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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 1 a), 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 1 b).[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 (Ln^{III}) 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]

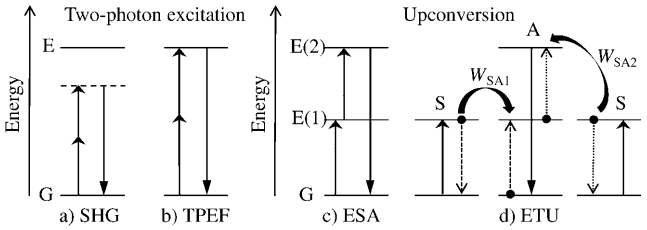

Figure 1. Energy schemes for selected nonlinear two-photon processes (G = ground state, E = excited state). a) Nonresonant second-harmonic generation (SHG), b) two-photon excitation fluorescence (TPEF), c) excited-state absorption (ESA), and d) sequential energy transfer upconversion (ETU, A = acceptor, S = sensitizer and $W_{SA} = S \rightarrow A$ energy transfer probability).[4]

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 1 c) or several (Figure 1 d) 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 1 c, d) can be considered as nonlinear because of the quadratic dependence of the efficiency (I) on the incident intensity of the excitation light ($I \propto P^2$).[4,6] Upconversion has been regularly reported for trivalent lanthanide cations doped into low-phonon inorganic matrices,[6] 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 $\hbar\omega_{eff} \approx 2000\ cm^{-1}$ 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 $Na_3[Ln(pyridine\text{-}2,6\text{-}dicarboxylate)_3]\cdot 13\,H_2O$ (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

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potentially overcome the purported theoretical limitation. Following Auzel's kinetic approach,[6b] the probabilities for the two-photon excitation processes $W_{G\to E(2)}$ shown in Figure 1c,d are given by Equations (1) and (2), respectively,

$$W^{ESA}_{G\to E(2)} = W_{G\to E(1)}\, W_{E\to E(2)} \quad (1)$$

$$W^{ETU}_{G\to E(2)} = \left(N^*_S W_{SA1}\right)\left(N^*_S W_{SA2}\right) = (N_S)^2 W_{SA1} W_{SA2} \left(W_{G\to E(1)}\right)^2 \quad (2)$$

where W_{SA} are the sensitizer→acceptor energy-transfer probabilities for each step and $N^*_S = N_S W_{G\to E(1)}$ is the concentration of the excited sensitizers that act as donors.

Assuming that $W_{G\to E(1)} \approx W_{E\to E(2)}$, 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_S around each acceptor and 2) efficient resonant S→A energy transfer processes that maximize W_{SA1} and W_{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→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 $Cr(^4T_2)$ 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 ^2E state of the Cr^{III} center to around 13400 cm^{-1}. These conditions are required for the fine-tuning of the target

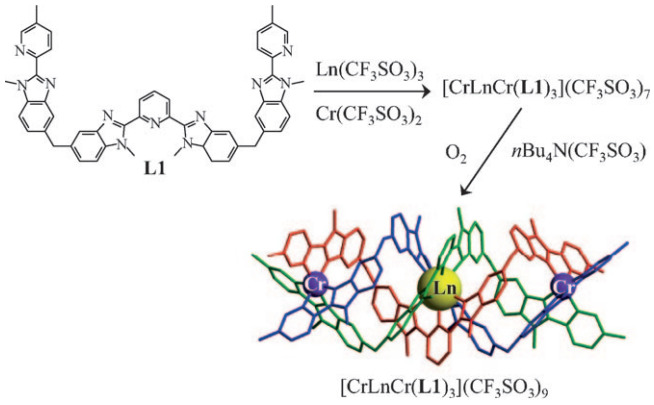

Figure 2. Synthesis of the kinetically inert dimetallic d–f–d complexes $[CrLnCr(\mathbf{L1})_3](CF_3SO_3)_9$. The molecular structure of the complex shown corresponds to one of the $[CrEuCr(\mathbf{L1})_3]^{9+}$ ions in the asymmetric unit of the crystal structure of $[CrEuCr(\mathbf{L1})_3]_2(CF_3SO_3)_{18}\cdot(C_3H_5N)_{30}$ (Cr1···Eu1 = 8.872(1) Å, Cr2···Eu1 = 8.811(1) Å).[13]

