Visible and Near-Infrared Luminescence of Lanthanide-Containing Dimetallic Triple-Stranded Helicates: Energy Transfer Mechanisms in the SmIII and YbIII Molecular Edifices

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The photophysical properties of the triple-stranded dimetallic helicates [{Ln₂(LC−2H)₂}·H₂O (Ln = Nd, Sm, Dy, Yb) are determined in water and D₂O solutions, and energy transfer processes are modeled for SmIII. The luminescence of NdIII, SmIII, and YbIII is sensitized by (LC−2H)₂, but the energy transfer from the ligand to the LnIII ions is not complete, resulting in residual ligand emission. The luminescence of the NdIII helicate is very weak due to nonradiative de-excitation processes. On the other hand, the YbIII and SmIII helicates exhibit fair quantum yields, 1.8% and 1.1% in deuterated water, respectively. The energy transfer rates between (LC−2H)₂ and SmIII levels are calculated by direct and exchange Coulomb interaction models. This theoretical modeling coupled to numerical solutions of the rate equations leads to an estimate of the emission quantum yields in H₂O and D₂O, which compares favorably with experimental data. The main component of the ligand-to-metal energy transfer (97.5%) goes through a 3πτπ → 3G5/2(11) path, and the operative mechanism is of the exchange type. For the YbIII helicate, minor effects of oxygen on the sensitization of YbIII and nanosecond time-resolved spectroscopy point to the energy transfer mechanism being consistent with a recently proposed pathway involving fast electron transfer and YbIII. No up-conversion process could be identified. Ligand-field splitting of the 2F5/2 (3E 1/2 + 4G5/2), and 2F7/2 (2E 1/2 + 4G3/2) levels of YbIII is consistent with D₃ symmetry.

I. Introduction

Luminescent lanthanide-containing compounds present unique spectroscopic properties, such as long luminescent lifetimes and line-like emission of the metal ions. These features are presently used in the design of structural1 and analytical2 luminescent probes, labels for proteins and nucleic acids,3 and of light-emitting sensors for hetero-4 and homogeneous5 fluoroimmunoassays. The development of Ln-containing responsive systems for biomedical analyses has long focused on EuIII and TbIII probes, as is the work aimed at engineering organic electro-luminescent devices for light emitting diodes.6 However, the need for multiple fluoroimmunoassays is now prompting the use of the luminescence of other LnIII ions, for instance, SmIII and DyIII,7 while probing chiro-optical effects is leading to pioneer work with LnIII ions emitting in the NIR, e.g., YbIII.8,9 The latter interest is further amplified by the development of organic lanthanide complexes for polymer-based optical amplifiers operating at 1.3 and 1.5 μm.10

We have recently synthesized a series of lanthanide dimetallic helicates [{Ln₂(LC−2H)₂}·H₂O obtained by self-assembly process in water from ligand LC and lanthanide salts, where LC=bis{1-ethyl-2-[(6’-carboxy)pyridin-2’-yl]benzimidazol-5-yl}-methane (see Chart 1).11 These molecular edifices represent a new class of highly stable carboxylates soluble in water, which is a mandatory characteristic for bioanalytical applications. In these triple-stranded helicates, the metal ion is well protected from solvent interaction and despite its lack of an efficient chromophoric substituent, (LC−2H)₂ sensitizes the EuIII luminescence reasonably well.11

Since these helicates are stable and water-insensitive, we now examine the ability of (LC−2H)₂ to sensitize other LnIII ions (Ln = Nd, Sm, Dy, and Yb) in aqueous solutions and in the pH range 7−12. The design of lanthanide-containing luminescent probes is not an easy task in view of the numerous energy transfer processes involved and of the many constraints on both the chemical and photophysical properties of the receptor.12 Therefore, efficient modeling of these processes would bring a

CHART 1

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better understanding of the crucial features needed and facilitate
the choice of a convenient synthetic strategy. Such modeling
has been proposed for Eu\textsuperscript{III} complexes,\textsuperscript{11} and we have recently
used this procedure to understand the luminescence quenching
in a triple helical monometallic Eu\textsuperscript{III} complex with a ligand
derived from bis(benzimidazole)pyridine (L).\textsuperscript{14} We now extend
this modus operandi to Sm\textsuperscript{III} and present, for the first time,
calculations of energy transfer rates and emission quantum yields
for this ion. The mechanism of Yb\textsuperscript{III} sensitization is also
discussed on the basis of time-resolved spectroscopy.

II. Experimental Part and Methods

Syntheses. Ligand L\textsubscript{C} was synthesized as previously
described.\textsuperscript{11} Solutions of the helicates were prepared as follows.
A solution of L\textsubscript{C} (6 mg, 0.010 mmol) in 4 mL of freshly bi-
distilled water or D\textsubscript{2}O (99.99\%, from ARMAR) was stirred at
295 K for 30 min; NaOH (from Merck) or NaOD (40\% in D\textsubscript{2}O,
Fluka) was added dropwise, and the mixture was stirred at 295
K for 30 min. A solution of 0.007 mmol of Ln(ClO\textsubscript{4})\textsubscript{3}•nH\textsubscript{2}O
(Ln = Sm, Yb, Dy, and Nd; n = 8.8, 6.34, 7, and 4.98,
respectively) in 2 mL of water or D\textsubscript{2}O was added dropwise,
and the mixture was stirred for 2 h at 295 K. The solvents used
to prepare these solutions were thoroughly degassed. The
 perchlorate salts Ln(ClO\textsubscript{4})\textsubscript{3}•nH\textsubscript{2}O were prepared from corre-
spending oxides (Rhône-Poulenc, 99.99\%) in the usual way.\textsuperscript{15}
(Caution! Perchlorate salts combined with organic ligands are
potentially explosive and should be handled in small quantities
and with adequate precautions.)\textsuperscript{16} The pH and pD of the
solutions were adjusted with NaOH and NaOD, respectively,
and were measured with a Metrohm 6.3013.210 glass electrode.
The final pH was corrected for a deuterium isotope effect by
using the equation pD = pH + 0.4.\textsuperscript{17}

