Sensitized near-infrared luminescence from polydentate triphenylene-functionalized Nd$^{3+}$, Yb$^{3+}$, and Er$^{3+}$ complexes

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Hexa-deutero dimethylsulfoxide (DMSO-$d_6$) solutions of terphenyl-based Nd$^{3+}$, Yb$^{3+}$, and Er$^{3+}$ complexes functionalized with a triphenylene antenna chromophore exhibit room temperature near-infrared luminescence at wavelengths of interest for the optical telecommunication network ($\sim 1330$ and $\sim 1550$ nm). The sensitizing process takes place through the triplet state of triphenylene as can be concluded from the oxygen dependence of the sensitized luminescence. A significant fraction of the excited triphenylene triplet state is quenched by oxygen, instead of contributing to the population of the lanthanide ion. The luminescence lifetimes of the triphenylene-functionalized lanthanide complexes (2)Ln are in the range of microseconds with a lifetime of 18.6 $\mu$s for 2Yb, 3.4 $\mu$s for 2Er, and 2.5 $\mu$s for 2Nd in DMSO-$d_6$. These luminescence lifetimes seem almost completely dominated by the vibrational quenching by the organic groups in the polydentate ligand and solvent molecules, which leads to low overall luminescence quantum yields. © 1999 American Institute of Physics. [S0021-8979(99)07615-X]

I. INTRODUCTION

The trivalent rare earth or lanthanide ions are known for their unique optical properties such as line-like emission spectra and long luminescence lifetimes.$^1$ Because of their intrinsically low absorption cross sections, the indirect excitation of lanthanide ions via an antenna chromophore has been studied in detail for europium (Eu$^{3+}$) and terbium (Tb$^{3+}$) luminescence.$^1,2$ The transfer of the excitation energy to the lanthanide ion is generally considered to take place through the triplet state of the antenna chromophore via an electron-exchange mechanism.$^3$ Recently, there has been a growing interest in polydentate complexes of the near-infrared (NIR) emitting lanthanide ions erbium (Er$^{3+}$), ytterbium (Yb$^{3+}$), and neodymium (Nd$^{3+}$) for applications in fluoroimmuno assays,$^4,5$ laser systems,$^6$ and optical amplification.$^7$ However, only a few studies have been reported on the sensitized emission of Nd$^{3+}$ and Yb$^{3+},$ and even fewer studies on Er$^{3+}.$

In the optical telecommunication network an optical transition of Er$^{3+}$, doped into an inorganic matrix such as silica, is used for amplification of light around 1550 nm.$^{10}$ An optical transition of praseodymium (Pr$^{3+}$) is used for the amplification of light around 1300 nm.$^{11}$ The ultimate goal of our research is the development of a polymer-based optical amplifier in which overall neutral organic lanthanide complexes are incorporated into polymer waveguides. In order to achieve an efficient population of the lanthanide luminescent state, these complexes will be functionalized with an antenna chromophore. We have reported the synthesis and photophysical properties of terphenyl-based Nd$^{3+}$ and Er$^{3+}$ complexes.$^9,12$ Recently, a polymeric waveguide doped with the neodymium chloride salt has been shown to amplify light of 1060 nm.$^{13}$

In the present article we report novel sensitizer-functionalized Nd$^{3+}$, Yb$^{3+}$, and Er$^{3+}$ complexes, and their sensitized NIR luminescence. The terphenyl-based ligand (1)H$_3$ and its triphenylene-functionalized derivative (2)H$_3$ were designed to provide eight oxygen donor atoms for the encapsulation of the lanthanide ion: three ether oxygens, three carboxylate oxygens, and two amide carbonyl oxygens (See Fig. 1).

The terphenylene antenna chromophore was incorporated into ligand (2)H$_3$, because it allows excitation up to 350 nm and it has a high intersystem crossing quantum yield (0.89).$^2$ This is favorable since the sensitized excitation of the lanthanide ion occurs via the triplet state of the chromophore.$^3$ The antenna chromophore will be positioned in close proximity to the lanthanide ion because of the coordination of the amide carbonyl (vide infra).