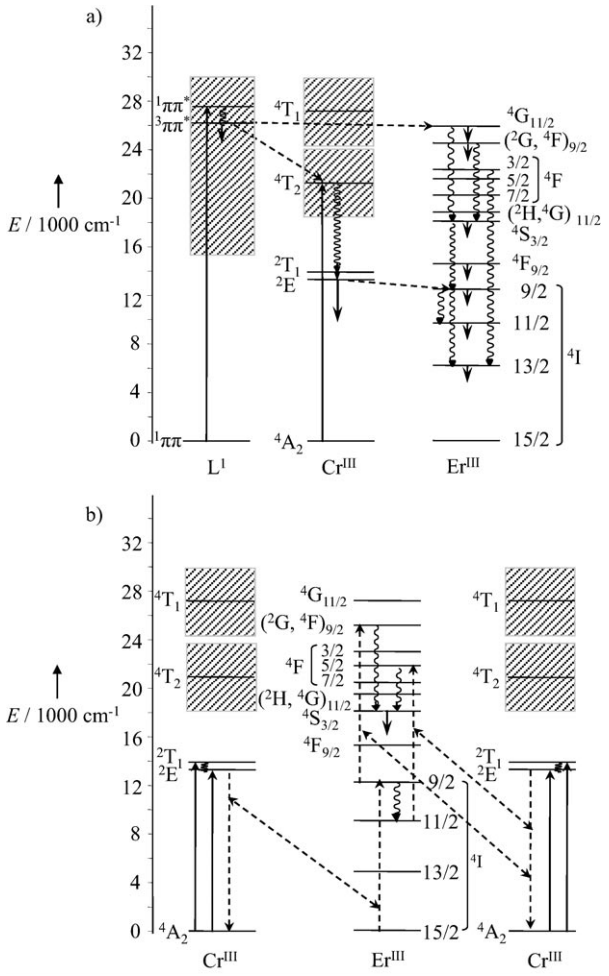

Figure 3. Jablonski diagrams for the different chromophores in $[CrErCr(\mathbf{L1})_3](CF_3SO_3)_9$ showing a) the linear downconversion luminescence (excitation = full upward arrows, internal conversion = curled down arrows, energy transfer = dotted arrows, emission = full downward arrows), and b) the nonlinear upconversion luminescence (excitation = full upward arrows, internal conversion = curled down arrows, ETU = dotted arrows, emission = full downward arrows).

intermetallic $Cr(^2E)\to Er(^4I_{9/2})$ energy transfer (Figure 3).[11] With these points in mind, we reacted the segmental ligand **L1** with stoichiometric amounts of $Ln(CF_3SO_3)_3\cdot x\,H_2O$ (Ln = Eu, Gd, Er, Yb) and $Cr(CF_3SO_3)_2\cdot H_2O$ in acetonitrile to give the self-assembled helical pseudo-cryptates $[CrLnCr(\mathbf{L1})_3]^{7+}$, which were subsequently oxidized into the kinetically inert triple-helical complexes $[CrLnCr(\mathbf{L1})_3]^{9+}$ (Figure 2).[12] Fine crystalline orange needles of $[CrLnCr(\mathbf{L1})_3]_2(CF_3SO_3)_{18}\cdot(C_3H_5N)_{30}$ ($P2_1/c$, Ln = 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.[13] All the Cr–N and Ln–N bond lengths are typical (Tables S2 and S3),[10] and the global pseudo-D_3 symmetrical triple-helical ion $[CrLnCr(\mathbf{L1})_3]^{9+}$ is made up of a pseudo-tricapped trigonal $\{LnN_9\}$ prism sandwiched between two pseudo-octahedral $\{CrN_6\}$ 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 S3), and we conclude that the three metals in $[CrLnCr(\mathbf{L1})_3]^{9+}$ are 1) aligned along a pseudo-threefold axis, 2) protected from the solvent by the wrapping of the three helical ligand strands (Table S4), and 3) regularly spaced with Cr···Eu = 8.8(1) Å and Cr···Yb = 8.9(1) Å. Based on the Jablonski diagram previously established for $[CrGdCr(\mathbf{L1})_3]^{9+}$ (termed CrGdCr; Figure 3a and Figures S4 and S5),[12] UV irradiation of the complexes $[CrErCr(\mathbf{L1})_3]^{9+}$ (CrErCr) efficiently populates ligand-centered ππ* excited states. Subsequent partial $\mathbf{L1}\rightarrow Cr^{III}$ and $\mathbf{L1}\rightarrow Er^{III}$ 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]

