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Transition Metal Complexes as Photosensitizers for Near-Infrared Lanthanide Luminescence**

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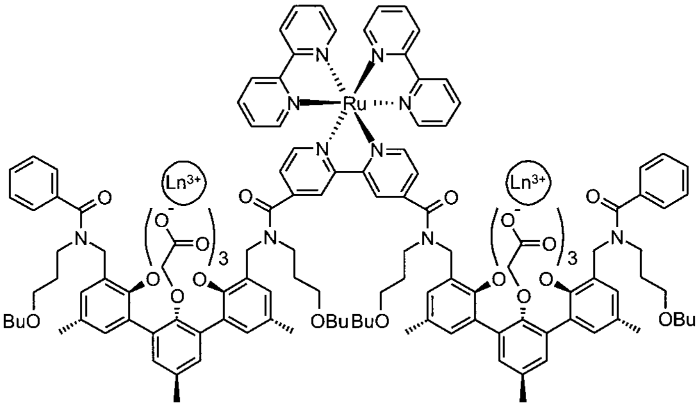
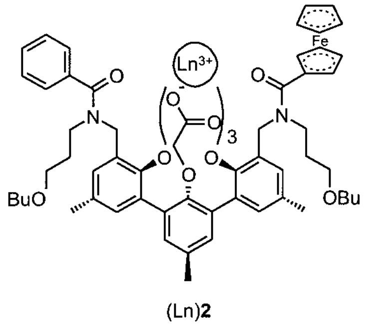
The design of sensitizer-functionalized lanthanide complexes that exhibit efficient luminescence in the near-infrared (NIR) region is currently of interest because of potential applications in fluoroimmuno-assays,[1] in laser systems,[2] and in polymer-based optical signal amplifiers.[3, 4] NIR luminescence of complexes of the lanthanide ions erbium(III), neodymium(III), and ytterbium(III) is readily observed in solution at room temperature, only when the ions are excited *indirectly* by energy transfer from the triplet state[5] of an incorporated organic chromophore (the antenna or 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 $1-10\,\mathrm{M^{-1}\,cm^{-1}}$) and the lifetimes of the excited states are relatively long (microseconds to milliseconds).

Herein, we report the first example of $\mathrm{Nd^{III}}$ and $\mathrm{Yb^{III}}$ luminescence sensitized by the transition metal complexes ruthenium(II) tris(bipyridine) ($[\mathrm{Ru(bpy)_3}]^{2+}$) and ferrocene. Investigations of sensitizers for NIR lanthanide luminescence have focused on conjugated organic molecules, nevertheless, there are only a few examples of sensitizers that enable visible light excitation instead of near-UV excitation.[1, 4, 6, 7] The $[\mathrm{Ru(bpy)_3}]^{2+}$ complex not only has an intersystem-crossing quantum yield near unity, but it should enable excitation of $\mathrm{Nd^{III}}$ and $\mathrm{Yb^{III}}$ with visible light of up to 500 nm. Compared to $[\mathrm{Ru(bpy)_3}]^{2+}$, ferrocene has weaker absorption bands in the visible region,[8] but its low-lying triplet state ($E_\mathrm{T} = 13\,300\,\mathrm{cm^{-1}}$)[9] closely matches the receiving luminescent states of $\mathrm{Nd^{III}}$ ($11\,300\,\mathrm{cm^{-1}}$) and $\mathrm{Yb^{III}}$ ($10\,250\,\mathrm{cm^{-1}}$).

Our systems $[(\mathrm{Ln_2\text{-}Ru})\mathbf{1}]^{2+}$ and $(\mathrm{Ln})\mathbf{2}$ are based on *m*-terphenyl-based lanthanide (Ln) complexes[10–12] that are covalently linked to the transition metal complexes. Experimental and physical data can be found in the Supporting Information.



