Near-Infrared—Visible Light Upconversion in a Molecular Trinuclear d–f–d Complex**

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Molecular nonlinear-optical (NLO) phenomena are currently being exploited for the design of visible emitting bioprobes with unprecedented properties that result from 1) the transparency of living tissues toward low-energy near-infrared (NIR) incident radiation and 2) the improved focusing of the light from an excitation laser beam within nanometric volumes.[1] Nonresonant multiphoton absorption produces a single emission during the irradiation; this emission corresponds to a multiple of the energy of the incident beam, as, for example, in second-harmonic generation (Figure 1a), while resonant multiphoton absorption populates a real excited state of the chromophore, which relaxes and fluoresces with the same characteristics as if sensitized by a linear excitation process (Figure 1b).[2] Beyond the optimization of polarizable push–pull π-aromatic molecules for NLO optical response,[2] and the related development of upconverted fluorescence signals in polyaromatic platforms produced by metal-sensitized triplet–triplet annihilation photochemistry.[3] Le Bozec, Maury, Andraud, and their respective co-workers demonstrated that trivalent lanthanide ions (LnIII) may efficiently contribute to the polarization of coordinated aromatic ligands for resonant multiphoton absorption.[4] Moreover, the wealth of accessible long-lived metal-centered luminescent emissive levels can be exploited for two-photon-excited time-gated fluorescence analyses of biological tissues.[5]

Interestingly, the existence of several real excited states located between the ground state and the target excited state of lanthanide acceptors opens novel perspectives for the operation of alternative sensitizing mechanisms that take advantage of these electronic relays for successive linear excitations by one (Figure 1c) or several (Figure 1d) moieties, thus leading to an excited-state absorption (ESA) process or sequential energy transfer upconversion (ETU), both of which are followed by luminescence.[6] Although they operate by different principles, that is, they involve real rather than virtual intermediate excited levels during the multiphoton absorption processes, two-photon upconversion fluorescence processes (Figure 1c,d) can be considered as nonlinear because of the quadratic dependence of the efficiency (θ) on the incident intensity of the excitation light (I) (θ ∝ I^2).[4, 6] Upconversion has been regularly reported for trivalent lanthanide cations doped into low-phonon inorganic matrices,[7] particularly for applications in bioanalyses, telecommunications, and solar energy conversion,[7] but it is still unknown in molecular erbium complexes[8] because of the high effective vibrational energy hν_{th} ≈ 2000 cm⁻¹ that is typical of the molecular vibrations of organic ligands or of closely interacting solvent molecules, which result in efficient nonradiative relaxation of 4f–4f transitions.[9] In their seminal contribution dedicated to the search for upconversion fluorescence in the molecular complexes Na3[Ln(pyridine-2,6-dicarboxylate)]·13H2O (Ln = Nd, Er, Yb), Reinhard and Güdel indeed concluded that “there is no chance to induce and observe upconversion luminescence in these molecular compounds”.[9] Such a statement usually stimulates synthetic chemists to design novel molecular systems that are able to

Figure 1. Energy schemes for selected nonlinear two-photon processes (G = ground state, E = excited state). a) Nonresonant second-harmonic generation (SHG), b) two-photon excitation fluorescence (TPEF), c) excited-state absorption (ESA), and d) sequential energy transfer upconversion (ETU, A = acceptor, S = sensitizer and W_{SA} = S → A energy transfer probability).[6]
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potentially overcome the purported theoretical limitation. Following Auzel’s kinetic approach,[6b] the probabilities for the two-photon excitation processes \( W_{G-E(2)} \), shown in Figure 1c,d are given by Equations (1) and (2), respectively,

\[
W_{\text{E(A)}} = W_{G-E(1)} W_{E-E(2)} \tag{1}
\]

\[
W_{\text{ETU}} = (N_e^A W_{\text{SA}})(N_e^S W_{\text{SA}}) = (N_e)^2 W_{\text{SA}} W_{\text{SA2}} (W_{G-E(1)})^2 \tag{2}
\]

where \( W_{\text{SA}} \) are the sensitizer→acceptor energy-transfer probabilities for each step and \( N_e = N_e W_{G-E(1)} \) is the concentration of the excited sensitizers that act as donors.

