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Diazatriphenylene complexes of Eu^{3+} and Tb^{3+}; promising light-converting systems with high luminescence quantum yields

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Abstract

Diazatriphenylene (**1**) displays the unique property that it sensitizes the long lived luminescence of both Tb^{3+} and Eu^{3+} with high efficiency (quantum yields of 0.55 and 0.41, respectively) while allowing near UV excitation (<340 nm), which makes the lanthanide complexes of **1** very suitable for time-resolved multi-probe detection.

Keywords: Diazatriphenylene; Luminescence; UV

1. Introduction

Molecular systems that combine binding ability and useful photophysical properties are of great interest for designing lanthanide luminescence probes [1–6]. In various applications, such as time-resolved fluorometry and optical amplification [7–10], the disadvantage of the low extinction coefficient of lanthanide ions can be overcome by an absorption-energy transfer process via a sensitizer ('antenna') moiety [11]. An important challenge in this field is to optimize the sensitizer enabling to excite via the same antenna different lanthanide ions with high efficiencies, allowing multi-probe analysis. Furthermore, the sensitizer should have an absorption in the near UV–Vis region to allow the application of glass optics in conjunction with standard excitation. Particularly the combination of Tb^{3+} and Eu^{3+} is very attractive because of the high intrinsic quantum yield and its relatively low susceptibility to non-radiative quenching effects of these ions, with Tb^{3+} being the most efficient emitter [12]. However, for the sensibilization of Tb^{3+} an antenna with a higher triplet energy than for Eu^{3+}, and thus an even higher singlet energy is required [13] which severely restrains the upper limit of the excitation wavelength of suitable sensitizers. In practice this means that only a small excitation window for the sensibilization of Tb^{3+} (ca. 330–350 nm) is allowed. Takalo et al. recently reported [14] that several bis-pyridine and bis-pyrazole tetraacids which absorb in this region are able to sensitize Tb^{3+} luminescence with an appreciable quantum yield (0.58), but regrettably the luminescence quantum yield for Eu^{3+} is quite low with these systems (0.03) as a result of competing dark processes (e.g., electron transfer).

Recently, we have reported that the triphenylene antenna is a good sensitizer for both Eu^{3+} and Tb^{3+} when they are encapsulated in calix[4]arene receptors carrying such an antenna [13]. Triphenylene derives these properties from the fact that its triplet state is generated with high efficiency ($\Phi_{ISC} = 0.89$), together with a long lifetime, and in particular because the energy gap separating its first excited singlet and triplet states ($\Delta E = 6500$ cm^{-1}) is unusually small for an aromatic species.[2] In spite of these useful properties the triphenylene antenna has severe disadvantages. Firstly, the molar extinction of its longest wavelength absorption band is quite low as for many aromatic hydrocarbons. Secondly, the triphenylene moiety itself is devoid of any significant complexing ability towards lanthanide ions. Therefore we concluded that introduction of hetero atoms in the triphenylene skeleton might eliminate both of these disadvantages while

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[2] These properties imply that relatively long wavelength excitation followed by intersystem crossing leads to a sensitizing triplet state of sufficiently high energy (23 400 cm^{-1}) for energy transfer to the luminescent state of Eu^{3+} (17 500 cm^{-1}) and even that of Tb^{3+} (20 400 cm^{-1}) in an essentially irreversible energy transfer step.

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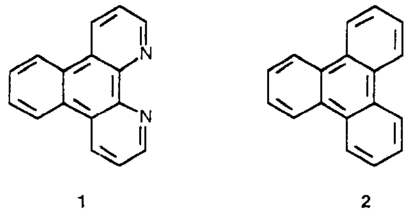

Scheme 1. Diazatriphenylene (**1**) and triphenylene (**2**).

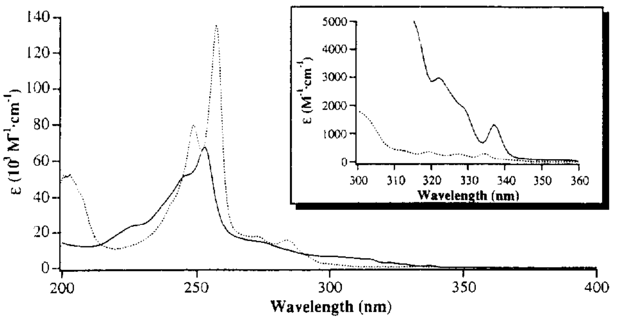

Fig. 1. Absorption spectra of **1** (—) and **2** (···) in acetonitrile.

preserving the excellent photophysical properties outlined above.