Physicochemical Measurements. UV/vis spectra were re-
corded at 22 °C on a Perkin-Elmer Lambda 900 spectrometer
with the help of quartz cells of 1 and 0.1 cm path length.
Excitation and emission spectra of the ligand and of its Sm\textsuperscript{III}
complex were recorded on a Perkin-Elmer LS-50B spectrometer
equipped for both room- and low-temperature measurements.
The luminescence spectra of the Nd\textsuperscript{III} and Yb\textsuperscript{III} helicates were recorded with a Fluorolog-3 (TRIAXSERIES 320) spectrometer
from Spex Industries. Luminescence and excitation spectra are
corrected for the instrumental function. Lifetimes are averages
of at least five independent determinations.

Continuous-wave luminescence and excitation measurements for the Yb\textsuperscript{III} helicate were performed by using a Ti:sapphire laser (Spectra Physics 3900S), pumped by an argon-ion laser (Spectra Physics 2060-10 SA) in all-lines mode. Wavelength control was achieved by an inchworm-driven (Burleigh PZ-501)
birefringent filter, and the wavelength was monitored with a Burleigh WA2100 wavemeter. The sample luminescence was
dispersed by a 0.85 m double monochromator (Spectra Physics 1402) using
500 nm blazed 1200 grooves/mm gratings and detected by a cooled photomultiplier (Hamamatsu R928), only three dynodes of which were employed. Light scattered by the sample and the cell walls was blocked before the
monochromator by a 400 nm cutoff filter. A 1 GHz band-
pass digital signal analyzer (Tektronix DSA 602A) was employed to
record the time course of the laser-induced emission.

The quantum yields were calculated using the following equation:

\[ Q = \frac{\langle \alpha \rangle}{Q_{r}} = \frac{[A_{r}(<\lambda_{r})][I(\lambda_{r})/I(\lambda_{0})][n_{2}^{2} \ln n_{2}^{2}][D_{r}/D_{0}]}{[\langle \alpha \rangle]} \]

in which subscript r stands for the reference and x for the samples; A is the absorbance at the excitation wavelength, \( I \) is the intensity of the excitation light at the same wavelength, \( n \) is the refractive index (\( n = 1.328 \), in D\textsubscript{2}O, and \( n = 1.333 \), in H\textsubscript{2}O), and \( D \) is the measured integrated luminescence intensity.

Emission band areas were corrected, when needed, for the Raman and Rayleigh diffusion bands, by subtracting the spectrum of the solvent alone. Concentrations and excitation wavelengths of the reference and sample were chosen to generate an absorbance \( < 0.05 \), for which a linear relationship between the intensity of the emitted light and the concentration of the absorbing species is found.\textsuperscript{18} Degassed solvents were used to avoid a possible quenching of the ligand triplet state by oxygen. The standards used to determine the quantum yield of the Sm\textsuperscript{III} helicate were quinine sulfate in 0.5 M H\textsubscript{2}SO\textsubscript{4} (\( n = 1.338, Q_{abs} = 0.546 \)), cresyl violet 1.4 × 10\textsuperscript{5} M in MeOH (\( n = 1.329, Q_{abs} = 0.542 \)), and [Ru(bipy)]\textsubscript{2}+ 6 × 10\textsuperscript{5} M in water (\( n = 1.333, Q_{abs} = 0.042 \)), where bipy stands for 2,2'-
bipyridine. These standards possess an absorbance in the UV region similar to that of the Sm\textsuperscript{III} helicate, and the last two ones exhibit emission in the same wavelength range than Sm\textsuperscript{III},
Ligand-centered luminescence was measured relative to quinine sulfate in 0.5 M H\textsubscript{2}SO\textsubscript{4}. The [Yb(TTA)]\textsubscript{3} complex, TTA =
thenyltrifluoroacetone, was used as reference to determine the quantum yield of the metal-centered luminescence in [Yb-
\( (\text{L}^2-2\text{H})_3 \)].