Assuming that \( W_{G-E(1)} \approx W_{E-E(2)} \), which is a common approximation for rare-earth ions,[6b] comparison of Equations (1) and (2) shows that the ETU process (Figure 1d) may benefit from chemical tuning by 1) a large local concentration of sensitizers, thus maximizing the value of \( N_e \) around each acceptor and 2) efficient resonant \( S \rightarrow A \) energy transfer processes that maximize \( W_{\text{SA}} \) and \( W_{\text{SA2}} \). An attractive sensitizer/acceptor pair for potential molecular upconversion should thus match the following three criteria: 1) each acceptor should be surrounded by at least two equidistant sensitizers, 2) the resonant \( S \rightarrow A \) energy transfer processes should be optimized for an efficient population of the excited levels of the acceptor, while ensuring that the excited-state lifetimes of the remaining sensitizers are long enough for the occurrence of sequential energy transfer in an isolated molecule,[3] and 3) the acceptor must be protected from high-frequency vibrations in order to minimize the average energy of the interacting phonons.

Based on previous studies,[10,11] a Cr\(^{III}/Er\(^{III}/Cr\(^{III} \) triad (Figure 2) appears to be a good candidate, as the two Cr\(^{III} \) sensitizers are in strong ligand-field environments and therefore can push both the Cr(4\(T_2 \)) excited states and the associated broad absorption bands to sufficiently high energy (Figure S1 in the Supporting Information), while the comparatively large nephelauxetic effect lowers the energy of the 2\(E_\) state of the Cr\(^{III} \) center to around 13,400 cm\(^{-1} \). These conditions are required for the fine-tuning of the target intermetallic Cr(\("E\)→Er(\("I_9/2 \)) energy transfer (Figure 3).[11]

With these points in mind, we reacted the segmental ligand \( L_1 \) with stoichiometric amounts of \( \text{Ln(CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O} \) (Ln = Eu, Gd, Er, Yb) and Cr(\(\text{CF}_3\text{SO}_3\))\(_2 \cdot \text{H}_2\text{O} \) in acetonitrile to give the self-assembled helical pseudo-cryptates \([\text{CrLnCr(L)}_3], \) which were subsequently oxidized into the kinetically inert triple-helical complexes \([\text{CrLnCr(L)}_3]^{x+}_x \) (Figure 2).[12] Fine crystalline orange needles of \([\text{CrLnCr(L)}_3]^{x+}_x \) (\(x\text{CF}_3\text{SO}_3\)\(_x\text{C}_3\text{H}_5\text{N})_{30} \) (\(P_{21/c}, \text{Ln} = \text{Eu, Yb, Table S1} \)) suitable for X-ray diffraction studies could be isolated by slow diffusion of diethyl ether into concentrated solutions of the complex in propionitrile.[12] All the Cr–N and Ln–N bond lengths are typical (Tables S2 and S3).[10] and the global pseudo-D\(^2\) symmetrical triple-helical ion \([\text{CrLnCr(L)}_3], \) is made up of a pseudo-tricapped trigonal \([\text{LnN}_3] \) prism sandwiched between two pseudo-octahedral \([\text{CrN}_6] \) moieties (Figure 2 and Figure S2). Two slightly different cations with opposite helicities exist in the asymmetric unit, but the geometrical differences, except for the chirality, are marginal.