In this communication we present the first successful implementation of this approach towards realization of a new and efficient class of sensitizers with strong complexing power for lanthanides as found in the diazatriphenylene system (Scheme 1). In this system we combine the superior photophysical properties of the triphenylene structure with the strong complexing ability of two nitrogen atoms as exploited before by Lehn [15] in their 2,2′-bipyridine type sensitizers or extended to three nitrogens in terpyridine antennas by Mukkala et al. [16].

2. Experimental details

Continuous emission and excitation spectra were recorded on a Spex Fluorolog 2 spectrofluorometer. Time resolved emission spectra were obtained using a Lumonics EX700 XeCl excimer laser (308 nm) as excitation source. The resulting luminescence was observed by a gated, intensified CCD camera from Princeton Instruments. Spectra were taken with a typical gatewidth of 25 μs, an initial delay of about 0.5 μs relative to the laser pulse maximum and 50 μs increment delay between spectra. At each delay, spectra were averaged over 50 laser shots to improve the signal to noise ratio. From these data luminescent lifetimes were calculated by fitting the wavelength integrated signal in time. Monoexponential decay was observed in all cases. Deoxygenation of the samples was performed by bubbling argon through the solutions for 5 min (excitation emission spectra) or by several freeze–pump–thaw cycles (phosphorescence spectrum). $Eu(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 5H_2O$, $DyCl_3 \cdot 5H_2O$, and $SmCl_3 \cdot 5H_2O$ were purchased from Aldrich.

3. Results and discussion

Incorporation of nitrogen atoms in a *cis* chelating manner as in diazatriphenylene (**1**) (Scheme 1) was achieved via a Skraup reaction of 2,3-diaminonaphthalene with acrolein according to a literature procedure [17]. The absorption spectra of **1** and the parent system triphenylene (**2**) are shown in Fig. 1.

As expected the spectrum of **1** is only marginally red shifted with respect to **2** ($^1E_{00}$ = 29 700 and 29 900 cm^{-1}, respectively), but strongly enhanced in intensity. Furthermore, for **1** no significant fluorescence could be detected, which indicates that its $S_1 \rightarrow T_1$ intersystem crossing efficiency is near unity. Indeed **1** was found to display a strong and structured phosphorescence at low temperature (77 K, in methanol/ethanol 4:1 glass) from which a triplet energy of 23 800 cm^{-1} was determined, which proves that in **1** the small singlet–triplet separation of ca. 6000 cm^{-1} typical for triphenylene, is maintained. While **1** is thus non-luminescent in solution, addition of lanthanide ions leads to strongly luminescent complexes with a spectral distribution typical for the lanthanide ion used.

Titration experiments of a 1.8×10^{-5} M solution of diazatriphenylene (**1**) with the lanthanide salts [$Eu(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 5H_2O$, $DyCl_3 \cdot 5H_2O$, and $SmCl_3 \cdot 5H_2O$] in acetonitrile show the formation of luminescent 2:1 complexes (Fig. 2). This complex stoichiometry

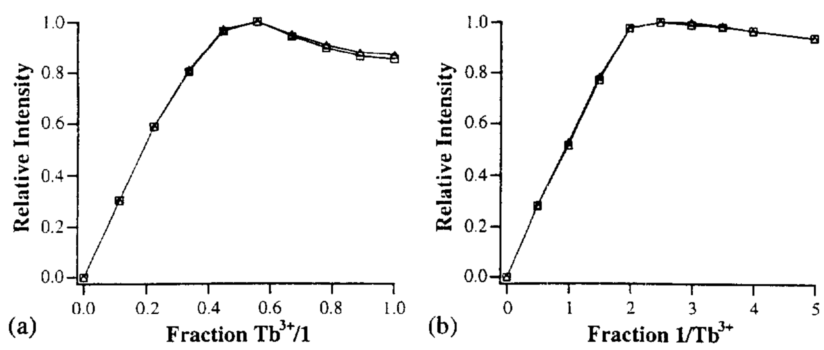

Fig. 2. Relative lanthanide luminescence intensity with increasing concentrations of Tb^{3+} relative to **1** (a) and **1** relative to Tb^{3+} (b) in acetonitrile solution; λ_{ex} = 334 nm, λ_{obs} = 530–565 nm (Δ) and 569–606 nm (□).