The \( Q_{abs} \) was taken as 0.35\%.\textsuperscript{23}

Theoretical Models Used.\textsuperscript{13,24} As previously shown, the various contributions to the ligand-to-rare earth ion energy transfer rates \( W_{ET} \) may be described by the following expressions

\[ W_{ET} = \frac{2\pi}{\hbar} \frac{e^2 S_{L}}{(2J+1)G} \sum_{\alpha'J'} \gamma_{L}^{\alpha} |U(\alpha')|^{2} |\alpha J_{x}^{2} \rangle \]  

(1a)

describes the contribution of the dipole-2\textsuperscript{nd} pole mechanism (\( \lambda = 2, 4, \) and 6), with

\[ \gamma_{L} = (\lambda + 1) \left( \frac{Q}{R_{L}^{2}+2} \right)^{2} (3 |C(\lambda)|^{2} |1 - \sigma_{x}^{2}|^{2} \]  

(1b)

Nd:YAG laser (Continuum Powerlite 7030, 30 Hz repetition rate, wavelength 355 nm, pulse width at half-height 7 ns). The pulse energy was typically restricted to less than 5 mJ to prevent rapid degradation of the sample. The emission from the solution was collected at right angle to the excitation beam by a 2” plano-
convex lens, passed through various optical elements, a 1/6 m grating monochromator (Oriel model 77250) and was finally detected by a fast red-sensitive photomultiplier tube (Hamamatsu R928), only three dynodes of which were employed. Light scattered by the sample and the cell walls was blocked before the
monochromator by a 400 nm cutoff filter. A 1 GHz band-
pass digital signal analyzer (Tektronix DSA 602A) was employed to
record the time course of the laser-induced emission.

Satisfactory signal-to-noise ratios were typically obtained by
averaging over several hundreds laser shots.
where $\langle r^3 \rangle$ is the radial expectation value of $r^3$ for 4f electrons, $C^L$ is a Racah tensor operator, and

$$ F = \frac{1}{\hbar \Delta \mathcal{A}_L} \sqrt{\ln (2\pi)} \exp \left[ -\left( \frac{\Delta E}{\hbar \Delta \mathcal{A}_L} \right)^2 \ln 2 \right] \tag{1c} $$

where $\Delta E$ is the energy difference between the ligand donor level and the lanthanide ion acceptor level and $\Delta \mathcal{A}_L$ is the bandwidth at half-height of the ligand state.

$$ W_{\text{DP}}^\lambda = \frac{2\pi}{\hbar} \frac{e^2 S_L}{(2J + 1) G R_L^\lambda} \sum_k \Omega_{k}^\lambda \langle \alpha J' \parallel \langle U^\lambda \rangle \parallel \alpha J \rangle^2 \tag{2} $$

corresponds to the dipole–dipole mechanism ($\lambda = 2, 4$, and 6), and

$$ W_{\text{EX}}^\lambda = \frac{8\pi}{3\hbar} \frac{e^2 (1 - \alpha_0)^2}{(2J + 1) R_L^\lambda} \sum_k \langle \phi \rangle \sum_{i,k} \mu_{ik}(k) \phi_{ij}^2 \tag{3} $$

generates the exchange mechanism. In the above equations, $J$ is the total angular momentum quantum number of the rare-earth ion and $\alpha$ specifies a 4f spectroscopic term. $G$ is the degeneracy of the ligand initial state, and $S_L$ is the electric dipole strength associated with the transition $\alpha \rightarrow \phi$ in the ligand. The quantities $\langle \parallel \parallel \rangle$ are reduced matrix elements of the unit tensor operators $U^\lambda$; $R_L^\lambda$ is the distance from the rare-earth ion nucleus to the region of the ligand molecule in which the ligand donor (or acceptor) state is localized. In eq 3, $S$ is the total spin operator of the rare-earth ion, $\mu_{ik}$ is the component of the electric dipole operator, $\phi_{ij}$ is the spherical component of the spin operator for the ligand electrons, and $\alpha_0$ is a distance-dependent screening factor.

The matrix elements $\langle \phi \rangle \sum_{i,k} \mu_{ik}(k) \phi_{ij}$ were calculated from the molecular orbital wave functions given by the Sparkle model, which optimizes the coordination geometry and electronic structure of the organic part of the complex. The quantities $\gamma_{ij}$ and $F$ were previously described. The selection rules that can be derived from the above equations are the following: $J + J' \geq \lambda \geq |J - J'|$ for the mechanisms expressed by eqs 1 and 2, and $\Delta J = 0, \pm 1$ for the exchange mechanism; in both cases, transitions with $J = J' = 0$ are excluded. The selection rules for the ligand levels involved can be derived from the electric dipole strength $S_L$ and the matrix element of the coupled operators $\mu_{ij}$ and $\phi_{ij}$ in eq 3.

The normalized populations of the electronic levels, $\eta_i$, are described by

$$ \frac{d\eta_i}{dt} = -\sum_{j \neq i}^N k_{ij} \eta_j + \sum_{j \neq i}^N k_{ji} \eta_i \tag{4} $$

where the indices $i$ and $j$ indicate the energy levels involved in the energy transfer process. The $k_{ij}$ or $k_{ji}$ symbols correspond to the decay rate constants between $i$ and $j$ or $j$ and $i$, respectively, and $N$ is the total number of levels involved. In the steady-state regime, all $d\eta_i/dt$ are equal to zero, and the set of algebraic equations can be solved analytically in terms of the transition and transfer rates. In the present case, the rate equations were solved numerically by using fourth-order Runge–Kutta method with an adaptive integration step. This set of coupled differential equations belongs to the initial value category, where the populations ($\eta_i$) at $t = 0$ are set equal to 1 for the ground state population and to zero for the other states. The total time of propagation was around 0.01 s, and the initial step size was equal to the inverse of the largest transfer rate constant (approximately $10^{-3}$ s). The numerical solutions of the rate equations yield the time dependence of the energy level populations, which reach the steady-state regime after $10^{-6}$ to $10^{-5}$ s.

