} \) (Table 1, columns 2 and 7). Although recent investigations\(^{32} \) suggest that long-distance intermetallic d-d energy transfers may include a competition between the electron-exchange mechanism (i.e., Dexter-type)\(^{33} \) and the (multipolar) Coulombic interaction between the donor and acceptor electric fields (i.e., Förster-type),\(^{34} \) the energy transfer efficiencies in [CrLn(L1)\(_3\)]\(^{6+} \) and [CrLnCr(L2)\(_3\)]\(^{19+} \) (Ln = Nd, Er, Yb) were analyzed within the strict limit of the long-range dipole–dipole formalism according to eq 6, in which \( R_{\text{DA},\text{C}} \) is the donor–acceptor distance separation taken as the intramolecular Cr-Ln contact distance in the complexes and \( R_{\text{DA},\text{C}} \) is the critical distance at which \( \eta_{\text{DA} \rightarrow \text{C}} = 0.5.\(^{12,35} \) This simplification is justified by the presence of m ethylene units linking the three tridentate coordination moieties in L2 acting as electronic insulators.

\[
\eta_{\text{Cr} \rightarrow \text{Ln}} = \left[ 1 + \left( \frac{R_{\text{DA},\text{C}}}{R_{\text{DA},\text{C}}} \right)^{6} \right]^{-1} = \frac{R_{\text{DA},\text{C}}^{6}}{R_{\text{DA},\text{C}}^{6} + R_{\text{DA},\text{C}}^{6}} \\
\]

(6)

We find critical distances for 50% energy transfer efficiencies in the nanometric range for all complexes with \( R_{\text{DA},\text{C}}^{6} > R_{\text{DA},\text{C}}^{6} > R_{\text{DA},\text{C}}^{6} \) (Table 1, column 9), a trend in line with the decreasing number of Ln-centered excited acceptor levels available on each cation for resonant or phonon-assisted energy transfer mechanisms (Figure 6).

We are now equipped for introducing the rate constants collected in Table 1 into eq 1 with the kinetic matrix adapted for [CrLnCr(L2)\(_3\)]\(^{19+} \) (Figure S3a). Steady-state simulations for Ln = Nd, Er, Yb using the simplified Jablonski diagram depicted in Figure 3b show that the slow decay rates of the Cr(2E) donor levels control the stepwise depopulation of the CrLnCr ground state to the benefit of the Cr-centered excited levels Cr*LnCr (low pumping power) and Cr*LnCr* (large pumping power, Figure S17, Supporting Information). The population density of the Ln-centered NIR emitting levels CrLn*Cr, Cr*Ln*Cr, and Cr*Ln*Cr* remains negligible (less than 1%) for any pumping power leading to weak NIR emission because of the low intrinsic luminescence quantum efficiency of the Yb luminescence (Figure S18). We however could notice that the predicted statistical 2-fold gain in intensity in going from [LnCr(L1)]\(^{6+} \) to [CrLnCr(L2)]\(^{19+} \) is verified for Ln = Nd (Figure S19), whereas some “positive cooperative effect” is observed for Ln = Yb, with a somewhat larger overall gain \( f_{\text{gain}} = 2.4 \) at low incident power and \( f_{\text{gain}} = 3.1 \) at high power, Figure 8. Interestingly, these slow Cr-Ln energy transfer rate constants can be converted into an advantage when one considers the apparent lifetimes of the Ln-centered NIR emission. For the short-time low-power light pulses used in this work, only the ground CrLnCr (0 level) and the two first excited states Cr*LnCr (\( \ell \alpha \)) and Cr*Ln*Cr (\( \ell \beta \)) contribute to the kinetic scheme. Equation 7 therefore satisfyingly models the relaxation processes originating from the initial density population matrix written as its transpose (\( N_{\text{tot}}^{(0)} = (N_{\text{tot}} - N_{\text{tot}}^{(0)})N_{\text{tot}}^{(0)}N_{\text{tot}}^{(0)} = 0 \)):

\[
\begin{array}{l}
\frac{dN_{\text{tot}}^{(0)}}{dt} = 0 \\
\frac{dN_{\text{tot}}^{(0)}}{dt} = -k_{\text{CrLnCr}} + W_{\text{CrLnCr} \rightarrow \text{Ln}} \\
\end{array}
\]

\[
\begin{align*}
\begin{bmatrix}
\frac{dN_{\text{tot}}^{(0)}}{dt} \\
\frac{dN_{\text{tot}}^{(0)}}{dt} \\
\frac{dN_{\text{tot}}^{(0)}}{dt} \\
\end{bmatrix}
&= 
\begin{bmatrix}
\frac{N_{\text{tot}}^{(0)}}{k_{\text{CrLnCr}} + W_{\text{CrLnCr} \rightarrow \text{Ln}}} \\
0 \\
\end{bmatrix}
\end{align*}
\]

(7)

Using projection operator solutions,\(^{20} \) we obtain (Appendix 1):
and [CrErCr(L2)]^{9+} (Figure S21) shows that, except for the first microseconds following the pulse, the decay rate of the Ln-centered NIR emission mirrors the Cr(2E) emission lifetimes and thus extends into the millisecond range. This prediction is confirmed by the apparent long experimental Nd(4F3/2), Er(4I13/2), and Yb(2F5/2) lifetimes observed in [CrLnCr(L2)]^{9+} (Figure S21), an exact comparison of experimental and calculated emission at the solid state, 295 K) are compatible with their use as long-lived NIR probes for analytical chemistry and biology. Last, but not least, the presence of two Cr(III) donors sandwiching the Ln(III) activator results in the non-negligible population of long-lived doubly excited states Cr*LnCr* (δβ) and Cr*Ln*Cr* (γβ), Figures 3b and S3) under reasonable pumping powers as illustrated for Yb on Figure 10 (see Figures S22–S23 for corresponding graphs for Nd and Er; equations are given in Appendix 2), a phenomenon that has no counterpart in the parent dinuclear complexes (Figure 2).

This work opens unprecedented perspectives for the programming of molecular Ln-centered energy transfer upconversion (ETU) processes exploiting lanthanide-centered CrLn*Cr doubly excited states when the activator possesses an adequate series of accessible spectroscopic levels as found in [CrErCr(L2)]^{9+}. We believe that such a supramolecular control of NIR luminescence parameters will be helpful for the design of materials and probes in fields as diverse as telecommunications, security devices, and bioimaging, especially that extension to multidimensional arrays can be envisaged.

