

Transition metal complexes as a new class of photosensitizers for near-infrared lanthanide luminescence

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Abstract

In this paper, we report the near-infrared lanthanide luminescence of neodymium(III) and ytterbium(III) sensitized by energy transfer from the triplet excited state of a transition metal complex. In the present systems, polydentate neodymium(III) and ytterbium(III) complexes have been functionalized with the transition metal complexes ruthenium-tris(bipyridine) or ferrocene as the light harvesting units. Ruthenium-tris(bipyridine) and ferrocene have suitable triplet state energies for energy transfer to neodymium(III) and ytterbium(III), and have absorption bands in the visible part of the electromagnetic spectrum. The energy transfer process in the ruthenium-tris(bipyridine) complexes could be studied in detail because the donating state of the antenna (the ³MLCT state) is luminescent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Transition metals; Lanthanides; Luminescence; Sensitizers

1. Introduction

The design of sensitizer-functionalized lanthanide complexes that exhibit efficient luminescence in the near-infrared (NIR) region is currently of great interest because of their potential applications in fluoroimmuno-assays [1] and in polymer-based optical signal amplifiers [2]. NIR luminescence of complexes of the lanthanide ions erbium(III) (Er³⁺), neodymium(III) (Nd³⁺) and ytterbium(III) (Yb³⁺) is readily observed in solution at room temperature only when the ions are excited *indirectly* by energy transfer from the triplet state [3] of an incorporated organic antenna chromophore (the *sensitizer*). Direct excitation is more demanding because of the forbidden optical transitions within the 4f subshells of lanthanide ions. As a result, the absorption coefficients are very low (typically 1–10 M⁻¹ cm⁻¹) and the lifetimes of the excited states are relatively long (microseconds to milliseconds).

In optical telecommunication networks, Er³⁺-doped silica fiber amplifiers (EDFAs) are currently used for the amplification of light with a wavelength of about 1550 nm [4], which corresponds to an optical transition of Er³⁺ (⁴I_{13/2} → ⁴I_{15/2} transition). Recently, a polymeric wave-

guide doped with neodymium(III) chloride (NdCl₃) has been shown to amplify light of 1060 nm [5]. The work presented in this paper is part of our research that is concerned with the development of a polymer-based optical amplifier in which lanthanide complexes bearing antenna chromophores are incorporated in planar polymeric waveguides [2,6]. The polymer-based amplifiers can be integrated in existing polymeric optical components such as splitters, switches and multiplexers [7]. The advantage of polymer-based components lies in their ease of processing, which enables low-cost manufacturing technologies to be applied.

We have recently developed a polydentate ligand based on the *m*-terphenyl platform which forms overall neutral complexes with various lanthanide cations such as Eu³⁺, Yb³⁺, Nd³⁺ and Er³⁺ [8]. In these complexes, the lanthanide ion is complexed by eight oxygen donor atoms: three oxyacetate and two amide carbonyl moieties. The synthesis route of this ligand allows the incorporation of different sensitizers without changing the coordinating nature of the ligand [9]. In this paper, we report the NIR luminescence of *m*-terphenyl-based complexes of Nd³⁺ and Yb³⁺ sensitized by the transition metal complexes ruthenium(II)-tris(bipyridine) ([Ru(bpy)₃]²⁺) and ferrocene. The polydentate neodymium(III) and ytterbium(III) complexes functionalized with the transition metal complexes ruthenium-tris(bipyridine) or ferrocene, [(Ln₂-Ru)1]²⁺ and (Ln)2, respectively, are depicted in Fig. 1 [10].

Until now, the investigations of sensitizers for NIR lanthanide luminescence have been focused on organic conjugated

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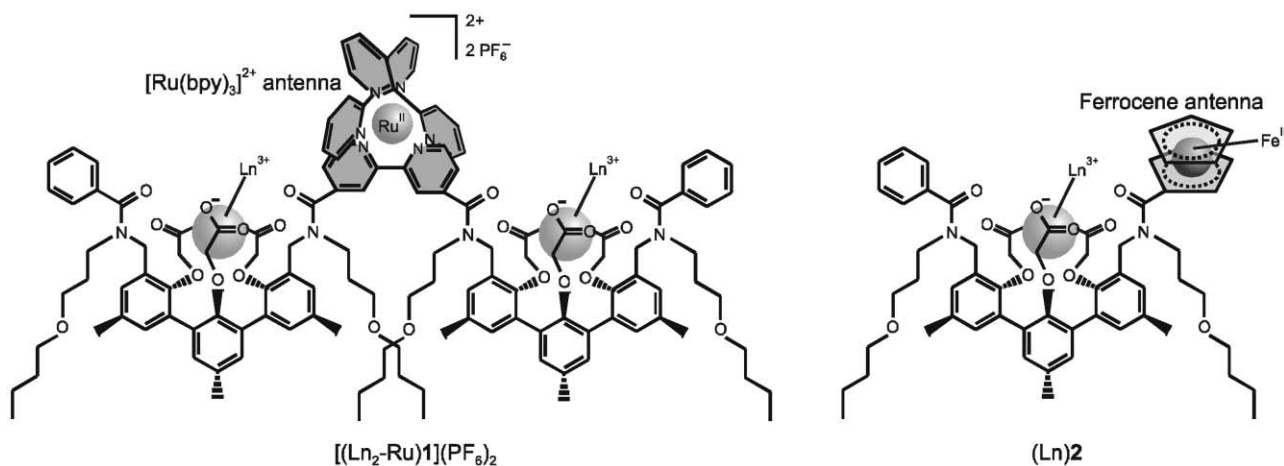