### Modeling Energy Transfer Processes in the SmIII Helicate

We have applied the above theory for the first time to analyze the energy transfer processes in a SmIII compound. The required parameters are listed in Table 1.

The criteria used to determine which of the SmIII excited levels could be potentially involved in the ligand-to-metal transfer processes were the following:

1. The energy differences $\Delta E(1,2,3,4)$, and $\Delta E(5,7,8)$ have been set to $\Delta E \leq \Delta \mathcal{A}_L/2$, to allow for a sufficient spectral overlap integral (Förster’s theory); $\Delta \mathcal{A}_L$ is around 2200 and 2100 cm$^{-1}$ for the emission bands corresponding to $1^2\pi^*$ and $3^2\pi^*$ states, respectively. According to this criterion, SmIII levels with energy in the ranges 28100–32500 and 16500–20700 cm$^{-1}$ only show appropriate resonance conditions and were taken into consideration.

2. In the case of SmIII, the selection rules derived for multipolar ($\Delta J = 2, 4, 6$) and exchange ($\Delta J = 0, \pm 1$) mechanisms further restrict the number of levels to 6 and 8, respectively.

3. For multipolar mechanisms, only four levels have significant matrix elements $U(\lambda, \lambda', \lambda''; \parallel \parallel \parallel)$. For the exchange mechanism, only two levels have a reduced matrix element $\langle \phi J' \parallel \langle U \parallel \phi J \rangle \parallel \phi J \rangle \neq 0$: $4G_{5/2}^{(1)}$ (ca. 17900 cm$^{-1}$) and $4G_{5/2}^{(2)}$ (ca. 30230 cm$^{-1}$).
TABLE 2: Absolute Quantum Yields ($Q_{abs}$ ± 20%) of the Metal-Centered Luminescence in the Sm$^{III}$ and Yb$^{III}$ Helicates, of the Ligand-Centered Luminescence for Free and Complexed (L$^C$–2H)$^2^+^+$ in the Dy$^{III}$, Sm$^{III}$, and Yb$^{III}$ Helicates, and Lifetimes ($\tau$) of Sm$^{III}$, Yb$^{III}$, and L$^C$, in Solution at 295 K

<table>
<thead>
<tr>
<th>compound$^a$</th>
<th>solvent</th>
<th>$c$/M</th>
<th>$\lambda_{exc}$/cm$^{-1}$</th>
<th>$Q_{abs}/%$</th>
<th>$Q_{rad}/%$</th>
<th>$\tau$/µs$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sm$^3$(L$^C$–2H)$_3$]</td>
<td>D$_2$O</td>
<td>$3.1 \times 10^{-6}$</td>
<td>27550</td>
<td>1.1</td>
<td>0.11</td>
<td>180 ± 1</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>$4.0 \times 10^{-6}$</td>
<td>27550</td>
<td>0.14</td>
<td>0.03</td>
<td>42.0 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40 ± 2</td>
</tr>
<tr>
<td>[Yb$(^3$L$^C$–2H)$_3$]</td>
<td>D$_2$O</td>
<td>$5.1 \times 10^{-6}$</td>
<td>32250</td>
<td>1.8</td>
<td>0.20</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>$2.0 \times 10^{-6}$</td>
<td>26700</td>
<td>--</td>
<td>0.18</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>[Dy$(^3$L$^C$–2H)$_3$]</td>
<td>D$_2$O</td>
<td>$1.1 \times 10^{-6}$</td>
<td>27000</td>
<td>--</td>
<td>0.08</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>$8.8 \times 10^{-7}$</td>
<td>29410</td>
<td>--</td>
<td>--</td>
<td>0.008 ± 0.0006</td>
</tr>
<tr>
<td>L$^C$</td>
<td>H$_2$O</td>
<td>$8.4 \times 10^{-7}$</td>
<td>29410</td>
<td>--</td>
<td>5.0±</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ At pH or pD 7.5. $^b$ Obtained monitoring the Sm$^{III}$(G$_{5/2}$ → $^4$H$_{5/2}$) transition, the $^3\pi\pi^*$ ligand emission, and the Yb$^{III}$(F$_{5/2}$ → $^2$F$_{7/2}$) transition. $^c$ As compared to 5.5% reported in ref 11.

very similar values with averages of 1.1% in D$_2$O and 0.14% in H$_2$O (6 determinations). In summary, and roughly speaking, complexation of the Sm$^{III}$ ion results in more than 99% of the energy of the excited ligand state being transferred onto the metal ion; on the other hand, only a very small part is emitted in a radiative way by Sm$^{III}$.

