

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

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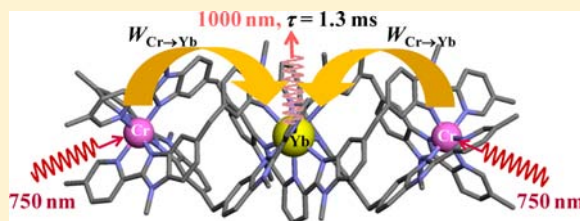
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## Supporting Information

**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 L2 with stoichiometric amounts of  $M(\text{CF}_3\text{SO}_3)_2$  ( $M = \text{Cr}, \text{Zn}$ ) and  $\text{Ln}(\text{CF}_3\text{SO}_3)_3$  ( $\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$ ) under aerobic conditions quantitatively yield the  $D_3$ -symmetrical trinuclear  $[\text{MLnM}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_n$  complexes ( $M = \text{Zn}, n = 7$ ;  $M = \text{Cr}, n = 9$ ), 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  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  induces rate-limiting intramolecular intermetallic Cr→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  $[\text{CrLn}(\text{L}1)_3]^{6+}$ , the connection of a second strong-field  $[\text{CrN}_6]$  sensitizer in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  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  $[\text{Cr}^*\text{LnCr}^*(\text{L}2)_3]^{9+}$  under reasonable pumping powers.



## INTRODUCTION

Formally, the near-infrared (NIR) spectral range starts at 750 nm ( $13\,333\text{ cm}^{-1}$ ), and many trivalent lanthanide ions,  $\text{Ln}(\text{III}) = \text{Pr}, \text{Nd}, \text{Sm}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$ , display radiative  $f-f$  transitions above this wavelength.<sup>1</sup> Those with  $\text{Ln} = \text{Nd}, \text{Er}$ , and  $\text{Yb}$  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  $\text{Er}(^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2})$  emission),<sup>2</sup> as laser materials (for instance, in Nd:YAG lasers based on the  $\text{Nd}(^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2})$  transition at 1060–1090 nm),<sup>3</sup> as NIR→visible light upconverting devices,<sup>4</sup> 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).<sup>5</sup> In this context, hundreds of lanthanide-containing NIR emitters were synthesized and investigated during the past decade,<sup>6</sup> 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.<sup>7</sup> 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,<sup>6</sup> highly conjugated polyaromatic antennae emitting in the red part of the electromagnetic spectrum<sup>7</sup> are actively investigated for improving the global sensitization process.<sup>8</sup> 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  $\hbar\omega_{\text{eff}} \approx 2000\text{ cm}^{-1}$  operative in molecular coordination complexes,<sup>9</sup> 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  $\text{Ln}(\text{III})$  ions,  $\tau_{\text{Ln}} = 1/k_{\text{Ln}}$ , are on the (sub)microsecond time scale, which is far below their predicted millisecond radiative decays.<sup>6,7</sup> 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.<sup>10</sup> 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.<sup>11</sup>

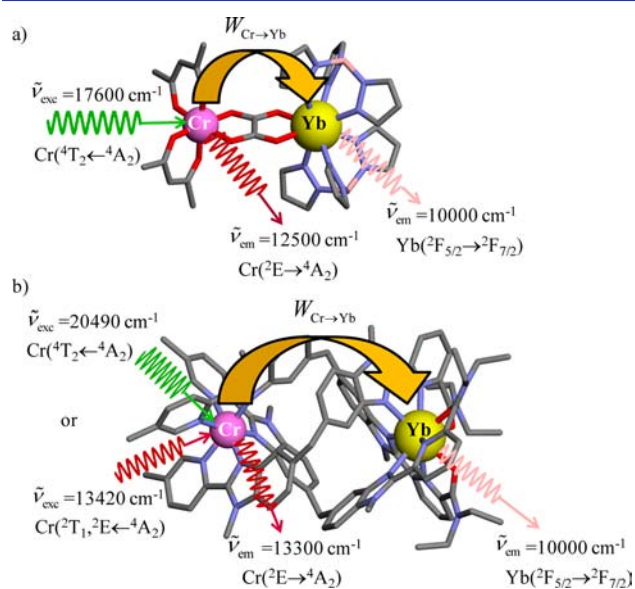
Pseudo-octahedral trivalent chromium chromophores are particularly attractive as sensitizers in this context<sup>12</sup> because two broad and spin-allowed transitions ( ${}^4T_1$ ,  ${}^4T_2 \leftarrow {}^4A_2$ ) are available in the UV–visible domain, while narrow spin-forbidden excited states are accessible in the visible ( ${}^2T_2 \leftarrow {}^4A_2$ ) and in the NIR region ( ${}^2T_1$ ,  ${}^2E \leftarrow {}^4A_2$ , Figure S1, Supporting Information).<sup>13</sup> For instance, cocrystallization of  $[\text{Cr}(\text{CN})_6]^{3-}$ <sup>14</sup> with Nd(III) and Yb(III) cations gives infinite  $[\text{Cr}(\text{CN})_4(\mu\text{-CN})_2\text{Ln}(\text{H}_2\text{O})_2(\text{dmf})_4]_\infty$  chains, in which the NIR emitting lanthanides could be indirectly sensitized by the blue excitation of the spin-allowed  $\text{Cr}({}^4T_2 \leftarrow {}^4A_2)$  transition.<sup>15</sup> However, the efficient intermetallic  $\text{Cr} \rightarrow \text{Ln}$  energy transfer processes operating in these coordination polymers ( $W_{\text{Cr} \rightarrow \text{Ln}} > 10^8 \text{ s}^{-1}$ ) did not offer a possibility for lengthening the Ln(III)-centered emission lifetimes.<sup>16</sup>

To restrain Cr/Ln communication to an isolated pair of metals, for which the intermetallic energy transfer rate constant can be controlled, Kaizaki<sup>17</sup> and Piguet<sup>18</sup> 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  $\text{Cr}({}^2E \rightarrow {}^4A_2)$  emission together with the target  $\text{Yb}({}^2F_{5/2} \rightarrow {}^2F_{7/2})$  fluorescence upon visible or NIR irradiation (Figure 1) confirmed that incomplete intramolecular  $\text{Cr} \rightarrow \text{Yb}$  energy transfers occur due to small  $W_{\text{Cr} \rightarrow \text{Yb}}$  rate constants, thus leading to long apparent Yb-centered NIR

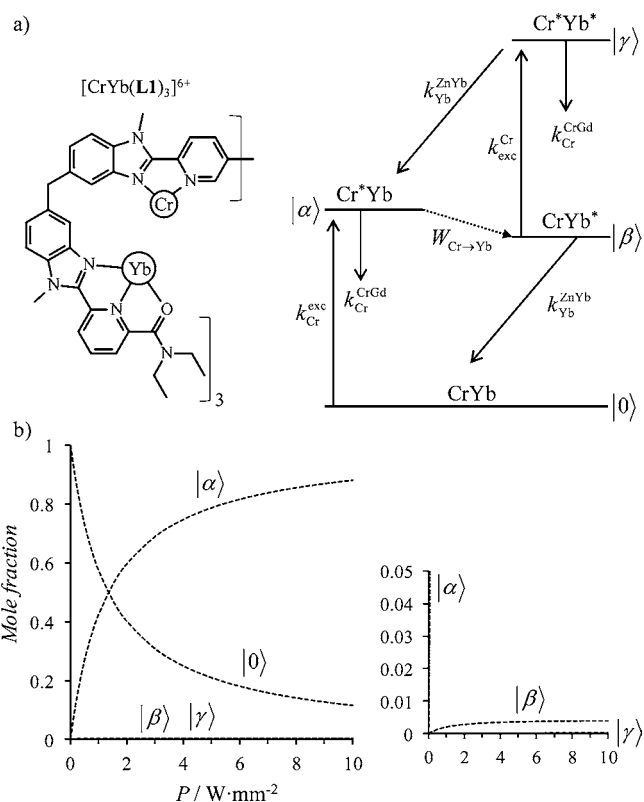
lifetimes mirroring the millisecond decay of the Cr(III) donor chromophore,<sup>10,16</sup> but to small quantum yields. In this Article, we propose a simple and efficient strategy for optimizing lanthanide-centered emission intensity in such edifices by increasing their nuclearity and apply it to  $\text{Ln} = \text{Nd}, \text{Er}, \text{and Yb}$ .