$[(\mathrm{Ln_2\text{-}Ru})\mathbf{1}]^{2+}$



$(\mathrm{Ln})\mathbf{2}$

Excitation of the $[(\mathrm{Nd_2\text{-}Ru})\mathbf{1}]^{2+}$ and $[(\mathrm{Yb_2\text{-}Ru})\mathbf{1}]^{2+}$ complexes in deoxygenated [D$_6$]DMSO ($10^{-5}\,\mathrm{M}$) with visible light resulted in $\mathrm{Ln^{III}}$-centered NIR luminescence. Figure 1 shows the emission bands of $[(\mathrm{Nd_2\text{-}Ru})\mathbf{1}]^{2+}$ at 1060 and 1330 nm corresponding to the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4I_{13/2}$ transitions of $\mathrm{Nd^{III}}$, respectively, and the emission band of $[(\mathrm{Yb_2\text{-}Ru})\mathbf{1}]^{2+}$ at

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

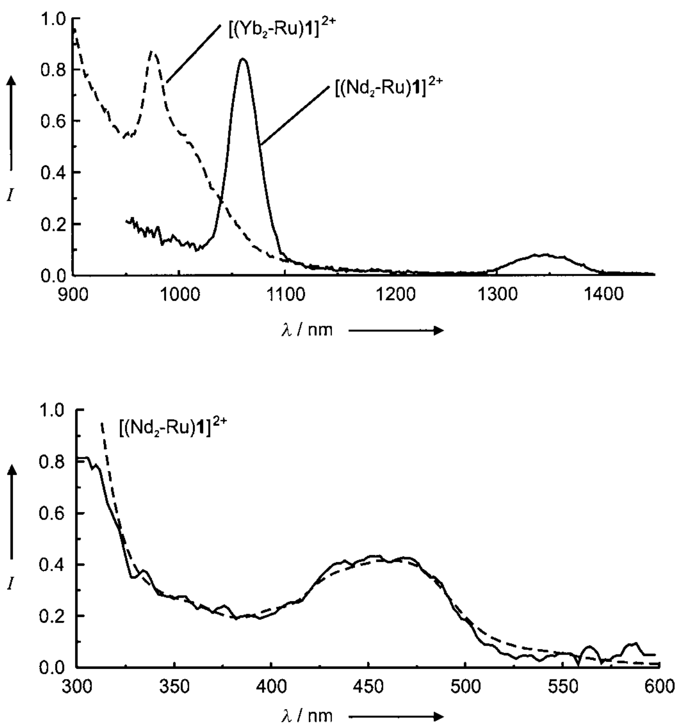

Figure 1. Top: the NIR luminescence spectrum of [(Nd$_2$-Ru)**1**]$^{2+}$ and [(Yb$_2$-Ru)**1**]$^{2+}$ in [D$_6$]DMSO (10^{-5} M) upon excitation at 450 nm. The spectra have been corrected for the absorbance of the samples. Bottom: the excitation spectrum of the Nd^{3+} luminescence of [(Nd$_2$-Ru)**1**]$^{2+}$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

975 nm corresponding to the $^4F_{5/2} \rightarrow {}^4F_{7/2}$ transition of Yb^{III}. The 1060 nm band of [(Nd$_2$-Ru)**1**]$^{2+}$ and the 975 nm band of [(Yb$_2$-Ru)**1**]$^{2+}$ are superimposed on the tail of the weak Ru(bpy)-antenna luminescence. The sensitized Yb^{III} luminescence of [(Yb$_2$-Ru)**1**]$^{2+}$ is less than the sensitized Nd^{III} luminescence of [(Nd$_2$-Ru)**1**]$^{2+}$. The excitation spectra closely resemble the absorption spectrum of the Ru(bpy) antenna, this obsevration clearly shows that the Ln^{III} ions are excited by the ^{1}MLCT (metal-to-ligand charge transfer) state of the Ru(bpy) antenna. The excitation and absorption spectra of [(Nd$_2$-Ru)**1**]$^{2+}$ are shown in Figure 1. The [(Yb$_2$-Ru)**1**]$^{2+}$ complex has identical excitation and absorption spectra.

