Tetraazatriphenylenes as Extremely Efficient Antenna Chromophores for Luminescent Lanthanide Ions**

Erik B. van der Tol, Hendrik J. van Ramesdonk, Jan W. Verhoeven,* Frank J. Steemers, Esther G. Kerver, Willem Verboom, and David N. Reinhoudt*

Abstract: A series of tetraazatriphenylene derivatives is presented that constitutes a new and efficient class of sensitisers with significant complexing power for lanthanide ions. These tetraazatriphenylenes have the ability to sensitise the luminescence of different lanthanide ions simultaneously within a practically suitable excitation window, and the 2:1 (ligand–ion) complexes are stable even at low concentrations in acetonitrile. The very high luminescence quantum yields obtained for both Eu^{3+} and Tb^{3+} (up to 0.41 and 0.67, respectively) in combination with the suitable excitation window and the appreciable molar extinction coefficient of tetraazatriphenylenes at $\lambda > 330$ nm make these sensitisers very attractive for incorporation as antenna chromophores in luminescent lanthanide probes (e.g. for time-resolved fluorometry).

Keywords: energy transfer · lanthanides · luminescence · sensitizers · time-resolved fluorometry

Introduction

The important role of lanthanide complexes as luminescent labels in bioaffinity assays is related to their unique luminescence characteristics, such as long luminescent lifetimes, large Stokes shifts and line-like emission of the lanthanide ions.[1] Particularly long-lived lanthanide luminescence probes are of considerable interest as alternatives for radioimmuno assay probes. Besides certain requirements to be fulfilled by the lanthanide complexes for practical purposes, for example, strong complexation with high thermodynamic and kinetic stability in water, an important aspect which determines the sensitivity of the probe is the sensitiser (antenna) unit. The sensitiser should allow excitation in the near UV/Vis region to overcome the low extinction coefficients of the lanthanide ions.[2] In order to ensure fast energy transfer a short distance between sensitiser and lanthanide ion is obviously desirable. Direct coordination of the antenna chromophore to the lanthanide ion has been mainly exploited with β-diketonate ligands[3] and aza-aromatics.[4] Concerning the latter, Lehn et al.[5] employed cryptates in which bipyridine or biquinoline (the antenna) is incorporated in the macrocyclic structure. Hemmilä et al.[6] investigated terpyridine structures and picolinic acid derivatives[7] in which the coordinating pyridine moiety serves as a sensitiser, giving high quantum yields for Eu^{3+} and Tb^{3+}.[8]

Recently, we showed[9] that the triphenylene antenna is a good sensitiser for both Eu^{3+} and Tb^{3+} when they are encapsulated in calix[4]arene receptors.[9, 10] Triphenylene derives these properties from the fact that its triplet state is generated with high efficiency ($\Phi_{ISC} = 0.89$),[11] together with a long lifetime, and, in particular, because the energy gap separating its first excited singlet and triplet states ($^1E_{00} = 29\,900\ cm^{-1}$, $^3E_{00} = 23\,400\ cm^{-1}$, and thus $\Delta E = 6500\ cm^{-1}$)[11] is unusually small for an aromatic species. These properties imply that relatively long wavelength excitation followed by intersystem crossing leads to a sensitising triplet state of sufficiently high energy 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. However, the triphenylene antenna has some disadvantages. Firstly, the molar extinction of its longest wavelength absorption band is, as for many aromatic hydrocarbons, quite low, because this 0–0 transition is in principle forbidden. Secondly, the triphenylene moiety itself is devoid of any significant affinity towards

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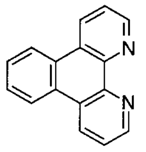
lanthanide ions, which implies, for example, that in the triphenylene-substituted calix[4]arenes we reported earlier[9] the average distance between the encapsulated lanthanide and the triphenylene antenna is too large for complete energy transfer. It is expected that introduction of heteroatoms (e.g., nitrogen) in the triphenylene skeleton might eliminate both of these disadvantages while preserving the excellent photophysical properties outlined above. The 0–0 transition is made more probable by a decrease in the symmetry of the molecule, while arranging the heteroatoms in a *cis* chelating manner is expected to allow the complexation of the lanthanide ion. Recently, we successfully applied this approach in the form of 1,12-diazatriphenylene (**1**), sensitising the long-lived luminescence of both Tb^{3+} and Eu^{3+} with high efficiencies (quantum yields of 0.55 and 0.41, respectively), while allowing near-UV excitation (< 340 nm), which makes it very suitable for time-resolved multi-probe analysis.[12] Although diazatriphenylene (**1**) is a powerful sensitiser for both the Eu^{3+} and Tb^{3+} ion, the synthetic possibilities of the Skraup reaction to obtain diazatriphenylene derivatives for incorporation of this type of sensitiser in lanthanide ionophores, for example, or subsequent fine-tuning of the luminescence properties, are rather limited.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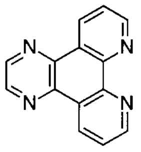
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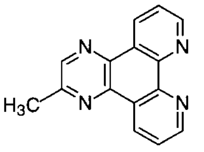
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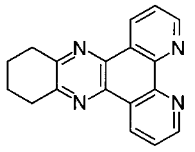
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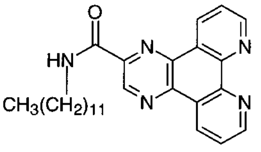
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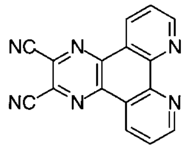
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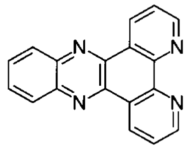
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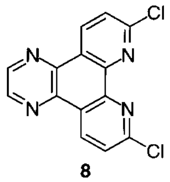
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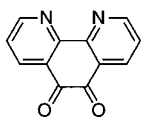
In this paper the synthesis and luminescence properties of novel tetraazatriphenylene derivatives **2**–**8** are presented. The motivation for the synthesis and photophysical characterisation of tetraazatriphenylenes is twofold. Firstly, structural variation is important in order to vary the absorption characteristics and to study to what extent additional functional groups influence the other photophysical characteristics of the sensitiser. Secondly, the synthetic route to tetraazatriphenylenes readily permits the introduction of a point of attachment on the phenazine ring of the tetraazatriphenylenes, allowing covalent coupling of these antenna systems to strongly chelating lanthanide ionophores such as calixarenes.