## EXPERIMENTAL SECTION

### Synthesis.

Chemicals were purchased from Strem, Acros, Fluka AG, and Aldrich, and used without further purification unless otherwise stated. The ligand L2 was prepared complexes Cr(CF3SO3)2.[ZnGdZn(L2)]2[CF3SO3]2, CrGdCrCl(L2)], [CF3SO3]2, and [CrErCr(L2)]2[CF3SO3]2.3,23b were prepared according to literature procedures. The triflate salts Ln(CF3SO3)2·nH2O were prepared from the corresponding oxide (Aldrich, 99.99%). Acetonitrile and dichloromethane were distilled over calcium hydride.

Preparation of [ZnLnZn(L2)]2[CF3SO3]2·nH2O (Ln = Nd, Er, Yb). Ln(CF3SO3)2·xH2O (17 μmol) in acetonitrile (2 mL) was added into a dichloromethane/acetonitrile (1:1, 24 mL) solution of L2 (41.3 mg, 51 μmol). After being stirred at room temperature for 24 h, the mixture was evaporated to dryness, the solid residue was dissolved into acetonitrile (10 mL), and Zn(CF3SO3)2 (12.4 mg, 34 μmol) in acetonitrile (2 mL) was added. The resulting solution was stirred for 24 h and concentrated. Slow diffusion of diethyl ether (12 h) eventually

**CONCLUSION**

The connection of a second strong-field [CrN6] chromophore to the C2-symmetrical dinuclear complexes [LnCr(L1)]^{6+} resulting in the formation of [CrLnCr(L2)]^{9+} does not significantly affect the ligand-centered and metal-centered photophysical properties. Excitation into the Cr(2E)-centered levels with NIR irradiation at 13 300 cm^{-1} induces intra-

molecular Cr→Ln energy transfers, which eventually sensitize low-energy luminescence for Ln = Nd, Er, or Yb in the spectral range 6000–10 000 cm^{-1}. As compared to the fast Ln-centered relaxation pathways operating in [ZnLnZn(L2)]^{9+}, the slow Cr→Ln energy transfer responsible for the feeding of the same Ln-centered excited levels in [CrLnCr(L2)]^{9+} acts as bottleneck, which controls the kinetics of the low-energy NIR emission. The apparent millisecond Ln-centered lifetimes thus mirror those of the Cr(2E) donor levels. This unusual property is obtained at the cost of the intensity of the NIR output, but the connection of a second Cr(III) donor in [CrLnCr(L2)]^{9+} partially overcomes this limitation because the predicted intensities are more than twice larger than those found in the related dinuclear [LnCr(L1)]^{6+} complexes. The effective experimental gain in NIR emission intensity further depends on the ratio between radiative and nonradiative de-excitation pathways for the emitting Nd(4F3/2), Er(4I13/2), and Yb(2F5/2) levels, a trend that can be addressed by measuring intrinsic and global quantum yields. Because no such data were recorded for [LnCr(L1)]^{6+} in ref 23a, an exact comparison of experimental NIR→NIR light-conversion efficiencies between dinuclear and trinuclear complexes is currently inaccessible, but the encouraging global quantum yields measured for [CrLnCr(L2)]^{9+} upon Cr-centered irradiation (η_Nd = 0.027(1) and η_Yb = 0.030(3), solid state, 295 K) are compatible with their use as long-lived NIR probes for analytical chemistry and biology.

The time evolution of the population densities computed for [CrYbCr(L2)]^{9+} (Figure 9), [CrNdCr(L2)]^{9+} (Figure S20), and [CrErCr(L2)]^{9+} (Figure S21) shows that, except for the first microseconds following the pulse, the decay rate of the Ln-centered NIR emission mirrors the Cr(2E) emission lifetimes and thus extends into the millisecond range. This prediction is confirmed by the apparent long experimental Nd(4F3/2), Er(4I13/2), and Yb(2F5/2) lifetimes observed in [CrLnCr(L2)]^{9+} (Table 1, column S).

\[ N_{t}^{(0)} = N_{t}^{(0)} - \frac{\eta_{\text{Cr}}^{(\alpha)}}{\eta_{\text{Ln}}^{(\beta)}} \times \frac{N_{t}^{(\alpha)}}{(k_{\text{Ln}}^{(\alpha)} - k_{\text{Cr}}^{(\alpha)})} \times \left( e^{-\left(k_{\text{Ln}}^{(\alpha)} + k_{\text{Cr}}^{(\alpha)}\right)t} \right) \]

\[ N_{t}^{(9)} = N_{t}^{(9)} - \frac{N_{t}^{(9)}}{(k_{\text{Ln}}^{(9)} - k_{\text{Cr}}^{(9)})} \times \left( e^{-\left(k_{\text{Ln}}^{(9)} + k_{\text{Cr}}^{(9)}\right)t} \right) \]

\[ N_{t}^{(10)} = \frac{N_{t}^{(10)}}{(k_{\text{Ln}}^{(10)} - k_{\text{Cr}}^{(10)})} \times \left( e^{-\left(k_{\text{Ln}}^{(10)} + k_{\text{Cr}}^{(10)}\right)t} \right) \]
prepared by Dr. H. Eder from the Microchemical Laboratory of the University of Geneva. Electronic spectra in the UV-vis were recorded at 293 K from solutions in MeCN with a Perkin-Elmer Lambda 900 spectrometer using quartz cells of 0.1 cm path length.

Photophysical investigations at 10 K were performed on powdered samples, which were mounted onto copper plates with either rubber cement or conductive silver glue; cooling was achieved either with a closed-cycle He cryostat (CTI-Cryogenics, Oxford Instruments, CICC110T) or with a liquid-helium bath cryostat (Oxford Instruments MD4). For room temperature or 77 K measurements, the samples were transferred into quartz tubes (Ω = 2.4 mm, Verre et Quarts Technique SA, Neuchâtel) or borosilicate glass tubes (Ω = 0.8–1.1 mm, Kimble Kontes), which were sealed with Parafilm. Room temperature and 77 K emission and excitation spectra were measured on a LS-50B fluorescence spectrometer (Perkin-Elmer) or a Fluorolog FL3-22 spectrometer (Horiba Jobin-Yvon Ltd.) equipped with a 450W Xe-lamp, two double-grating emission monochromators, and three different detectors, a Hamamatsu R927 photomultiplier (300–750 nm), a solid-state InGaAs detector cooled at 77 K (range 800–1600 nm), and a Peltier-cooled (≈60 °C) Hamamatsu H9170-75 photomultiplier (950–1700 nm) for measuring the Er3+ (4I13/2 → 4I15/2) emission. High-resolution room temperature and low temperature emission spectra were recorded upon excitation with an Ar laser (Coherent Innova 90C) at 488 nm or with Nd:YAG laser (Quantel Brilliant B) at 355 nm. The emitted light was analyzed at 90° with a Spex 270 M monochromator blazed at 600 nm with holographic gratings (150 L/mm). Light intensity was measured by a photomultiplier or CCD detectors. Appropriate filters were utilized to remove the laser light, the Rayleigh scattered light, and associated harmonics from the emission spectra. Luminescent lifetimes were measured using excitation provided by a Quantum Brilliant or Quantel YG 980 (Nd:YAG laser equipped with frequency doubler, tripler, and quadrupler as well as with an OPOTEK MagicPrism TM OPO crystal and a Quantel TDL + dye laser. The output signal of the photomultiplier was fed into a Stanford Research SR-400 multichannel scaler or to a 500 MHz Tektronix TDS724C and transferred to a PC for treatment with Origin 8. Lifetimes are averages of three independent determinations. Resonant excitation into the Cr(5E→5A) transition in CrLnCr was achieved with a tunable Ti:sapphire laser (Spectra Physics 3900S) pumped by the 532 nm excitation of a Nd:YVO4 laser (Spectra Physics Millennia-105J). The excitation was tuned to 13 360–13 890 cm−1. A short pass filter that cuts the scattered laser light and allows the passing of green light was used for these measurements. Residual pump laser light was removed at the exit of the Ti:sapphire laser with an RG 715 nm color filter. All excitation spectra were corrected for the emission of the xenon lamp, and all emission spectra were corrected for the instrumental response. The spectra were displayed as photons versus energy (cm−1). Quantum yield measurements of the solid state samples were measured on quartz tubes with the help of an integration sphere developed by Frédéric Gumy at the Laboratory of Lanthanide Supramolecular Chemistry, EPFL and commercialized by GMP S.A. (Renens, Switzerland, www.gmp.ch).60

