Synergistic Complexation of Eu^{3+} by a Polydentate Ligand and a Bidentate Antenna to Obtain Ternary Complexes with High Luminescence Quantum Yields

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A series of ternary Eu^{3+} complexes are presented consisting of a polydentate *m*-terphenyl-based Eu^{3+} complex (Eu)**1** and different antenna chromophores possessing lanthanide(III) ion coordinating properties. The series of investigated antenna chromophores consist of 1,10-phenanthroline, tetraazatriphenylene, and three *β*-diketonates, namely dibenzoylmethane, benzoyltrifluoroacetylacetonate, and hexafluoroacetylacetonate. As a result of the synergistic complexation of Eu^{3+} by the polydentate ligand and the bidentate antenna, the distance between the antenna and lanthanide ion has been minimized and the Eu^{3+} ion has been shielded completely from the solvent. These are two important requirements to obtain efficiently emitting lanthanide-(III) complexes. The formation of the ternary complexes and their photophysical properties, in particular the population of the Eu^{3+} excited states and the efficiency of the sensitization process, have been studied in detail. Based on these measurements, it can be concluded that the aforementioned strategy of synergistic complexation has indeed led to the construction of efficiently emitting Eu^{3+} complexes. The *β*-diketonate ternary Eu^{3+} complexes combine a high stability ($K = 3.8 \pm 0.2 \times 10^7$ M^{-1}) with high overall luminescence quantum yields of up to 0.29. The energy transfer from the sensitizer to the Eu^{3+} is exclusively to the $^5D_1$ level, from which the $^5D_0$ level is populated.

Introduction

The design of molecular systems that combine binding abilities and useful photophysical properties for the construction of efficient photoluminescent lanthanide(III) complexes continues to be an active area of research. The long lifetimes of the excited states of lanthanide ions and their distinct narrow emission bands ranging from the UV−visible to the near-infrared region are ideally suited for applications as fluorescent probes[1,2] and as optical signal amplifiers.[3] The long luminescent lifetimes of lanthanide ions are due to the forbidden character of their intra-4f transitions, which unfortunately also result in low absorption coefficients (typically $1-10$ M^{-1}cm^{-1}).[4] For this reason, the excited state of a luminescent lanthanide(III) ion is generally populated by energy transfer from the triplet state of an organic antenna chromophore (the *sensitizer*).[5,6] The quantum yield of the overall process, which involves the excitation of the antenna chromophore and intersystem crossing to the triplet state, energy transfer to the lanthanide ion and subsequent lanthanide emission (see Figure 1), depends on the efficiency of these individual steps: the intersystem crossing efficiency (η_{ISC}), the energy transfer efficiency (η_{ET}), and the lanthanide-(III) luminescence quantum yield (ϕ_{Ln}). Eu^{3+} is one of the best studied lanthanide ions, and the research of the sensitization process of this ion has resulted in a better understanding of the

sensitization process of other lanthanide ions, in particular the near-infrared emitting lanthanide ions.[7,8] For example, it is obvious that ideally η_{ISC} should be (close to) unity. However, it has been shown that by positioning the antenna chromophore in close proximity of the lanthanide ion, η_{ISC} is enhanced as a result of an external heavy atom effect.[9,10,11] This understanding has led to the application of fluorescent dyes, which have very low intrinsic intersystem crossing quantum yields, as efficient sensitizers for near-infrared Nd^{3+}, Er^{3+}, and Yb^{3+} luminescence.[11,12]

Based on the knowledge of antenna-functionalized Eu^{3+} complexes, the antenna triplet state should be higher in energy than the receiving lanthanide 4f state by approximately 2000 cm^{-1} [6] and the antenna should be coordinated to the lanthanide ion in order to obtain the maximum heavy atom effect and a fast energy transfer process, which are both strongly distance dependent. In general, the energy transfer process is an electron-exchange mechanism.[13,14] At the same time, the lanthanide ion should be shielded by the ligand from their environment because high-frequency oscillators, like the O−H and C−H vibrations of the solvent, play an important role in removing energy nonradiatively from the lanthanide excited state.[15]