Time-resolved luminescence measurements of the antenna and Nd^{III} demonstrated that the pathway of the sensitized emission indeed involves the ^{3}MLCT state of the antenna. During the time that the energy transfer from the antenna triplet state to the lanthanide ion is in progress, the lanthanide luminescence intensity is expected to rise with a rate equal to the decay rate of antenna triplet state. Upon excitation of [(Nd$_2$-Ru)**1**]$^{2+}$, antenna luminescence was observed at 660 nm originating from the ^{3}MLCT state and decayed with a time-constant of 420 ± 10 ns. At the same time, the Nd^{III} emission at 1060 nm rose with the same time-constant of 420 ± 20 ns, after which it decayed with a time-constant of 2.1 ± 0.2 s, which is the lifetime of the Nd^{III} luminescence.[11]

As a reference compound, the [(Gd$_2$-Ru)**1**]$^{2+}$ complex allows the study of the antenna luminescence in the absence of energy transfer, because Gd^{III} 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 [(Nd$_2$-Ru)**1**] is less than the antenna luminescence intensity of [(Gd$_2$-Ru)**1**]$^{2+}$ (Figure 2). Also the antenna luminescence lifetime of [(Nd$_2$-Ru)**1**]$^{2+}$ is shorter than the 770 ± 20 ns of [(Gd$_2$-Ru)**1**]$^{2+}$. Since the antenna luminescence lifetime of [(Gd$_2$-Ru)**1**]$^{2+}$ represents the ^{3}MLCT-state lifetime in the absence of energy transfer, the energy transfer rate (k_{ET}) in the [(Nd$_2$-Ru)**1**]$^{2+}$ complex can thus be calculated from $k_{\mathrm{ET}} = 1/\tau_{\mathrm{RuNd}} - 1/\tau_{\mathrm{RuGd}} = 1.1 \times 10^6\,\mathrm{s}^{-1}$, where τ = luminescence lifetime.

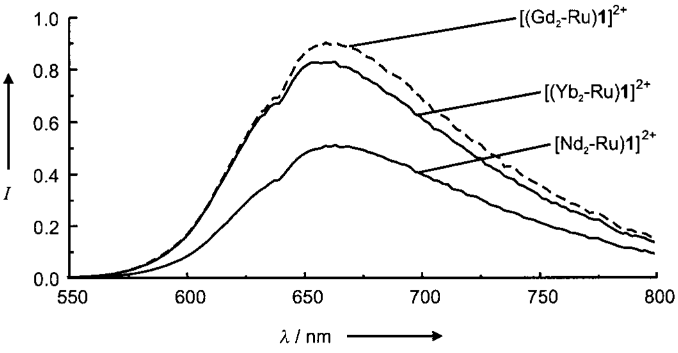

Figure 2. Emission spectra of the Ru(bpy)-centered luminescence of [(Gd$_2$-Ru)**1**]$^{2+}$, [(Yb$_2$-Ru)**1**]$^{2+}$, and [(Nd$_2$-Ru)**1**]$^{2+}$ in [D$_6$]DMSO (10^{-5} M) upon excitation at 450 nm. The spectra have been corrected for the absorbance of the samples.

Closer examination of the antenna luminescence properties of [(Yb$_2$-Ru)**1**]$^{2+}$ revealed that the antenna luminescence intensity (see Figure 2) and lifetime of [(Yb$_2$-Ru)**1**]$^{2+}$ are equal, within the experimental error, to the antenna luminescence intensity and lifetime of [(Gd$_2$-Ru)**1**]$^{2+}$. This indicates that the rate of the energy transfer process in [(Yb$_2$-Ru)**1**]$^{2+}$ is at least an order of magnitude lower than $10^6\,\mathrm{s}^{-1}$, the decay rate of the ^{3}MLCT level of the antenna. The rise-time of the Yb^{III} luminescence at 980 nm could not be measured because the first microseconds (after the laser pulse) of the time-resolved emission spectrum are 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 Figure 1). The luminescence decay of [(Yb$_2$-Ru)**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^{III} luminescence).[11]