**Computational Details.** The gas-phase geometry of the complex [ZnEuZn(L2)3]− was optimized by Density Functional Theory using the PW91PW91 exchange-correlation functional41 implemented in Gaussian 03.32 The DZVP double-ζ basis set developed by Godbout et al. was used for the H, C, N, and Zn atoms, and the europium cation was described by the quasi-relativistic pseudopotential of Dolg et al. for the 52 + 4f core electrons and by a (7s, 6p, 5d)/(5s, 4p, 3d)
Gaussian basis set for the valence electrons. All kinetic calculations were performed with EXCEL.

ASSOCIATED CONTENT

Supporting Information
Details for the determination of matrix differential equations (appendices 1 and 2); tables of $^1$H NMR shifts, elemental analyses, ESI-MS molecular peaks, characteristic emission lifetimes; figures showing $^1$H NMR spectra, ESI-MS spectra, molecular structure models, computed steady-state and time-evolution of population densities, computed dependences of the intensity on the incident pump power, electronic excitation and emission spectra, and Tanabe–Sugano diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(22) If $m_1^1u$, then $κ_e = 3.8 \times 10^{−2} f$ for the molar absorption coefficient $f$ taken in $M^−1 cm^1$.
deduce that the crystal for [CrGd(L2)]3+ despite the replacement of LnN6O3 with LnN9 coordination spheres.16

The analysis of high-resolution emission spectra for [ZnLaZn(L2)]3+[Ln = Nd, Yb, Figure S13] leads to the identification of ligand-field sublevels (Figure S14), from which we deduce that the crystal field effects in [ZnLaZn(L2)]3+ are identical, within 10 cm−1, with those reported for [LnZn(L1)]3+ despite the replacement of LnN6O3 with LnN6 coordination spheres.16


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Supporting Information

(33 pages)
X-Ray Crystallography.\textsuperscript{23b}

Extensive tabular information concerning the crystal structures of [CrEuCr(L\textsubscript{2})\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{9}(C\textsubscript{2}H\textsubscript{5}N)\textsubscript{30} (CCDC-806425) and [CrYbCr(L\textsubscript{2})\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{9}(C\textsubscript{2}H\textsubscript{5}N)\textsubscript{30} (CCDC-806426) can be found in reference 23b. The cif files can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+ 44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Due to the disorder exhibited by solvent molecules and by the counter-anions, the high-angle data were of low quality and the data were cut to a resolution of 0.95 Å for the CrEuCr compound and 1.1 Å for the CrYbCr compound. Among the eighteen triflate anions, fifteen were localized for CrEuCr and thirteen for CrYbCr. Restraints were applied on their C-S, S-O, C-F bond length, on the internal triflate bond angles and on their anisotropic displacement parameters. For CrYbCr restraints were also applied on some bond lengths of the ligands. For both compounds, the anisotropic displacement parameters of the ligands were restrained. Seven planar aromatic groups were defined for each ligand and similitude restraints were applied within the groups. Of the 2889 restraints used for CrEuCr, 77 corresponded to geometrical parameters (triflates), whereas 2812 concerned anisotropic displacement parameters. For CrYbCr, 487 constraints were applied on geometrical parameters (triflates and ligands), whereas 2238 constraints concerned the anisotropic displacement parameters. The interstitial solvent molecules were disordered and the “SQUEEZE/BYPASS” procedure was used within PLATON.\textsuperscript{S1} Using this procedure, 4538 electrons located in a void of 18190 Å\textsuperscript{3} were accounted for in the case of CrEuCr, while 5590 electrons located in a void of 19999 Å\textsuperscript{3} were accounted for in the case of CrYbCr. These electrons were assigned to the missing triflate molecules required for neutrality and to the disordered acetonitrile solvent molecules. Figures S7 and S8 show ORTEP plots of the crystal structures of [CrEuCr(L\textsubscript{2})\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{9}(C\textsubscript{2}H\textsubscript{5}N)\textsubscript{30} and [CrYbCr(L\textsubscript{2})\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{9}(C\textsubscript{2}H\textsubscript{5}N)\textsubscript{30}, respectively.

