

Extending Lifetimes of Lanthanide-Based Near-Infrared Emitters (Nd, Yb) in the Millisecond Range through Cr(III) Sensitization in Discrete Bimetallic Edifices

Daniel Imbert,[†] Martine Cantuel,[‡] Jean-Claude G. Bünzli,^{*,†} Gérald Bernardinelli,[§] and Claude Piguet^{*,‡}

Institute of Molecular and Biological Chemistry, Swiss Federal Institute of Technology, BCH 1402, 1015 Lausanne, Switzerland, and Department of Inorganic, Analytical, and Applied Chemistry and Laboratory of X-ray Crystallography, University of Geneva, 30 quai E. Ansermet, 1211 Geneva 4, Switzerland

Received September 22, 2003; E-mail: jean-claude.bunzli@epfl.ch; claude.piguet@chiam.unige.ch

Near-infrared (NIR) lanthanide-based emitters (1–1.6 μm) are attracting considerable interest as potential stains for immunoassays or for the imaging of biological cells using time-resolved luminescence¹ because biological tissues are fairly transparent in this spectral range. However, these ions have two intrinsic drawbacks: a low quantum yield due to the small energy gap between their excited- and ground-state levels, and short lifetimes (nanoseconds to microseconds) which limit the efficiency of time-resolved detection. In most published systems, excitation of the luminescent ion is achieved through chromophoric groups absorbing in the near UV or in the visible,² followed by efficient energy transfer onto the metal ion (antenna effect). As a consequence, the NIR luminescence lifetime is controlled by the intrinsic properties of the emitting Ln^{III} level. Recently, d-block metal ions Pt^{II} ,³ Ru^{II} ,⁴ and Cr^{III} ,⁵ inserted into discrete bimetallic d–f edifices, have been tested as alternative sensitizers for Nd^{III} , Er^{III} , or Yb^{III} . Extremely efficient $\text{M} \rightarrow \text{Ln}^{\text{III}}$ energy transfer processes take place, but the short lifetimes of the Ru- or Pt-centered feeding levels result in Ln^{III} -centered luminescence decays controlled by the lanthanide, in the nanosecond to microsecond range. On the other hand, slightly longer $\text{Yb}(\text{}^2\text{F}_{5/2})$ lifetimes have been reported by Kaizaki et al.⁵ for oxalate-bridged $\text{Cr}^{\text{III}}\text{--Yb}^{\text{III}}$ complexes ($\tau = 48 \mu\text{s}$).

Here, we present a strategy for extending the NIR emitter lifetime in the millisecond (ms) range by controlling the population of the Ln^{III} excited level through $\text{Cr}^{\text{III}} \rightarrow \text{Ln}^{\text{III}}$ energy transfers in bimetallic edifices where the intrinsic Cr^{III} lifetime is long. For instance, $[\text{Cr}(\alpha, \alpha'\text{-diimine})_3]^{3+}$ chromophores display Cr^{III} lifetimes in the range 1–5 ms,⁶ an adequate value for our purpose. We therefore build on our know-how of 3d–4f bimetallic functional edifices to insert $\text{Cr}^{\text{III}}\text{--Ln}^{\text{III}}$ pairs into triple-stranded helicates.^{7,8} The isolated complexes $[\text{LnCr}^{\text{III}}\text{L}_3](\text{CF}_3\text{SO}_3)_6(\text{CH}_3\text{CN})_4$ ($\text{Ln} = \text{Nd}$, **1**; Yb , **2**)⁹ are isostructural with the previously reported helicates with $\text{Ln} = \text{La}$, Eu , Gd , Tb , and Lu (monoclinic, $P2_1/n$, $Z = 4$, Figure 1).⁸ In these compounds, the ligand strands form rather rigid coordination environments, in which the two metal ions lie ca. 9.3 Å apart, a suitable distance for efficient dipole–dipole energy transfer processes (a 70% yield is reported for the $\text{Eu}^{\text{III}} \rightarrow \text{Cr}^{\text{III}}$ transfer).⁸

Both CrNd (**1**) and CrYb (**2**) complexes display two main absorption bands around 40 490 and 29 940 cm^{-1} , assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions, with shoulders on the low energy side characteristic of spin-allowed Cr^{III} -centered ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2, {}^4\text{T}_1$ transitions mixed with charge transfer transitions.⁸ As for the compounds reported by Kaizaki et al.,⁵ the two helicates display simultaneous emission from Cr^{III} and Ln^{III} . The chromium emission