## 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  $\text{Ln} = \text{Yb}$ .<sup>19</sup> The



**Figure 1.** Cr(III)-sensitized Yb-centered NIR emission occurring in isolated dinuclear complexes (a)  $[(\text{acac})_2\text{Cr}(\text{ox})\text{Yb}(\text{HB}(\text{pz})_3)_2]$  ( $\text{Cr} \cdots \text{Yb} = 5.67 \text{ \AA}$ )<sup>17</sup> and (b)  $[\text{CrYb}(\text{L1})_3]^{6+}$  ( $\text{Cr} \cdots \text{Yb} = 9.33 \text{ \AA}$ ).<sup>18</sup>



**Figure 2.** (a) Kinetic scheme for modeling the light-conversion process operating in  $[\text{CrYb}(\text{L1})_3]^{6+}$  upon irradiation into the Cr-centered absorption bands<sup>19</sup> and (b) computed steady-state population densities for the various levels (the 0–0.05 population density range is highlighted on the right) by using  $W_{\text{Cr} \rightarrow \text{Yb}} = 240 \text{ s}^{-1}$ ,  $k_{\text{Cr}}^{\text{CrGd}} = 270 \text{ s}^{-1}$ , and  $k_{\text{Yb}}^{\text{ZnYb}} = 5 \times 10^4 \text{ s}^{-1}$  with increasing incident pump power  $P$  ( $\text{Cr} = \text{Cr}({}^4A_2)$  ground state,  $\text{Yb} = \text{Yb}({}^2F_{7/2})$  ground state,  $\text{Cr}^* = \text{Cr}({}^2E)$  excited state, and  $\text{Yb}^* = \text{Yb}({}^2F_{5/2})$  excited state).<sup>16</sup>

solutions of the associated kinetic differential equations, given in matrix form in eq 1,<sup>20</sup> under continuous-wave irradiation of the Cr-centered transitions yield the variations of the steady-state population densities  $N^{(j)}$  versus increasing pump power shown in Figure 2b. In eq 1,  $W_{\text{Cr} \rightarrow \text{Yb}}$  is the energy transfer rate constant measured in  $[\text{CrYb}(\text{L1})_3]^{6+}$ ,  $k_{\text{Cr}}^{\text{CrGd}}$  is the decay rate constant of Cr( ${}^2E$ ) in the absence of an acceptor and measured in  $[\text{CrGd}(\text{L1})_3]^{6+}$ , while  $k_{\text{Yb}}^{\text{ZnYb}}$  is the decay rate constant of Yb( ${}^2F_{5/2}$ ) in the absence of a donor and measured in  $[\text{ZnYb}(\text{L1})_3]^{5+}$ . The pumping rate constant,  $k_{\text{Cr}}^{\text{exc}}$ , is given by eq 2<sup>21</sup> in which  $\sigma_{\text{Cr}}^{22}$  is the absorption cross section of the Cr-centered transition<sup>22</sup> and  $\lambda_p$  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.

$$\left[ \frac{dN^{(i)}}{dt} \right] = \mathbf{M} \times [N^{(i)}] \text{ with } \mathbf{M} =$$

$$\begin{pmatrix} -k_{\text{Cr}}^{\text{exc}} & k_{\text{Cr}}^{\text{CrGd}} & k_{\text{Yb}}^{\text{ZnYb}} & 0 \\ k_{\text{Cr}}^{\text{exc}} & -(k_{\text{Cr}}^{\text{CrGd}} + W_{\text{Cr} \rightarrow \text{Yb}}) & 0 & k_{\text{Yb}}^{\text{ZnYb}} \\ 0 & W_{\text{Cr} \rightarrow \text{Yb}} & -(k_{\text{Yb}}^{\text{ZnYb}} + k_{\text{Cr}}^{\text{exc}}) & k_{\text{Cr}}^{\text{CrGd}} \\ 0 & 0 & k_{\text{Cr}}^{\text{exc}} & -(k_{\text{Cr}}^{\text{CrGd}} + k_{\text{Yb}}^{\text{ZnYb}}) \end{pmatrix} \quad (1)$$

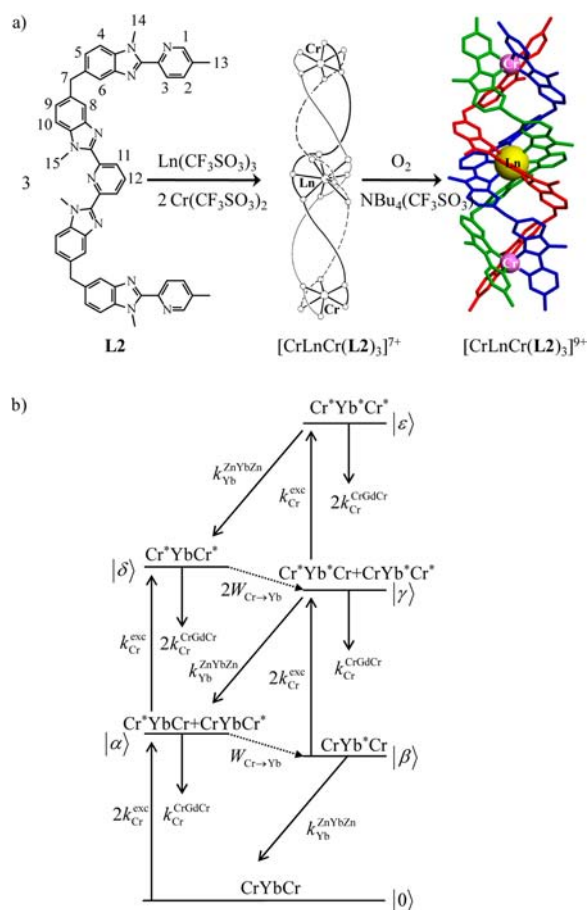
$$k_{\text{Cr}}^{\text{exc}} = \frac{\lambda_p}{hc\pi(\omega_p)^2} P\sigma_{\text{Cr}} = fP\sigma_{\text{Cr}} \quad (2)$$

Because  $(k_{\text{Cr}}^{\text{CrGd}} + W_{\text{Cr} \rightarrow \text{Yb}}) \ll k_{\text{Yb}}^{\text{ZnYb}}$ , the population densities of the Yb-centered excited levels  $|\beta\rangle$  and  $|\gamma\rangle$  remain negligible for all incident pump powers, and as the intrinsic luminescence quantum efficiency of the Yb luminescence,  $\eta_{\text{Yb}}^{\text{Yb}}$  is low, the intensity of the NIR emission remains marginal ( $I \propto \eta_{\text{Yb}}^{\text{Yb}} (N^{|\beta\rangle} + N^{|\gamma\rangle})$ , Figure S2, Supporting Information). However, its apparent exponential decay  $\tau_{\text{Yb}}^{\text{CrYb}} = 1/k_{\text{CrYb}}^{\text{CrYb}} = 1.96$  ms in  $[\text{CrYb}(\text{L1})_3]^{6+}$  mirrors the long  $\text{Cr}(^2\text{E})$  donor lifetime.<sup>16</sup>

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 dimetallic complex  $[\text{CrYbCr}(\text{L2})_3]^{9+}$  is expected to meet the above-mentioned criterion (Figure 3a):<sup>23</sup> introduction of the rate constants obtained for  $[\text{CrYb}(\text{L1})_3]^{6+}$  into a kinetic scheme adapted to  $[\text{CrYbCr}(\text{L2})_3]^{9+}$  (Figure 3b,  $k_{\text{Cr}}^{\text{CrGdCr}} \equiv k_{\text{Cr}}^{\text{CrGd}}$ ,  $k_{\text{Yb}}^{\text{ZnYbZn}} \equiv k_{\text{Yb}}^{\text{ZnYb}}$ , and  $W_{\text{Cr} \rightarrow \text{YbCr}} \equiv W_{\text{Cr} \rightarrow \text{Yb}} = W_{\text{Cr} \rightarrow \text{Yb}}$ ) logically predicts a statistical increase of the intensity of the NIR emission by a factor:  $f_{\text{gain}} = 2$  (Figure S2, Supporting Information). It is worth noting here that the Yb-centered NIR luminescence in  $[\text{CrYbCr}(\text{L2})_3]^{9+}$  is expected to mainly originate from the singly excited state  $\text{CrYb}^*\text{Cr}$  ( $|\beta\rangle$  in Figure 3b) at low incident pump power, as found for  $[\text{CrYb}(\text{L1})_3]^{6+}$ , whereas the doubly excited state  $\text{Cr}^*\text{Yb}^*\text{Cr}$  ( $|\gamma\rangle$  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  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  (Ln = Nd, Er, Yb) in which the twin d-block metal ions act as sensitizers, as well as for the reference helicates  $[\text{ZnLnZn}(\text{L2})_3]^{7+}$  for which no d-block sensitization is present.