Table S1  Elemental Analyses for [ZnLnZn(L2)_3](CF_3SO_3)_7·nH_2O and [CrLnCr(L2)_3](CF_3SO_3)_9·mTBAf·nH_2O Complexes (Ln = Nd, Er, Yb; TBAf = Bu_4NCF_3SO_3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>MM/ g·mol⁻¹</th>
<th>%C found</th>
<th>%H found</th>
<th>%N found</th>
<th>%C calc</th>
<th>%H calc</th>
<th>%N calc</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="CF%E2%82%83SO%E2%82%83">Zn₂Nd(L₂)₃</a>₇·6H₂O</td>
<td>3853.7</td>
<td>49.85</td>
<td>3.53</td>
<td>11.97</td>
<td>49.87</td>
<td>3.68</td>
<td>11.99</td>
</tr>
<tr>
<td><a href="CF%E2%82%83SO%E2%82%83">Zn₂Er(L₂)₃</a>₇·9H₂O</td>
<td>3937.8</td>
<td>48.77</td>
<td>3.45</td>
<td>11.67</td>
<td>48.80</td>
<td>3.76</td>
<td>11.74</td>
</tr>
<tr>
<td><a href="CF%E2%82%83SO%E2%82%83">Zn₂Yb(L₂)₃</a>₇·9H₂O</td>
<td>3929.6</td>
<td>48.88</td>
<td>3.52</td>
<td>11.71</td>
<td>48.90</td>
<td>3.76</td>
<td>11.76</td>
</tr>
<tr>
<td><a href="CF%E2%82%83SO%E2%82%83">Cr₂Nd(L₂)₃</a>₉·0.25TBAf·2H₂O</td>
<td>4151.5</td>
<td>48.11</td>
<td>3.79</td>
<td>11.46</td>
<td>48.11</td>
<td>3.44</td>
<td>11.22</td>
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<tr>
<td><a href="CF%E2%82%83SO%E2%82%83">Cr₂Er(L₂)₃</a>₉·17H₂O</td>
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<td>44.70</td>
<td>3.56</td>
<td>10.48</td>
<td>44.71</td>
<td>3.78</td>
<td>10.62</td>
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<tr>
<td><a href="CF%E2%82%83SO%E2%82%83">Cr₂Yb(L₂)₃</a>₉·0.5TBAf·3H₂O</td>
<td>4284.0</td>
<td>47.67</td>
<td>3.92</td>
<td>11.19</td>
<td>47.67</td>
<td>3.57</td>
<td>10.94</td>
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</table>
**Table S2** Molecular Peaks and their Triflate Adducts Observed by ESI-MS (positive mode) for $\text{[Zn}Ln\text{Zn(L2)}_3](\text{CF}_3\text{SO}_3)_7\cdot n\text{H}_2\text{O}$ and $\text{[Cr}Ln\text{Cr(L2)}_3](\text{CF}_3\text{SO}_3)_9\cdot m\text{TBAF}\cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd, Er, Yb}$, acetonitrile, $3-5\cdot 10^{-4}$ M).

<table>
<thead>
<tr>
<th>Cationic species</th>
<th>Ln = Nd m/z</th>
<th>Ln = Er m/z</th>
<th>Ln = Yb m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Zn}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)]^{6+}$</td>
<td>-</td>
<td>479.9</td>
<td>480.9</td>
</tr>
<tr>
<td>$\text{[Zn}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_2]^{5+}$</td>
<td>-</td>
<td>605.4</td>
<td>606.6</td>
</tr>
<tr>
<td>$\text{[Zn}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_3]^{4+}$</td>
<td>-</td>
<td>794.1</td>
<td>795.2</td>
</tr>
<tr>
<td>$\text{[Zn}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_4]^{3+}$</td>
<td>1099.9</td>
<td>1107.7</td>
<td>1110.6</td>
</tr>
<tr>
<td>$\text{[Cr}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_2]^{7+}$</td>
<td>425.3</td>
<td>428.7</td>
<td>429.2</td>
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<tr>
<td>$\text{[Cr}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_3]^{6+}$</td>
<td>521.1</td>
<td>524.9</td>
<td>526.0</td>
</tr>
<tr>
<td>$\text{[Cr}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_4]^{5+}$</td>
<td>654.9</td>
<td>659.5</td>
<td>660.8</td>
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<td>$\text{[Cr}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_5]^{4+}$</td>
<td>856.1</td>
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<td>$\text{[Cr}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_6]^{3+}$</td>
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<td>1198.5</td>
<td>1200.6</td>
</tr>
<tr>
<td>$\text{[Cr}_2\text{Ln(L2)}_3(\text{CF}_3\text{SO}_3)_7]^{2+}$</td>
<td>1860.4</td>
<td>1872.0</td>
<td>1875.3</td>
</tr>
</tbody>
</table>
Table S3  $^1$H NMR Chemical Shifts (δ/ppm with Respect to TMS)) for L2 and [ZnLnZn(L2)$_3$]$^{7+}$
(Ln = Nd, Yb, Er; CD$_3$CN, 293 K).$^a$

<table>
<thead>
<tr>
<th></th>
<th>L2</th>
<th>[Zn$_2$Nd(L2)$_3$]$^{7+}$</th>
<th>[Zn$_2$Yb(L2)$_3$]$^{7+}$</th>
<th>[Zn$_2$Er(L2)$_3$]$^{7+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>8.48</td>
<td>7.44</td>
<td>8.95</td>
<td>$^b$</td>
</tr>
<tr>
<td>H2</td>
<td>7.61</td>
<td>7.51</td>
<td>8.43</td>
<td>$^b$</td>
</tr>
<tr>
<td>H3</td>
<td>8.19</td>
<td>7.69</td>
<td>9.04</td>
<td>$^b$</td>
</tr>
<tr>
<td>H4</td>
<td>7.32</td>
<td>6.67</td>
<td>7.12</td>
<td>$^b$</td>
</tr>
<tr>
<td>H5</td>
<td>7.21</td>
<td>6.78</td>
<td>6.37</td>
<td>$^b$</td>
</tr>
<tr>
<td>H6</td>
<td>7.67</td>
<td>3.05</td>
<td>9.02</td>
<td>$^b$</td>
</tr>
<tr>
<td>H7,7’</td>
<td>4.25</td>
<td>3.07, 3.19</td>
<td>4.42, 3.30</td>
<td>7.28, 7.46</td>
</tr>
<tr>
<td>H8</td>
<td>7.63</td>
<td>-0.07</td>
<td>17.46</td>
<td>10.43</td>
</tr>
<tr>
<td>H9</td>
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<td>7.30</td>
<td>8.69</td>
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<td>H15</td>
<td>4.17</td>
<td>5.28</td>
<td>1.36</td>
<td>$^b$</td>
</tr>
</tbody>
</table>

$^a$ Numbering scheme is given in Fig. S5. $^b$ Incomplete assignments due to strong paramagnetic effects (Fig. S5c).$^{23}$
**Table S4** Selected Characteristic Luminescence Lifetimes for Ligand-Centred and Metal-Centred Excited States in L2, [ZnLnZn(L2)3]7+ and [CrLnCr(L2)3]9+ (Ln = Nd, Gd Yb, Er) in the Solid State Under Various Conditions