II. EXPERIMENT

The synthesis of the ligands (1)H$_3$ and (2)H$_3$ is depicted in Fig. 2. Full details of the synthesis will be reported in a forthcoming publication. The key step is the asymmetric functionalization of 4. Reaction of bis(amine) 4 with 1.3 equivalents of benzoyl chloride gave the mono(amine) 5 in
20% yield and bis(amide) 7 in 50% yield. The mono(amide) 5 was reacted with triphenylene carboxylic acid chloride yielding 6 in 70% yield. After hydrolysis of the tert-butylesters of 6 and 7 with trifluoroacetic acid, the corresponding complexes were readily formed upon addition of the lanthanide nitrate salts to the ligands in the presence of Et₃N as a base.

Fast atom bombardment mass spectrometry indicated that the complexes have a 1:1 stoichiometry. The IR spectra showed that all carboxylic acid groups are deprotonated and that the amide carbonyls are also coordinated to the lanthanide ion.

Steady state photoluminescence measurements in the NIR region were performed using the 351.1/363.8 nm lines of an Ar ion pump laser at a power of 60 mW for excitation. The laser beam was modulated with an acousto-optic modulator at a frequency of 40 Hz. The luminescence signal was focused into a monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques. The spectral resolution was 6 nm. When a Xe lamp was used as the excitation source, the steady state measurements were performed according to Ref. 12. Luminescence lifetime measurements were performed by monitoring the luminescence decay after excitation with a 0.5 ns pulse of a N₂ laser (λₑₓ = 337 nm, pulse energy 20 µJ, 10 Hz repetition rate). Decay signals were recorded using a liquid-nitrogen-cooled Ge detector with a time resolution of 0.3 µs. The signals were averaged using a digitizing oscilloscope. All decay curves were analyzed by deconvolution of the measured detector response.

III. RESULTS AND DISCUSSION

The processes that follow the excitation of the antenna chromophore into its singlet excited state are intersystem crossing to the triplet state, energy transfer to the lanthanide ion, and subsequent lanthanide luminescence (See Fig. 3). The overall quantum yield of sensitized emission \( \phi_{se} \) is therefore the product of the triplet yield \( \phi_{isc} \), the energy transfer yield \( \phi_{et} \), and the intrinsic luminescence quantum yield \( \phi_{lum} \), hence:

\[
\phi_{se} = \phi_{isc} \phi_{et} \phi_{lum}.
\]  

Hexa-deutero dimethylsulfoxide (DMSO-\( d₆ \)) solutions of the NIR emitting (2)Ln complexes (1 mM) exhibit the
typical line-like lanthanide emission upon excitation of the triphenylene antenna chromophore. At room temperature sensitized emission at 1540 nm \((4_{13/2} \rightarrow 4_{15/2})\) transition is observed for \((2)\)Er, at 880, 1060, and 1330 nm \((4F_{3/2} \rightarrow 4I_{9/2}, 4I_{11/2}, \) and \(4I_{13/2})\) transition, respectively) for \((2)\)Nd, and at 980 nm \((2F_{5/2} \rightarrow 2F_{7/2})\) transition for \((2)\)Yb (See Fig. 4).

The luminescence intensity is enhanced by 35% for \((2)\)Nd, 120% for \((2)\)Er, and 90% for \((2)\)Yb upon deoxygenation of the samples, indicating that oxygen quenching of the triplet state of triphenylene is competing with the energy transfer to the encapsulated lanthanide ion. The energy transfer rate can be estimated from this oxygen dependence by using the Stern–Volmer equation\(^{16}\) for the diffusion-controlled oxygen quenching of the triplet state of triphenylene:

\[
I_0 / I = 1 + k_{\text{diff}} \tau_T [O_2],
\]

where \(I_0\) and \(I\) are the lanthanide luminescence intensities in the absence and presence of oxygen, respectively, \(k_{\text{diff}}\) is the diffusion-controlled quenching rate constant, \(\tau_T\) is the lifetime of the triplet state of triphenylene, and [O\(_2\)] is the oxygen concentration in DMSO at room temperature. In the availability of energy transfer, \(k_{\text{diff}}\) is the same order of magnitude as the oxygen quenching rate, and thus

\[
k_{\text{et}} = 1 / \tau_T.
\]

If \(k_{\text{diff}}\) is taken as \(10^{10} \text{M}^{-1} \text{s}^{-1}\) and [O\(_2\)] is taken as 0.46 mM\(^{18}\) the triphenylene triplet state lifetime and energy transfer rate constants in the different complexes can be calculated (see Table I).