Previously, we have reported the synthesis and photophysical properties of a series of neutral *m*-terphenyl-based polydentate lanthanide complexes.[16,17] In the well-defined and stable complex (Ln)**1**, the lanthanide ion is coordinated by eight hard oxygen donor atoms, whereas the ninth coordination site of the

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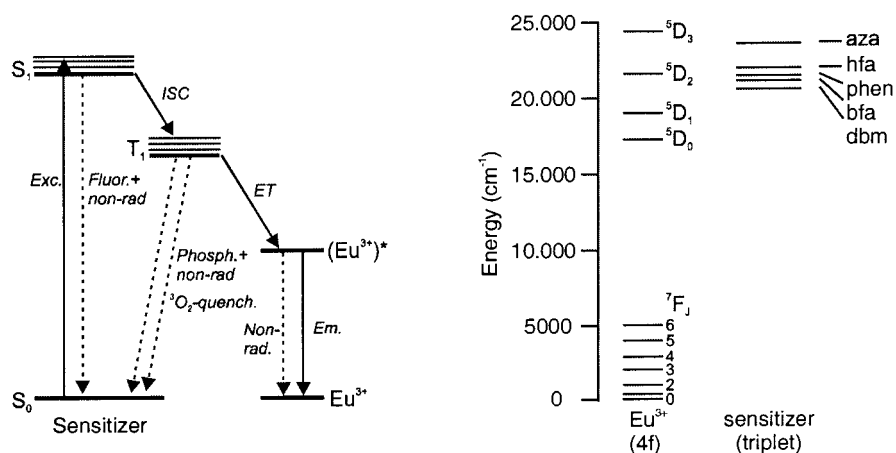
Figure 1. Left: Schematic representation of the photophysical pathway of the sensitization process. The solid arrows indicate the pathway of the sensitization process, whereas the dashed arrows indicate the competing processes. Right: The relevant 4f energy levels of Eu^{3+} as well as the triplet state energies of hexafluoroacetylacetonate (hfa, 22,000 cm^{-1}), benzoyltrifluoroacetylacetonate (bfa, 21,400 cm^{-1}), dibenzoylmethane (dbm, 20,600 cm^{-1}), 1,10-phenanthroline (phen, 21,480 cm^{-1}) and tetraazatriphenylene (aza, 23,800 cm^{-1}).

CHART 1

(Eu)**1**
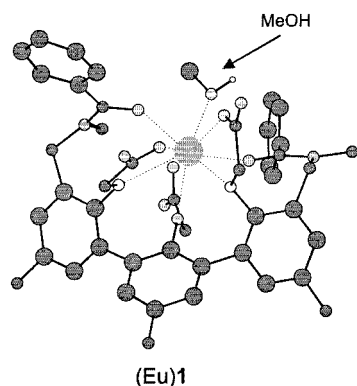
lanthanide ion is occupied by a solvent molecule (depicted in Chart 1).[17,18]

In this article, ternary complexes are reported in which the ninth coordination site of (Eu)1 is occupied by an antenna chromophore. In this way the antenna-Eu^{3+} distance has been minimized and at the same time the lanthanide ion is completely shielded from the solvent. The coordinating antenna chromophores are a series of three β-diketonates (dibenzoylmethane (dbm), benzoyltrifluoroacetylacetonate (bfa), and hexafluoroacetylacetonate (hfa)), 1,10-phenanthroline (phen), and tetraazatriphenylene (aza). The triplet-state energies of these sensitizers and the relevant 4f energy levels of Eu^{3+} are depicted in Figure 1.

The 1:3 Eu^{3+}/β-diketonate,[5,6,19,20] the 1:2 Eu^{3+}/1,10-phenanthroline,[21] and the 1:2 Eu^{3+}/tetra-azatriphenylene[22] complexes are well-known and have been studied extensively. The sensitization process in these complexes is very efficient. However, a drawback of these complexes is their limited stability and the incomplete shielding of the Eu^{3+} ion from the solvent. In the present ternary complexes the excellent sensitizing capabilities of these bidentate antennas have been combined with the stability and shielding properties of polydentate complexes. Besides the preparation and characterization of the ternary complexes, we have determined the luminescence quantum yields and studied in detail the time-evolution of the luminescence of the two emissive states of Eu^{3+}, namely the $^5D_1$ (at ~19,000 cm^{-1}) and $^5D_0$ (at ~17,500 cm^{-1}) state. We have found that in these complexes the energy transfer from the antenna triplet to Eu^{3+} exclusively takes place to the $^5D_1$ state. There is no *direct* energy transfer to the $^5D_0$ state, but