Fig. 1.

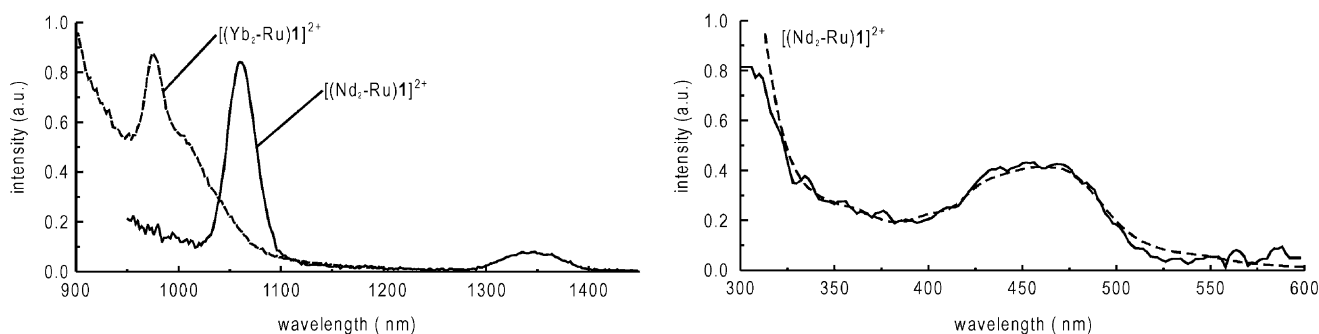


Fig. 2. Left: the steady-state NIR luminescence spectrum of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ and $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ in $[\text{D}_6]\text{DMSO}$ (10^{-5} M) upon excitation at 450 nm. The spectra have been corrected for the absorbance of the samples. Right: the solid line is the excitation spectrum of the Nd^{3+} luminescence of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ while monitoring the 1060 nm emission band, the dashed line is the absorption spectrum of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$.

molecules. Nevertheless, there are only a few examples of sensitizers that enable visible light instead of near-UV excitation [1,11,12]. The $[\text{Ru}(\text{bpy})_3]^{2+}$ complex not only has an intersystem crossing quantum yield near unity, but it would also enable excitation of Nd^{3+} and Yb^{3+} with visible light of up to 500 nm. Compared to $[\text{Ru}(\text{bpy})_3]^{2+}$, ferrocene has weaker absorption bands in the visible region [13], but its low lying triplet state ($E_T = 13,300 \text{ cm}^{-1}$) [14] closely matches the receiving luminescent states of Nd^{3+} ($11,300 \text{ cm}^{-1}$) and Yb^{3+} ($10,250 \text{ cm}^{-1}$).

2. Results and discussion

Excitation of the $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ and $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ complexes in deoxygenated $[\text{D}_6]\text{DMSO}$ (10^{-5} M) with visible light resulted in Ln^{3+} -centered NIR luminescence. Fig. 2 shows the emission bands of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ at 1060 and 1330 nm corresponding to the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$ transitions of Nd^{3+} , respectively, and the emission band

of $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ at 975 nm corresponding to the ${}^4\text{F}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ transition of Yb^{3+} . The 1060 nm band of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ and the 975 nm band of $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ are superimposed on the tail of the Ru-bpy antenna luminescence that originates from the ${}^3\text{MLCT}$ state. The excitation spectra closely resemble the absorption spectrum of the Ru-bpy antenna which proves that the Ln^{3+} ions are excited via the ${}^1\text{MLCT}$ state of the Ru-bpy antenna. The excitation and absorption spectra of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ are shown in Fig. 2. The $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ complex has identical excitation and absorption spectra.