In the system. First, there is a distance of approximately 5 Å between the center of the sensitizer and the lanthanide ion.\(^{19}\) Second, there is a large energy difference between the triplet state of triphenylene \((22,900 \text{ cm}^{-1})\)\(^{20}\) and the luminescent state of especially Yb\(^{3+}\). The lanthanide-sensitizer distance and the energy difference between the triplet state and the lanthanide luminescent state are known to strongly influence the energy transfer process in the sensitized emission of Eu\(^{3+}\) and Tb\(^{3+}\).\(^{2,3}\)

Recently, an internal redox mechanism was proposed for the sensitized Yb\(^{3+}\) luminescence that takes place through the singlet state of the antenna chromophore.\(^{8}\) Since such an internal redox energy transfer mechanism takes place through the triphenylene singlet state, the triphenylene fluorescence of \((2)\)Yb must not only be competing with intersystem crossing, but also with the redox energy transfer mechanism. However, the intensity of the triphenylene fluorescence of \((2)\)Yb and \((2)\)Nd (the internal redox energy transfer mechanism does not take place in the latter complex) is the same. Furthermore, the overall sensitized luminescence is oxygen dependent. These observations strongly indicate that the energy transfer pathway takes place through the triplet state of triphenylene.

### Table I

The ratio of the sensitized lanthanide luminescence intensities in the absence and presence of oxygen (1 mM DMSO-d\(_6\) solutions), as well as the calculated energy transfer rate constants \(k_{\text{et}}\) using the Stern–Volmer equation (Xe lamp: \(k_{\text{esc}} = 320 \text{ nm}\)).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(I_0/I)</th>
<th>(\tau_T) (ns) (^a)</th>
<th>(k_{\text{et}}) ((\text{M}^{-1} \text{s}^{-1})) (^b)</th>
<th>(\phi_{\text{et}}) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((2))Yb</td>
<td>1.90</td>
<td>196</td>
<td>0.51</td>
<td>0.53</td>
</tr>
<tr>
<td>((2))Er</td>
<td>2.20</td>
<td>261</td>
<td>0.38</td>
<td>0.45</td>
</tr>
<tr>
<td>((2))Nd</td>
<td>1.35</td>
<td>76</td>
<td>1.32</td>
<td>0.74</td>
</tr>
</tbody>
</table>

\(^a\)\(\tau_T = (I_0/I-1)/(k_{\text{diff}}[O_2])\), \(k_{\text{diff}} = 10^{10} \text{M}^{-1} \text{s}^{-1}\), [O\(_2\)] = 0.46 mM. 
\(^b\)\(k_{\text{et}} = 1/\tau_T\). 
\(^c\)\(\phi_{\text{et}} = k_{\text{et}} / (k_{\text{et}} + k_{\text{diff}}[O_2])\).
Time-resolved luminescence measurements showed that the observed luminescence lifetimes of the complexes in DMSO-$d_6$ are in the range of microseconds (See Table II), with the Yb$^{3+}$ complexes having the longest lifetimes and the Nd$^{3+}$ complexes the shortest. Our present results compare favorably with the recently published luminescence lifetimes of Nd$^{3+}$ and Yb$^{3+}$ complexes,$^{5,21}$ and our previously published lifetimes of Eu$^{3+}$. In DMSO-$h_6$ the luminescence lifetimes are decreased significantly due to the fact that the methyl groups (–CD$_3$) of DMSO-$h_6$ are more efficient quenchers of the lanthanide excited state than the deuto methyl groups (–CD$_2$) of DMSO-$d_6$. Our observation that the rate constants of the quenching by the methyl groups of the solvent DMSO-$h_6$ is the largest for Nd$^{3+}$ and the smallest for Yb$^{3+}$ (See Table II) is in agreement with the energy gap law, as is the case for the well-documented quenching by hydroxyl groups (–OH) of Eu$^{3+}$ and Tb$^{3+}$ luminescence. According to the energy gap law the smaller the harmonic number of vibrational quanta that is required to match the energy gap between the lowest luminescent state and the highest nonluminescent state of the lanthanide ion, the more effective the vibronic quenching will be. For the C–H vibration, which has vibrational quanta of 2950 cm$^{-1}$, the number of harmonics needed to match the energy gap is largest for Yb$^{3+}$, and smallest for Nd$^{3+}$ (see Fig. 5).