Results and Discussion

Synthesis: The tetraazatriphenylene derivatives **2**–**7** were synthesised starting from 1,10-phenanthroline-5,6-quinone (**9**), obtained by oxidation of phenanthroline monohydrate with Br_2 (generated in situ from H_2SO_4 and NaBr) and HNO_3, according to a literature procedure.[13, 14] Reaction of 1,10-phenanthroline-5,6-quinone (**9**) with the diamines *o*-diaminobenzene (**10**),[15] *cis*-1,2-diaminocyclohexane (**11**), diaminomaleonitrile (**12**), ethylenediamine (**13**), D,L-2,3-diaminopropionic acid dodecylamide (**14**) and 1,2-diaminopropane (**15**) in EtOH (or THF) gave the corresponding Schiff bases, which upon oxidation (oxygen from the air) generally afforded the tetraazatriphenylenes **2**–**7** in yields ranging from 71–92%.[13, 16]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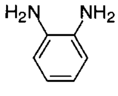
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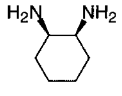
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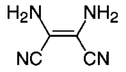
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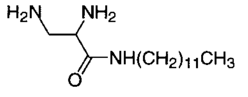
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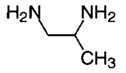
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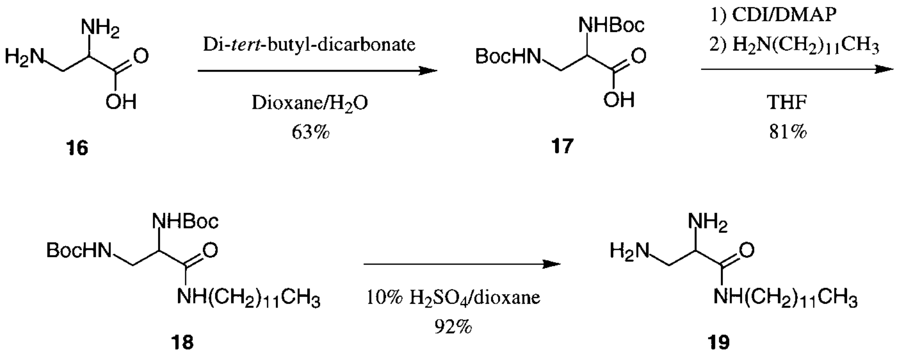
In the case of diaminomaleonitrile (**12**),[17] however, more severe conditions had to be applied. Due to the influence of the cyano groups, not the Schiff base but the hemiaminal was obtained. Subsequent heating of the diol in DMF in the presence of triethylamine as a base gave 2,3-dicyanodipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (**6**) in 71% overall yield. D,L-2,3-Diaminopropionic acid dodecylamide (**14**) was synthesised starting from D,L-2,3-diaminopropionic acid (**16**) by a sequence of Boc-protection (**17**), amidation (**18**) and Boc-deprotection (**19**), as depicted in Scheme 1. The long aliphatic chain in diamine **19** was introduced for solubility reasons which facilitate workup procedures. Due to the high symmetry of the tetraazatriphenylene derivatives **2**–**7** the ^1H NMR spectra are simple, showing the characteristic tetraazatriphenylene protons around $\delta = 9.5$ and 7.8.

Introduction of chlorine atoms at the α-positions of the cis-chelating nitrogen atoms as in tetraazatriphenylene **8** was achieved starting from the known 2,9-dichloro-1,10-phenanthroline-5,6-quinone.[13, 14] Schiff-base formation with ethylenediamine (**13**) in EtOH, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CH_2Cl_2, gave dichlorotetraazatriphenylene **8** in 71% yield.

Photophysical properties: Recently we have shown that 1,12-diazatriphenylene (**1**) forms 2:1 complexes with trivalent lanthanide ions (Eu^{3+}, Tb^{3+}, Dy^{3+}, Sm^{3+}) that exhibit sensitised lanthanide luminescence upon excitation of the azatriphenylene moiety.[12] The tetraazatriphenylenes described here combine direct complexation to the lanthanide ions with variation of substituents on the azatriphenylene skeleton.



Scheme 1. Reaction scheme for the preparation of **19**.

These substituents can improve either the photophysical properties or contain a reactive group, which can be used for labelling purposes, for example, to biological material.

In Figure 1 the absorption spectra of 1,12-diazatriphenylene (**1**) and the various tetraazatriphenylenes are depicted. It can be seen that the introduction of two more nitrogen atoms (going from diazatriphenylene **1** to the otherwise similar tetraazatriphenylene **2**) into the system decreases the extinction coefficient in the wavelength region around 250 nm, while the absorption maximum does not shift. However, at longer wavelengths (>300 nm) the absorption is significantly enhanced relative to that of **1**; the long-wavelength absorption edge is also red-shifted. Introducing substituents on the tetraazatriphenylene moiety further improves the absorption characteristics in the important wavelength region above 330 nm.

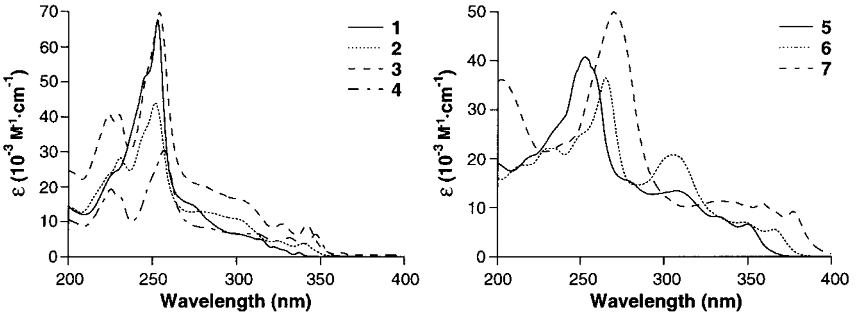


Figure 1. Absorption spectra of **1** and the tetraazatriphenylenes in MeCN. Because of the extremely poor solubility of tetraazatriphenylene **8** in organic solvents, the spectrum of this compound is not shown.

Upon addition of lanthanide ions (Eu^{3+}, Tb^{3+}) to an acetonitrile solution of **2**–**8** only a small hypsochromic shift in the absorption spectrum of these compounds occurred (a typical example is shown in Figure 2), while the absorbance remains essentially constant. That complexation occurs is nevertheless evident, especially from the fact that except for **7** and **8** very bright lanthanide luminescence is observed from the solutions under near-UV light. The excitation spectrum of this luminescence exactly matches the absorption of the particular ligand as exemplified in Figure 2 for the combination **4**·Tb^{3+}. It should be stressed that we have not pursued extensive identification of the antenna–lanthanide complex stability because, as stated above, the main aim of the present study is to find efficient antennae with significant lanthanide affinity; these could then be incorporated in a further stage into a supramolecular structure containing more strongly lanthanide-binding ligands that allow the overall system to be stable in water. Although, as expected, the present complexes were found to dissociate upon addition of water and other strongly competing solvents, they turned out to be stable in dry acetonitrile. Luminescence titration experiments identical to those described before for diazatriphenylene (**1**),[12] established that in acetonitrile the tetraazatriphenylene compounds also form a 2:1 (antenna–ion) complex, which appears to be stable down to a concentration $\leq 10^{-5}$ M.

In Table 1 some relevant photophysical data of the tetraazatriphenylene compounds and their Eu^{3+} and Tb^{3+} complexes are compiled. The luminescence quantum yields of the lanthanide complexes were measured with the lowest-energy maximum in the excitation spectrum (i.e., the 0–0 transition of the antenna) as the excitation wavelength. All quantum yields were measured with aerated solutions, but deoxygenation does not lead to a measurable change in the quantum yield.

