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Near-Infrared Luminescence of Yb^{3+}, Nd^{3+}, and Er^{3+} Azatriphenylene Complexes

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Abstract

Near-infrared luminescent ytterbium(III), neodymium(III), and erbium(III) complexes containing novel organic chromophores derived from azatriphenylene have been prepared and spectroscopically studied. The complexes can be excited from 350 to 450 nm, leading after intramolecular energy transfer to intense lanthanide luminescence in acetonitrile. Quenching of the luminescence of the complexes by molecular oxygen reveals information on the rate of energy transfer from the "antenna" to the lanthanide ion.

Keywords: Aza compounds; lanthanides; luminescence

Introduction

Whereas the luminescence characteristics of Eu^{3+} and Tb^{3+} are widely studied, the NIR (Near Infrared) emitting lanthanide ions like Er^{3+}, Nd^{3+}, and Yb^{3+} are relatively unexplored. The ability of Er^{3+}, Nd^{3+}, and Yb^{3+} to emit in the near-IR (beyond 800 nm) makes them of interest for diagnostic or tagging applications.[1,2] Although the luminescent lifetimes of NIR lanthanide ions are short (0.5-20 μs in solution) compared to the rare earth ions which emit in the visible part of the spectrum, these lanthanide ions have several advantages. The near infrared emission bands offer good penetration into scattering media such as biological systems and the characteristic emission bands of Nd^{3+} and Yb^{3+} are in the 850-1100 nm range, which allows sensitive detection with Si-based detectors. Moreover, their emissive state is lower compared to the lanthanide ions Eu^{3+} and Tb^{3+} and also to Dy^{3+} and Sm^{3+}. Therefore it can be accomplished by excitation in the near-infrared region, or by energy transfer from an aromatic chromophore which absorbs in the visible part of the spectrum. Only a few examples of these chromophores are known, namely, triphenylmethane-derived indicators (e.g. xylenol orange),[3] porphyrins,[4] and fluorescein or eosin derivatives incorporated in diethylenetriaminepentaacetic acid.[5]

Very recently, we reported that diaza-[6] and tetraazatriphenylenes[7] combine complexation strength and an extremely efficient energy transfer ability to the lanthanide ions Eu^{3+}, Tb^{3+} (Dy^{3+} and Sm^{3+}). In this communication we describe that diaza- and tetraazatriphenylenes are also very promising antenna chromophores for the NIR emitting lanthanide ions Er^{3+}, Nd^{3+}, and Yb^{3+}.

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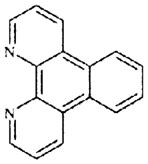
Results and Discussion

All azatriphenylene-lanthanide complexes were prepared by adding a known amount of lanthanide salt to the sensitizer (**1**, **2**, **3**, and **4**) in acetonitrile. In these experiments the molar ratio sensitizer/lanthanide ion of 2/1 was obtained as was evident from titration experiments with sensitizers **1-3**. For sensitizer **4** the maximum signal for sensitized Yb luminescence was obtained for the molar ratio sensitizer/lanthanide ion of 1/1. The results obtained for sensitizers **1-3** are in accordance with experiments performed with diaza- and tetraaza-triphenylenes.[6,7] Evidence for sensitized emission came from luminescence experiments in which the sensitizer is directly excited in one of its absorption bands (e.g. at about 335 and 280 nm for diaazatriphenylene **1**, 375, 360, 320 or 280 nm for tetraazatriphenylenes **2** and **3**, and 450, 411, 390, 370, and 325 nm for tetraazatriphenylene **4**) after which the typical lanthanide emission is observed. From these experiments it is clear that in all cases the NIR luminescent lanthanide ions show sensitized luminescence. For Nd^{3+} emission at about 880, 1070, and 1340 nm is observed, for Yb^{3+} at about 980 nm, and for Er^{3+} at about 1540 nm. Moreover, the excitation spectra show features which correspond to the absorption spectra of the azatriphenylenes. Emission spectra for the Yb^{3+}, Nd^{3+}, and Er^{3+} complexes with tetraazatriphenylene **2** and the excitation spectra of the Yb^{3+} complexes of **2**, **3**, and **4** are shown in Figures 1 and 2, respectively. It is evident from Figure 2 that upon going from azatriphenylene **2** to **3** and **4** the longest wavelength of absorption shifts to higher values. This indicates a gradual lowering of the energy of the lowest excited singlet state of the azatriphenylenes, and a concomitant shift of the lowest excited triplet state, as exemplified in Table 1. Moreover, the absorption spectra of the azatriphenylenes do not change significantly upon complexation.