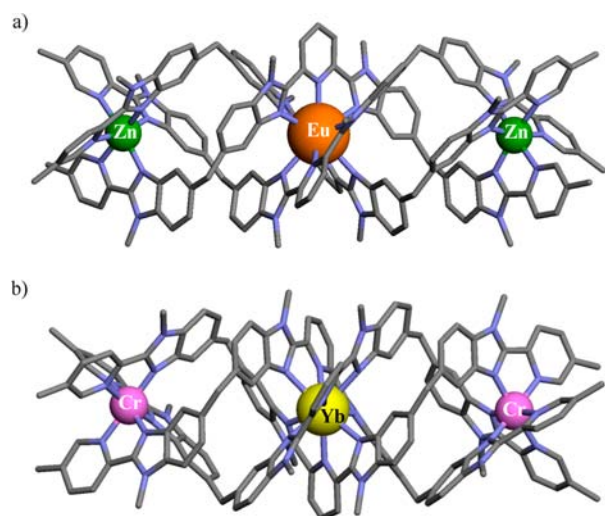
**Synthesis and Structural Characterization of  $[\text{ZnLnZn}(\text{L2})_3](\text{CF}_3\text{SO}_3)_7$  and  $[\text{CrLnCr}(\text{L2})_3](\text{CF}_3\text{SO}_3)_9$  (Ln = Nd, Er, Yb).** Stoichiometric mixing of  $M(\text{CF}_3\text{SO}_3)_2 \cdot x\text{H}_2\text{O}$  ( $M = \text{Cr}(\text{II}), \text{Zn}(\text{II}); 2$  equiv) and  $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$  (Ln = Nd, Er, Yb; 1 equiv) with the segmental tridentate ligand **L2** (3 equiv) in acetonitrile quantitatively yields the targeted self-assembled triple-stranded complexes  $[\text{MLnM}(\text{L2})_3]^{7+}$  as previously established for Ln = La, Eu, Gd, Tb, and Lu (Figure 3a).<sup>23a</sup> Whereas the air-sensitive dinuclear chromium(II) complexes are not isolated, slow diffusion of diethyl ether into concentrated acetonitrile solutions of the zinc(II) complexes gives 75–80% yield of  $[\text{ZnLnZn}(\text{L2})_3](\text{CF}_3\text{SO}_3)_7 \cdot n\text{H}_2\text{O}$  (Table S1) whose ESI-MS (Table S2 and Figure S4a) and



**Figure 3.** (a) Self-assembly of the trinuclear complexes  $[\text{CrLnCr}(\text{L2})_3]^{9+23}$  and (b) adapted kinetic scheme for modeling the light-conversion process operating in  $[\text{CrYbCr}(\text{L2})_3]^{9+}$  upon irradiation of the Cr-centered transitions (Cr =  $\text{Cr}(^4\text{A}_2)$  ground state, Yb =  $\text{Yb}(^2\text{F}_{7/2})$  ground state,  $\text{Cr}^* = \text{Cr}(^2\text{E})$  excited state, and  $\text{Yb}^* = \text{Yb}(^2\text{F}_{5/2})$  excited state).<sup>18b</sup>

paramagnetically shifted  $^1\text{H}$  NMR spectra (Ln = Nd, Yb, Table S3 and Figure S5) are diagnostic for the systematic formation of  $D_3$ -symmetrical triple-stranded helicates  $[\text{ZnLnZn}(\text{L2})_3]^{7+23}$ . Despite several attempts, we were unable to obtain X-ray quality crystals for these complexes. Therefore, a DFT-optimized gas-phase molecular structure was computed for  $[\text{ZnEuZn}(\text{L2})_3]^{7+}$  (Figure 4a). For  $M = \text{Cr}$ , the intermediate  $[\text{CrLnCr}(\text{L2})_3]^{7+}$  complexes undergo fast air oxidation to give  $[\text{CrLnCr}(\text{L2})_3](\text{CF}_3\text{SO}_3)_9 \cdot m\text{TBAF} \cdot n\text{H}_2\text{O}$  after slow diffusion of diethyl ether into concentrated acetonitrile solutions containing an excess of  $\text{Bu}_4\text{N}(\text{CF}_3\text{SO}_3)$  (=TBAF, Table S1). Because of the slow electronic relaxation rate of the nondegenerate  $\text{Cr}(^4\text{A}_2)$  ground state,<sup>24</sup>  $^1\text{H}$  NMR spectra are too broad for any reliable characterization of these complexes (Figure S6), but ESI-MS data strongly support the exclusive formation of  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  in acetonitrile (Table S2 and Figure S4b). Recrystallization by slow diffusion of diethylether into propionitrile solutions yields fragile orange needles of  $[\text{CrLnCr}(\text{L2})_3](\text{CF}_3\text{SO}_3)_9(\text{C}_3\text{H}_5\text{N})_{30}$  (Ln = Eu, Gd, Tb, Er, Yb, Lu) suitable for X-ray diffraction studies. All complexes are isostructural (monoclinic,  $P2_1/c$ ) with huge unit cells ( $V \approx 48$  000  $\text{\AA}^3$ ,  $Z = 4$ ) and limited diffraction intensities, which require synchrotron facilities for collecting suitable sets of diffraction data. Ln = Eu (midrange sized lanthanide) and Ln = Yb (small sized lanthanide) have been selected for further structural





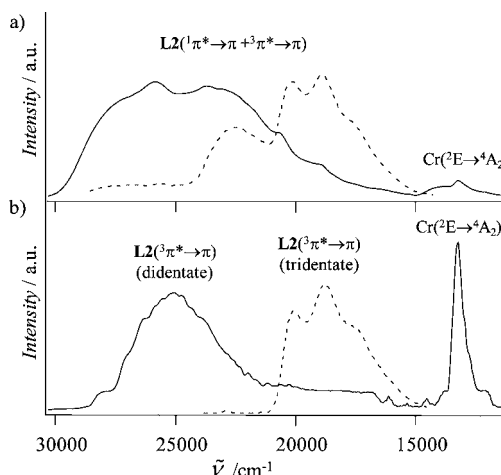
**Figure 4.** Color-coded perspective views of (a) the DFT-optimized gas-phase structure of  $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$  and (b) the molecular structure of  $[\text{CrYbCr}(\text{L}2)_3]^{9+}$  in the crystal structure of  $[\text{CrYbCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{C}_3\text{H}_5\text{N})_{30}$ . Hydrogen atoms have been omitted for clarity (C = gray, N = blue).

analyses, and their crystal structures indeed confirm the existence of almost superimposable pseudo- $D_3$  symmetrical triple-stranded helical cations (Figures S7–S9), together with disordered noncoordinated triflate anions and propionitrile molecules (Figure 4b).<sup>25</sup> DFT-optimized Zn–N and Eu–N bond lengths in  $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$ , and observed Cr–N and Ln–N bond lengths in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$ , have standard values.<sup>18,26</sup> 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 pseudo-tricapped trigonal prismatic cavities provided by the nine heterocyclic nitrogen atoms of the three wrapped tridentate segments. The average intramolecular intermetallic Zn...Ln distance of 9.74 Å estimated for  $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$  in the gas phase is marginally longer than related Cr...Ln separations measured in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (8.59–9.02 Å; average 8.86 Å).<sup>23b</sup> These values compare well with 8.96 and 9.33 Å distances previously reported for the parent dinuclear  $[\text{ZnEu}(\text{L}1)_3]^{5+26}$  and  $[\text{CrLn}(\text{L}1)_3]^{6+18}$  complexes in the solid state.