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(T)/K</th>
<th>(\nu_{\text{exc}})/(\text{cm}^{-1})</th>
<th>(\nu_{\text{an}})/(\text{cm}^{-1})</th>
<th>(\tau)/(\mu\text{s})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2</td>
<td>77</td>
<td>31505</td>
<td>22780</td>
<td>-</td>
<td>(L(^1\pi^\ast\rightarrow\pi))</td>
</tr>
<tr>
<td>[ZnGdZn(L2)3]7+</td>
<td>77</td>
<td>24690</td>
<td>22520</td>
<td>20100</td>
<td>(L(^1\pi^\ast\rightarrow\pi)) (tridentate)</td>
</tr>
<tr>
<td>[CrGdGd(L2)3]7+</td>
<td>10</td>
<td>31250</td>
<td>24510</td>
<td>24105</td>
<td>(L(^3\pi^\ast\rightarrow\pi)) (didentate)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12168</td>
<td>(L(^3\pi^\ast\rightarrow\pi)) (tridentate)</td>
</tr>
<tr>
<td>[ZnNdZn(L2)3]7+</td>
<td>40</td>
<td>24390</td>
<td>11494</td>
<td>1.67(1)</td>
<td>(\text{Nd}(^4F_{3/2} \rightarrow ^4I_{9/2}))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24390</td>
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<td>(L(^3\pi^\ast\rightarrow\pi))</td>
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<td>28170</td>
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<td>(\text{Yb}(^2F_{5/2} \rightarrow ^2F_{7/2}))</td>
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Table S4  Continuation

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<th>Transition</th>
<th>Wavelength</th>
<th>Life Time (ns)</th>
<th>Excitation Energy</th>
<th>Excitation Level</th>
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<td>22.1(2)</td>
<td>Cr(2E → 4A_2)</td>
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Figure S1  Energy level diagram (Tanabe-Sugano) for $d^3$ ion in an octahedral field ($C = 4.5 \, B$).\textsuperscript{14a}
Figure S2  Computed linear dependence of Yb-centered emission intensity with respect to incident pump power (in W/mm²) of the Cr-centered transition in [CrYb(L1)3]⁶⁺ (full trace),¹⁶ and related dependence for [CrYbCr(L2)₃]⁹⁺ (dashed trace) predicted by using the same rate constants (CrYbCr ≡ CrYb CrYb Cr Yb Cr Yb Cr Yb ≡ 240 s⁻¹, CrGdCr ≡ CrGd ≡ 270 s⁻¹ and ZnYbZn ≡ ZnYb ≡ 5·10⁴ s⁻¹).
Figure S3  

a) Kinetic matrix for the Jablonski diagram shown in Fig. 3b and b) predicted steady-state population densities for the various levels (the 0-0.05 population density range is highlighted on the right) for \([\text{CrYbCr(L2)}_3]^{9+}\) upon irradiation of the Cr-centered transitions \((k_{\text{Cr}}^{\text{GdCr}} \equiv k_{\text{Cr}}^{\text{Gd}} = 270 \text{ s}^{-1}, \ k_{\text{Yb}}^{\text{ZnYbZn}} \equiv k_{\text{Yb}}^{\text{ZnYb}} = 5 \cdot 10^4 \text{ s}^{-1}, \ W_{\text{Cr} \rightarrow \text{Yb}}^{\text{CrYbCr}} \equiv W_{\text{Cr} \rightarrow \text{Yb}}^{\text{GdYb}} = W_{\text{Cr} \rightarrow \text{Yb}} = 240 \text{ s}^{-1})\) with increasing incident pump power \(P\).  

\[
M = \begin{pmatrix}
-2k_{\text{Cr}}^{\text{exc}} & k_{\text{Cr}}^{\text{CrGdCr}} & k_{\text{Yb}}^{\text{ZnYbZn}} & 0 & 0 & 0 \\
2k_{\text{Cr}}^{\text{exc}} & \left(\frac{k_{\text{Cr}}^{\text{GdCr}} + k_{\text{Cr}}^{\text{exc}}}{W_{\text{Cr} \rightarrow \text{Yb}}} \right) & 0 & k_{\text{Yb}}^{\text{ZnYbZn}} & 0 & 2k_{\text{Cr}}^{\text{GdCr}} \\
0 & W_{\text{Cr} \rightarrow \text{Yb}} & \left(-2k_{\text{Cr}}^{\text{exc}} + k_{\text{Yb}}^{\text{ZnYbZn}} \right) & k_{\text{Cr}}^{\text{CrGdCr}} & 0 & 0 \\
0 & 0 & 2k_{\text{Cr}}^{\text{exc}} & -\left(\frac{k_{\text{Cr}}^{\text{exc}} + k_{\text{Cr}}^{\text{CrGdCr}}}{W_{\text{Cr} \rightarrow \text{Yb}}} \right) & 2W_{\text{Cr} \rightarrow \text{Yb}} & 2k_{\text{Cr}}^{\text{GdCr}} \\
0 & k_{\text{Cr}}^{\text{exc}} & 0 & 0 & -\left(\frac{2k_{\text{Cr}}^{\text{exc}}}{W_{\text{Cr} \rightarrow \text{Yb}}} \right) k_{\text{Yb}}^{\text{ZnYbZn}} & k_{\text{Yb}}^{\text{ZnYbZn}} \\
0 & 0 & 0 & k_{\text{Cr}}^{\text{exc}} & 0 & -\left(\frac{2k_{\text{Cr}}^{\text{exc}}}{W_{\text{Cr} \rightarrow \text{Yb}}} \right) + k_{\text{Yb}}^{\text{ZnYbZn}}
\end{pmatrix}
\]
Figure S4  ESI-MS spectra of a) [ZnYbZn(L2)₃](CF₃SO₃)₇ and b) [CrErCr(L2)₃](CF₃SO₃)₉ (3-5·10⁻⁴ M, CH₃CN, 298 K, Otf⁻ = CF₃SO₃⁻).
Figure S5  $^1$H NMR spectra of a) [ZnNdZn(L2)$_3$]$^{7+}$, b) [ZnYbZn(L2)$_3$]$^{7+}$ and c) [ZnErZn(L2)$_3$]$^{7+}$ (CD$_3$CN, 293 K).
Figure S6  Part of the $^1$H NMR spectrum of $[\text{CrNdCr(L2)}_3]^{9+}$ (CD$_3$CN, 293 K).
Figure S7 Perspective ORTEP views of a) the asymmetric unit and b) the molecular structures of the two triple-helical \([\text{CrEuCr(L2)}_3]^{9+}\) cations along their pseudo-threefold axes in the asymmetric unit of \([\text{CrEuCr(L2)}_3]_{25}\text{(CFSO}_3\text{)}_{18}\text{(C}_3\text{H}_2\text{N})_{30}\). Ellipsoids are represented at the 50% probability level. Hydrogen atoms are omitted for clarity.
Figure S8  Perspective ORTEP views of a) the asymmetric unit and b) the molecular structures of the two triple-helical [CrYbCr(L2)]$^{3+}$ cations along their pseudo-threefold axes in the asymmetric unit of [CrYbCr(L2)$_3$]$_2$(CF$_3$SO$_3$)$_{18}$(C$_3$H$_7$N)$_{30}$. Ellipsoids are represented at the 50% probability level. Hydrogen atoms are omitted for clarity.
**Figure S9** Superimposition of the molecular structures of \([\text{CrEuCr(L2)}_3]^{9+}\) (red) and \([\text{CrYbCr(L2)}_3]^{9+}\) (green) in the crystal structures of \([\text{CrLnCr(L2)}_3](\text{CF}_3\text{SO}_3)_9(\text{C}_3\text{H}_5\text{N})_{30}\). Hydrogen atoms have been omitted for clarity.