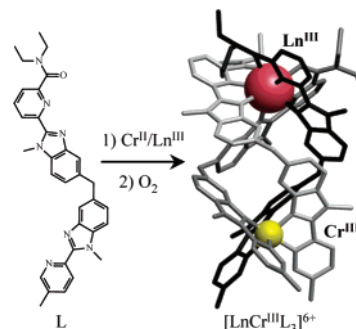


Figure 1. Self-assembly of the triple-stranded helicates $[\text{LnCr}^{\text{III}}\text{L}_3]^{6+}$ (the crystal structure of $[\text{YbCr}^{\text{III}}\text{L}_3]^{6+}$ is shown).

appears as a strong band centered at 13 320 cm^{-1} , with Stokes phonon sidebands on the low energy side, and originating from the $\text{Cr}(\text{}^2\text{E})$ level, whatever the excitation mode is, in the ligand or in the Cr^{III} levels. At room temperature, the $\text{Cr}(\text{}^2\text{E})$ luminescence becomes less intense, with additional appearance of anti-Stokes sidebands at higher energy.

The Yb^{III} emission in the 0.98–1.03 μm range displays four peaks, assigned to the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition. The crystal field splitting of the ${}^2\text{F}_{7/2}$ level can be interpreted as arising from metal ions in a trigonal site, reflecting the approximate D_3 symmetry of the helicates.¹⁰ The Nd^{III} luminescence translates into three bands in the NIR region (0.87–0.92, 1.06–1.09, 1.32–1.39 μm) having five, five, and seven main components, respectively, assigned to transitions from the ${}^4\text{F}_{3/2}$ level to the ${}^4\text{I}_{9/2}$, ${}^4\text{I}_{11/2}$, and ${}^4\text{I}_{13/2}$ sublevels; again, the crystal field splitting of the ground-state sublevels reflects a trigonal symmetry around the Nd^{III} ion. Direct radiative transfer from Cr^{III} to Nd^{III} in CrNd is proved by the observation of several dips in the $\text{Cr}(\text{}^2\text{E})$ emission spectrum which perfectly match the $\text{Nd}({}^4\text{F}_{7/2}, {}^4\text{S}_{3/2}) \leftarrow {}^4\text{I}_{9/2}$ absorption spectrum. Insight into the intermetallic energy transfer processes occurring in these CrLn helicates can be gained by measuring the lifetimes of the Cr^{III} - and Ln^{III} -centered luminescence displayed by solid-state samples at 10 and 295 K.

In CrGd , for which the Gd-centered excited levels are not accessible for energy transfer from Cr^{III} , the lifetime of the $\text{Cr}(\text{}^2\text{E})$ emission is long and decreases from 3.66(3) ms at 10 K to 0.29(3) ms at room temperature,⁸ indicating the existence of thermally activated nonradiative vibrational quenching processes. In the presence of $\text{Ln} = \text{Nd}$, Yb as acceptors, intramolecular $\text{Cr}^{\text{III}} \rightarrow \text{Ln}^{\text{III}}$ energy transfers occur and the $\text{Cr}(\text{}^2\text{E})$ luminescence lifetime becomes substantially shorter, reaching 0.48(1) and 2.02(1) ms (10 K), or 0.11(2) and 0.23(1) ms (295 K) for CrNd and CrYb , respectively.¹¹ The postulated $\text{Cr}^{\text{III}} \rightarrow \text{Ln}^{\text{III}}$ intramolecular energy transfer processes are eventually demonstrated by the long Ln -

[†] Swiss Federal Institute of Technology.

[‡] Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva.

[§] Laboratory of X-ray Crystallography, University of Geneva.

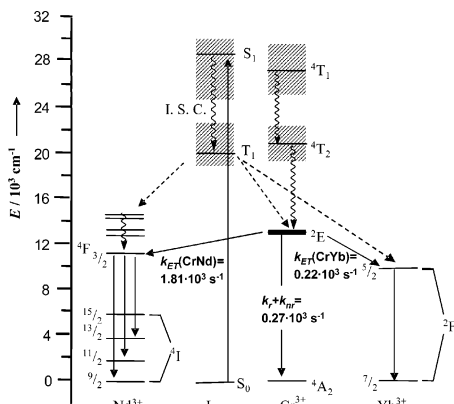


Figure 2. Partial energy level diagram (i) showing ground and excited levels centered on the metal ions and ligand and (ii) summarizing the excitation processes, energy transfer, and radiative processes occurring in $[\text{LnCrL}_3]^{6+}$ ($\text{Ln} = \text{Nd}, \text{Yb}$).

centered luminescence decays in the CrLn complexes which exactly match those measured for the $\text{Cr}(^2\text{E})$ donor level: 0.46(1) ms (Nd , $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{I}_{11/2}$ transitions) and 2.05(3) ms (Yb) at 10 K; 0.11(2) ms (Nd) and 0.24(2) ms (Yb) at room temperature.¹² In other words, the population of the $\text{Nd}(^4\text{F}_{3/2})$ and $\text{Yb}(^2\text{F}_{5/2})$ accepting levels is controlled by the de-excitation of the long-lived $\text{Cr}(^2\text{E})$ level, resulting in a Ln^{III} NIR emission with lifetimes in the millisecond range.