Beyond the helical twist, which is increased by a half turn on going from  $[\text{CrLn}(\text{L}1)_3]^{6+}$  (0.78 turn for a total linear progression of 12.01 Å, pitch = 15.4 Å)<sup>18</sup> to  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (1.30 turns for a total linear progression of 19.78 Å, pitch = 15.2 Å), the connection of the second Cr(III) sensitizer in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  further affects the lanthanide coordination sphere because the terminal pseudo- $C_3$  nine-coordinated  $\text{LnN}_6\text{O}_3$  metallic unit in  $[\text{CrLn}(\text{L}1)_3]^{6+}$  (Figure 1b) is transformed into a central pseudo- $D_3$   $\text{LnN}_9$  entity in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (Figure 4b).

**Photophysical Properties of Isolated Ligand-Centered and Metal-Centered Chromophores in  $[\text{ZnLnZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7$  (Ln = Gd, Nd, Er, Yb) and  $[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ .** The free polyaromatic ligand L2 strongly absorbs UV irradiation via a series of allowed  $\pi \rightarrow \pi^*$  transitions whose apparent maximum band envelope lies at 31 500  $\text{cm}^{-1}$  (Table S4, Supporting Information). UV-photoexcitation into these bands produces a structured blue-green fluorescence arising from the lowest singlet state ( $^1\pi^* \rightarrow \pi$ ; 22 780  $\text{cm}^{-1}$ ), but no

phosphorescence was detectable.<sup>23a</sup> Upon coordination to optically inactive metallic cations in the trinuclear complex  $[\text{ZnGdZn}(\text{L}2)_3]^{7+}$ ,<sup>27</sup> standard excitonic coupling between the three bound wrapped aromatic binding units splits the  $\pi \rightarrow \pi^*$  transitions into two principal components (30 675 and 26 180  $\text{cm}^{-1}$ ).<sup>28</sup> This gives an opportunity for extending ligand-centered excitation from UV to visible, and irradiation of  $[\text{ZnGdZn}(\text{L}2)_3]^{7+}$  in the 30 770–24 690  $\text{cm}^{-1}$  domain indeed produces fluorescence ( $^1\pi^* \rightarrow \pi$  at 22 520  $\text{cm}^{-1}$ ) and phosphorescence ( $^3\pi^* \rightarrow \pi$  at 20 100  $\text{cm}^{-1}$ ,  $\tau = 2.45(9)$  ms, Figure 5).<sup>23a</sup>

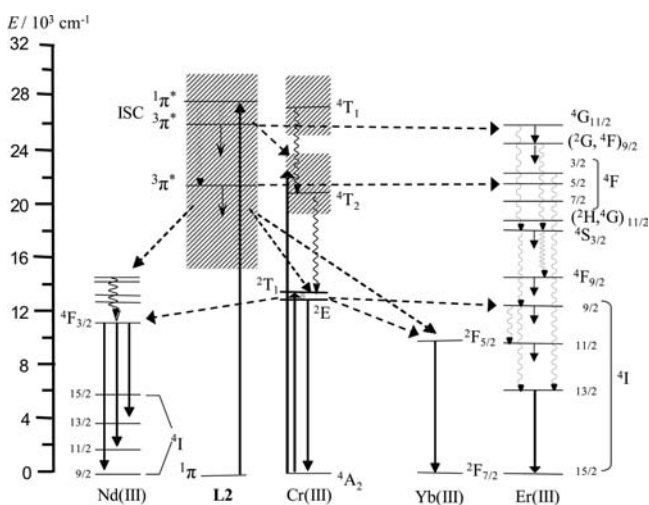


**Figure 5.** (a) Fluorescence and (b) phosphorescence (delay time after flash = 0.05 ms) spectra recorded for  $[\text{ZnGdZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7$  (dashed line,  $\tilde{\nu}_{\text{exc}} = 30\,770\text{ cm}^{-1}$ ) and  $[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$  (full line,  $\tilde{\nu}_{\text{exc}} = 31\,250\text{ cm}^{-1}$ ) upon ligand-centered excitation (solid state, 77 K).

The replacement of the terminal diamagnetic Zn(II) with open-shell Cr(III) in  $[\text{CrGdCr}(\text{L}2)_3]^{9+}$  enhances the paramagnetic coupling mechanism responsible for the increasing intensity of the spin-forbidden  $^3\pi^* \rightarrow \pi$  phosphorescence<sup>29</sup> arising at 24 510  $\text{cm}^{-1}$  (didentate unit,  $\tau = 5.19(1)$  ms) and 21 050  $\text{cm}^{-1}$  (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  $\text{Cr}^2(\text{E})$  excited state evidenced by intramolecular  $\text{L}2 \rightarrow \text{Cr}$  energy transfer processes sensitizing the famous long-lived  $\text{Cr}^2(\text{E} \rightarrow ^4\text{A}_2)$  luminescence at 13 240  $\text{cm}^{-1}$  in  $[\text{CrGdCr}(\text{L}2)_3]^{9+}$  ( $\tau_{\text{Cr}^2(\text{E})}^{\text{CrGdCr}} = 1/k_{\text{Cr}^2(\text{E})}^{\text{CrGdCr}} = 2.27(2)$  ms at 10 K, Table 1, column 2, Figure 5, and Figure S10).

The associated excitation profile recorded for  $[\text{CrGdCr}(\text{L}2)_3]^{9+}$  upon monitoring the  $\text{Cr}^2(\text{E} \rightarrow ^4\text{A}_2)$  transition unravels that both Cr-centered  $\text{Cr}^2(\text{E} \rightarrow ^4\text{A}_2)$  at 13 330  $\text{cm}^{-1}$ ;  $\text{Cr}^2(^2\text{T}_1 \leftarrow ^4\text{A}_2)$  at 13 910/14 090  $\text{cm}^{-1}$ ;  $\text{Cr}^4(^4\text{T}_2 \leftarrow ^4\text{A}_2)$  at 19 970/21 780  $\text{cm}^{-1}$  and ligand-centered ( $>24\,500\text{ cm}^{-1}$ ) excitation processes (Figure S11) contribute to NIR phosphorescence centered at 13 240  $\text{cm}^{-1}$  (Figure 6). Because of the pseudo- $D_3$  symmetry in  $[\text{CrGdCr}(\text{L}2)_3]^{9+}$ , the  $\text{Cr}^4(^4\text{T}_2)$  and  $\text{Cr}^2(^2\text{T}_1)$  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  $\Delta = 20\,880\text{ cm}^{-112-14}$  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).<sup>30</sup>



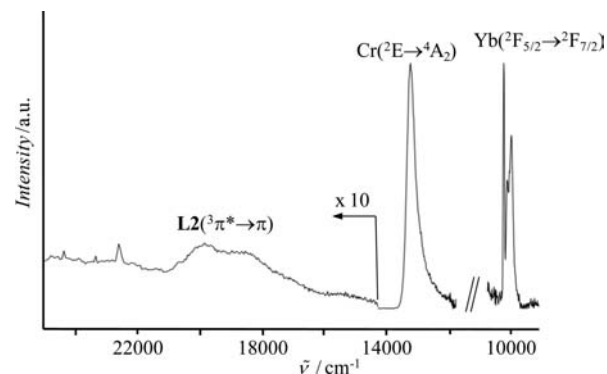
**Figure 6.** Partial energy level diagram with pertinent excited states for individual components summarizing the excitation processes (straight upward arrows), resonant energy transfer processes (horizontal dashed arrows), phonon-assisted energy transfer processes (diagonal dashed arrows), nonradiative multiphonon relaxation (undulating arrows), and observed radiative emission processes (straight downward arrows) occurring in  $[\text{ZnLnZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7$  and  $[\text{CrLnCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$  (Ln = Nd, Er, Yb). The  $\text{Cr}(^2\text{T}_2)$  levels are omitted for clarity, although they can act as a relay for energy transfer processes.