Figure 2. Synthesis of the kinetically inert dimetallic d–f–d complexes \([\text{CrLnCr(L)}_3]\)\(_x\text{CF}_3\text{SO}_3\)\(_x\). The molecular structure of the complex shown corresponds to one of the \([\text{CrEuCr(L)}_3]^{x+}_x \) ions in the asymmetric unit of the crystal structure of \([\text{CrEuCr(L)}_3]\)\(_x\text{CF}_3\text{SO}_3\). The crystal structure of \([\text{CrEuCr(L)}_3], \)\(_x\text{CF}_3\text{SO}_3\)\(_x\text{C}_3\text{H}_5\text{N})_{30} \) (Cr(1–Eu1 = 8.872(1) \(\text{Å}, \text{Cr2–Eu1 = 8.811(1) Å} \) [7].

Figure 3. Jablonski diagrams for the different chromophores in \([\text{CrErCr(L)}_3]\)\(_x\text{CF}_3\text{SO}_3\) showing a) the linear downconversion luminescence (excitation = full upward arrows, internal conversion = curled downward arrows, energy transfer = dotted arrows, emission = full downward arrows), and b) the nonlinear upconversion luminescence (excitation = full upward arrows, internal conversion = curled down arrows, ETU = dotted arrows, emission = full downward arrows).
and $S_5$), [12] UV irradiation of the complexes \([\text{CrErCr(L1)}]^{3+}\) (term CrGdCr; Figure 3a and Figures S4 and S5). [12] UV irradiation of the complexes \([\text{CrErCr(L1)}]^{3+}\) (CrErCr) efficiently populates ligand-centered $\pi^*\pi^*$ excited states. Subsequent partial $L_1$—Cr$^{III}$ and $L_1$—Er$^{III}$ energy transfer processes followed by internal relaxation processes (see Figure 3a) result in rich mixed ligand-centered and metal-centered luminescence, as previously described for several Cr$^{III}$/Ln$^{III}$ pairs in molecular complexes (Figure 4). [10,12,14]

From the excitation spectrum of CrErCr recorded upon monitoring the Cr(2$E$→4$A_2$) emission band at 13380 cm$^{-1}$ (in the red region; Figure S6a), we can easily locate the low-energy spin-allowed Cr($T_2$→$A_2$) transition at around 20980 cm$^{-1}$, a band which is further split by pseudo-$D_3$ symmetry into $A_+$ + $E$ components (Tables S6 and S7, and Figure S7). Since the energy of the latter transition exactly matches the ligand-field strength for $d^3$ metals in an octahedral geometry, [15] we deduce that 10$Dq$(Cr) ≈ 20980 cm$^{-1}$ in CrErCr; this value is consistent with the value of 23240 cm$^{-1}$ found for [Cr(bpy)$_3$] (bpy is the strong-field dientate 2,2'-bipyridine ligand). [13]

In agreement with our hypothesis, the coordination spheres around the Cr$^{III}$ ions in the trinuclear complexes CrLnCr indeed discriminate the energies of the Cr($T_2$) and Cr($E$) levels to such an extent ($\Delta E$ = 20980–13380 = 7600 cm$^{-1}$, Figure S1) that only the latter excited state can act as a feeding level for energy transfer towards the Er$^{III}$ ion, while Cr($T_2$) is inefficient (Figure S6b). This situation is ideal for a quantitative analysis of the intermetallic energy transfer process. Upon selective irradiation of the Cr($T_2$→$A_2$) transition in CrErCr at 22220 cm$^{-1}$, internal relaxation by intersystem crossing rapidly feeds the Cr($E$) excited states, which simultaneously luminesce in the red region (Cr(E→4$A_2$), $\nu_{em}$ = 13380 cm$^{-1}$, full width at half height, fwhh = 420 cm$^{-1}$) and transfer energy to the Er$^{III}$ ion (Cr(E→Er($4I_9/2$)), Figure 3a). Basic rate equations written for the time evolution of the population of the Cr(E) excited states in CrGdCr [Eq. (3), $k_{rad}$ and $k_{em}$ are the intrinsic radiative and nonradiative relaxation rate constants] and in CrErCr [Eq. (4)], $k_{Er^{III}}^{0}$ is the rate constant for Cr→Er energy transfer allow the estimation of the rate [Eq. (5)], $k_{Er^{III}}^{0}$ = 4.9(2) × 10$^{-5}$ s$^{-1}$ and efficiency [Eq. (6), $\eta Er^{III}$ = 53(2%) of the intramolecular Cr(E→Er($4I_9/2$)) energy transfer by simply using the characteristic Cr(E) lifetimes experimentally measured for CrGdCr ($\tau_{em}^{0}$ (CrGdCr) = 2.27(1) ms at 10 K) and for CrErCr ($\tau_{em}^{0}$ (CrErCr) = 1.07(5) ms at 10 K). [10]