**Figure S10** Emission spectra for \([\text{CrGdCr(L2)}_3](\text{CF}_3\text{SO}_3)_9\) at 10 K and 295 K (\(\tilde{\nu}_{\text{exc}} = 28170 \text{ cm}^{-1}\)).
**Figure S11** Sensitization of the Cr$^2E \rightarrow ^4A_2$ NIR emission in [CrGdCr(L1)$_3$](CF$_3$SO$_3$)$_9$. A) Low-energy excitation spectrum (black trace, $\nu$$_{an}$ = 12821 cm$^{-1}$, 10 K) and emission spectrum (red trace, $\nu$$_{exc}$ = 13888 cm$^{-1}$, 10 K). B) High-energy excitation spectrum recorded upon monitoring the Cr$^2E \rightarrow ^4A_2$ emission (solid state). The shaded areas correspond to the region of high absorption coefficients of the ligand-centred $1\pi^* \rightarrow 1\pi$ transitions leading to artefacts due to the lack of penetration of the incident light. C) Deconvolution of the Cr$^4T_2 \rightarrow ^4A_2$ transition ($O_h$ symmetry) into its A+E components in $D_3$-symmetry in [CrGdCr(L1)$_3$](CF$_3$SO$_3$)$_9$ (solid state, 295 K).
Figure S12  Solid state excitation (grey traces) and emission (black traces, $\tilde{\nu}_{\text{exc}} = 28170 \text{ cm}^{-1}$) spectra recorded for a) [ZnNdZn(L2)3](CF3SO3)7 ($\tilde{\nu}_{\text{an}}[\text{Nd}(^{4}\text{F}_{3/2} \rightarrow ^{4}\text{I}_{3/2})], 295 \text{ K}$), b) [ZnErZn(L2)3](CF3SO3)7 (10 K) and c) [ZnYbZn(L2)3](CF3SO3)7 ($\tilde{\nu}_{\text{an}}[\text{Yb}(^{2}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2})], 295 \text{ K}$). The shaded areas correspond to the region of high absorption coefficients of the ligand-centred $^{1}\pi^{*} \rightarrow ^{1}\pi$ transitions leading to artefacts due to the lack of penetration of the incident light.
**Figure S13**  High-resolution solid state NIR emission spectra ($\nu_{\text{exc}} = 24690 \text{ cm}^{-1}, 10 \text{ K}$) recorded for [ZnNdZn(L$_2$)$_3$](CF$_3$SO$_3$)$_7$ (red trace) and [ZnYbZn(L$_2$)$_3$](CF$_3$SO$_3$)$_7$ (blue trace).
**Figure S14** a) High-resolution solid state emission spectra of $[\text{ZnNdZn(\text{L2})}_3](\text{CF}_3\text{SO}_3)_7$ and $[\text{CrNdCr(\text{L2})}_3](\text{CF}_3\text{SO}_3)_9$ showing isostructurality around Nd(III) and b) associated crystal-field splittings.
Figure S15  Emission spectra recorded for a) [CrNdCr(L2)3](CF3SO3)9 and b) [CrErCr(L2)3](CF3SO3)9 upon ligand-centered excitation ($\tilde{\nu}_{\text{exc}} = 37037$ cm$^{-1}$, solid state, 77 K).
Figure S16 Solid state excitation spectra recorded at 77 K for a) [CrNdCr(L1)3](CF3SO3)9. (\(\tilde{\nu}_\text{an} \left( ^4F_{3/2} \rightarrow ^4I_{11/2} \right) = 9314 \text{ cm}^{-1}\)), b) [CrErCr(L1)3](CF3SO3)9. (\(\tilde{\nu}_\text{an} \left( ^4I_{13/2} \rightarrow ^4I_{15/2} \right) = 6569 \text{ cm}^{-1}\)) and c) [CrYbCr(L1)3](CF3SO3)9. (\(\tilde{\nu}_\text{an} \left( ^2F_{5/2} \rightarrow ^2F_{7/2} \right) = 10294 \text{ cm}^{-1}\)). The shaded areas correspond to the region of high absorption coefficients of the ligand-centred \(^1\pi^* \leftarrow ^1\pi\) transitions leading to artefacts due to the lack of penetration of the incident light.
Figure S17 Computed steady-state population densities for the various levels (the 0-0.05 population density range is highlighted on the right) for a) [CrNdCr(L2)3]9+, b) [CrErCr(L2)3]9+ and c) [CrYbCr(L2)3]9+ upon irradiation of the Cr-centered transitions with increasing incident pump power $P$ (pertinent rate constants are collected in Table 1).
Figure S18 Computed linear dependences of Ln-centered emission intensity with respect to incident pump power (in W/mm$^2$) of the Cr-centered transitions in [CrNdCr(L2)$_3$]$^{9+}$ (blue trace), [CrErCr(L2)$_3$]$^{9+}$ (black trace) and [CrYbCr(L2)$_3$]$^{9+}$ (red trace).

Figure S19 Computed linear dependences of Nd-centered emission intensity with respect to incident pump power (in W/mm$^2$) of the Cr-centered transition in [CrNd(L1)$_3$]$^{6+}$ and [CrNdCr(L2)$_3$]$^{9+}$ (full traces, solid state, 10K). The statistical behavior ($f_{\text{gain}} = 2.0$) predicted for [CrNdCr(L2)$_3$]$^{9+}$ by using the rate constants of [CrNd(L1)$_3$]$^{6+}$ is shown as a dotted trace.
Figure S20  Computed time evolution of the population densities of the ground state CrNdCr ($\ket{0}$), dashed trace, eq. 8), and of the lowest excited states Cr*NdCr ($\ket{\alpha}$, full trace, eq. 9) and CrNd*Cr ($\ket{\beta}$, dotted trace, eq. 10) in [CrNdCr(L2)3]9+ after 500 µJ/mm² pulse of 10 ns in the Cr-centered transition (solid state, 10K).
Figure S21  Computed time evolution of the population densities of the ground state CrErCr ($|0\rangle$), dashed trace, eq. 8), and of the lowest excited states Cr*ErCr ($|\alpha\rangle$, full trace, eq. 9) and CrEr*Cr ($|\beta\rangle$, dotted trace, eq. 10) in [CrErCr(L2)$_3$]$^{9+}$ after a 500 $\mu$J/mm$^2$ pulse of 10 ns in the Cr-centered transition (solid state, 10K).
Figure S22 Time evolution of the population densities for the ground state CrNdCr ($|0\rangle$, blue trace) and of the excited states Cr*NdCr ($|\alpha\rangle$, red trace), CrNd*Cr ($|\beta\rangle$, black trace), Cr*Nd*Cr ($|\gamma\rangle$, violet trace), Cr*NdCr* ($|\delta\rangle$, green trace) and Cr*Nd*Cr* ($|\epsilon\rangle$, orange trace) in [CrNdCr(L2)3]^{9+} following a 3 W/mm² presaturation (solid state, 10K, eq S13).
Figure S23 Time evolution of the population densities for the ground state CrErCr (|0⟩, blue trace) and of the excited states Cr*ErCr (|α⟩, red trace), CrEr*Cr (|β⟩, black trace), Cr*Er*Cr (|γ⟩, violet trace), Cr*ErCr* (|δ⟩, green trace) and Cr*Er*Cr* (|ε⟩, orange trace) in [CrErCr(L2)]³⁺ following a 3 W/mm² presaturation (solid state, 10K, eq S13).
Appendix 1. Projection operator solutions of eq. 7