$$\begin{aligned} \Delta E &= E[\text{Cr}(^2\text{E})] - E[\text{Cr}(^4\text{A}_2)] \\ &= (9B + 3C - 90B^2/\Delta) \\ &= 13\,330\text{cm}^{-1} \end{aligned} \quad (3)$$

The energies of the Ln-centered excited levels are deduced from excitation of the ligand-centered  $^1\pi^*$  singlet states in  $[\text{ZnLnZn}(\text{L}2)_3]^{7+}$  (Ln = Nd, Er, Yb), which produces residual ligand-centered emission because of incomplete  $\text{L}2 \rightarrow \text{Ln}(\text{III})$  energy transfer, together with Ln-centered luminescence assigned to specific  $4f \rightarrow 4f$  transitions (Figure 6 and Figure S12).<sup>31</sup> The characteristic lifetimes of the Ln-centered NIR emissions are within the microsecond range as expected for molecular complexes with reasonably protected coordination sites ( $\tau_{\text{Nd}(^4\text{F}_{3/2})}^{\text{ZnNdZn}} = 1/k_{\text{Nd}}^{\text{ZnNdZn}} = 1.60(6) \mu\text{s}$ ,  $\tau_{\text{Er}(^4\text{I}_{13/2})}^{\text{ZnErZn}} = 1/k_{\text{Er}}^{\text{ZnErZn}} =$

$4.54(4) \mu\text{s}$ , and  $\tau_{\text{Yb}(^2\text{F}_{5/2})}^{\text{ZnYbZn}} = 1/k_{\text{Yb}}^{\text{ZnYbZn}} = 31.0(2) \mu\text{s}$ , solid state 10 K, Table 1, column 4).<sup>9</sup>

Finally, irradiation into the ligand-centered  $\pi \rightarrow \pi^*$  transitions in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (Ln = Nd, Er, Yb) induces a luminescence produced by three components: (i) the residual ligand-centered  $^3\pi^* \rightarrow \pi$  phosphorescence (incomplete  $\text{L}2 \rightarrow \text{Cr}$ , Ln energy transfers), (ii) the Cr(III) sensitized emission at  $13\,300\text{cm}^{-1}$ ; and (iii) the Ln(III) sensitized NIR emission at  $\sim 10\,000\text{cm}^{-1}$  for Yb( $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ ) (Figure 7), at  $\sim 11\,000/9500/7500\text{cm}^{-1}$



**Figure 7.** Emission spectrum recorded for  $[\text{CrYbCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$  upon ligand-centered excitation ( $\bar{\nu}_{\text{exc}} = 37\,037\text{cm}^{-1}$ , solid state, 77 K).

for Nd( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ ,  $^4\text{I}_{11/2}$ ,  $^4\text{I}_{13/2}$ ) (Figure S15a), and at  $\sim 6500\text{cm}^{-1}$  for Er( $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ) (Figure S15b). The excitation spectra recorded upon monitoring the Ln-centered NIR emission demonstrate that the Cr( $^2\text{E}$ ) excited state can be systematically used as a feeding level for lanthanide sensitization in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (Ln = Nd, Er, Yb, Figure S16). Consequently, selective laser excitation of the Cr( $^2\text{E} \leftarrow ^4\text{A}_2$ ) transition at  $13\,330\text{cm}^{-1}$  produces dual emission arising from Cr( $^2\text{E}$ )/Nd( $^4\text{F}_{3/2}$ ) in  $[\text{CrNdCr}(\text{L}2)_3]^{9+}$ , Cr( $^2\text{E}$ )/Er( $^4\text{I}_{13/2}$ ) in  $[\text{CrErCr}(\text{L}2)_3]^{9+}$ , and Cr( $^2\text{E}$ )/Yb( $^2\text{F}_{5/2}$ ) in  $[\text{CrYbCr}(\text{L}2)_3]^{9+}$  with characteristic lifetimes  $\tau_{\text{Cr}(^2\text{E})}^{\text{CrLnCr}} = 1/k_{\text{Cr}}^{\text{CrLnCr}}$  and  $\tau_{\text{Ln}}^{\text{CrLnCr}} = 1/k_{\text{Ln}}^{\text{CrLnCr}}$  collected in Table 1 (columns 3 and 5).

**Intermetallic Energy Transfer and Light-Conversion Processes in  $[\text{CrLnCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$  (Ln = Nd, Er, Yb).** The use of short-time and low-power light pulses for pumping the Cr( $^2\text{E} \leftarrow ^4\text{A}_2$ ) transition in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  at  $13\,330\text{cm}^{-1}$

**Table 1.** Rate Constants ( $k/\text{s}^{-1}$ ), Efficiencies ( $\eta$ , eq 5), Intramolecular Intermetallic Ln $\cdots$ Cr Distances ( $R_{\text{D,A}}^{\text{Cr,Ln}}/\text{\AA}$ ), and Critical Distances for 50% Energy Transfer ( $R_0^{\text{Cr,Ln}}/\text{\AA}$ , eq 6) in  $[\text{LnCr}(\text{L}1)_3]^{6+}$  and  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (Ln = Gd, Nd, Er, Yb; 10 K)<sup>a</sup>

compd	$k_{\text{Cr}}^{\text{CrGd}}$	$k_{\text{Cr}}^{\text{CrLn}}$	$k_{\text{Ln}}^{\text{ZnLn}}$	$k_{\text{Ln}}^{\text{CrLn}}$	$W_{\text{Cr} \rightarrow \text{Ln}}$	$\eta_{\text{Cr} \rightarrow \text{Ln}}$	$R_{\text{D,A}}^{\text{Cr,Ln}}$	$R_0^{\text{Cr,Ln}}$	ref
$[\text{GdCr}(\text{L}1)_3]^{6+}$	$2.73(8) \times 10^2$								16
$[\text{NdZn}(\text{L}1)_3]^{6+}$			$6.85(5) \times 10^5$						16
$[\text{YbZn}(\text{L}1)_3]^{6+}$			$5.0(3) \times 10^4$						16
$[\text{NdCr}(\text{L}1)_3]^{6+}$		$2.13(7) \times 10^3$		$2.1(3) \times 10^3$	$1.86(8) \times 10^3$	0.87(4)	9.28	12.8(2)	16
$[\text{YbCr}(\text{L}1)_3]^{6+}$		$5.1(2) \times 10^2$		$5.0(5) \times 10^2$	$2.4(1) \times 10^2$	0.46(2)	9.33	9.1(1)	16
$[\text{CrGdCr}(\text{L}2)_3]^{9+}$	$4.40(9) \times 10^2$								this work
$[\text{ZnNdZn}(\text{L}2)_3]^{9+}$			$6.2(1) \times 10^5$						this work
$[\text{ZnYbZn}(\text{L}2)_3]^{9+}$			$3.2(1) \times 10^4$						this work
$[\text{ZnErZn}(\text{L}2)_3]^{9+}$			$2.20(3) \times 10^5$						this work
$[\text{CrNdCr}(\text{L}2)_3]^{9+}$		$2.00(6) \times 10^3$		$4.0(4) \times 10^3$	$1.56(6) \times 10^3$	0.78(3)	8.9	11.0(1)	this work
$[\text{CrYbCr}(\text{L}2)_3]^{9+}$		$6.9(2) \times 10^2$		$7.6(8) \times 10^2$	$2.50(9) \times 10^2$	0.36(2)	8.9	8.10(9)	this work
$[\text{CrErCr}(\text{L}2)_3]^{9+}$		$9.3(3) \times 10^2$		$9.3(5) \times 10^2$	$4.9(2) \times 10^2$	0.53(3)	8.9	9.1(1)	this work