$$k_{rad}^{0} (\text{CrGdCr}) = k_{rad}^{0} + k_{em}^{0} = 1/\tau_{em}^{0} (\text{CrGdCr})$$

$$k_{rad}^{0} (\text{CrErCr}) = k_{rad}^{0} + k_{em}^{0} + k_{Er^{III}}^{0} = 1/\tau_{em}^{0} (\text{CrErCr})$$

$$k_{Er^{III}}^{0} = k_{rad}^{0} (\text{CrErCr}) - k_{em}^{0} (\text{CrGdCr}) = 1/\tau_{em}^{0} (\text{CrErCr}) - 1/\tau_{em}^{0} (\text{CrGdCr})$$

$$\eta Er^{III} = \frac{k_{rad}^{0} (\text{CrErCr}) + k_{em}^{0} + k_{Er^{III}}^{0}}{k_{rad}^{0} (\text{CrErCr})} = \frac{1 - k_{em}^{0} (\text{CrErCr})}{\tau_{em}^{0} (\text{CrGdCr})}$$

We can now explore the sequential energy transfer upconversion (ETU) phenomenon in the molecular CrErCr complex, in which the central Er$^{III}$ acceptor is sandwiched between two strong-field Cr$^{III}$ sensitizers that possess Cr($E$) levels adapted for feeding the Er($4I_9/2$) level (i.e. ca. 50% efficiency at 10 K with millisecond residual lifetimes). Although the transitions are very weak because of the spin selection rules, the excitation spectra of CrErCr indicate that direct excitation of the Cr($T_2$,E→A$_2$) transitions with NIR light is conceivable (13200–13800 cm$^{-1}$). Figure S8. Consequently, irradiation at 13333 cm$^{-1}$ with a tunable Ti:sapphire laser with power in the range 195–690 mW mm$^{-2}$ [16] indeed produces upconversion luminescence with the detection of the characteristic Er($4I_9/2$→$4I_{15/2}$) green emission at 18400 cm$^{-1}$ (Figure 5a). [11] The approximate quadratic dependence of the photoluminescence intensity on the incident laser power ($I \propto P^{1/2}$, Figure 5a) supports the nonlinear ETU mechanism (Figure 3b). However, the existence of a non-negligible amount of intermolecular Cr–Ln contact distances shorter than 15 Å in the crystalline state (Table S4) suggests that upconversion luminescence may benefit from both intra- and intermolecular processes, but that it may also be susceptible to concentration quenching. When comparing the metal concentrations within a single [CrErCr(L1)]$^{3+}$ ion, [Cr$^{III}$]$_{mol}$ = 2 $\text{Ln}^{III}$]$_{mol}$ = 2 $\text{Na}_2\text{V}_{10}\text{O}_{28}$ = 1.4 M $\text{Na}_2$ = 6.02 × 10$^{23}$ is Avogadro's number and V$_{10}\text{O}_{28}$ = 2376 Å$^3$ = 2376 × 10$^{-23}$ dm$^3$ is the molecular volume of the cation) with their average concentration in the crystal [Cr$^{III}$]$_{cryst}$ = 2 $\text{Na}_2\text{V}_{10}\text{O}_{28}$ = 2 $\text{V}_{10}\text{O}_{28}$ = 2 M $\text{V}_{10}\text{O}_{28}$ = 0.55 M ($\alpha_{cryst}$ = 1340 g dm$^{-3}$ is the calculated density in the crystal of [CrYbCr(L1)]$_{7+}$(CF$_3$SO$_3$)$_{9+}$, (C$_2$H$_5$)$_3$) and $\text{MM}$ = 4872 g mol$^{-1}$ is the molecular weight of the complex), it is
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Figure 5. Nonlinear green upconversion luminescence in [CrErCr(L1)](CF3SO3)3, obtained upon irradiation of the Cr(4f→2A2) transition at varying laser powers (P): a) in the solid state (4 K, \( \nu_{\text{exc}} = 13333 \text{ cm}^{-1} \)) and b) in acetonitrile solution (10 mm, \( \nu_{\text{exc}} = 13360 \text{ cm}^{-1} \), 30.6 K).