It is noteworthy that the quantum yields determined can be considered as being relatively large for a Sm$^{III}$-containing compound: the energy gap between the lowest sublevel of $^4$G$_{5/2}$ and the highest sublevel of the $^6$F multiplet, $^6$F$_{1/2}$, is known to be around 7400 cm$^{-1}$, which favors nonradiative deexcitation processes, especially in compounds with organic ligands possessing several vibrations of relatively high energy. As a comparison, a quantum yield of 0.20% in water has been reported for the Sm$^{III}$ complex with a pyrazole-containing ligand, NN,N$'_N,N$'-$^3$(aminomethyl)pyrazol-1-yllpyrazine)tetraakis(acetic acid), L$^1$,$^3$, which displays good chromophoric and energy transfer properties, while a quantum yield of 2% has been reported for an especially well protected micellar system suitable for fluoroimmunoassays and containing 1,1,1-trifluoro-4-(2-naphthyl)-butane-2,4-dione, trioctylphosphine oxide and Triton X-100.$^4$

The lifetime of the $^4$G$_{5/2}$ level increases from 42 to 180 µs in going from H$_2$O to D$_2$O. Using Kimura’s equation,$^{15}$ we calculate that essentially no water is bound into the first coordination sphere, in line with previous observations for the Eu$^{III}$ and Tb$^{III}$ helicates.$^{11}$ Therefore, the large effect of H$_2$O on the radiative rate constant is due to second-sphere interactions. The lifetime of 180 µs in D$_2$O is long, compared with $^4$G$_{5/2}$ lifetimes reported previously: 79-96 µs in several systems used for fluoroimmunoassays and containing a β-diketone, Triton X-100 and Y$^III$ as co-luminescence enhancement ion.$^{3}$ However, µs for Sm$^{III}$ chelated by 2-naphthylitrifuorooctoate in benzene$^{15}$, and 30 µs for the complex with ligand L$^1$.$^3$

A relatively intense metal-centered NMR emission is observed for the Yb$^{III}$ helicate in D$_2$O upon excitation at 32258 cm$^{-1}$, while it is extremely weak in H$_2$O, which prevented us to measure the corresponding lifetime. The spectrum is depicted in Figure 2. It displays a band centered at ca. 10000 cm$^{-1}$ with four main components at 10493 (0$^0$–0$^0$), 10224 (0$^0$–0$^0$), 10091 (0$^0$–2$^0$), and 9852 (0$^0$–3$^0$) cm$^{-1}$, assigned to the $^4$F$_{5/2}$ → $^4$F$_{7/2}$ transitions. They arise from the $M_f$ splitting of the emitting and/or fundamental state, as a consequence of ligand field effects.

The line at 10224 cm$^{-1}$ corresponds to the lowest component of $^4$F$_{5/2}$, since at this wavelength the excitation and emission lines overlap. Excitation spectrum in the infrared region of the Yb$^{III}$ helicate, recorded by monitoring the emission from Yb$^{III}$ at 10200 cm$^{-1}$, presents three very weak bands centered at 10500, 10800, and 11110 cm$^{-1}$ (right side of Figure 2, see scale). Only the first one is of electronic nature, the latter two being of vibronic origin. The total ligand-field splitting amounts to
emission is around 10 in ionic systems, the photon ratio between visible and NIR cannot, however, be drawn from this experiment: averaged NMR measurements indicating that the helicates retain time-

to 269 and 372 cm$^\text{-1}$ and 372 cm$^\text{-1}$ respectively. Level 1$^\text{′(2F}_{5/2}$ has not been formally identified.

to 269 and 372 cm$^\text{-1}$ for the $^{2}\text{F}_{5/2}$ and $^{2}\text{F}_{7/2}$ levels, respectively (Figure 3). Analyzing these splittings in terms of group theory allowed us to assess the site symmetry of the Yb$^\text{III}$ ions, which is consistent with $D_3$. Determination of the irreducible representations of the angular momentum operator $J$ in this symmetry leads to four sublevels ($3E_{\text{1/2}} + E_{\text{3/2}}$) for $^{2}\text{F}_{5/2}$ and three sublevels ($2E_{\text{1/2}} + E_{\text{3/2}}$) for $^{2}\text{F}_{7/2}$. This is in agreement with the number of experimentally determined sublevels, with paramagnetic NMR measurements indicating that the helicates retain time-
averaged $D_3$ symmetry along the entire Ln$^\text{III}$ series, and with the X-ray crystal structure of the Yb$^\text{III}$ helicate. Up-conversion processes have been evidenced in Yb dimers in nonmolecular ionic lattices. To investigate whether such a process takes place in the Yb$^\text{III}$ helicate, we have recorded its emission spectrum upon direct metal excitation in the infrared region, at $\nu_{\text{exc}} = 10753$ cm$^\text{-1}$, but no visible emission was observed. A definitive conclusion cannot, however, be drawn from this experiment: in ionic systems, the photon ratio between visible and NIR emission is around $10^{-6}$ and if it does exist, we expect a less efficient up-conversion process in the dimetallic helicate in view of the large Yb$^\text{III}$–Yb$^\text{III}$ separation ($9.1$–$9.3$ Å) so that an extremely faint signal would be expected. On the other hand, direct metal excitation leads to a very weak Yb$^\text{III}$-centered emission, compared with ligand excitation, in line with the very weak excitation spectrum shown on Figure 2. This points to an appreciable sensitization of the Yb$^\text{III}$ by the ligand, as shown by the following data.

The lifetime of the Yb$^\text{III}(^{2}\text{F}_{5/2})$ state is long in D$_2$O, 40 μs (Table 2) compared to solution data reported previously, e.g., 18.6 μs in DMSO–d$_6$ for a $m$-terphenyl-based complex bearing a triphenylene chromophore and 6.2 μs in D$_2$O for a complex with a chiral macrocyclic tetra-amide. As a result, the quantum yield of the metal-centered luminescence amounts to 1.8% (D$_2$O) upon ligand excitation which, again is fairly large compared with the values reported in the literature for other Yb$^\text{III}$ complexes, e.g., 0.45% for the complex with fluorexon in D$_2$O or 0.5% for a terphenyl-based complex in DMSO.