Time-resolved luminescence measurements of the earlier mentioned antenna luminescence originating from the ${}^3\text{MLCT}$ state and the sensitized Nd^{3+} luminescence of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ proved that the pathway of the sensitized emission indeed involves the ${}^3\text{MLCT}$ state of the antenna (see Fig. 3, right). During the time that the energy transfer from the ${}^3\text{MLCT}$ to the lanthanide ion is in progress, the lanthanide luminescence intensity is expected to rise with a rate equal to the decay rate of the ${}^3\text{MLCT}$ state. Upon pulsed laser excitation of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$, antenna luminescence was observed at 660 nm and decayed with a time constant of $420 \pm 10 \text{ ns}$ (τ_{RuNd}). At the same time, the Nd^{3+} emission at 1060 nm rose with the same time constant of $420 \pm 20 \text{ ns}$,

² Nd^{3+} also has an emission band around 880 nm corresponding to the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ transition, but this band could not be measured accurately with the detector that was used in the experimental set-up.

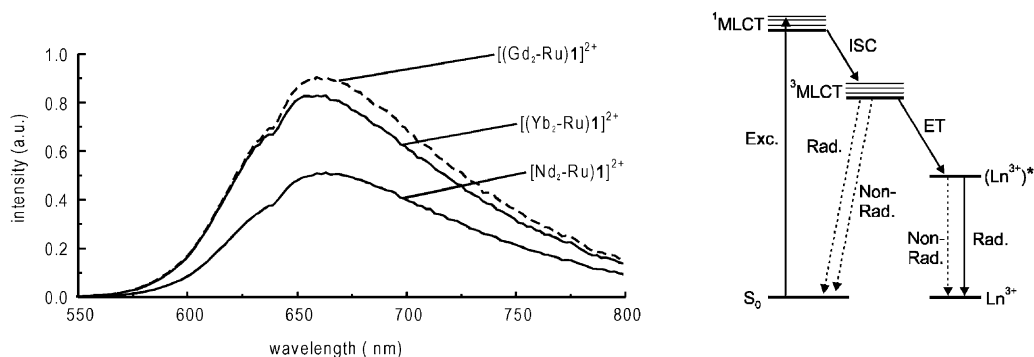


Fig. 3. Left: emission spectra of Ru-bpy-centered luminescence of $[(\text{Gd}_2\text{-Ru})\mathbf{1}]^{2+}$, $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ and $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ in deoxygenated $[\text{D}_6]\text{DMSO}$ (10^{-5} M) upon excitation at 450 nm. The spectra have been corrected for the absorbance of the samples. Right: the photophysical pathway of the sensitization process of $[(\text{Ln}_2\text{-Ru})\mathbf{1}]^{2+}$ that involves the excitation of the antenna into its $^1\text{MLCT}$ state, intersystem crossing to the $^3\text{MLCT}$ state, the population of the lanthanide excited state by energy transfer from the $^3\text{MLCT}$ state and subsequent lanthanide emission. The solid arrows indicate the photophysical pathway and the dashed arrows indicate the competing processes.

after which it decayed with a time constant of 2.1 ± 0.2 μs , which is the lifetime of the Nd^{3+} luminescence [8].

As a reference compound, the $[(\text{Gd}_2\text{-Ru})\mathbf{1}]^{2+}$ complex allows the study of the antenna luminescence in the absence of energy transfer because Gd^{3+} has no energy levels below $32,000$ cm^{-1} and therefore cannot accept any energy from the antenna triplet state. As expected, the antenna luminescence intensity of $[(\text{Gd}_2\text{-Ru})\mathbf{1}]^{2+}$ is higher than the antenna luminescence intensity of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ due to the absence of energy transfer process (see Fig. 3). Also its antenna luminescence lifetime of 770 ± 20 ns (τ_{RuGd}) is longer than that of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$. Since the antenna luminescence lifetime of $[(\text{Gd}_2\text{-Ru})\mathbf{1}]^{2+}$ represents the $^3\text{MLCT}$ state lifetime in the absence of energy transfer, the energy transfer rate (k_{ET}) in the $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ complex can thus be calculated from $k_{\text{ET}} = 1/\tau_{\text{RuNd}} - 1/\tau_{\text{RuGd}}$ and is 1.1×10^6 s^{-1} .

Closer examination of the antenna luminescence properties of $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ revealed that the antenna luminescence intensity and lifetime of $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ are equal within the experimental error to the antenna luminescence intensity and lifetime of $[(\text{Gd}_2\text{-Ru})\mathbf{1}]^{2+}$. This indicates that the rate of the energy transfer process in $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ is at least an order of magnitude lower than 10^6 s^{-1} , which is the decay rate of the $^3\text{MLCT}$ level of the antenna. The rise-time of the Yb^{3+} luminescence at 980 nm could not be measured because the first few microseconds (after the laser pulse) of the time-resolved emission spectrum were dominated by the decay of the Ru-bpy antenna luminescence. This is not surprising since the emission spectrum shows that there is an appreciable amount of antenna luminescence at 980 nm (see Fig. 2). The luminescence decay of $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ at 980 nm could be fitted with a bi-exponential curve with lifetimes of 780 ± 20 ns (corresponding to the antenna luminescence) and 18.2 ± 0.8 μs (corresponding to the Yb^{3+} luminescence) [8].