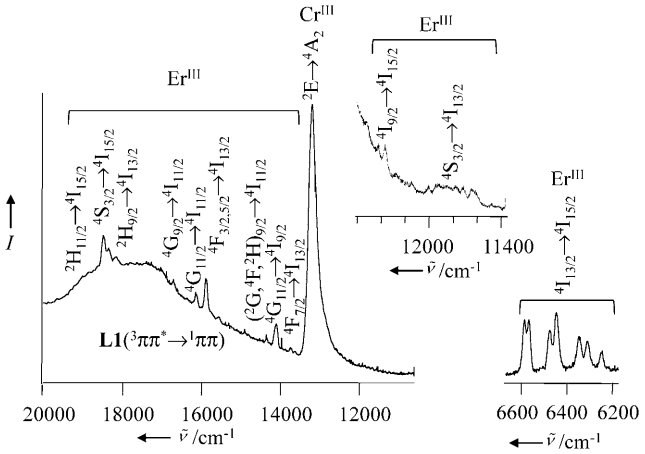

Figure 4. Emission spectrum of $[CrErCr(\mathbf{L1})_3](CF_3SO_3)_9$ (solid state, $\tilde{\nu}_{exc} = 28170\ cm^{-1}$, 3.5 K).

From the excitation spectrum of CrErCr recorded upon monitoring the $Cr(^2E\rightarrow{}^4A_2)$ emission band at 13380 cm^{-1} (in the red region; Figure S6a), we can easily locate the low-energy spin-allowed $Cr(^4T_2\leftarrow{}^4A_2)$ 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 $10Dq(Cr) \approx 20980\ cm^{-1}$ in CrErCr; this value is consistent with the value of 23240 cm^{-1} found for $[Cr(bpy)_3]^{3+}$ (bpy is the strong-field didentate 2,2′-bipyridine ligand).[15]

In agreement with our hypothesis, the coordination spheres around the Cr^{III} ions in the trinuclear complexes CrLnCr indeed discriminate the energies of the $Cr(^4T_2)$ and $Cr(^2E)$ 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 $Cr(^4T_2)$ is inefficient (Figure S6b). This situation is ideal for a quantitative analysis of the intermetallic energy transfer process. Upon selective irradiation of the $Cr(^4T_2\leftarrow{}^4A_2)$ transition in CrErCr at 22220 cm^{-1}, internal relaxation by intersystem crossing rapidly feeds the $Cr(^2E)$ excited states, which simultaneously luminesce in the red region ($Cr(^2E\rightarrow{}^4A_2)$, $\tilde{\nu}_{em} = 13380\ cm^{-1}$, full width at half height, fwhh = 420 cm^{-1}) and transfer energy to the Er^{III} ion ($Cr(^2E)\rightarrow Er(^4I_{9/2})$, Figure 3a). Basic rate equations written for the time evolution of the population of the $Cr(^2E)$ excited states in CrGdCr [Eq. (3), k_{rad} and k_{nr} are the intrinsic radiative and nonradiative relaxation rate constants] and in CrErCr [Eq. (4), $k_{EnT}^{Cr,Er}$ is the rate constant for Cr→Er energy transfer] allow the estimation of the rate [Eq. (5), $k_{EnT}^{Cr,Er} = 4.9(2)\times 10^2\ s^{-1}$) and efficiency [Eq. (6), $\eta_{EnT}^{Cr,Er} = 53(2)\%$) of the intramolecular $Cr(^2E)\rightarrow Er(^4I_{9/2})$ energy transfer by simply using the characteristic $Cr(^2E)$ lifetimes experimentally measured for CrGdCr ($\tau_{obs}^{Cr}(CrGdCr) = 2.27(1)$ ms at 10 K) and for CrErCr ($\tau_{obs}^{Cr}(CrErCr) = 1.07(5)$ ms at 10 K).[10]

$$k_{obs}^{Cr}(CrGdCr) = k_{rad}^{Cr} + k_{nr}^{Cr} = 1/\tau_{obs}^{Cr}(CrGdCr) \quad (3)$$

$$k_{obs}^{Cr}(CrErCr) = k_{rad}^{Cr} + k_{nr}^{Cr} + k_{EnT}^{Cr,Er} = 1/\tau_{obs}^{Cr}(CrErCr) \quad (4)$$

$$k_{EnT}^{Cr,Er} = k_{obs}^{Cr}(CrErCr) - k_{obs}^{Cr}(CrGdCr) = 1/\tau_{obs}^{Cr}(CrErCr) - 1/\tau_{obs}^{Cr}(CrGdCr) \quad (5)$$

$$\eta_{EnT}^{Cr,Er} = \frac{k_{EnT}^{Cr,Er}}{k_{rad}^{Cr} + k_{nr}^{Cr} + k_{EnT}^{Cr,Er}} = \frac{k_{obs}^{Cr}(CrErCr) - k_{obs}^{Cr}(CrGdCr)}{k_{obs}^{Cr}(CrErCr)} = 1 - \frac{\tau_{obs}^{Cr}(CrErCr)}{\tau_{obs}^{Cr}(CrGdCr)} \quad (6)$$