<sup>a</sup> $k_{\text{Cr}}^{\text{CrGd}}$ ,  $k_{\text{Cr}}^{\text{CrLn}}$ ,  $k_{\text{Ln}}^{\text{ZnLn}}$ , and  $k_{\text{Ln}}^{\text{CrLn}}$  are reported with their experimental standard deviations. All other uncertainties are calculated by using standard mathematical propagations.<sup>38</sup>

produces a non-negligible transient population only for the lowest excited  $\text{Cr}^*\text{LnCr}$  state ( $|\alpha\rangle$ ) level in Figure 3b), which relaxes (i) via radiative and nonradiative pathways ( $k_{\text{Cr}}^{\text{CrGdCr}}$ ) toward the  $\text{CrLnCr}$  ground state ( $|0\rangle$ ) level in Figure 3b) and (ii) via energy transfer  $W_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}}$  toward the  $\text{CrLn}^*\text{Cr}$  state ( $|\beta\rangle$ ) level in Figure 3b). This simple kinetic scheme allows straightforward estimates of energy transfer rate constants ( $W_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}}$ , eq 4) and efficiencies ( $\eta_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}}$ , eq 5) by using the experimental characteristic lifetimes of the  $\text{Cr}(^2\text{E})$  excited state measured for the isostructural  $[\text{CrGdCr}(\text{L2})_3]^{9+}$  ( $\tau_{\text{Cr}}^{\text{CrGdCr}}$ ) and  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  ( $\tau_{\text{Cr}}^{\text{Cr}(\text{E})}$ ) complexes (Ln = Nd, Er, Yb, Table 1).<sup>12</sup>

$$W_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}} = k_{\text{Cr}}^{\text{CrLnCr}} - k_{\text{Cr}}^{\text{CrGdCr}} \\ = \left(\tau_{\text{Cr}}^{\text{CrLnCr}}\right)^{-1} - \left(\tau_{\text{Cr}}^{\text{CrGdCr}}\right)^{-1} \quad (4)$$

$$\eta_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}} = \frac{W_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}}}{W_{\text{Cr}\rightarrow\text{Ln}}^{\text{CrLnCr}} + k_{\text{Cr}}^{\text{CrGdCr}}} \\ = 1 - \frac{k_{\text{Cr}}^{\text{CrGdCr}}}{k_{\text{Cr}}^{\text{CrLnCr}}} \\ = 1 - \frac{\tau_{\text{Cr}}^{\text{CrLnCr}}}{\tau_{\text{Cr}}^{\text{CrGdCr}}} \quad (5)$$

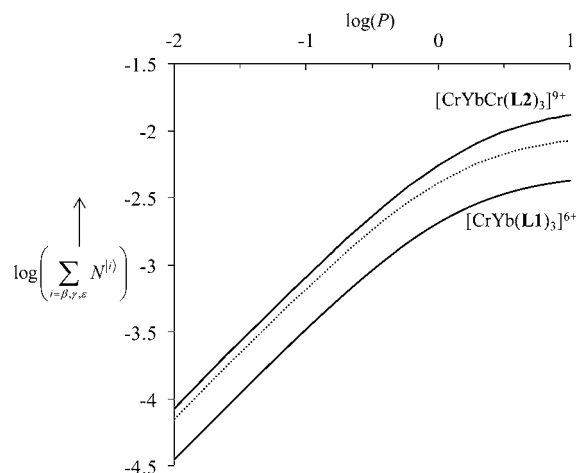
The calculated rate constants for the intramolecular  $\text{Cr}\rightarrow\text{Ln}$  energy transfer processes are similar for the dinuclear  $[\text{CrLn}(\text{L1})_3]^{6+}$  and trinuclear  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  complexes (Ln = Nd, Yb, Table 1, column 6), in line with the starting hypothesis. This leads to slightly less efficient energy transfer for the latter complexes because of the shorter intrinsic  $\text{Cr}(^2\text{E})$  lifetime in  $[\text{CrGdCr}(\text{L2})_3]^{9+}$  (Table 1, columns 2 and 7). Although recent investigations<sup>32</sup> suggest that long-distance intermetallic  $d\rightarrow f$  energy transfers may include a competition between the electron-exchange mechanism (i.e., Dexter-type)<sup>33</sup> and the (multipolar) Coulombic interaction between the donor and acceptor electric fields (i.e., Förster-type),<sup>34</sup> the energy transfer efficiencies in  $[\text{CrLn}(\text{L1})_3]^{6+}$  and  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  (Ln = Nd, Er, Yb) were analyzed within the strict limit of the long-range dipole–dipole formalism according to eq 6, in which  $R_{\text{D,A}}^{\text{Ln,Cr}}$  is the donor–acceptor distance separation taken as the intramolecular  $\text{Cr}\cdots\text{Ln}$  contact distance in the complexes and  $R_0^{\text{Ln,Cr}}$  is the critical distance at which  $\eta_{\text{Ln}\rightarrow\text{Cr}} = 0.5$ .<sup>12,35</sup> This simplification is justified by the presence of methylene units linking the three tridentate coordination moieties in L2 acting as electronic insulators.

$$\eta_{\text{Cr}\rightarrow\text{Ln}} = \left[ 1 + \left( \frac{R_{\text{D,A}}^{\text{Ln,Cr}}}{R_0^{\text{Ln,Cr}}} \right)^6 \right]^{-1} = \frac{(R_0^{\text{Ln,Cr}})^6}{(R_0^{\text{Ln,Cr}})^6 + (R_{\text{D,A}}^{\text{Ln,Cr}})^6} \quad (6)$$

We find critical distances for 50% energy transfer efficiencies in the nanometric range for all complexes with  $R_0^{\text{Nd,Cr}} > R_0^{\text{Er,Cr}} > R_0^{\text{Yb,Cr}}$  (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  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  (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  $\text{Cr}(^2\text{E})$  donor levels control the stepwise depopulation of the  $\text{CrLnCr}$  ground state to the benefit of the Cr-centered excited levels  $\text{Cr}^*\text{LnCr}$  (low pumping power) and  $\text{Cr}^*\text{LnCr}^*$  (large pumping power, Figure S17, Supporting Information). The population density of the Ln-centered NIR emitting levels  $\text{CrLn}^*\text{Cr}$ ,  $\text{Cr}^*\text{Ln}^*\text{Cr}$ , and  $\text{Cr}^*\text{Ln}^*\text{Cr}^*$  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  $[\text{LnCr}(\text{L1})_3]^{6+}$  to  $[\text{CrLnCr}(\text{L2})_3]^{9+}$  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  $\text{Cr}\rightarrow\text{Ln}$  energy transfer rate



**Figure 8.** Computed linear dependences of Yb-centered emission intensity with respect to incident pump power (in  $\text{W}/\text{mm}^2$ ) of the Cr-centered transitions in  $[\text{CrYb}(\text{L1})_3]^{6+}$  and  $[\text{CrYbCr}(\text{L2})_3]^{9+}$  (full traces, solid state, 10 K). The statistical behavior ( $f_{\text{gain}} = 2.0$ ) predicted for  $[\text{CrYbCr}(\text{L2})_3]^{9+}$  by using the rate constants measured for  $[\text{CrYb}(\text{L1})_3]^{6+}$  is shown as a dotted trace.