The triplet energies of the tetraazatriphenylenes were determined by taking the shortest-wavelength transition in the phosphorescence spectrum at 77 K in an EtOH/MeOH (4:1) glass. These low-temperature spectra are depicted in Figure 3. The excitation wavelengths used to obtain these spectra were set at the 0–0 transition of the absorption spectrum of each compound. Only for tetraazatriphenylene **6** could some fluorescence be observed at low temperature, while at ambient temperature

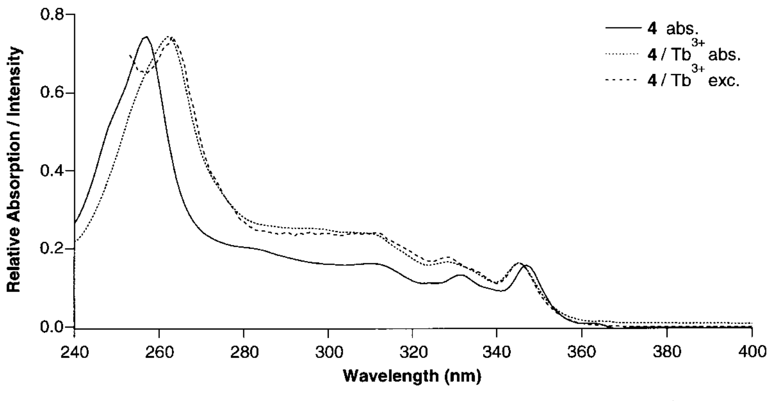


Figure 2. Normalised absorption spectra of tetraazatriphenylene **4** and its Tb^{3+} complex, as well as the excitation spectrum of the latter (λ_{obs} = 544 nm).

Table 1. Singlet ($^1E_{00}$) and triplet energies ($^3E_{00}$) of tetraazatriphenylenes and the extinction coefficient of their 0–0 absorption band and the lanthanide luminescence quantum yields of their Eu^{3+} and Tb^{3+} complexes in dry MeCN. Quantum yields refer to aerated solutions at 20°C. Deoxygenation and temperature have no significant influence except in the case of **6**/Tb^{3+}.

	$^1E_{00}$ [cm^{-1} (nm)][a]	ε [M^{-1}cm^{-1}][a]	$^3E_{00}$ [cm^{-1} (nm)][d]	Φ_{Eu}	Φ_{Tb}
1[f]	29700 (337)	1300	23800 (420)	0.41	0.55
2	29400 (340)	3800	23800 (420)	0.41	0.67
3	29400 (340)	8500	23600 (424)	0.43	0.51
4	28800 (347)	6440	23400 (428)	0.37	0.62
5	28600 (350)	6630	22500 (444)	0.29	0.30
6	27300 (366)	5520	21700 (460)	0.25	(0.14)[g]
7	26500 (377)	9160	≈18500 (542)[e]	0	0
8	29600 (338)[b]	[c]	≈23000 (435)[e]	0	0

[a] In acetonitrile unless stated otherwise. [b] In EtOH. [c] Solubility too low. [d] From the 0–0 transition of the phosphorescence measured in EtOH:MeOH (4:1) glass at 77 K (see Figure 3). [e] Broad band. [f] From ref. [12]. [g] Increases slightly (≈15%) upon deoxygenation, but strongly upon cooling.

virtually no fluorescence is observed for any of the tetraazatriphenylenes. This indicates that the triplet quantum yield for these compounds exceeds that of triphenylene ($\Phi_T = 0.89$),[11] and must be close to unity. Furthermore, it should be noted that in particular the phosphorescence spectra of **2**–**4** are rather similar in structure to each other as well as to those of **1** and of triphenylene itself. This strongly suggests that at least for these systems the lowest triplet state is $\pi-\pi^*$ in nature, as it is for triphenylene. In the case of **5** and **6** the phosphorescence is sufficiently different in structure to allow—in principle—for a different nature of the lowest triplet state, such as an admixture of a low-lying $n-\pi^*$ state due to the strongly electron-withdrawing substituents that are expected to stabilise such a state by lowering the energy of the LUMO. For **7** and **8**, which lack such strongly electron-withdrawing substituents the structure of the phosphorescence spectra again resembles that of **2**–**4**, although, especially for **7**, a strong bathochromic shift results from the extension of the π-system. With respect to a possible change of the nature of the lowest triplet state it should be noted that this is not reflected in a change of the triplet lifetime, which is in the seconds regime for **2**–**8** at 77 K.

From Table 1 it can be seen that the tetraazatriphenylenes without substituents (tetraazatriphenylene **2**) or with alkyl substituents at the noncoordinating side of the molecule (**3** and **4**) have a triplet energy close to those of triphenylene and of diazatriphenylene (**1**), while the other substituents (phenyl, cyano or amide groups) lower the triplet (and singlet) energy significantly.

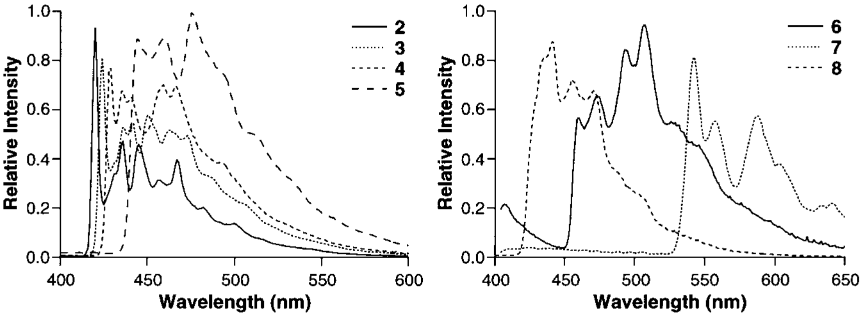


Figure 3. Total luminescence spectra of tetraazatriphenylenes at 77 K in EtOH/MeOH (4:1).

The lanthanide luminescence quantum yields for the complexes of **1**–**4** are similar, as are the triplet energies for these compounds (see above). This is very useful for further extension of the azatriphenylene system to couple it to a calix[4]arene or another strongly lanthanide-binding unit, for example, because apparently the alkyl substituent can be varied without loss of the very efficient sensitising properties.

While with **1**–**4** the quantum yield is consistently higher for Tb^{3+} than for Eu^{3+}, the introduction of an amido substituent on tetraazatriphenylene **5** leads to a stronger decrease in luminescence quantum yield for Tb^{3+} than for Eu^{3+}, and as a result the quantum yield for the Tb^{3+} complex is now almost equal to that of the Eu^{3+} complex (which is still very respectable!). Upon introduction of two cyano substituents (**6**) the quantum yield for the Tb^{3+} complex becomes lower than that of the Eu^{3+} complex, and with the benzannulated tetraazatriphenylene **7** neither sensitisation of Tb^{3+} nor of Eu^{3+} could be detected.

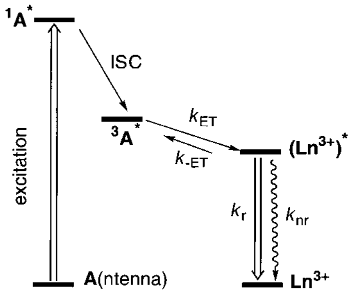


Figure 4. Scheme indicating sensitised formation of the lanthanide luminescent state and its radiative and nonradiative decay in an antenna–lanthanide complex.