The metal-centered emission quantum yields for the Sm$^\text{III}$ and Yb$^\text{III}$ helicates are large, compared to literature data, despite their absolute low values. Usually the nonradiative de-excitation of the metal-ion emitter level is related to the energy gap between the lowest luminescent excited state and the highest sublevel of the ground multiplet. These gaps amount to ~7400 cm$^{-1}$ for the $^{4}\text{G}_{5/2} \rightarrow ^{4}\text{F}_{7/2}$ transition of Sm$^\text{III}$ and to ~10200 cm$^{-1}$ for the $^{2}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2}$ transition of Yb$^\text{III}$. Therefore, overtones and/or combinations of high-energy vibrational modes, such as C–H and C=N oscillators, are in principle able to match these gaps, resulting in efficient quenching of the luminescent states. Such quenching mechanisms appear however to be not very efficient in the studied helicates given that the lifetimes, which are among the largest reported for Sm$^\text{III}$ and Yb$^\text{III}$ compounds, are quite longer in D$_2$O compared to H$_2$O. This can be traced back to the rigidity of the coordination environment in these molecular dimetallic edifices.

IV. Modeling of the Energy Transfer Processes

We have attempted to rationalize the quantitative data described above for Sm$^\text{III}$ and Yb$^\text{III}$ by an adequate modeling. The diagram sketched in Figure 4 shows the energy transfer processes taken into consideration for the sensitization of the Sm$^\text{III}$ compound. This model is based on the observed photophysical properties of this helicate and allows ligand-to-metal energy transfers to occur through either the singlet or triplet state. The initial excitation takes place through UV absorption in the Yb$^\text{III}$ singlet state. The initial excitation takes place through UV absorption in the Yb$^\text{III}$ singlet state. The initial excitation takes place through UV absorption in the Yb$^\text{III}$ singlet state.

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process is important for lanthanide containing compounds because intersystem crossing rates (isc) are enhanced by paramagnetic and heavy atom effects.43 This is exemplified by the quantum yield of the ligand-centered fluorescence of the GdIII helicate in H2O which amounts to only 0.93%,11 down from 5% for the free ligand. A similar, but much more pronounced trend is observed for the SmIII helicate that presents a very small quantum yield in D2O, 0.03%, compared to 12% for the free ligand. These data point to the intersystem crossing in the ligand increasing upon complexation with a concomitant energy transfer onto the metal ion and a large decrease in the emission from the singlet state.

The SmIII ion possesses a wealth of electronic levels, which have been identified and labeled by Carnall et al.31 We have used several criteria to select the levels most amenable to energy transfer, in particular resonance conditions and selection rules (see Experimental Section), which limited the number of potentially interesting levels to six: (i) an exchange mechanism is operative for the two 4G5/2 levels (30230 and 17900 cm−1), and multipolar mechanisms are effective for the 4H9/2, 4H11/2, 4H13/2, and 4G9/2 levels. To apply the selection rules, we have considered solely the ground state 4H5/2; at room temperature, population of the 4H7/2 level is around 0.06% only, and we think that the benefit introduced by taking the latter level into consideration would have been largely outweighed by the severe complications brought in the model.

The parameters used in the calculation of the energy transfer rate constants and quantum yield were the following: A1 (spontaneous emission coefficient) = 880 s−1 and 1/τ = 23998 s−1 in H2O, and A1 = 894 s−1 and 1/τ = 5531 s−1 in D2O. The 4G5/2 → 4H5/2 transition was taken as reference in the estimate of the spontaneous emission coefficient because the quantities (UJ) are very small for this transition. The R1 and (ϕ) values have been calculated previously for the following compounds: [Eu(NO3)3(L-MeOH)].14 Eu(TTA)2:2H2O and Eu(TTA)3:2DBSO,29 where L = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine, TTA = thonytrilfluoracetone and DBSO = dibenzyl sulfoxide. In these compounds, R1 ranges between 4.3 and 4.5 Å and (ϕ) between 0.8 × 10−36 and 1.9 × 10−36 esu2 cm2. In view of their relative insensitivity to the nature of the complex, we have chosen the same values as those calculated by the Sparkle model for [Eu(NO3)3(L-MeOH)].43 Å and 1.9 × 10−36 esu2 cm2, respectively.14 The other parameters were set to ΔA1(1/τ*π) = 4200 cm−1, from the phosphorescence spectra of the GdIII helicate,11 ΔA1(1/τ*π) = 4400 cm−1, from the absorption band of the lower energy singlet centered at 30300 cm−1, and α = 0.99, from the structural data reported for the EuIII and TbIII helicates.11 The transfer rate constant ks1 = ϕ = 109 s−1 was assumed to be identical with those found for other coordination compounds,7 while the rate constants for nonradiative decays from the excited SmIII levels have been set to 108 s−1.