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 $Cr(^2E)$ 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 $Cr(^2T_1,{}^2E\leftarrow{}^4A_2)$ transitions with NIR light is conceivable (13200–13800 cm^{-1}, Figure S8). Consequently, irradiation at 13333 cm^{-1} with a tuneable Ti–sapphire laser with power in the range 195–690 mW mm^{-2} [16] indeed produces upconversion luminescence with the detection of the characteristic $Er(^4S_{3/2}\rightarrow{}^4I_{15/2})$ green emission at 18400 cm^{-1} (Figure 5a).[11] The approximate quadratic dependence of the photoluminescence intensity on the incident laser power ($I \propto P^{1.8(7)}$, 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 $[CrErCr(\mathbf{L1})_3]^{9+}$ ion, $|Cr^{III}|_{mol} = 2\,|Ln^{III}|_{mol} = 2/(N_{Av}V_{mol}^{CrLnCr}) = 1.4$ M ($N_{Av} = 6.02\times10^{23}$ is Avogadro's number and $V_{mol}^{CrLnCr} = 2376\ Å^3 = 2376\times10^{-27}\ dm^3$ is the molecular volume of the cation) with their average concentration in the crystal $|Cr^{III}|_{cryst} = 2\,|Ln^{III}|_{cryst} = 2\,d_{cryst}/MM^{CrLnCr} = 0.55$ M ($d_{cryst} = 1340\ g\,dm^{-3}$ is the calculated density in the crystal of $[CrYbCr(\mathbf{L1})_3]_2(CF_3SO_3)_{18}\cdot(C_3H_5N)_{30}$ and $MM^{CrLnCr} = 4872\ g\,mol^{-1}$ is the molecular weight of the complex), it is

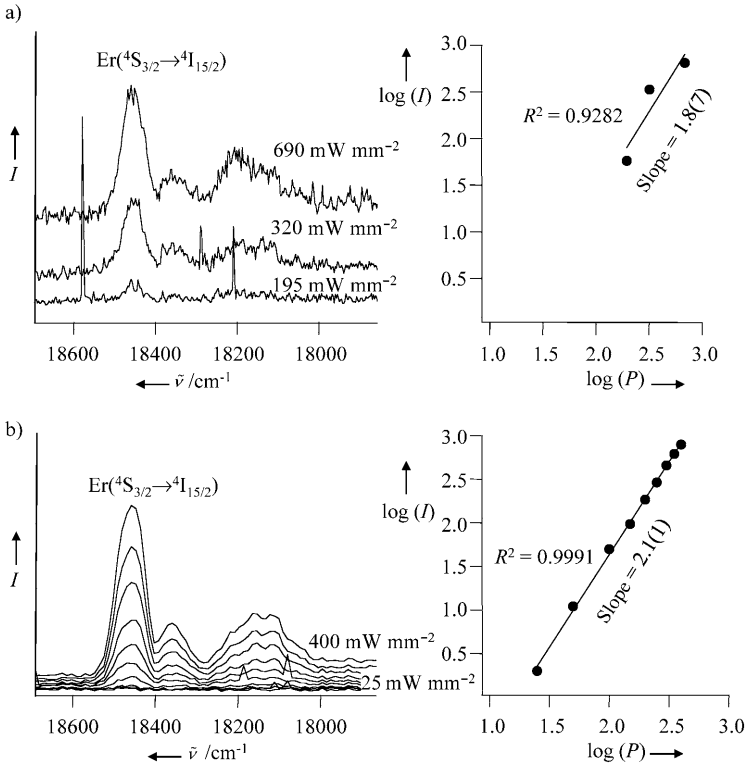

Figure 5. Nonlinear green upconversion luminescence in $[CrErCr(\mathbf{L1})_3](CF_3SO_3)_9$ obtained upon irradiation of the $Cr(^2E\leftarrow{}^4A_2)$ transition at varying laser powers (P): a) in the solid state (4 K, $\tilde{\nu}_{exc} = 13\,333\ cm^{-1}$) and b) in acetonitrile solution (10 mM; $\tilde{\nu}_{exc} = 13\,360\ cm^{-1}$, 30.6 K).