In Figure 4 a simplified scheme is given of the antenna excitation/intersystem crossing (ISC)/energy transfer (k_{ET}) sequence that populates the lanthanide luminescent state. It is tempting to assume that the effects of structural variation in the antenna on the quantum yield of the lanthanide luminescence are related to the energy gap between the triplet level of the antenna and the luminescent level of the lanthanide ion since this provides the driving force for the energy-transfer process required to populate the luminescent state. In Figure 5 a summary is given of the differences between the triplet energies of azatriphenylenes and the energies of the excited lanthanide levels in relation to the quantum yields observed. The quantum yields for **1**–**7** with Eu^{3+} and **1**–**6** with Tb^{3+} versus the energy difference $^3E_{00} - E_{Ln^*}$ are plotted.

Although the lines drawn in Figure 5 are merely intended as guides to the eye and should not lead to the conclusion that the quantum yield varies linearly with the energy difference between the two states involved in the energy-transfer process, the trend seems quite evident and at least suggests that optimal conditions require an energy gap of ≥3000 cm^{-1} for Tb^{3+} and ≥6000 cm^{-1} for Eu^{3+}. It should be

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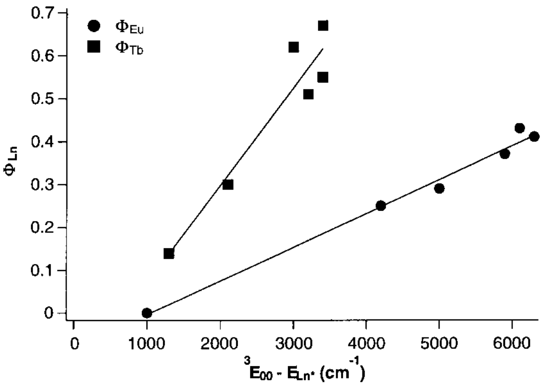

Figure 5. Luminescence quantum yields of azatriphenylene **1**–**7**/Eu^{3+} and **1**-**6**/Tb^{3+} complexes in MeCN as a function of the difference between the triplet state of the azatriphenylene ($^3E_{00}$) and the luminescent level of the lanthanide ion (17500 and 20400 cm^{-1} for Eu^{3+} and Tb^{3+}, respectively).

stressed that larger energy gaps are not automatically beneficial. Overlap between levels in the energy donor and acceptor is required, and raising the triplet energy too much can in principle cause a loss in this overlap. Apparently this problem does not occur up to at least $\Delta E = 3400\ cm^{-1}$ for Tb^{3+} and $\Delta E = 6300\ cm^{-1}$ for Eu^{3+}. To find out whether it becomes significant at still higher ΔE values, a series of analogous antenna chromophores with higher triplet energies would be required.[18]

In this context an important question is why are the quantum yields obtained with antennae **5**, **6** and especially with **7** significantly lower than with **1**–**4**? For **7**·Tb^{3+} this is probably trivial because the triplet energy of **7** (18500 cm^{-1}) is below that of the main luminescent level of Tb^{3+} (20400 cm^{-1}). However, in **7**·Eu^{3+} energy transfer is still predicted to be exergonic by about 1000 cm^{-1}, and nevertheless no sensitised luminescence could be detected. Also the absence of any effect of deoxygenation on the luminescence of the complexes **1**–**6**·Eu^{3+} and **1**–**5**·Tb^{3+}, and the minor effect of deoxygenation on the luminesecence of **6**·Tb^{3+} (<25% at room temperature), indicate that the differences in quantum yields between these complexes cannot simply be related to slow and thereby incomplete energy transfer in those for which the quantum yield is lower; this would make the intermediate antenna triplet sufficiently long-lived to be intercepted by triplet–triplet annihilation with oxygen (see below).

The complexity of the relationship between triplet energy and sensitising efficiency is further demonstrated by the fact that tetraazatriphenylene **8** is unable to sensitise either Eu^{3+} or Tb^{3+}, although the triplet energy of this compound is quite high ($^3E_{00} = 23000\ cm^{-1}$). A possible explanation in this latter case is that **8** is sterically unable to complex the lanthanide ions.

In order to obtain more insight into the factors governing the efficiency of the azatriphenylenes as antenna chromophores for Eu^{3+} and Tb^{3+}, time-resolved luminescence spectra were measured for the complexes involving the antennae **1**–**6**. These measurements were performed with a streak camera system (see Experimental Section) employing excitation in the long-wavelength absorption of the antennae at 337 nm by a pulsed nitrogen laser. The first striking observation is that in all cases the rise time of the lanthanide emission falls within the time resolution obtainable (≤20 ns, see Experimental Section). Thus, energy transfer from the triplet antenna to the lanthanide must also occur within this time scale; this explains the virtual insensitivity to oxygen quenching. This of course fully corroborates the observation mentioned above that in all cases, except for **6**·Tb^{3+}, the lanthanide emission intensity is insensitive to deoxygenation of the solution. More importantly it also shows that the apparent correlation between triplet energy and sensitising efficiency evidenced in Figure 5 is not simply a result of diminished energy transfer upon lowering of the triplet energy.

Because the decay of the lanthanide excited state is clearly the slowest step in the overall relaxation process following excitation of the antenna, the luminescence decay time τ (see Table 2) is directly related to the radiative (k_r) and nonradiative (k_{nr}) decay rates of the lanthanide ion [see Figure 4 and Eq. (1)]. The luminescence quantum yield of the lanthanide ion itself is given by Equation (2).

Table 2. Luminescence lifetimes (τ) of azatriphenylene–lanthanide complexes in MeCN measured at room temperature ($\lambda_{ex} = 337$ nm). Except for **6**/Tb^{3+}, lifetimes are not significantly influenced by deoxygenation. Furthermore the radiative (k_r) and nonradiative (k_{nr}) rate constants are given as calculated from the lifetimes and the quantum yields (see Table 1).

	τ_{Eu} [ms]	k_r [ms^{-1}][b]	k_{nr} [ms^{-1}][b]	τ_{Tb} [ms]	k_r [ms^{-1}][b]	k_{nr} [ms^{-1}][b]
1[a]	1.20 ± 0.02	0.34	0.49	1.31 ± 0.02	0.42	0.34
2	1.37 ± 0.02	0.30	0.43	1.67 ± 0.02	0.40	0.20
3	1.40 ± 0.02	0.31	0.40	1.60 ± 0.02	0.32	0.30
4	1.41 ± 0.02	0.26	0.45	1.41 ± 0.02	0.44	0.27
5	1.34 ± 0.03	0.22	0.53	1.37 ± 0.02	0.22	0.50
6	1.18 ± 0.02	0.21	0.64	0.76 ± 0.04[c]	(0.18)	(1.136)
				1.16 ± 0.04[d]	(0.12)	(0.74)

[a] Data for **1** from ref. [12]. [b] Calculated under the assumption that $\Phi_{lum} = \Phi_{ln}$, which does not apply for **6**/Tb^{3+} (see text). [c] In aerated solution. [d] In deoxygenated solution.

$$\tau = \frac{1}{(k_r + k_{nr})} \tag{1}$$

$$\Phi_{Ln} = k_r \times \tau \tag{2}$$

The overall luminescence quantum yield (Φ_{lum}) resulting from the absorption/intersystem crossing/energy transfer/luminescence sequence in antenna–lanthanide complexes is in principle determined not only by Φ_{Ln}, but also by the quantum yields of the intersystem crossing (Φ_{ISC}) and energy transfer (Φ_{ET}) steps, leading to Equation (3).

$$\Phi_{lum} = \Phi_{ISC} \times \Phi_{ET} \times \Phi_{Ln} = \Phi_{ISC} \times \Phi_{ET} \times k_r \times \tau \tag{3}$$

However, in the case of the Eu^{3+} and Tb^{3+} complexes of azatriphenylenes **1**–**6**, (except for **6**·Tb^{3+} as discussed below), the efficiencies of intersystem crossing (Φ_{ISC}) as well as energy transfer (Φ_{ET}) seem to be close to unity, implying that $\Phi_{lum} = \Phi_{Ln}$ and is thus only governed by k_r and k_{nr} of the lanthanide ion as it resides in the coordination sphere of the complex and the surrounding medium. Under this assumption, values for k_r and k_{nr} of the lanthanide in the complexes can then be calculated and are compiled in Table 2.