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  $\text{CrLnCr}$  ( $|0\rangle$ ) and the two first excited states  $\text{Cr}^*\text{LnCr}$  ( $|\alpha\rangle$ ) and  $\text{CrLn}^*\text{Cr}$  ( $|\beta\rangle$ ) contribute to the kinetic scheme. Equation 7 therefore satisfyingly models the relaxation processes originating from the initial density population matrix written as its transpose ( $N_0^{(0)} = (N_{\text{tot}} - N_0^{(\alpha)})N_0^{(\alpha)}N_0^{(\beta)} = 0$ )<sup>T</sup>:

$$\begin{pmatrix} dN_t^{(0)}/dt \\ dN_t^{(\alpha)}/dt \\ dN_t^{(\beta)}/dt \end{pmatrix} = \begin{pmatrix} 0 & k_{\text{Cr}}^{\text{CrGdCr}} & k_{\text{Ln}}^{\text{ZnLnZn}} \\ 0 & -(k_{\text{Cr}}^{\text{CrGdCr}} + W_{\text{Cr}\rightarrow\text{Ln}}) & 0 \\ 0 & W_{\text{Cr}\rightarrow\text{Ln}} & -k_{\text{Ln}}^{\text{ZnLnZn}} \end{pmatrix} \times \begin{pmatrix} N_t^{(0)} \\ N_t^{(\alpha)} \\ N_t^{(\beta)} \end{pmatrix} \quad (7)$$

Using projection operator solutions,<sup>20</sup> we obtain (Appendix 1):

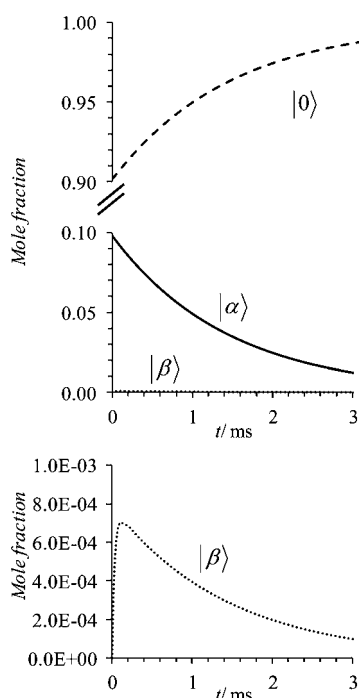


$$N_t^{(0)} = N_{\text{tot}} - \frac{N_0^{(\alpha)}}{(k_{\text{Ln}}^{\text{ZnLnZn}} - k_{\text{Cr}}^{\text{CrGdCr}} - W_{\text{Cr} \rightarrow \text{Ln}})} \left[ (k_{\text{Ln}}^{\text{ZnLnZn}} - k_{\text{Cr}}^{\text{CrGdCr}}) e^{-(k_{\text{Cr}}^{\text{CrGdCr}} + W_{\text{Cr} \rightarrow \text{Ln}})t} - W_{\text{Cr} \rightarrow \text{Ln}} e^{-k_{\text{Ln}}^{\text{ZnLnZn}}t} \right] \quad (8)$$

$$N_t^{(\alpha)} = N_0^{(\alpha)} e^{-(k_{\text{Cr}}^{\text{CrGdCr}} + W_{\text{Cr} \rightarrow \text{Ln}})t} \quad (9)$$

$$N_t^{(\beta)} = \frac{W_{\text{Cr} \rightarrow \text{Ln}} N_0^{(\alpha)}}{(k_{\text{Ln}}^{\text{ZnLnZn}} - k_{\text{Cr}}^{\text{CrGdCr}} - W_{\text{Cr} \rightarrow \text{Ln}})} \left[ e^{-(k_{\text{Cr}}^{\text{CrGdCr}} + W_{\text{Cr} \rightarrow \text{Ln}})t} - e^{-k_{\text{Ln}}^{\text{ZnLnZn}}t} \right] \quad (10)$$

The time evolution of the population densities computed for  $[\text{CrYbCr}(\text{L}2)_3]^{9+}$  (Figure 9),  $[\text{CrNdCr}(\text{L}2)_3]^{9+}$  (Figure S20),



**Figure 9.** Computed time evolution of the population densities of the ground state  $\text{CrYbCr}$  ( $|0\rangle$ , dashed trace, eq 8), and of the lowest excited states  $\text{Cr}^*\text{YbCr}$  ( $|\alpha\rangle$ , full trace, eq 9) and  $\text{CrYb}^*\text{Cr}$  ( $|\beta\rangle$ , dotted trace, eq 10) in  $[\text{CrYbCr}(\text{L}2)_3]^{9+}$  after a  $500 \mu\text{J}/\text{mm}^2$  pulse in the Cr-centered transition (solid state, 10 K).

and  $[\text{CrErCr}(\text{L}2)_3]^{9+}$  (Figure S21) shows that, except for the first microseconds following the pulse, the decay rate of the Ln-centered NIR emission mirrors the  $\text{Cr}(\text{E})$  emission lifetimes and thus extends into the millisecond range. This prediction is confirmed by the apparent long experimental  $\text{Nd}(^4\text{F}_{3/2})$ ,  $\text{Er}(^4\text{I}_{13/2})$ , and  $\text{Yb}(^2\text{F}_{5/2})$  lifetimes observed in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  (Table 1, column 5).

## CONCLUSION

The connection of a second strong-field  $[\text{CrN}_6]$  chromophore to the  $C_3$ -symmetrical dinuclear complexes  $[\text{LnCr}(\text{L}1)_3]^{6+}$  resulting in the formation of  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  does not significantly affect the ligand-centered and metal-centered photophysical properties. Excitation into the  $\text{Cr}(\text{E})$ -centered levels with NIR irradiation at  $13\,300 \text{ cm}^{-1}$  induces intra-

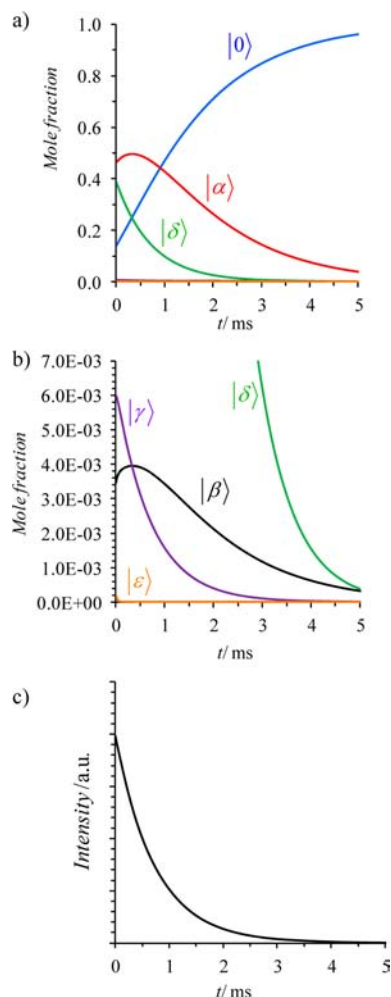
molecular  $\text{Cr} \rightarrow \text{Ln}$  energy transfers, which eventually sensitize low-energy luminescence for  $\text{Ln} = \text{Nd}, \text{Er}, \text{or Yb}$  in the spectral range  $6000\text{--}10\,000 \text{ cm}^{-1}$ . As compared to the fast Ln-centered relaxation pathways operating in  $[\text{ZnLnZn}(\text{L}2)_3]^{9+}$ , the slow  $\text{Cr} \rightarrow \text{Ln}$  energy transfer responsible for the feeding of the same Ln-centered excited levels in  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  acts as bottleneck, which controls the kinetics of the low-energy NIR emission. The apparent millisecond Ln-centered lifetimes thus mirror those of the  $\text{Cr}(\text{E})$  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  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  partially overcomes this limitation because the predicted intensities are more than twice larger than those found in the related dinuclear  $[\text{LnCr}(\text{L}1)_3]^{6+}$  complexes. The effective experimental gain in NIR emission intensity further depends on the ratio between radiative and nonradiative de-excitation pathways for the emitting  $\text{Nd}(^4\text{F}_{3/2})$ ,  $\text{Er}(^4\text{I}_{13/2})$ , and  $\text{Yb}(^2\text{F}_{5/2})$  levels, a trend that can be addressed by measuring intrinsic and global quantum yields. Because no such data were recorded for  $[\text{LnCr}(\text{L}1)_3]^{6+}$  in ref 23a, an exact comparison of experimental NIR  $\rightarrow$  NIR light-conversion efficiencies between dinuclear and trinuclear complexes is currently inaccessible, but the encouraging global quantum yields measured for  $[\text{CrLnCr}(\text{L}2)_3]^{9+}$  upon Cr-centered irradiation ( $\eta_{\text{Nd}}^{\text{Cr}} = 0.027(1)$  and  $\eta_{\text{Yb}}^{\text{Cr}} = 0.030(3)$ , 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  $\text{Cr}^*\text{LnCr}^*$  ( $|\delta\rangle$ ) and  $\text{Cr}^*\text{Ln}^*\text{Cr}$  ( $|\gamma\rangle$ , 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  $\text{CrLn}^*\text{Cr}$  doubly excited states when the activator possesses an adequate series of accessible spectroscopic levels as found in  $[\text{CrErCr}(\text{L}2)_3]^{9+}$ .<sup>23b</sup> 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.<sup>36</sup>