<table>
<thead>
<tr>
<th>TABLE 3: Experimental Transition Energies (cm−1) from and to the Singlet and Triplet States of [Ln(L−2H)2]</th>
<th>Ln = Gd</th>
<th>Ln = Sm</th>
<th>Ln = Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>triplet state</td>
<td>singlet state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ln = Gd</td>
<td>Ln = Sm</td>
<td>Ln = Yb</td>
<td></td>
</tr>
<tr>
<td>16560</td>
<td>28490 sh</td>
<td>28460 sh</td>
<td></td>
</tr>
<tr>
<td>17950</td>
<td>30300</td>
<td>30380</td>
<td></td>
</tr>
<tr>
<td>19340</td>
<td>34600 sh</td>
<td>34550 sh</td>
<td></td>
</tr>
<tr>
<td>20660</td>
<td>40065 sh</td>
<td>40000 sh</td>
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</tr>
<tr>
<td></td>
<td>50000</td>
<td>50250</td>
<td></td>
</tr>
</tbody>
</table>

a From phosphorescence spectra at 10 K for Gd helicate, obtained from ref 11. b From absorption spectra in H2O at 293 K; sh = shoulder.

<table>
<thead>
<tr>
<th>TABLE 4: Calculated Energy Transfer Rates (s−1) for [Sm2(L−2H)3]</th>
<th>E(1 state)/cm−1</th>
<th>E(4f state)/cm−1</th>
<th>transfer rate WET/s−1</th>
<th>back-transfer rate WBT/s−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/τ<em>π</em>(18 620) → 4G5/2(17900)</td>
<td>8.4 × 109</td>
<td>2.72 × 109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/τ<em>π</em>(18 620) → 4H9/2 (20500)</td>
<td>4.67 × 109</td>
<td>601</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/τ<em>π</em>(30 300) → 4H5/2 (29000)</td>
<td>6.0 × 109</td>
<td>1.23 × 109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/τ<em>π</em>(30 300) → 4H9/2 (39000)</td>
<td>1.37 × 109</td>
<td>1.27 × 109</td>
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<td></td>
</tr>
<tr>
<td>1/τ<em>π</em>(30 300) → 4G5/2 (30100)</td>
<td>1.52 × 109</td>
<td>5.87 × 109</td>
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<td></td>
</tr>
<tr>
<td>1/τ<em>π</em>(30 300) → 4G5/2 (30232)</td>
<td>1.75 × 109</td>
<td>1.27 × 109</td>
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<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE 5: Calculated Quantum Yield (%) of [Sm2(L−2H)3] at 300 K for Several Values of the Transition Rates</th>
<th>ks1 (s−1)</th>
<th>ks2 (s−1)</th>
<th>ks2 (s−1)</th>
<th>Q(H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
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<td>106</td>
<td>0.271</td>
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<tr>
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<td>0.27</td>
<td>0.25</td>
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<tr>
<td>106</td>
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<td>104</td>
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<tr>
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<td>104</td>
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<td>0.014</td>
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<td>95</td>
<td>0.0300</td>
<td>0.0280</td>
</tr>
<tr>
<td>96</td>
<td>95</td>
<td>94</td>
<td>0.25</td>
<td>0.23</td>
</tr>
</tbody>
</table>

a See Figure 4 for the numbering of the states and, therefore, the labeling of the rate constants. Italicized values reproduce best the experimental data.

The theoretical values for the forward and back-transfer rate constants calculated from eqs 1−3 are listed in Table 4. They vary widely for the different levels involved, between 108 and 109 s−1, a range comparable to that found for the transfer rate constants in the 1:1 and 1:3 complexes of EuIII with L.45 The largest rate constants correspond to both 4G5/2 levels and a first conclusion is that these levels are implicated in the main path(s) of the energy transfer process. The numerical solutions of the rate equations were used to calculate the populations of the levels (eq 4) which, in turn, were used to estimate the emission quantum yields.

We have performed a variable analysis to investigate the dependence of the quantum yield upon the rate constants k91, k12, and k32 (Table 5). A quite satisfactory match between the calculated (1.2%) and experimental (1.1%) quantum yields in D2O solution was found by setting k91 = 109 s−1, k12 = 108 s−1, and k32 = 108 s−1. For H2O solution, k91 = 109 s−1, k12 = 109 s−1, and k32 = 108 s−1 gave a calculated quantum yield = 0.12%, as compared to 0.14% for the experimental one. It is noteworthy that, as expected, the only rate constant influenced by the solvent change is k91, which becomes 10 times larger in H2O compared to that in D2O, while the intersystem crossing rate constant remains the same (108 s−1) and is comparable to that found in the complexes with L (107−108 s−1)42 and in metallotaxaphyrins containing coordinated NdIII and YIII ions.46 This means that second sphere interactions of water molecules with the carboxylic groups not only depopulate the emitter level of the SmIII ion, but also the triplet state level, consistent with the quantum yields for the ligand-centered luminescence discussed above. The large k32 value is typical of a heavy-atom effect.43

The lifetime of the 1/τ*π* emission in the helicate depends on the energy transfer rate constants to the SmIII upper excited...
levels, on \( k_{32} \), and on the internal conversion rate constant \( k_{31} \). The same lifetime in the uncoordinated ligand depends only on \( k_{31} \) and \( k_{32} \), and the latter rate constant is smaller in the ligand than in the complex, as describe above. Therefore, the internal conversion rate constant \( k_{31} \) in the Sm\( ^{III} \) helicate should be comparable to the inverse of the singlet emission lifetime (1/\( \tau_s \)) in the uncoordinated ligand, which is the case: \( 1/\tau_s = 1.2 \times 10^8 \) s\(^{-1} \) compares well with the \( k_{31} \) value of \( 10^8 \) s\(^{-1} \) reproducing best the experimental quantum yields in both water and deuterated water.