In light of the competing antenna processes the energy transfer rates in [(Nd$_2$-Ru)**1**]$^{2+}$ ($\sim 10^6\,\mathrm{s}^{-1}$) and [(Yb$_2$-Ru)**1**]$^{2+}$ ($\leq 10^5\,\mathrm{s}^{-1}$) are too low for a complete energy transfer. The energy transfer process is most likely to involve an electron-exchange mechanism[13] that requires a physical overlap between the 4f orbitals of the lanthanide ion and the ground state HOMO and LUMO of the antenna. Although the antenna ground state LUMO is probably localized on the amide-functionalized bpy moiety,[14] which is closest to the lanthanide ions (separation ~5 Å), the antenna ground state HOMO is localized on the Ru^{II} center,[15] which is further away from the lanthanide ions (>5 Å). 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, that is, how well the donating and receiving energy levels match. The energy-transfer rate in $[(Yb_2\text{-}Ru)\mathbf{1}]^{2+}$ will be even slower than in $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$, because the antenna triplet state ($E_T = 17\,400\ cm^{-1}$)[16] matches the $Nd^{III}\ {}^4G_{5/2}$ state at $17\,100\ cm^{-1}$, whereas the overlap with the only Yb^{III} energy level, the ${}^2F_{5/2}$ state which is at $10\,240\ cm^{-1}$, is much smaller.

Deoxygenated $[D_6]$DMSO solutions of the ferrocene-functionalized (Nd)**2** and (Yb)**2** complexes (10^{-4} M) exhibit the typical linelike lanthanide emission upon excitation of the ferrocene antenna at 320 nm.[17] At room temperature, sensitized emission at 1060 and 1330 nm (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, and ${}^4I_{13/2}$ transitions, respectively) is observed for (Nd)**2**, and at 980 nm (${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) for (Yb)**2** (see Figure 3). The excitation spectra of (Nd)**2** and (Yb)**2** (not shown), closely follow the absorption spectrum of the ferrocene antenna and confirm unambiguously that excitation takes place through the antenna. Upon excitation at 337 nm the lanthanide luminescence decay curves could be fitted mono-exponentially with lifetimes of 2.0 ± 0.2 μs for (Nd)**2** and 18.8 ± 0.8 μs for (Yb)**2**.

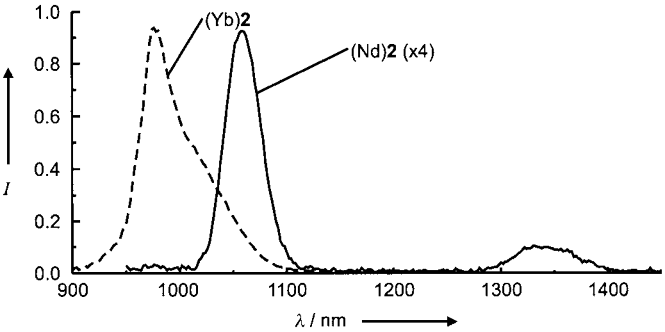

Figure 3. Emission spectra of (Yb)**2** and (Nd)**2** in $[D_6]$DMSO (10^{-4} M) upon excitation at 320 nm. The spectra have been corrected for the absorbance of the samples.

In conclusion, the transition metal complexes $[Ru(bpy)_3]^{2+}$ and ferrocene are able to sensitize both Nd^{III} and Yb^{III}. Moreover, these sensitizers enable excitation with visible light. The luminescent nature of the $[Ru(bpy)_3]^{2+}$ ^{3}MLCT state has allowed a direct study of the sensitization process. It has been established for the $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ complex that the energy transfer takes place in a "classical way" through the antenna triplet state with a rate of $1.1 \times 10^6\ s^{-1}$. The sensitization process of $[(Yb_2\text{-}Ru)\mathbf{1}]^{2+}$ follows the same pathway, although the energy transfer rate is lower ($\leq 10^5\ s^{-1}$).

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[14] Comparison of the antenna luminescence spectrum of $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ with the standard $[Ru(bpy)_3]^{2+}$ complex in DMSO shows that the emission maximum of $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ has shifted to the red: from 634 nm to 666 nm. The amide groups stabilize the ^{3}MLCT state, and probably the excited electron is localized on the amide-functionalized bpy ligand.

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

A Novel Iron-Based Catalyst for the Biphasic Oxidation of Benzene to Phenol with Hydrogen Peroxide

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Direct oxidation of benzene to phenol is an important reaction in organic chemistry. Often, however, its selectivity is rather poor since phenol is more reactive toward oxidation than benzene itself, and substantial formation of over-oxygenated by-products (catechol, hydroquinone, benzoquinones, and tars) also occurs.[1]

Similar over-oxidation problems are efficiently solved in biological systems by segregating catalysts and products into

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