The natural lifetimes $\tau_0$ of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er$^{3+}$ and the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb$^{3+}$ have been calculated from the absorption spectra of these transitions$^{21}$ to be 14 ms for (I)Er and 2 ms for (I)Yb. The natural lifetime of Nd$^{3+}$ cannot be determined in this way, since the 1060 and 1330 nm emissions do not involve a transition back to the ground state. Instead a literature value of 0.25 ms was taken for Nd$^{3+}$. The intrinsic luminescence quantum yield $\phi_{\text{lum}}$ of the complexes ions follows

$$\phi_{\text{lum}} = k_0/k = k_0/(k_0 + k_{\text{rad}}) = \tau/\tau_0,$$

where $k_0$ is the natural radiative decay rate, $k$ is the observed radiative decay rate, $k_{\text{rad}}$ the nonradiative decay rate, $\tau$ is the observed lifetime, and $\tau_0$ is the natural lifetime. The calculated intrinsic luminescence quantum yields are summarized in Table II. This value of $\phi_{\text{lum}}$ is also the upper limit of the overall quantum yield of sensitized emission $\phi_{\text{isc}}$, because this is the product of the triplet yield $\phi_{\text{isc}}$, the energy transfer yield $\phi_{\text{et}}$, and the intrinsic luminescence quantum yield $\phi_{\text{lum}}$. This means that, even when $\phi_{\text{isc}}$ and $\phi_{\text{et}}$ are close to unity, the overall quantum yield is low, because the transferred energy is lost mainly via nonradiative processes involving the luminescent states of the lanthanide ions. High-frequency oscillators such as C–H vibrations in the ligand and the solvent molecules, provide a very efficient nonradiative pathway for relaxation of the luminescent state of the NIR emitting lanthanide ions via vibronic coupling.

**IV. CONCLUSIONS**

In summary, these novel sensitizer functionalized Er$^{3+}$, Nd$^{3+}$, and Yb$^{3+}$ complexes exhibit sensitized NIR emission with luminescence lifetimes in the microsecond range. The energy transfer rate from the antenna chromophore to the lanthanide ion should be optimized by incorporating sensitizers with lower triplet energy states in even closer proximity of the lanthanide ion. Substitution of the CH groups in our ligand system for CD groups will further increase the overall luminescence quantum yield.

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**TABLE II.** The luminescence lifetimes of the terphenyl-based complexes in DMSO-$d_6$ ($\tau_d$) and DMSO-$h_6$ ($\tau_h$), the calculated luminescence quenching rates by the CH$_3$ groups of DMSO-$h_6$ ($k_q$), as well as the calculated lanthanide luminescence quantum yield ($\phi_{\text{lum}}$ for DMSO-$d_6$ and $\phi_{\text{lum}}$ for DMSO-$h_6$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\tau_d$ (µs)</th>
<th>$\tau_h$ (µs)</th>
<th>$k_q$ ($10^4$ s$^{-1}$)</th>
<th>$\phi_{\text{lum}}$ (DMSO-$d_6$)</th>
<th>$\phi_{\text{lum}}$ (DMSO-$h_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)Yb</td>
<td>19.9</td>
<td>9.1</td>
<td>6.0</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>(2)Yb</td>
<td>18.6</td>
<td>9.4</td>
<td>5.3</td>
<td>0.009</td>
<td>0.005</td>
</tr>
<tr>
<td>(1)Er</td>
<td>3.3</td>
<td>2.1</td>
<td>17.3</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>(2)Er</td>
<td>3.4</td>
<td>2.4</td>
<td>12.3</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>(1)Nd</td>
<td>2.5</td>
<td>1.2</td>
<td>43.3</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>(2)Nd</td>
<td>2.5</td>
<td>1.4</td>
<td>31.4</td>
<td>0.01</td>
<td>0.006</td>
</tr>
</tbody>
</table>

$k_q = 1/\tau_h - 1/\tau_d$. 

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**FIG. 5.** Energy diagram of the $4f$ levels responsible for the lanthanide luminescence (a filled circle denotes the lowest luminescent state, an open circle denotes the highest nonluminescent state). Adapted from Ref. 21.
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