We can thus conclude that a molecular upconversion process is responsible for the Er(III)-centered green emission obtained upon NIR irradiation of the complex [CrErCr(L1)](CF3SO3)3. This result strongly contrasts with previous predictions based on the detailed analysis of nonradiative relaxation processes that operate in standard mononuclear Er(III) complexes, but is consistent with upconversion luminescence, also with an exact quadratic dependence (\( I \propto P^2 \)).

Keywords: helical structures – lanthanides – photochemistry – self-assembly – upconversion.


The synthesis and characterization of the ligand $L_1$ and of its complexes $[\text{CrLnCr}(L_1)_3](\text{CF}_3\text{SO}_3)_9$ (Ln = La, Eu, Gd, Tb, Lu) were reported in M. Cantuel, F. Gumy, J.-C. G. Bünzli, C. Piguet, Dalot Trans. 2006, 2647–2660, while that for Ln = Er can be found in the Supporting Information.

CCDC 806425 ($[\text{CrErCr}(L_1)_3]_2(\text{CF}_3\text{SO}_3)_{18} \cdot (\text{C}_3\text{H}_5\text{N})_{30}$) and 806426 ($[\text{CrYbCr}(L_1)_3]_2(\text{CF}_3\text{SO}_3)_{18} \cdot (\text{C}_3\text{H}_5\text{N})_{30}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Pertinent ORTEP figures and tabular materials are given in the Supporting Information.

We did not detect measurable upconverted emission below 195 mW mm$^{-2}$, and the sample was photobleached above 720 mW mm$^{-2}$.

For 1.0 dm$^3$ of $[\text{CrLnCr}(L_1)_3]^{3+}$ ions at concentration $C$, the extra volume amounts to $V_{\text{extra}} = 1.0 \times 10^{-27} \sum V_{\text{mol}} = 1.0 \times 10^{-22} - (C N_{\text{Av}} V_{\text{mol}})$ in Å$^3$. The statistical distribution of the extra volume around each cation leads to a total volume per cation of $V_{\text{tot}} = V_{\text{mol}} + (V_{\text{mol}}/C N_{\text{Av}})$ in Å$^3$. Assuming a compact cubic arrangement of these volume elements, we eventually compute $d = \sqrt[3]{V_{\text{tot}}}$ as the average distance that separates the barycenters of two adjacent $[\text{CrLnCr}(L_1)_3]^{3+}$ cations. Taking $V_{\text{mol}} = 2376$ Å$^3$, we calculate a pseudo-spherical radii of $R_{\text{sphere}} = \sqrt[3]{3V_{\text{mol}}/4\pi} = 8.2$ Å and average intermolecular contact distances of $d = 14.5$ Å in the crystal ($C = 0.55$ m) and $d = 55$ Å in the frozen acetonitrile solution ($C = 0.01$ m).
Giving the green light: The connection of two Cr$^{	ext{III}}$ sensitizers around a central Er$^{	ext{III}}$ acceptor in a self-assembled cation provides high local metal concentrations that favor efficient nonlinear energy transfer upconversion luminescence (see picture). Upon selective low-energy near-infrared irradiation of Cr$^{	ext{III}}$-centered transitions, 1 displays an unprecedented molecular two-photon upconverted green Er$^{	ext{III}}$-centered emission.