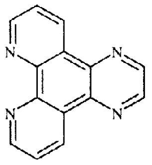
Table 1. Photophysical Data of the Azatriphenylenes **1-4** in Acetonitrile.

Compound	$^3E_{00}$ (cm^{-1}) (nm)	$^1E_{00}$ (cm^{-1}) (nm)
1	23800 (420)	29400 (340)
2	23600 (424)	29400 (340)
3	~18500 (542)	26500 (377)
4	*a*	20400 (490)

[a] This value cannot be determined but it is much lower than that of compound **3**.



1



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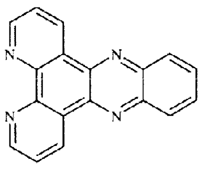

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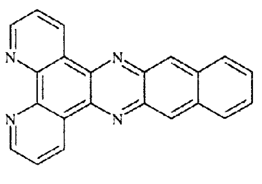

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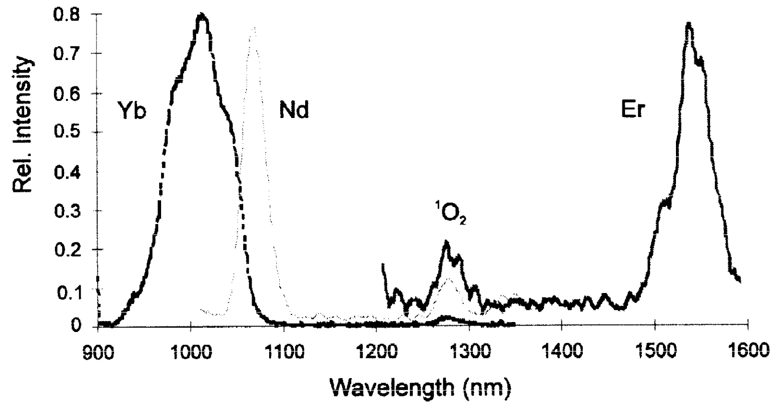

Figure 1. Normalized Emission Spectra of Yb^{3+}, Nd^{3+}, and Er^{3+} upon Ligand Excitation of **2** in Acetonitrile.

Although no quantum efficiency could be determined for the NIR lanthanide ions due to the lack of a suitable reference compound with known efficiency[8] (e.g. quinine bisulfate for Eu^{3+}), an estimation of the efficiency of energy transfer has been made by studying the effect of deaeration on the luminescence intensity. Oxygen competes with the excited state of the sensitizer. Energy transfer from sensitizer to oxygen results in the formation of singlet oxygen which is visible as an emission at 1275 nm. In particular, the luminescence emission spectra of the Er^{3+} and Nd^{3+} complexes show the signal of singlet oxygen which was significantly reduced upon deaeration.

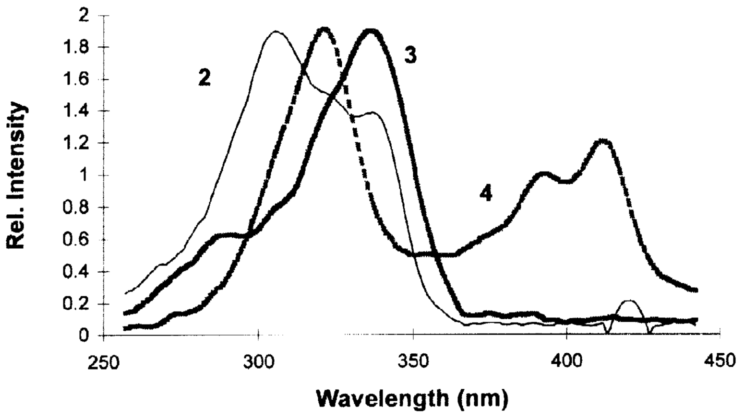

Figure 2. Normalized Excitation Spectrum of Yb^{3+} with **2**, **3**, and **4**; λ_{em} = 980 nm in Acetonitrile.

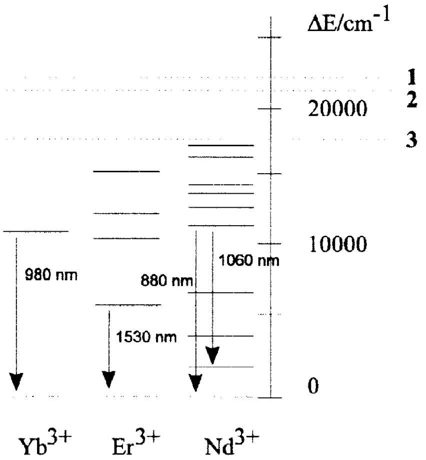

Figure 3. Energy Level Diagram of the Lanthanide Ions and the Triplet Levels of the Azatriphenylenes.