In view of the long intermetallic $\text{Cr}-\text{Ln}$ distance and of the presence of the methylene bridges which block potential electronic transfer between them, we assume a dipole–dipole mechanism for the $\text{Cr}^{\text{III}} \rightarrow \text{Ln}^{\text{III}}$ intermetallic transfer. The yield is given by

$$\eta = 1 - (\tau/\tau_0) = [1 + (R/R_0)^6]^{-1} \quad (1)$$

where τ and τ_0 are the $\text{Cr}(^2\text{E})$ lifetimes in the presence (CrYb , CrNd) and in the absence (CrGd) of Ln^{III} acceptor, respectively, R is the donor–acceptor distance ($R = 9.282(1) \text{ \AA}$ in $[\text{NdCrL}_3]^{6+}$ and $R = 9.334(1) \text{ \AA}$ in $[\text{YbCrL}_3]^{6+}$), and R_0 is the distance for 50% transfer. From the data reported above, we calculate $\eta_{\text{CrNd}} = 87(1)\%$, $R_0^{\text{CrNd}} = 12.7 \text{ \AA}$, $\eta_{\text{CrYb}} = 45(1)\%$, and $R_0^{\text{CrYb}} = 9.0 \text{ \AA}$ at 10 K. The better yield for CrNd may be explained by a favorable overlap integral between the $\text{Cr}(^2\text{E})$ emission spectrum and the $\text{Nd}(^4\text{F}_{3/2})$ absorption spectrum; this is exemplified by an energy gap $\Delta E(\text{Cr}(^2\text{E}) - \text{Nd}(^4\text{F}_{3/2})) = 1850 \text{ cm}^{-1}$ smaller than $\Delta E(\text{Cr}(^2\text{E}) - \text{Yb}(^2\text{F}_{5/2})) = 3050 \text{ cm}^{-1}$ in CrYb . The rate constant k_{ET} (2) associated with the energy transfer process may be estimated from $\tau = (k_r + k_{nr} + k_{ET})^{-1}$ and $\tau_0 = (k_r + k_{nr})^{-1}$ (k_r and k_{nr} are the radiative and nonradiative deactivation rates).

$$k_{ET} = \tau^{-1} - \tau_0^{-1} \quad (2)$$

In the absence of acceptor (CrGd) at 10 K, the $\text{Cr}(^2\text{E})$ de-excitation rate $\tau_0^{-1} = 0.27 \times 10^3 \text{ s}^{-1}$ is smaller than the transfer rate $k_{ET}(\text{CrNd}) = 1.81 \times 10^3 \text{ s}^{-1}$, but similar to the transfer rate to Yb^{III} : $k_{ET}(\text{CrYb}) = 0.22 \times 10^3 \text{ s}^{-1}$, reflecting a less efficient transfer in the latter helicate. It is worth noting that the comparable magnitude of the energy transfer rate constants $k_{ET}(\text{CrLn})$ with the decay rate constant (τ_0^{-1}) of the feeding $\text{Cr}(^2\text{E})$ level is the first required condition for extending the Nd - and Yb -centered NIR lifetimes in the millisecond range (Figure 2). The second condition implies that $k_{ET}(\text{CrLn}) \ll k_{\text{lum}}(\text{Ln})$ ¹² and is indeed fulfilled because the decays of the Ln -centered luminescence in the related $[\text{LnZnL}_3]^{5+}$ helicates retain their classical values in the microsecond range ($<2 \mu\text{s}$ for Nd corresponding to $k_{\text{lum}}(\text{Nd}) > 5 \times 10^5 \text{ s}^{-1}$, and $20 \mu\text{s}$ for Yb corresponding to $k_{\text{lum}}(\text{Yb}) = 5 \times 10^4 \text{ s}^{-1}$).