From the results it appears that in fact the lowered efficiency of **5** and especially **6** as a sensitiser towards Eu^{3+} and Tb^{3+} is related to a decrease of k_r and a simultaneous increase of k_{nr}. As we will discuss later on, the complexation with the azatriphenylenes apparently induces a higher k_r in the lanthanide ion and also shields it from quenching by the environment, thereby lowering k_{nr}. We therefore tentatively propose that the lowering of k_r and the increase of k_{nr} observed with **5** and **6** as compared with **1**–**4** is at least partly due to a weakening of the complexing ability of the azatriphenylenes upon introduction of electron-withdrawing groups (i.e., an amide group in **5** and two cyano groups in **6**).

For $\mathbf{6}\cdot Tb^{3+}$ an additional deactivation mechanism of the lanthanide luminescence is, however, evident from the fact that this is the only complex for which the lifetime significantly increases upon deoxygenation. Furthermore, we found that the lifetime of this complex strongly decreases and the effect of oxygen simultaneously increases when the temperature is raised. Together with the effect of oxygen on the luminescence quantum yield of this complex these observations imply that the energy transfer from the triplet of **6** to Tb^{3+} is thermally reversible. This is quite feasible because the energy gap is only 1300 cm^{-1} (3.7 $kcal\,mol^{-1}$), which allows for significant back energy transfer (k_{-ET} in Figure 4) within the millisecond lifetime of the lanthanide luminescence.

Thus the k_{nr} values calculated for $\mathbf{6}\cdot Tb^{3+}$ must contain a large contribution from this back energy transfer, a contribution which increases upon raising the temperature and also if the product of this process (i.e., the antenna triplet) is intercepted by oxygen. Under these conditions, application of Equations (1) and (2) of course only yields apparent rates; these results are therefore given in brackets for $\mathbf{6}\cdot Tb^{3+}$ in Table 2.

It is clear that **1**–**5** and to a somewhat lesser degree also **6** are good sensitisers for Eu^{3+} and Tb^{3+} not only because Φ_{ISC} and Φ_{ET} are close to unity, but also because the k_r/k_{nr} ratio of the lanthanide ions surrounded by these ligands is high. While a comparison of the k_{nr} values with literature data is complicated by the fact that these are certainly determined not only by the antenna ligands, but also to a large extent by the degree to which the lanthanide ion is still accessible to the quenching action of solvent molecules and counter-ions, the k_r values calculated (see Table 2) deserve some additional comment. In aqueous solution k_r has been reported as 0.19 ms^{-1} and 0.11 ms^{-1} for Eu^{3+} and Tb^{3+} ions, respectively[19]. Organic ligands[20] and solvents,[21] however, are known to induce a significant increase of the transition probability for the forbidden transitions underlying the low k_r values of the lanthanides. The spectral distribution of the lanthanide luminescence in the Eu^{3+} and Tb^{3+} complexes presented here (see Figure 6) indeed differs significantly from that of the free hydrated ions, indicating the well-known[20] differentiating effect of the organic ligands on the various transitions, and thereby enhancing the overall radiative decay probability.

Some lower limits on k_r implied by quantum yields and lifetimes reported in recent literature for organic ligand complexes of Eu^{3+} include 0.38 ms^{-1} with a bis-isoquinoline-*N*-oxide ligand,[22] 0.43 ms^{-1} with 4-(phenylethynyl)pyridine-2,6-dicarboxylic acid as a ligand,[8] 0.5 ms^{-1} with a bis-isoquinoline-*N*-oxide based cryptate[23, 24] and 0.52 ms^{-1} with a polymeric pyridinedicarboxylic acid based ligand.[25] Lower limits on k_r implied by quantum yields and lifetimes reported in recent literature for organic ligand complexes of Tb^{3+} are: 0.26 ms^{-1} with a terpyridine-based ligand,[26] 0.29 ms^{-1} with a 2,2′-bipyridine-based branched macrocyclic,[24] 0.30 ms^{-1} with a 2,6-bis-(*N*-pyrazolyl)pyridine-based ligand,[27] 0.33 ms^{-1} with pyridine-2,6-dicarboxylic acid,[28] and 0.42 ms^{-1} with 4-(2,4,6-trimethoxyphenyl)pyridine-2,6-dicarboxylic acid.[29] In fact, it has been mentioned earlier that for complexes of Eu^{3+} and Tb^{3+} upper values of $k_r = 0.60\ ms^{-1}$ and $k_r = 0.55\ ms^{-1}$, respectively, may be expected.[30] The k_r values we find (see Table 2) for Eu^{3+} and especially with Tb^{3+} complexes of ligands **1**–**4** are close to these upper limits, which clearly must be one of the sources of the extremely high luminescence efficiency of these complexes. Of course it remains to be seen whether such high k_r values will also be available in systems in which the complexation is enhanced by ligands with a higher affinity for the lanthanide ion and in which one or more azatriphenylenes serve as antennae to harvest the excitation light and not as the major ligands coordinating the lanthanide ion.

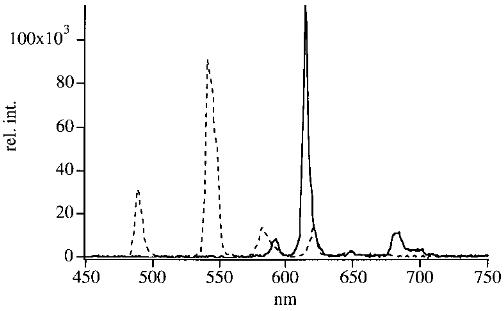

Figure 6. Luminescence spectra of the complexes of tetraazatriphenylene **4** with Eu^{3+} (—) and Tb^{3+} (- - -) in MeCN; $\lambda_{ex} = 345$ nm.

In conclusion, the compounds investigated, especially **1**–**5**, have the rather unique property of forming strongly luminescent complexes both with Eu^{3+} and with Tb^{3+}, while until now antenna chromophores absorbing in the region > 330 nm have mainly been reported that are only able to sensitise efficiently either Eu^{3+} or Tb^{3+}. Inefficiency towards Tb^{3+} seems primarily related to a lack of sufficient triplet energy, whereas inefficiency towards Eu^{3+} has generally been attributed to the occurrence of electron-transfer quenching by LMCT. The present azatriphenylenes combine high triplet energy with a strong resistance to oxidative quenching (E_{ox} has been found to exceed 2.5 V, measured relative to the saturated calomel electrode in acetonitrile[31]).