Compared to the competing processes that deactivate the $^3\text{MLCT}$ state (see Fig. 3), the energy transfer rate is too slow in $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ ($\sim 10^6$ s^{-1}) and $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ ($\leq 10^5$ s^{-1}) for a complete energy transfer. The energy transfer process

from an antenna triplet to a lanthanide(III) ion is generally assumed to involve an electron-exchange mechanism [15] which requires a physical overlap between the 4f orbitals of the lanthanide ion and the HOMO and LUMO of the antenna. Although in this case the antenna LUMO is probably localized on the amide-functionalized bipyridine moiety³, which is the closest to the lanthanide ions (~ 5 \AA), the antenna HOMO is localized on the Ru^{II} center [16], which is further away from the lanthanide ions (>5 \AA). This results in a weaker electron-exchange interaction and thus a slow energy transfer rate. The energy transfer rate is further determined by the so-called spectral overlap of the antenna and the lanthanide ion, i.e. how well the donating and receiving energy levels match. Compared to $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$, the energy transfer rate in $[(\text{Yb}_2\text{-Ru})\mathbf{1}]^{2+}$ will be even slower because the antenna triplet state at $17,400$ cm^{-1} [17] matches the Nd^{3+} $^4\text{G}_{5/2}$ state at $17,100$ cm^{-1} , whereas the overlap with the only available Yb^{3+} energy level, which is the $^2\text{F}_{5/2}$ state at $10,240$ cm^{-1} , is much smaller.

Deoxygenated $[\text{D}_6]\text{DMSO}$ solutions of the ferrocene-functionalized (Nd)**2** and (Yb)**2** complexes (10^{-4} M) exhibit the typical line-like lanthanide emission upon excitation of the ferrocene antenna at 320 nm.⁴ At room temperature, sensitized emission at 1060 and 1330 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ transition, respectively) is observed for (Nd)**2** and at 980 nm ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition) for (Yb)**2** (see Fig. 4).

The excitation spectra of (Nd)**2** and (Yb)**2** (not shown) closely follow the absorption spectrum of the ferrocene antenna and confirm that the population of the lanthanide(III) excited state takes place via the antenna. Upon excitation at 337 nm, the lanthanide luminescence decay

³ Comparison of the antenna luminescence spectrum of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ with the standard $[\text{Ru}(\text{bpy})_3]^{2+}$ complex in DMSO shows that the emission maximum of $[(\text{Nd}_2\text{-Ru})\mathbf{1}]^{2+}$ has shifted to the red: from 634 to 666 nm. The amide groups stabilize the $^3\text{MLCT}$ state, and probably the excited electron is localized on the amide-functionalized bpy ligand.

⁴ Excitation in the weaker ferrocene absorption band at 440 nm ($\epsilon = 200$ M^{-1} cm^{-1}) also resulted in sensitized lanthanide luminescence.

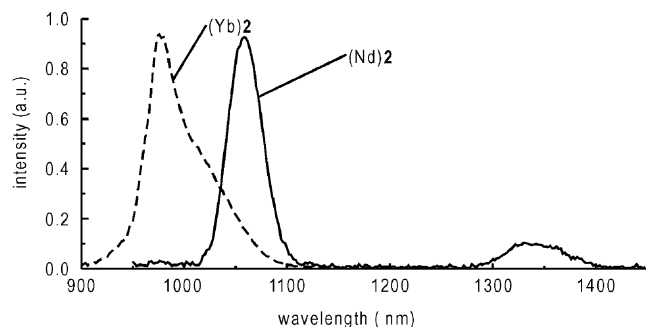


Fig. 4. Emission spectra of (Yb)2 and (Nd)2 in [D₆]DMSO (10⁻⁴ M) upon excitation at 320 nm.

curves could be fitted mono-exponentially with lifetimes of $2.0 \pm 0.2 \mu\text{s}$ for (Nd)2 and $18.8 \pm 0.8 \mu\text{s}$ for (Yb)2.

3. Conclusion

In conclusion, the transition metal complexes [Ru(bpy)₃]²⁺ and ferrocene are able to sensitize both Nd³⁺ and Yb³⁺. Moreover, these sensitizers enable excitation with visible light. The luminescent nature of the [Ru(bpy)₃]²⁺ ³MLCT state has allowed a direct study of the sensitization process. It has been established for the [(Nd₂-Ru)1]²⁺ complex that the energy transfer takes place in a 'classical way' via the antenna triplet state with a rate of $1.1 \times 10^6 \text{ s}^{-1}$. The sensitization process of [(Yb₂-Ru)1]²⁺ follows the same pathway although the energy transfer rate is lower ($\leq 10^5 \text{ s}^{-1}$).

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