At room temperature, both Cr^{III} - and Ln^{III} -centered luminescence is less intense due to temperature-dependent vibrational and electronic de-excitation modes, but similarly to the low-temperature situation, the Ln^{III} emitters have still lifetimes in the millisecond range and the yields of the $\text{Cr}^{\text{III}} \rightarrow \text{Ln}^{\text{III}}$ energy transfer remain sizable: 62(11)% for Nd and 21(11)% for Yb in the solid state. In acetonitrile solution, the absolute quantum yields of the emission of the $\text{Cr}(^2\text{E})$ level in $[\text{LnCrL}_3]^{6+}$ are modest ($\Phi_{\text{Cr}} = 7.4 \times 10^{-3}$, 1.8×10^{-3} , and 6.1×10^{-3} % for $\text{Ln} = \text{Gd}, \text{Nd}$, and Yb , respectively). However, if we consider that the intramolecular $\text{Cr}^{\text{III}} \rightarrow \text{Ln}^{\text{III}}$ transfer is the only additional nonradiative process affecting deactivation of the $\text{Cr}(^2\text{E})$ level when Nd^{III} or Yb^{III} replaces Gd^{III} , its efficiency is given by

$$\eta = 1 - (\Phi_{\text{CrNd,Yb}}/\Phi_{\text{CrGd}}) \quad (3)$$

and we calculate $\eta_{\text{CrNd}} = 0.8(1)$ and $\eta_{\text{CrYb}} = 0.2(1)$, in excellent agreement with the values found in the solid state, given the experimental uncertainties. This result is evidence for sizable $\text{Cr}-\text{Ln}$ intramolecular energy transfers taking place both in the solid state and in solution, at low and room temperatures.

In conclusion, we have shown that the $\text{Cr}(^2\text{E})$ level is a good feeding level for sensitizing Nd^{III} and Yb^{III} NIR luminescence in discrete bimetallic helicates. In addition, the resulting Ln^{III} emission lifetimes are controlled by the de-excitation rate of the $\text{Cr}(^2\text{E})$ level, which extends their values in the millisecond range at 10 K, and $>100 \mu\text{s}$ at 295 K. This opens startling perspectives for the use of discrete CrLn pairs in *in vitro* biomedical analyses and imaging where time-resolved spectroscopy is needed to discriminate the background luminescence and to reach a high signal-to-noise ratio. In particular, Nd^{III} is a fascinating partner in CrNd systems with long-lived emission in three NIR spectral ranges.

Acknowledgment. This research is supported through grants from the Swiss National Science Foundation. We thank Mr. Frédéric Gummy for his technical help.

Supporting Information Available: Experimental details (PDF) and crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Werts, M. H. V.; Woudenberg, R. H.; Emmerink, P. G.; van Gassel, R.; Hofstraat, J. W.; Verhoeven, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4542 and references therein.
- (a) Shavaleev, N. M.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Dalton Trans.* **2003**, 808. (b) Hebbink, G. A.; Grave, L.; Woltering, L. A.; Reinhoudt, D. N.; van Veggel, F. C. J. M. *J. Phys. Chem. A* **2003**, *107*, 2483.
- Shavaleev, N. M.; Moorcraft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Chem. Commun.* **2003**, 1134.
- Klink, S. I.; Keizer, H.; van Veggel, F. C. J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4319.
- Subhan, M. A.; Nakata, H.; Suzuki, T.; Choi, J.-H.; Kaizaki, S. *J. Lumin.* **2003**, *101*, 307.
- Langford, V. S.; von Arx, M. E.; Hauser, A. *J. Phys. Chem. A* **1999**, *103*, 7161.
- Bünzli, J.-C. G.; Piguët, C. *Chem. Rev.* **2002**, *102*, 1897.
- Cantuel, M.; Bernardinelli, G.; Imbert, D.; Bünzli, J.-C. G.; Hopfgartner, G.; Piguët, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1929.
- CCDC-220050 and CCDC-220051 contain the supplementary crystallographic data in cif format for $[\text{LnCrL}_3](\text{CF}_3\text{SO}_3)_2(\text{CH}_3\text{CN})_4$ ($\text{Ln} = \text{Nd}$, **1**; Yb , **2**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- Goncalves e Silva, F. R.; Malta, O. L.; Reinhard, C.; Güdel, H.-U.; Piguët, C.; Moser, J. E.; Bünzli, J.-C. G. *J. Phys. Chem. A* **2002**, *106*, 1670.
- These lifetimes do not depend on the excitation mode via the ligand ($\tilde{\nu}_{\text{exc}} = 28\,169 \text{ cm}^{-1}$) or via the Cr^{III} levels ($\tilde{\nu}_{\text{exc}} = 20\,492 \text{ cm}^{-1}$).
- There is no residual Cr^{III} emission at the wavelength used for Nd and Yb lifetime determination, as ascertained by blank measurements on the CrEu compound.
- Beeby, A.; Faulkner, S.; Williams, J. A. G. *J. Chem. Soc., Dalton Trans.* **2002**, 1918.

JA0386501