It should be stressed that the actual efficiency of a luminescent label, for example in a microscopic study or biological assay, cannot be deduced from the quantum yield alone. Factors like spectral distribution of the excitation source used and the wavelength-dependent response of all other equipment make it very hard to predict the effectiveness of a label. The extinction coefficient at the excitation wavelength also plays a major role. A common way of taking the latter two factors into account is to calculate the so-called luminescence intensity, by taking the product of the extinction coefficient and the quantum yield ($\Phi_{\text{lum}} \times \varepsilon$). In Table 3 these values are compiled for the Eu^{3+} and Tb^{3+} complexes of **1**–**6** assuming excitation in the longest-wavelength maximum of the antenna.

Table 3. Product of the extinction coefficient at the 0–0 transition (position in nm given between brackets) for the azatriphenylene/lanthanide complexes in MeCN.

	$\Phi_{\text{Eu}} \cdot \varepsilon$[a] ($^1E_{00}$ [nm])	$\Phi_{\text{Tb}} \cdot \varepsilon$[a] ($^1E_{00}$ [nm])
2	3120 (340)	5100 (340)
3	7320 (340)	8680 (340)
4	4760 (347)	7980 (347)
5	3840 (350)	3980 (350)
6	2760 (366)	[b]

[a] The molar extinction of the complex was calculated for the 2:1 ligand/lanthanide stoichiometry. [b] Strongly dependent on temperature and presence of oxygen (see text).

It is important to note that the ε values are taken at the 0–0 transition, and not at the strongest absorption maximum of the azatriphenylenes. Otherwise much higher values would be obtained, for example, for tetraazatriphenylene **3** $\Phi_{\text{Eu}} \times \varepsilon_{\max} = 60\,000$ and $\Phi_{\text{Tb}} \times \varepsilon_{\max} = 75\,000$ around 260 nm. Much more important, however, is that with, for example, **3** a $\Phi \times \varepsilon > 7000$ can be achieved at such a long excitation wavelength as 340 nm and with **5** $\Phi \times \varepsilon \approx 4000$ even at 350 nm for both Eu^{3+} and Tb^{3+}. In this important excitation wavelength region these values seem quite competitive with the highest reported in the literature for either Eu^{3+} or Tb^{3+} complexes,[6, 8, 26, 29] while the combination of such high $\Phi \times \varepsilon$ values at an excitation wavelength above 335 nm for both these lanthanide ions with a single sensitiser seems to be unprecedented.

From just the $\Phi \times \varepsilon$ data in Table 3 it might be concluded that the tetraazatriphenylenes with alkyl substituents (**3** and **4**) are the best candidates for further extension into a label for biological material. However, the 0–0 transition of these tetraazatriphenylenes is situated at significantly shorter wavelength than that of the amide-substituted tetraazatriphenylene **5**. For the complexes of the latter compound the lower value of $\Phi \times \varepsilon$ could in fact be easily compensated by the much stronger excitation intensity at 350 nm, compared with 340 nm, when a conventional light source, such as a mercury lamp, is used. On the other hand, if a nitrogen laser (337 nm) is used as the excitation source, **3** and **4** clearly come out as the most efficient antennae.

Conclusion

Various tetraazatriphenylenes appear to be excellent antenna chromophores as well as reasonably strong ligands towards both Eu^{3+} and Tb^{3+} ions. Furthermore, coordination of a number of these azatriphenylenes with lanthanide ions appears to significantly enhance the radiative-transition probability of these ions relative to their hydrated state. The exceptionally high luminescence quantum yields of the resulting lanthanide complexes and their long-wavelength absorption characteristics make them very interesting compounds for further investigation. Moreover, these azatriphenylenes represent a new class of sensitisers, a number of which display very high sensitising efficiency towards both Eu^{3+} and Tb^{3+}, allowing ultimately multicolour luminescent labels. In this context it should be mentioned that we have shown earlier[12] that azatriphenylenes are also able to sensitise the luminescence of other lanthanides (e.g., Dy^{3+} and Sm^{3+}) although the low inherent luminescence quantum yields of these ions make them less attractive for the development of luminescent labels. Importantly, the synthesis route of tetraazatriphenylenes allows easy modification and consequent fine-tuning of the required photophysical characteristics, by means of the diamine reagent. Also the fact that azatriphenylenes show no fluorescence, and the fast (and thus effective) energy transfer to lanthanide ions are advantages over many of the sensitisers investigated so far. Furthermore, the insensitivity towards quenching by oxygen (related to the fast energy transfer), which was observed for the quantum yields as well as the luminescence lifetimes, is quite advantageous.

Experimental Section

General procedures: Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC250 spectrometer in [D$_1$]chloroform with Me_4Si as the internal standard unless stated otherwise. Fast-atom-bombardment (FAB) and electron-impact (EI) spectra were obtained with a Finnigan MAT 90 spectrometer. Magic bullet (MB) and *m*-nitrobenzyl alcohol (NBA) were used as matrices for the FAB mass measurements. All other chemicals were analytically pure and were used without further purification. Hexane refers to the fraction with b.p. 40–60 °C. Standard work-up means that the organic layers were washed with water, dried over magnesium sulfate ($MgSO_4$), filtered, and concentrated in vacuo. Preparative column separations for compounds **2**–**7** were performed on Merck neutral Al_2O_3 (activity 5). Preparative column chromatography separation for compound **8** was performed on Merck silica gel 60 (230–400 mesh), while precoated silica gel plates (Merck, 60 F_{254}) were used for analytical TLC. 1,10-Phenanthroline-5,6-quinone (**9**)[13, 14] and 2,9-dichloro-1,10-phenanthroline-5,6-quinone[13, 14] were synthesised according to literature procedures. The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy.

Dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (**2**): Compound **2** was prepared according to a slightly modified literature procedure.[15] A solution of ethylenediamine (**13**; 0.19 g, 2.85 mmol) in THF (10 mL) was added dropwise to a solution of **9** (0.60 g, 2.85 mmol) in THF (600 mL), and the resulting mixture was refluxed for 4 h. The solution was concentrated in vacuo, and the slightly yellow solid was dissolved in CH_2Cl_2 (100 mL) and washed with 1 N HCl (50 mL). The aqueous solution was adjusted to pH 9.0 and cooled with an ice bath. The precipitate formed was filtered, and after purification with column chromatography (Al_2O_3, CH_2Cl_2) and trituration with CH_2Cl_2/hexane, compound **2** was obtained as a pure, white solid. Yield: 92 %; m.p. 253–255 °C (lit.[15] m.p. 250 °C); ^1H NMR: $\delta = 9.45$ (dd, $^3J(H,H) = 8.3$, 0.1 Hz, 2H), 9.3–9.2 (m, 2H), 9.18 (s, 2H), 7.97 (dd, $^3J(H,H) = 12.5$, 4.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 152.3$ (d), 147.5 (s), 144.5 (d), 140.6 (s), 133.2 (d), 127.5 (s), 124.0 (d); HRMS: *m*/*z* : 232.0785 ([M^+], calcd 232.0789); $C_{14}H_8N_4 \cdot 0.5\,H_2O$: calcd C 69.70, H 3.76, N 23.22; found C 69.66, H 3.40, N 23.03.