Finally, we have evaluated the contributions of the various energy-transfer processes to the overall quantum yield by performing the theoretical calculations for each separate level. It turns out that \( ^3\pi^* \rightarrow ^4G_{52}(1) \) accounts for ca. 97.5% of the total energy transfer while \( ^1\pi^* \rightarrow ^4G_{52}(2) \) accounts for 1% and all the other processes for the remaining 1.5%. Therefore, the common, and simplified, thinking that ligand-to-metal energy transfers in lanthanide-containing compounds goes essentially through the triplet state is validated in our particular case. One difference is that the main operative mechanism is an exchange one and not a Förster-type mechanism, pointing to some orbital overlap between the ligand and 4f states.

The Yb\( ^{III} \) helicate in D\(_2\)O presents a much stronger metal-centered emission in the infrared upon ligand excitation than upon direct excitation of the metal ion, clearly establishing the sensitizing role of the ligand. The oxygen effect on the sensitized luminescence intensity and time-resolved luminescence were investigated with the objective of determining which energy transfer mechanism is operative in this compound, since there is very little overlap between the ligand \(^1\pi^* \) and \(^3\pi^* \) states and the \(^2F_{5/2} \) level. Oxygen may deactivate the triplet level, and if the main path of the ligand-to-metal energy transfer goes through the \(^3\pi^* \) level, this is reflected in a concomitant decrease in the lanthanide-centered emission. The emission spectra of the Yb\( ^{III} \) helicate were therefore measured for both deoxygenated and nondeoxygenated solutions and they did not show significant intensity change. The rate constant of oxygen quenching of the triplet state \( (k_{oa}) \) is equal to the product of the diffusion-controlled quenching rate constant by the oxygen concentration, \( k_{oa} = k_{oa}(O_2) \). In D\(_2\)O, \( [O_2] = 0.265 \text{ mM} \) and \( k_{oa} \) is on the order of \( 10^{10} \text{ M}^{-1} \text{ s}^{-1} \),38 therefore, \( k_{oa} = 2.7 \times 10^8 \) s\(^{-1} \). Since oxygen has no effect on the metal-centered luminescence of the Yb\(^{III} \) helicate, \( W_{ET} \) must be significantly larger than \( k_{oa} \). This is unexpected given that the energy transfer rate constant of the triplet state to the \(^2F_{5/2} \) emitter level is usually considered to be \( 10^8 \) s\(^{-1} \). In view of the extremely small spectral overlap between the emission spectrum from the triplet state and the absorption spectrum of the Yb\(^{III} \) ion,38,41,41 One may therefore suspect that another mechanism is operative for the ligand-to-Yb\(^{III} \) energy transfer. In the cases of lanthanide chelates bearing an aromatic side-chain48 and of complexes with proteins,49 other authors have proposed that sensitization of Yb\(^{III} \) occurs via a long-range electron transfer process involving Yb\(^{II} \).

Such a mechanism has been confirmed for a variety of complexes.49 More recently, ultrafast time-resolved spectroscopy has also authenticated this mechanism for the (bipy:bipy:bipy) cryptand.2 We have investigated the Yb\(^{III} \) helicate under similar experimental conditions and found that the rise time of the metal-centered emission is extremely fast (\( t_{\text{rise}} < 8 \) ns). In summary, this information, combined with the absence of oxygen quenching and the fact that the intensity of the \(^3\pi^* \) emission decreases drastically upon formation of the helicate, points to a very fast energy transfer process, compatible with the electron transfer mechanism, although not proving it.

V. Conclusion

Metal-centered luminescence is fairly well sensitized in the three stranded homodimetallic helicates [Ln\(_2\)(L\(^5\)−OH)\(_2\)], Ln = Sm (H\(_2\)O, D\(_2\)O) and Yb (D\(_2\)O). The absolute quantum yield of the ligand-centered luminescence decreases dramatically upon formation of the helicates because of a large enhancement in the intersystem crossing rate constant and subsequent energy transfer onto the metal ions results in the observation of metal-centered luminescence. Both the quantum yields and lifetimes of the metal-centered luminescence of the helicates in D\(_2\)O are large compared to other values reported in the literature, pointing to these systems as potential luminescent probes for applications in bioanalyses. Indeed, ligand L\(^5\) can be easily derivatized in the 4-position of the pyridines50 so that grafting of adequate sensitizing groups is within reach.

Pioneering work for the calculation of energy transfer rates and emission quantum yield in the Sm\(^{III} \) helicate leads to a good agreement between experimental and theoretical quantum yield of the metal centered emission, indicating that the theoretical approach used is adequate. We have shown that the main energy stream from the ligand to the metal ion goes through the triplet state through an exchange mechanism. This type of theoretical modeling of energy transfer processes opens the way for a more rational design of samarium luminescent probes.

Acknowledgment. We gratefully acknowledge Professor Jörna Hölsä (University of Turku) for providing the wave functions of Sm\(^{III} \) in SmOCl and Mr M. Hollowenstein (University of Bern) for the synthesis of the ligand. F.R.G.S. is indebted to CNPq (Brazilian agency) for a stipend. This work is supported through grants from the Swiss National Science Foundation.

References and Notes