instead the $^5D_0$ state is populated via the $^5D_1$ state. Furthermore, we demonstrate a principle that has not been applied consciously until now to obtain efficiently emitting lanthanide complexes. The long-lived excited states of lanthanide(III) ions, make them very sensitive to quenching processes. By *increasing the radiative rate* of Eu^{3+} as a result of the composition of its coordination sphere, the radiative lifetime of the excited state is shortened making it less sensitive to nonradiative deactivation processes and the overall effect is an increased quantum yield. β-Diketonates are a proper choice in this respect, because the emission of complexes with Eu^{3+} are characterized by a very strong $^5D_0$-$^7F_2$ transition (see "Results and Discussion" for more details).
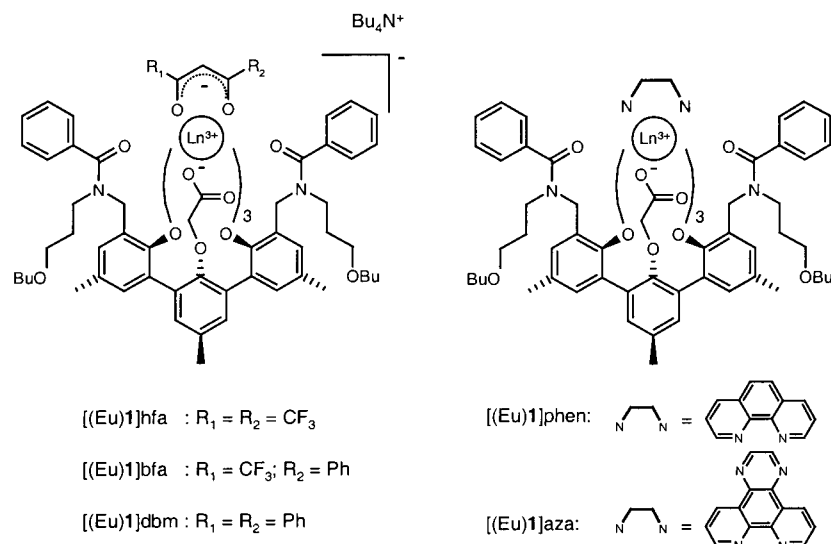
Experimental Section

Mass spectra were recorded with a Finnigan MAT 90 spectrometer using a mixture of dithiothreitol and dithioerythritol (5:1 (v/v)), known as Magic Bullet, as the matrix. IR spectra were obtained using a Perkin-Elmer Spectrum BX FT-IR System. CH_2Cl_2 was of spectroscopic grade and used without further purification. The β-diketones, 1,10-phenanthroline and NBu$_4$OH (1 M solution in methanol) were purchased from Aldrich and used without further purification. Tetraazatriphenylene and the (Eu)**1** complex were synthesized according to literature procedures.[17,22]

General Procedure for the Preparation of the m-terphenyl-based Complexes. The β-diketonate complexes were prepared by mixing a dichloromethane solution (10 mL) of (Eu)-**1** (30 mg, 0.026 mmol), 0.026 mmol of the appropriate β-diketone, and 27 μL of a 1 M aqueous NBu$_4$OH solution. After stirring for 0.5 h, the solvent was removed in vacuo. The neutral tetraazatriphenylene and phenanthroline complexes were prepared in a similar way. The complexes were characterized by FAB-MS spectrometry (see Table 1) and IR spectroscopy. The IR spectra of the β-diketonate complexes show a peak at 1650−1640 cm^{-1} ($\nu_{NC=O}$ and $\nu_{C=O,\beta-diketone}$), with a shoulder around 1610−1600 cm^{-1} (ν_{COO}), whereas the IR spectra of [(Ln)**1**]aza and [(Ln)**1**]phen show a peak at 1635−1630 cm^{-1} ($\nu_{NC=O}$) with a shoulder around 1590−1600 cm^{-1} (ν_{COO}).