2-Methyldipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (**3**): Compound **3** was prepared and purified starting from **9** (0.6 g, 2.9 mmol) and 1,2-diaminopropane (**15**; 0.21 g, 2.9 mmol) with the procedure described for compound **2**. Yield: 83 %; white solid; m.p. 271 °C; ^1H NMR: $\delta = 9.49$ (dd, $^3J(H,H) = 8.4$, 0.8 Hz, 1H), 9.44 (dd, $^3J(H,H) = 8.4$, 0.8 Hz, 1H), 9.3–9.2 (m, 2H), 8.82 (s, 1H), 7.79 (d, $^3J(H,H) = 8.4$ Hz, 1H), 7.77 (d, $^3J(H,H) = 8.4$ Hz, 1H), 1.68 (s, 3H); ^{13}C NMR: $\delta = 22.5$ (q); HRMS: *m*/*z* : 246.0897 ([M^+], calcd 246.0905); $C_{14}H_8N_4 \cdot 0.1\,H_2O$: calcd C 72.63, H 4.14, N 22.58; found C 72.30, H 4.04, N 22.72.

10,11,12,13-Tetrahydrodipyrido[3,2-*a*:2′,3′-*c*]phenazine (4): *cis*-1,2-Diaminocyclohexane (**11;** 0.53 g, 4.6 mmol) was added to a solution of **9** (0.99 g, 4.7 mmol) in EtOH (75 mL), and the resulting mixture was refluxed for 4 h. After removal of the solvent in vacuo, the brown residue was subjected to column chromatography (Al_2O_3, CH_2Cl_2) to give **4**, which after recrystallisation from CH_2Cl_2/hexane was obtained as a pure white solid. Yield: 86%; m.p. 292–295°C; ^1H NMR ([D$_8$]THF): δ = 9.49 (dd, $^3J(H,H)$ = 8.3,0.8 Hz, 2H), 9.3–9.1 (m, 2H), 7.82 (dd, $^3J(H,H)$ = 12.5, 4.2 Hz, 2H), 3.4–3.2 (m, 4H), 2.2–2.1 (m, 4H); ^{13}C NMR (CD_2Cl_2): δ = 154.4 (s), 151.6 (d), 147.5 (s), 137.9 (s), 132.8 (d), 127.6 (s), 124.0 (d), 33.2 (t), 23.2 (t); HRMS: m/z : 286.1225 ([M^+], calcd 286.1218); $C_{18}H_{14}N_4 \cdot 0.5\,H_2O$: calcd C 73.20, H 5.12, N 18.97; found C 73.47, H 4.68, N 19.16.

2-Dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline acid dodecylamide (5): Compound **5** was prepared and purified starting from **9** (0.50 g, 1.06 mmol) and D,L-2,3-diaminopropionic acid dodecylamide (**14**; 0.50 g, 1.06 mmol) with the procedure described for compound **2**. Yield: 81%; m.p. 172–174°C; ^1H NMR: δ = 9.76 (s, 1H), 9.47 (d, $^3J(H,H)$ = 8.3 Hz, 1H), 9.38 (d, $^3J(H,H)$ = 8.3 Hz, 1H), 9.35–9.2 (m, 2H), 8.01 (br t, $^3J(H,H)$ = 6.7 Hz, 1H), 7.83 (d, $^3J(H,H)$ = 5.0 Hz, 1H), 7.79 (d, $^3J(H,H)$ = 5.0 Hz, 1H), 3.62 (q, $^3J(H,H)$ = 7.5 Hz, 2H), 1.76 (t, $^3J(H,H)$ = 8.0 Hz, 2H), 1.6–1.2 (m, 20H), 0.87 (t, $^3J(H,H)$ = 7.5 Hz, 3H); ^{13}C NMR: δ = 162.9 (s), 153.0 (d), 152.7 (d), 143.9 (d), 143.4 (s), 133.7 (d), 132.8 (d), 126.1 (s), 124.3 (d), 123.9 (d), 39.8 (t), 31.9 (t), 29.8 (t), 29.6 (t), 29.3 (t), 27.1 (t), 22.7 (t), 14.1 (q); HRMS: m/z : 443.269 ([M^+], calcd 443.269); $C_{27}H_{33}N_5O \cdot 0.25\,H_2O$: calcd C 72.37; H 7.42; N 15.63; found C 72.57, H 7.50, N 15.69.

2,3-Dicyanodipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (6): Dicyanomaleonitrile (**12**; 0.43 g, 4.0 mmol) was added to a solution of **9** (0.85 g, 4.0 mmol) in THF (100 mL), and the solution was refluxed for 1 h. The solution was filtered, and the slightly red solid was triturated with CH_2Cl_2. The solid was redissolved in DMF (50 mL), and 2 equiv of triethylamine were added subsequently. The mixture was heated at 90°C for 30 min, after which the solvent was removed in vacuo. The residue was redissolved in CH_2Cl_2 (100 mL) and washed with 1N HCl (100 mL). Compound **6** was obtained after column chromatography (Al_2O_3, CH_2Cl_2) and trituration with hexane/CH_2Cl_2 as a pure white solid. Yield: 71%; m.p. > 300°C; ^1H NMR: δ = 9.5–9.3 (m, 4H), 8.2–8.0 (m, 2H); ^{13}C NMR: δ = 155.1 (d), 148.9 (s), 141.95 (s), 134.5 (d), 131.1 (s), 125.1 (d), 124.9 (s), 113.3 (s); HRMS: m/z : 282.0649 ([M^+], calcd 282.0654), 255.0543 ([$M^+ - HCN$]; $C_{16}H_6N_6 \cdot 0.5\,H_2O$: calcd C 65.98, H 2.42, N 28.85; found C 65.74, H 2.14, N 28.71.

Dipyrido[3,2-*a*:2′,3′-*c*]phenazine (7): Compound **7** was prepared according to a literature procedure starting from **9** (0.6 g, 2.9 mmol) and *o*-diaminobenzene (**10**; 0.3 g, 2.9 mmol).[15] Additional purification was necessary to obtain **7** as a pure white solid: column chromatography (Al_2O_3, CH_2Cl_2) and crystallisation from CH_2Cl_2/hexane. Yield: 81% (lit.[15] 80%); all spectroscopic data corresponded to those given in the literature.

2,9-Dichlorodipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (8): Ethylenediamine (**13**) (0.27 g, 4.0 mmol) was added to a solution of 2,9-dichloro-1,10-phenanthroline-5,6-quinone[13, 14] (0.85 g, 4.0 mmol) in EtOH (100 mL), and the solution was refluxed for 1 h. The solution was concentrated in vacuo, and the residue was subjected to column chromatography (Al_2O_3, CH_2Cl_2). The Schiff-base adduct was redissolved in CH_2Cl_2 (50 mL), and DDQ (2 equiv, 1.8 g, 8.0 mmol) was subsequently added. The mixture was stirred for 1 h at RT. Again, the solution was concentrated in vacuo, and the residue was subjected to column chromatography (Al_2O_3, CH_2Cl_2). After trituration with hexane/CH_2Cl_2 compound **8** was obtained as a pure white solid. Yield: 71%; m.p. 252–254°C; ^1H NMR ([D$_1$]TFA): δ = 9.99 (d, $^3J(H,H)$ = 8.3 Hz, 2H), 9.44 (s, 2H), 8.37 (d, $^3J(H,H)$ = 8.3 Hz, 2H); HRMS: m/z : 299.997 ([M^+], calcd 299.997), 265.0 ([$M^+ - Cl$]; $C_{14}H_6Cl_2N_4 \cdot 0.25\,H_2O$: calcd C 55.02, H 2.14, N 18.33; found C 55.28, H 1.96, N 18.52.