## EXPERIMENTAL SECTION

**Synthesis.** Chemicals were purchased from Strem, Acros, Fluka AG, and Aldrich, and used without further purification unless otherwise stated. The ligand  $\text{L}2$ <sup>37</sup> and complexes  $\text{Cr}(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ ,<sup>23a</sup>  $[\text{ZnGdZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7$ ,<sup>23a</sup>  $[\text{CrGdCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ ,<sup>23a</sup> and  $[\text{CrErCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9$ <sup>23b</sup> were prepared according to literature procedures. The triflate salts  $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$  were prepared from the corresponding oxide (Aldrich, 99.99%).<sup>39</sup> Acetonitrile and dichloromethane were distilled over calcium hydride.

**Preparation of  $[\text{ZnLnZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_7 \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$ ).**  $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot x\text{H}_2\text{O}$  (17  $\mu\text{mol}$ ) in acetonitrile (2 mL) was added into a dichloromethane/acetonitrile (1:1, 24 mL) solution of  $\text{L}2$  (41.3 mg, 51  $\mu\text{mol}$ ). 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  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  (12.4 mg, 34  $\mu\text{mol}$ ) in acetonitrile (2 mL) was added. The resulting solution was stirred for 24 h and concentrated. Slow diffusion of diethylether (12 h) eventually



**Figure 10.** (a) 0–1.0 mol fraction and (b) 0–0.007 mol fraction 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  $[\text{CrYbCr}(\text{L}2)_3]^{9+}$  and (c) Yb-centered emission intensity following a  $3 \text{ W}/\text{mm}^2$  photonic presaturation (solid state, 10 K, eq S13).

gave 75–80%  $[\text{ZnLnZn}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_{7-n}\text{H}_2\text{O}$  ( $\text{Ln} = \text{Nd, Er, Yb}$ ) as yellow microcrystals, which were characterized by  $^1\text{H}$  NMR, ESI-MS, and elemental analyses (Table S1).

**Preparation of  $[\text{CrLnCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9 \cdot m\text{TBAF} \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Nd, Er, Yb}$ ).**  $\text{Ln}(\text{CF}_3\text{SO}_3)_3 \cdot x\text{H}_2\text{O}$  (17  $\mu\text{mol}$ ) in acetonitrile (2 mL) was added into a dichloromethane/acetonitrile (1:1, 24 mL) solution of **L2** (41.3 mg, 51  $\mu\text{mol}$ ). After being stirred at room temperature for 24 h, the mixture was evaporated to dryness, and the pale yellow solid was transferred into a glovebox and dissolved in degassed acetonitrile (25 mL). A blue degassed acetonitrile solution (1 mL) of  $\text{Cr}(\text{CF}_3\text{SO}_3)_2 \cdot 1\text{H}_2\text{O}$  (12.6 mg, 34  $\mu\text{mol}$ ) was added, and the resulting mixture slowly turned brown, then green. After being stirred for 12 h under an inert atmosphere, solid  $\text{Bu}_4\text{NCF}_3\text{SO}_3$  (TBAF, 13.3 mg, 34  $\mu\text{mol}$ ) was added and air was slowly bubbled through the solution for 2 h. The yellow solution was evaporated, and the solid residue was dissolved in a minimum amount of acetonitrile. Slow diffusion of diethyl ether (24 h) yielded 92–95% of  $[\text{CrLnCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9 \cdot m\text{TBAF} \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Nd, Er, Yb}$ ) as pale microcrystalline powders, which were separated by filtration, washed with diethylether, dried under vacuum, and characterized by ESI-MS and elemental analyses (Table S1). Slow diffusion of diethylether into a concentrated propionitrile solution of  $[\text{CrYbCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9 \cdot 0.5\text{TBAF} \cdot 3\text{H}_2\text{O}$

gave fragile X-ray quality prisms of  $[\text{CrYbCr}(\text{L}2)_3](\text{CF}_3\text{SO}_3)_9(\text{C}_3\text{H}_5\text{N})_{30}$ .

**Spectroscopic Measurements.**  $^1\text{H}$  NMR spectra were recorded at 298 K on a Bruker Avance 400 MHz spectrometer. Chemical shifts were given in ppm with respect to TMS. Pneumatically assisted electrospray (ESI-MS) mass spectra were recorded from  $3$  to  $5 \times 10^{-4}$  M solutions on an Applied Biosystems API 150EX LC/MS System equipped with a Turbo Ionspray source, on a Finnigan-mat SSQ 7000, or on an Applied Biosystem API III. Elemental analyses were performed 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, CCC1100T) or with a liquid-helium bath cryostat (Oxford Instruments MD4). For room temperature or 77 K measurements, the samples were transferred into quartz tubes ( $\varnothing_{\text{in}} = 2.4$  mm, Verre et Quartz Technique SA, Neuchâtel) or borosilicate glass tubes ( $\varnothing = 0.8$ –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 R928 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  $\text{Er}^{3+}({}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2})$  emission. High-resolution room temperature and low temperature emission spectra were recorded upon excitation with an  $\text{Ar}^+$  laser (Coherent Innova 90C) at 488 nm or with Nd:YAG laser (Quantel Brilliant B) at 355 nm. The emitted light was analyzed at  $90^\circ$  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<sup>TM</sup> 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 Tektronics TDS724C and transferred to a PC for treatment with Origin 8. Lifetimes are averages of three independent determinations. Resonant excitation into the  $\text{Cr}({}^2\text{E} \leftarrow {}^4\text{A}_2)$  transition in  $\text{CrLnCr}$  was achieved with a tunable Ti:sapphire laser (Spectra Physics 3900S) pumped by the 532 nm excitation of a Nd:YVO<sub>4</sub> laser (Spectra Physics Millennia-10S). The excitation was tuned to  $13\,360$ – $13\,890$   $\text{cm}^{-1}$ . 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 ( $\text{cm}^{-1}$ ). Quantum yield measurements of the solid state samples were measured on quartz tubes with the help of an integration sphere developed by Frédéric Gummy at the Laboratory of Lanthanide Supramolecular Chemistry, EPFL and commercialized by GMP S.A. (Renens, Switzerland, www.gmp.ch).<sup>40</sup>

**Computational Details.** The gas-phase geometry of the complex  $[\text{ZnEuZn}(\text{L}2)_3]^{7+}$  was optimized by Density Functional Theory using the PW91PW91 exchange-correlation functional<sup>41</sup> implemented in Gaussian 03.<sup>42</sup> The DZVP double- $\zeta$  basis set developed by Godbout et al.<sup>43</sup> 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.<sup>44</sup> for the  $52 + 4f^6$  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  $^1\text{H}$  NMR shifts, elemental analyses, ESI-MS molecular peaks, characteristic emission lifetimes; figures showing  $^1\text{H}$  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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(31) The analysis of high-resolution emission spectra for  $[\text{ZnLnZn}(\text{L2})_3]^{7+}$  (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  $[\text{ZnLnZn}(\text{L2})_3]^{7+}$  are identical, within  $10\text{ cm}^{-1}$ , with those reported for  $[\text{LnZn}(\text{L1})_3]^{5+}$  despite the replacement of  $\text{LnN}_6\text{O}_3$  with  $\text{LnN}_9$  coordination spheres.<sup>16</sup>

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