clear that the upconversion experiment should be repeated in a frozen 0.01 M solution of $[CrErCr(\mathbf{L1})_3]^{9+}$ in acetonitrile in order to eliminate intermolecular interactions.[17] Firstly, we recorded the ESI mass spectrum of $[CrErCr(\mathbf{L1})_3](CF_3SO_3)_9$ in acetonitrile, and unambiguously confirmed that the kinetically inert ions $[CrErCr(\mathbf{L1})_3]^{9+}$ remain intact in solution for concentrations larger than 10^{-4} M (Figure S9).[12] Secondly, the selective irradiation of the $Cr(^2E\leftarrow{}^4A_2)$ transition at $13\,360\ cm^{-1}$ in the frozen 10^{-2} M solution of $[CrErCr(\mathbf{L1})_3]^{9+}$ in acetonitrile using laser powers in the range 25–400 mW mm^{-2} successfully produced easily detectable green upconverted Er($^4S_{3/2}\rightarrow{}^4I_{15/2}$) emission at $18\,400\ cm^{-1}$, with an exact quadratic dependence ($I \propto P^{2.1(1)}$, Figure 5b). Alternative excitation of the $Cr(^2T_1\leftarrow{}^4A_2)$ transition at $13\,889\ cm^{-1}$ provides similar upconversion luminescence, also with an exact quadratic dependence ($I \propto P^{1.98(2)}$, Figure S10).

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 $[CrErCr(\mathbf{L1})_3]^{9+}$. This result strongly contrasts with previous predictions based on the detailed analysis of nonradiative relaxation processes that operate in standard mononuclear Er^{III} complexes,[9] but is consistent with upconversion luminescence reported for thin films of [Er(8-hydroxyquinolinate)$_3$] complexes[18] or for Er^{III}-doped yttrium organic frameworks.[19] To the best of our knowledge, $[CrErCr(\mathbf{L1})_3]^{9+}$ is the first reported isolated molecular system that displays NIR→visible upconversion. This rare phenomenon is induced by the specific molecular and electronic design, which favors a sequential energy transfer upconversion (ETU) mechanism.[20] The high local concentration of sensitizers combined with 1) the tuned 50% efficiency of the intramolecular Cr→Er energy transfer, 2) the strong ligand-field environments around the Cr^{III} ion, 3) the long residual lifetime of the sensitizer excited states, and 4) the protection of the Er^{III} ion from high-energy oscillators contribute to the detection of measurable molecular upconversion in a diluted medium. It is worth noting that a strict two-photon upconversion process operates when two Cr^{III} ions sandwich the Er^{III} ion in CrErCr. Since the Er^{III} ion possesses several closely spaced excited states that cover the infrared to ultraviolet range,[18] we tentatively infer that the connection of three strong-field Cr^{III} ions around this specific trivalent lanthanide may lead to unprecedented molecular three-photon upconversion luminescence.

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[13] CCDC 806425 ($[CrErCr(\mathbf{L1})_3]_2(CF_3SO_3)_{18}\cdot(C_3H_5N)_{30}$) and 806426 ($[CrYbCr(\mathbf{L1})_3]_2(CF_3SO_3)_{18}\cdot(C_3H_5N)_{30}$)) 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.

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

[17] For 1.0 dm^3 of $[CrLnCr(\mathbf{L1})_3]^{9+}$ ions at concentration C, the extra volume amounts to $V_{extra} = 1.0\times10^{27} - \sum V^i_{mol} = 1.0\times10^{27} - (C N_{Av} V_{mol})$ in $Å^3$. The statistical distribution of the extra volume around each cation leads to a total volume per cation of $V_{tot} = V_{mol} + (V_{extra}/C N_{Av})$ in $Å^3$. Assuming a compact cubic arrangement of these volume elements, we eventually compute $d = \sqrt[3]{V_{tot}}$ as the average distance that separates the barycenters of two adjacent $[CrLnCr(\mathbf{L1})_3]^{9+}$ cations. Taking $V_{mol} = 2376$ $Å^3$, we calculate a pseudo-spherical radii of $R_{sphere} = \sqrt[3]{3V_{mol}/4\pi} =$ 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).

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