D,L-*N*,*N*′-Di-*tert*-butoxycarbonyl-2,3-diaminopropionic acid (17): Di-*tert*-butyl dicarbonate (17.1 g, 78.3 mmol) was added to a solution of D,L-2,3-diaminopropionic acid monohydrochloride (**16**; 5.0 g, 35.6 mmol) and triethylamine (18 g, 0.18 mol) in 1,4-dioxane/H_2O (75 mL, 1:1). The solution was stirred at RT for 10 h. After completion of the reaction, ethyl acetate (100 mL) and 1N HCl (100 mL) were added. The organic layer was washed with brine (2 × 100 mL), followed by standard work-up to give **17** as a white solid. Yield 91%; m.p. 162–164°C; ^1H NMR ([D$_6$]DMSO): δ = 6.89 (d, $^3J(H,H)$ = 8.3 Hz, 1H), 6.79 (br t, $^3J(H,H)$ = 6.7 Hz, 1H), 4.00 (dd, $^3J(H,H)$ = 8.3, 6.7 Hz, 1H), 3.24 (t, $^3J(H,H)$ = 6.7 Hz, 2H), 1.37 (s, 18H); MS (FAB): m/z : 303.2 ([$M^+ - H$], calcd for $C_{13}H_{23}N_2O_6$ 303.2).

D,L-*N*,*N*′-Di-*tert*-butoxycarbonyl-2,3-diaminopropionic acid dodecylamide (18): A solution of acid **17** (4.1 g, 13.3 mmol), 1,1′-carbonyldiimidazole (CDI; 3.0 g, 13.3 mmol), and 4-dimethylaminopyridine (DMAP; catalyst, 0.1 g) in THF (75 mL) was stirred at RT for 1 h. Subsequently, dodecylamine (2.7 g, 13.3 mmol) was added, and the solution was allowed to stir overnight. The solution was concentrated in vacuo. CH_2Cl_2 (100 mL) was added to the residue, and the resulting solution washed with 1N HCl (aq), followed by standard workup. The crude reaction product was purified by column chromatography (SiO_2, CH_2Cl_2) to give pure **18** as a white solid. Yield: 85%; m.p. 103-105°C; ^1H NMR: δ = 6.65 (br s, 1H), 5.80 (br s, 1H), 4.2–2.1 (m, 1H), 3.5–3.4 (m, 2H), 3.2–3.1 (m, 2H), 1.45 (s, 20H), 1.25 (s, 18H), 0.89 (t, $^3J(H,H)$ = 7.8 Hz, 3H); ^{13}C NMR: δ = 170.4 (s), 157.1 (s), 156.1 (s), 80.1 (s), 79.9 (s), 55.5 (d), 42.5 (t), 39.5 (t), 31.9 (t), 29.8 (s), 29.6 (t), 29.58 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.28 (t), 28.3 (d), 26.8 (t), 22.6 (t), 14.1 (q); MS (FAB): m/z : 470.1 [$M^+ - H$], 624.2 [M^++NBA]; $C_{25}H_{49}N_3O_5$: calcd C 63.66, H 10.47, N 8.91; found C 63.95, H 10.73, N 8.84.

D,L-2,3-Diaminopropionic acid dodecylamide (19): Amide **18** (0.80 g, 1.7 mmol) was added slowly to a solution of 10% H_2SO_4/dioxane (75 mL) at 0°C. After the addition was complete the mixture was stirred at RT for 4 h. The precipitate formed was filtered, dissolved in CH_2Cl_2 (100 mL), and the resulting solution was subsequently washed with 1M NaOH (aq) (50 mL) and brine (50 mL), followed by standard workup. The product was obtained, after trituration with MeOH, as a pure, white solid. Yield 77%; m.p. 88–90°C; ^1H NMR ([D$_6$]DMSO): δ = 7.48 (br s, 4H), 3.28 (t, $^3J(H,H)$ = 7.5 Hz, 1H), 3.20 (q, $^3J(H,H)$ = 7.5 Hz, 2H), 3.0–2.8 (m, 2H), 1.21 (br s, 20H), 0.83 (t, $^3J(H,H)$ = 7.6 Hz, 3H); ^{13}C NMR: δ = 173.7 (s), 56.5 (d), 46.1 (t), 39.1 (t), 31.9 (t), 29.62 (t), 29.57 (t), 29.5 (t), 29.3 (t), 29.28 (t), 27.0 (t), 22.7 (t), 14.1 (q); MS (FAB, MB): m/z : 272.4 ([M^++H], calcd for $C_{15}H_{34}N_3O$ 272.3).

Luminescence measurements: Continuous emission and excitation spectra were recorded on a Spex Fluorolog 2 spectrofluorimeter. Solutions for lanthanide luminescence measurements were prepared in spectrograde acetonitrile (Merck, Uvasol) dried over molecular sieves before use. The lanthanides were added in the form of $Eu(NO_3)_3 \cdot 6\,H_2O$ and $Tb(NO_3)_3 \cdot 5\,H_2O$ (Aldrich).

Titration experiments to determine the stoichiometry of the luminescent complexes in solution were carried out as described previously.[12] Full data on the results of these luminescence titrations are available as Supporting Information. These results show that, as already reported for **1**, the other luminescent complexes also have a 2:1 (ligand:lanthanide) stoichiometry in acetonitrile down to a concentration of $\approx 10^{-5}$M or less.

Luminescence quantum yields were determined relative to a reference solution of quinine sulfate in 1N sulfuric acid ($\Phi = 0.546$)[32] or Ru–tris-(bipyridine) in deoxygenated water ($\Phi = 0.042$)[33] and corrected for the refractive index of the solvent. All samples were prepared with an absorbance between 0.05 and 0.2 at the excitation wavelength, implying an antenna concentration in the range $1-5 \times 10^{-5}$M. Over this range no significant influence of the concentration on the quantum yield can be detected. Deoxygenation was performed by thoroughly purging with argon for 10–15 minutes.

Time-resolved emission spectra were obtained by the use of a Hamamatsu C-5680 streak camera equipped with an M 5677 sweep unit. Excitation at 337 nm was achieved by a pulsed (FWHM 600 ps) nitrogen laser (LTB, MSG 405 TD) operating at a repetition rate of 20 Hz. Monoexponential decay of the lanthanide luminescence was observed in all cases. Although the time resolution of this set-up is ca. 200 ps, it should be noted that the small radiant flux, together with the long lifetime of lanthanide luminescence, prevents full use of this time resolution in practice. The shortest sweep time employed was 100 microseconds, corresponding to a time resolution of about 20 ns.

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