Moreover, at the same time the intensity of the lanthanide luminescence increased. It is noteworthy that with the Eu^{3+} and Tb^{3+} complexes no oxygen quenching was observed. Obviously, the energy gap between the emitting levels and the sensitizing donor states is much larger for the NIR emitting ions so that less efficient energy transfer may be anticipated. Hence, when a lanthanide ion is complexed by the sensitizer, the formation of singlet oxygen is reduced compared to the free sensitizer but still a substantial signal at 1275 nm is present. In order to reduce the energy gap, the annellated tetraazatriphenylene derivative **4** [mp 295-297 °C; ^{1}H NMR (TFA) δ 10.40 (d, 2 H, J = 8.4 Hz), 9.65 (d, 2 H, J = 4.2 Hz), 9.62 (s, 2 H), 8.8-8.5 (m, 4 H), 8.3-8.1 (m, 2 H)] was synthesized in 84% yield by condensation of 2,3-diaminonaphthalene and 1,10-phenanthroline-5,6-quinone in refluxing ethanol.

Initial results show that energy transfer occurs from **4** to Nd^{3+}, Er^{3+}, and Yb^{3+} with excitation wavelengths extending beyond 450 nm. The influence of oxygen is strongly reduced as compared to the other sensitizers, which indicates a faster energy transfer in the complex with sensitizer **4**.

Table 2. Photophysical Data of Azatriphenylene-based Yb^{3+}, Nd^{3+}, and Er^{3+} Complexes in Acetonitrile.[a]

Compound	$\tau^{Yb,ox}$ (μs)	$\tau^{Yb,deox}$ (μs)	$\tau^{Nd,ox}$ (μs)	$\tau^{Nd,deox}$ (μs)	$\tau^{Er,ox}$ (μs)	$\tau^{Er,deox}$ (μs)
1	7.4	nd	0.4	nd	1.7	nd
2	6.2	nd	0.3	nd	2.0	nd
3	10.6	8.5	0.7	0.3	2.6	2.3
4	7.9	7.8	0.3	0.3	2.5	2.6

[a] $\tau^{(de)ox}$ (μs) = luminescence lifetime of the rare-earth ion luminescence in (de)oxygenated solution; the error is 0.05-0.1 μs; nd = not determined.

In Table 2 luminescence lifetimes of the Yb^{3+} , Nd^{3+}, and Er^{3+} complexes with the antenna chromophores **1**, **2**, **3**, and **4** are listed. All the measured luminescent lifetimes do not display a significant change upon deoxygenation and have typical lifetimes of the luminescent NIR lanthanide ions in solution as reported in the literature.[1]

Concluding Remarks

In conclusion, the azatriphenylenes **1**, **2**, **3**, and **4** give energy transfer to the NIR luminescent lanthanide ions Nd^{3+}, Er^{3+}, and Yb^{3+} (for an energy diagram see Figure 3), allowing excitation in the visible part of the electromagnetic spectrum. It has been demonstrated that the structure of azatriphenylenes can be adapted to allow fine-tuning of the triplet state of the sensitizer compared to the luminescent level of the near-infrared luminescent lanthanide ions. The energy transfer to these NIR emitting lanthanide ions occurs approximately on the same time scale as oxygen quenching, and consequently less efficiently than in the case of the Eu^{3+} and Tb^{3+} ions. The energy gap between the triplet state of the sensitizer and the luminescent level of the lanthanide ions is probably still too large for fast energy transfer. Another explanation for the observed Yb^{3+} NIR luminescence is a recently proposed electron transfer mechanism from sensitizer to lanthanide ion.[9] However, in the present work we found no evidence for this mechanism, since the data obtained for the three lanthanides studied show the same trends and the reduction potentials for both Nd^{3+} and Er^{3+} are much lower than that of Yb^{3+}, precluding effective electron transfer in the latter ions. Moreover, the oxidation potentials of the azatriphenylenes are very high; with cyclic voltammetry it proved impossible to measure oxidation potentials for solutions of diazatriphenylene **1** and tetraazatriphenylenes **2-4** in acetonitrile up to 2.5 V (relative to SCE).

Further investigations include the preparation of azatriphenylenes which have a lower triplet energy or a suitable oxidation potential for more efficient energy transfer to the near-IR lanthanide ions. The synthesis route for the tetraazatriphenylenes (e.g. **2**, **3**, and **4**) allows simple modifications to afford derivatives with more efficient energy transfer properties.

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