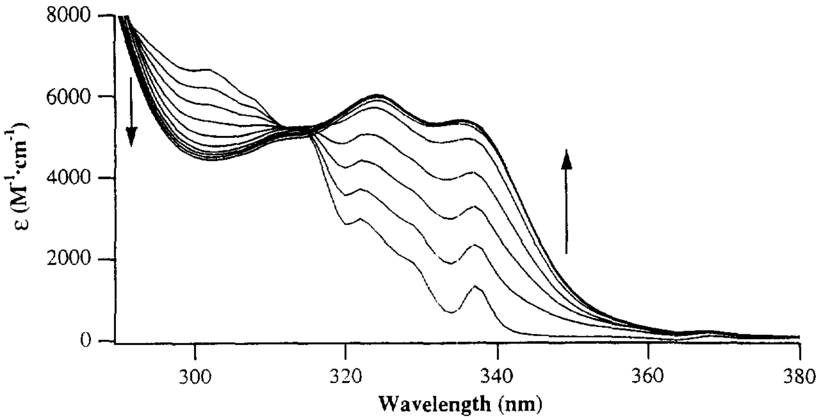

Fig. 3. Absorption spectra of **1** with increasing amounts of Tb^{3+} (Tb^{3+}:**1** molar ratio increasing from zero in the bottom spectrum to one in nine equal steps).

is analogous to that found for complexes of lanthanides with 1,10-phenanthroline [18–20]. The latter presents a very similar orientation of the chelating nitrogen atoms, but has a much lower triplet energy (S_1–T_1 separation ca. 7400 cm^{-1}) which impedes its sensitizing ability especially with respect to Tb^{3+}. The structure of the complexes that these planar diaza-ligands (Lig) form with trivalent lanthanides can be represented as $Lig_2LnX_3(H_2O)_n$, where n varies between zero and two depending on the solvent composition and the anion (X).

It is noteworthy that there is a four-fold increase in the extinction coefficient of the 0–0 transition of the diazatriphenylene moiety compared to the free ligand upon complexation with lanthanide ions to **1** (Fig. 3). This might be related to the fact that the sensitizer is in a less symmetric environment than when it is free in solution, enhancing the probability of the S_0–S_1 transition.[3] The excitation spectra of the complexes are identical to their absorption spectra.

The luminescence quantum yields of the 2:1 sensitizer:lanthanide complexes were determined in aerated acetonitrile solution (λ_{ex} = 334 nm) with the method of Haas and Stein [21]. Exceptionally high values for both the Eu^{3+} and the Tb^{3+} complexes, of 0.41 and 0.55, respectively, were observed in combination with long lifetimes (τ = 1.20 and 1.31 ms, respectively). Clearly the energy transfer from the sensitizer to the lanthanide ion is very efficient. Moreover, the luminescence lifetimes and the quantum yields are not influenced by oxygen, indicating that the energy transfer from the sensitizer to the lanthanide ion takes place sufficiently rapid to prevent quenching of the sensitizer triplet by oxygen.[4] It is interesting that the luminescence lifetime of the Tb^{3+} complex is only little longer than that of the Eu^{3+} complex. This may be due to the presence of one or two (see above) water molecules in the coordination sphere of the former complex, which leaves room for improvement of its quantum yield beyond the now already impressive 55%!

As already mentioned above the absorption spectra of **1** and its lanthanide complexes are strongly enhanced and slightly red-shifted as compared to that of triphenylene (**2**). Interestingly, the longest wavelength maximum (λ = 337 nm) with an extinction coefficient of ε = 5500 M^{-1} cm^{-1} in the 2:1 complexes of **1** allows application in conjunction with glass optics and the use of convenient excitation sources.

4. Conclusions

In conclusion, diazatriphenylene is able to sensitize both Tb^{3+} and Eu^{3+} with extremely high efficiencies (quantum yields of 0.55 and 0.41, respectively) with luminescent lifetimes in the ms range. Moreover, the diazatriphenylene/Eu^{3+} combination is not subject to the detrimental dark processes (probably electron transfer) that plague other efficient sensitizers of Tb^{3+} [14]. These properties, together with the suitable excitation window and the appreciable molar absorptivity coefficient of the sensitizer at λ > 330 nm, makes diazatriphenylene very promising for incorporation in lanthanide probes that can be used in time-resolved fluorometry including multi-color labelling approaches. Currently, the covalent incorporation of this type of sensitizer in lanthanide receptors suitable for application in aqueous solution and derivatized to allow conjugation with (bio)macromolecules is under investigation.

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[3] This effect is as pronounced for Eu^{3+} as for Tb^{3+} showing that this is not due to a LMCT transition.

[4] The quantum yields of the Sm^{3+} and Dy^{3+} complexes, 0.01 and 0.002, respectively, are similar to literature values and are inherently limited by the intrinsic quantum yields and shorter decay times of these ions [22].

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