The solution of the matrix differential eq. (7) is\textsuperscript{20}

\[
\begin{pmatrix}
N^0_{i} \\
N^1_{i} \\
N^2_{i}
\end{pmatrix} = \exp \begin{pmatrix}
0 & k_{Cr}^{GdCr} & k_{Ln}^{ZnLn} \\
0 & -(k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln}) & 0 \\
0 & W_{Cr\rightarrow Ln} & -k_{Ln}^{ZnLnZn}
\end{pmatrix} t \times \begin{pmatrix}
N^0_{i} \\
N^1_{i} \\
N^2_{i}
\end{pmatrix}
\]

(S1)

The matrix exponential can be written as a sum of scalar functions by introducing the eigenvalues $\lambda_i$ and projection operators $P_i$\textsuperscript{20}

\[
\begin{pmatrix}
N^0_{i} \\
N^1_{i} \\
N^2_{i}
\end{pmatrix} = \sum_{i=1}^{3} e^{\lambda_i} P_i \times \begin{pmatrix}
N^0_{0} \\
N^1_{0} \\
N^2_{0}
\end{pmatrix} = \sum_{i=1}^{3} e^{\lambda_i} P_i \times \begin{pmatrix}
N^0_{0} - N^0_{i} \\
N^1_{0} - N^1_{i} \\
N^2_{0} - N^2_{i}
\end{pmatrix}
\]

(S2)

where $P_i$ is given by the Lagrange-Sylvester formula

\[
P_i = \prod_{j=1, j\neq i}^{3} \begin{pmatrix}
0 & k_{Cr}^{GdCr} & k_{Ln}^{ZnLn} \\
0 & -(k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln}) & 0 \\
0 & W_{Cr\rightarrow Ln} & -k_{Ln}^{ZnLnZn}
\end{pmatrix} - \lambda_j \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix} \prod_{j=1, j\neq i}^{3} (\lambda_i - \lambda_j)
\]

(S3)

The eigenvalues are determined from the secular determinant

\[
\begin{vmatrix}
-\lambda & k_{Cr}^{GdCr} & k_{Ln}^{ZnLnZn} \\
0 & -(k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln}) - \lambda & 0 \\
0 & W_{Cr\rightarrow Ln} & -k_{Ln}^{ZnLnZn} - \lambda
\end{vmatrix} = (-\lambda)((k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln}) + \lambda)(k_{Ln}^{ZnLnZn} + \lambda) = 0
\]

(S4)

leading to $\lambda_1 = 0$, $\lambda_2 = -(k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln})$ and $\lambda_3 = -k_{Ln}^{ZnLnZn}$

The introduction of these eigenvalues into eq. S3 gives the three projection operators

\[
P_{\lambda=0} = (k_{Ln}^{ZnLnZn})^{-1} \begin{pmatrix}
k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln} & k_{Cr}^{GdCr} & k_{Ln}^{ZnLnZn} \\
0 & 0 & 0 \\
0 & W_{Cr\rightarrow Ln} & (k_{Ln}^{ZnLnZn} + k_{Cr}^{GdCr}) + W_{Cr\rightarrow Ln}
\end{pmatrix} \times \begin{pmatrix}
k_{ZnLnZn} & k_{Cr}^{GdCr} & k_{Ln}^{ZnLnZn} \\
0 & k_{Ln}^{ZnLnZn} & (k_{Cr}^{GdCr} + W_{Cr\rightarrow Ln}) \\
0 & 0 & W_{Cr\rightarrow Ln}
\end{pmatrix}
\]

(S5)
\[
\mathbf{P}_{\Delta_{t} \rightarrow \Delta_{t}^{(CrGdCr_{t=ls})}} = \left( k_{Cr}^{CrGdCr} + \frac{1}{W_{Cr\rightarrow Ln}} - k_{ZnLnZn} \right)^{-1} \left( \begin{array}{ccc}
0 & k_{Cr}^{CrGdCr} & k_{ZnLnZn} \\
0 & k_{Cr}^{CrGdCr} + W_{Cr\rightarrow Ln} & 0 \\
0 & W_{Cr\rightarrow Ln} - k_{ZnLnZn} 
\end{array} \right) \times \left( \begin{array}{ccc}
k_{ZnLnZn} & k_{Cr}^{CrGdCr} & k_{ZnLnZn} \\
0 & k_{Cr}^{CrGdCr} + W_{Cr\rightarrow Ln} & 0 \\
0 & W_{Cr\rightarrow Ln} - k_{ZnLnZn} 
\end{array} \right)
\]

\[\Rightarrow \mathbf{P}_{\Delta_{t} \rightarrow \Delta_{t}^{(CrGdCr_{t=ls})}} = \left( \begin{array}{ccc}
0 & k_{ZnLnZn} & k_{Cr}^{CrGdCr} - k_{ZnLnZn} \\
0 & k_{Cr}^{CrGdCr} - W_{Cr\rightarrow Ln} & 0 \\
0 & 1 & 0 
\end{array} \right) \]

\[\Rightarrow \mathbf{P}_{\Delta_{t} \rightarrow \Delta_{t}^{(CrGdCr_{t=ls})}} = \left( \begin{array}{ccc}
0 & W_{Cr\rightarrow Ln} & 0 \\
0 & k_{ZnLnZn} - k_{Cr}^{CrGdCr} - W_{Cr\rightarrow Ln} & 0 \\
0 & -k_{ZnLnZn} & 1 
\end{array} \right)
\]

The final introduction of eqs S5-S7 into eq S2 yields

\[\begin{align*}
N_{t}^{(k)} &= N_{tot} + N_{0}^{(k)} e^{\left(k_{Cr}^{CrGdCr_{t=ls}} \right)} \\
N_{t_0}^{(k)} &= 0 \\
N_{t_1}^{(k)} &= 0
\end{align*}
\]

The matrix notation is eventually transformed into the common analytical formula

\[N_{t}^{(k)} = N_{tot} - \frac{N_{0}^{(k)}}{\left(k_{ZnLnZn} - k_{Cr}^{CrGdCr} - W_{Cr\rightarrow Ln} \right)} \left[ k_{ZnLnZn} e^{\left(k_{Cr}^{CrGdCr_{t=ls}} \right)} - W_{Cr\rightarrow Ln} e^{-k_{ZnLnZn}} \right]
\]

\[N_{t_0}^{(k)} = N_{0}^{(k)} e^{\left(k_{Cr}^{CrGdCr_{t=ls}} \right)}
\]

\[N_{t_1}^{(k)} = \frac{W_{Cr\rightarrow Ln} N_{t}^{(k)}}{\left(k_{ZnLnZn} - k_{Cr}^{CrGdCr} - W_{Cr\rightarrow Ln} \right)} e^{\left(k_{Cr}^{CrGdCr_{t=ls}} \right)} - e^{-k_{ZnLnZn}}
\]
Appendix 2. Projection operator solutions for the complete kinetic scheme modeling 
$[\text{CrLnCr(L2)3}]^{3+}$.

The complete matrix differential equation for relaxation after presaturation is given by

$$\begin{bmatrix}
\frac{dN_i^{(1)}}{dt} \\
\frac{dN_i^{(2)}}{dt} \\
\frac{dN_i^{(3)}}{dt} \\
\frac{dN_i^{(4)}}{dt} \\
\frac{dN_i^{(5)}}{dt} \\
\frac{dN_i^{(6)}}{dt}
\end{bmatrix} =
\begin{bmatrix}
k_{\text{CrGdCr}} & k_{\text{ZnLaZn}} & 0 & 0 & 0 & 0 \\
0 & -k_{\text{CrGdCr}} & k_{\text{ZnLaZn}} & 2k_{\text{CrGdCr}} & 0 & 0 \\
0 & W_{\text{Cr→Ln}} & -k_{\text{ZnLaZn}} & 0 & 0 & 0 \\
0 & 0 & 0 & -\left(k_{\text{CrGdCr}} + k_{\text{ZnLaZn}}\right) & 2W_{\text{Cr→Ln}} & 2k_{\text{CrGdCr}} \\
0 & 0 & 0 & 0 & -\left(2k_{\text{CrGdCr}} + 2W_{\text{Cr→Yb}}\right) & k_{\text{ZnLaZn}} \\
0 & 0 & 0 & 0 & 0 & -\left(2k_{\text{CrGdCr}} + k_{\text{ZnLaZn}}\right)
\end{bmatrix}
\begin{bmatrix}
N_i^{(1)} \\
N_i^{(2)} \\
N_i^{(3)} \\
N_i^{(4)} \\
N_i^{(5)} \\
N_i^{(6)}
\end{bmatrix}$$

whose solution is

$$\begin{bmatrix}
N_i^{(1)} \\
N_i^{(2)} \\
N_i^{(3)} \\
N_i^{(4)} \\
N_i^{(5)} \\
N_i^{(6)}
\end{bmatrix} = \exp\left(\begin{bmatrix}
0 & -k_{\text{CrGdCr}} & k_{\text{ZnLaZn}} & 0 & 0 & 0 \\
0 & k_{\text{CrGdCr}} & -k_{\text{ZnLaZn}} & 2k_{\text{CrGdCr}} & 0 & 0 \\
0 & W_{\text{Cr→Ln}} & k_{\text{ZnLaZn}} & 0 & 0 & 0 \\
0 & 0 & 0 & -\left(k_{\text{CrGdCr}} + k_{\text{ZnLaZn}}\right) & 2W_{\text{Cr→Ln}} & 2k_{\text{CrGdCr}} \\
0 & 0 & 0 & 0 & -\left(2k_{\text{CrGdCr}} + 2W_{\text{Cr→Yb}}\right) & k_{\text{ZnLaZn}} \\
0 & 0 & 0 & 0 & 0 & -\left(2k_{\text{CrGdCr}} + k_{\text{ZnLaZn}}\right)
\end{bmatrix} \right) \times t$$

Please note that the eigenvalues $\lambda_i$ ($i = 1-6$) of the kinetic matrix are simply given by the opposite values of the six diagonal elements, on which the method of projection operator is applied (see appendix 1).
Numerical calculations of the projection operators are performed for each lanthanide and for each presaturation pumping power. For \( \text{Ln} = \text{Yb} \), a presaturation of 0.1 W/mm\(^2\) yields eq. (S12) and Fig. S24, whereas a presaturation of 3 W/mm\(^2\) yields eq. (S13) and Fig. 10.
\begin{equation}
\begin{pmatrix}
N_{r}^{(0)} \\
N_{r}^{(1)} \\
N_{r}^{(2)} \\
N_{r}^{(3)}
\end{pmatrix}
= \begin{pmatrix}
1 \\
0 \\
0 \\
0
\end{pmatrix}
+ \begin{pmatrix}
-1.25 \\
0.001 \\
0 \\
0
\end{pmatrix} e^{-6.90\times10^{-2}t}
+ \begin{pmatrix}
0.00025 \\
-0.00025 \\
0 \\
0
\end{pmatrix} e^{-3.20\times10^{4}t}
+ \begin{pmatrix}
-2.385\times10^{-5} \\
5.525\times10^{-5} \\
2.345\times10^{-5} \\
-5.485\times10^{-5}
\end{pmatrix} e^{-3.24\times10^{4}t}
\end{equation}

$$
\begin{pmatrix}
0.3955 \\
-0.782 \\
-0.006 \\
0.006 \\
0.387
\end{pmatrix} e^{-1.38\times10^{3}t}
+ \begin{pmatrix}
-3.78\times10^{-5} \\
0.00017 \\
3.64\times10^{-5} \\
-0.00017 \\
0.00021
\end{pmatrix} e^{-3.29\times10^{4}t}$$

**Figure S24** Time evolution of the population densities for the ground state CrYbCr (|0\rangle, blue trace) and of the excited states Cr*YbCr (|\alpha\rangle, red trace), CrYb*Cr (|\beta\rangle, black trace), Cr*Yb*Cr (|\gamma\rangle, violet trace), Cr*YbCr* (|\delta\rangle, green trace) and Cr*Yb*Cr* (|\epsilon\rangle, orange trace) in [CrYbCr(L2)3]^{9+} following a 0.1 W/mm² presaturation (solid state, 10K, eq. S12).