Photophysical Studies. Steady-state luminescence measurements were performed with a Spex Fluorolog 3−22 instrument or an Edinburgh FS900 spectrofluorimeter. In the Spex Fluorolog 3−22 instrument the samples were excited with a 450 W Xe lamp via a double-grating monochromator. The emitted light

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CHART 2

[(Eu)**1**]hfa : R$_1$ = R$_2$ = CF$_3$

[(Eu)**1**]bfa : R$_1$ = CF$_3$; R$_2$ = Ph

[(Eu)**1**]dbm : R$_1$ = R$_2$ = Ph

[(Eu)**1**]phen:

[(Eu)**1**]aza:

TABLE 1: Identification of the Ternary Complexes by Mass Spectrometry (FAB)

complex	measured m/z	calcd m/z
N(Bu)$_4$[(Eu)**1**]hfa	1343.0 (M−N(Bu)$_4$)$^-$	1343.4
N(Bu)$_4$[(Eu)**1**]bfa	1351.3 (M−N(Bu)$_4$)$^-$	1351.4
N(Bu)$_4$[(Eu)**1**]dbm	1359.4 (M−N(Bu)$_4$)$^-$	1359.4
[(Eu)1]phen	1261.9 (M-CH$_2$COO)$^{+a)}$	1261.4
[(Eu)1]aza	1371.0 (M+H)$^+$	1371.4
[(Tb)1]aza	1377.4 (M+H)$^+$	1377.5

^{a} This type of fragmentation is commonly observed in FAB MS experiments, see for instance ref 16a.

was detected at an angle of 90° by a Peltier cooled Hamamatsu R636−10 photomultiplier operating in the photon counting mode. In the Edinburgh FS900 spectrofluorimeter, the samples were excited by a 450 W xenon lamp via a single grating monochromator. The emitted light was detected at an angle of 90° by a Peltier cooled Hamamatsu R928 photomultiplier, and subsequently fed to a photon-counting interface. The spectra were corrected for the wavelength dependence of the detection sensitivity.

The time-resolved measurements were performed using an LTB MSG 400 nitrogen laser ($\lambda_{exc.}$ 337 nm) as the pulsed laser excitation source and a streak camera system (Hamamatsu) as the detector to simultaneously probe wavelength and time-dependence of the luminescence signals in the millisecond and microsecond domain. The streak images were analyzed with a mathematical procedure involving singular value decomposition.[32,33]

All photophysical measurements were performed on aerated samples at room temperature, unless otherwise stated. The overall quantum yields of the ternary complexes were determined relative to a reference solution of quinine sulfate in 1 M H$_2$SO$_4$ (ϕ = 0.546),[23] and corrected for the refractive index of the solvent according to Equation 1.[24]

$$\Phi_u = \frac{n_u^2 A_{ref} I_u}{n_{ref}^2 A_u I_{ref}} \Phi_{ref} \qquad (1)$$

In Equation 1, n_u, I_u, and A_u are the refractive index, the area of the corrected emission spectrum, and the absorbance at the excitation wavelength, respectively, for the sample of which

the quantum yield is unknown. n_{ref}, I_{ref}, and A_{ref} are the same observables for the reference sample (quinine sulfate in 1 M H$_2$SO$_4$).

The ternary complexes were dissolved to a concentration of 10^{-5} M in dichloromethane, to keep the absorption of samples below 0.2 at the excitation wavelength. At this concentration, the three ternary β-diketonate complexes are not dissociated. Since the formation constant of [(Eu)**1**]aza is 1.4 ± 0.1 × 10^5 M^{-1} (vide infra), the fraction of this ternary complex at 10^{-5} M is only 44%. Based on the structural similarity of phen and aza, it is assumed that [(Eu)**1**]phen has a similar formation constant. The emission, excitation spectra, and lifetimes represent the photophysical properties of the ternary complex, because only the ternary complex exhibits sensitized luminescence upon excitation above 300 nm. The measured luminescence quantum yields of [(Eu)**1**]aza and [(Eu)**1**]phen were corrected for the amount of ternary complex in solution. This was done by multiplying the measured absorbance at the excitation wavelength of the [(Eu)**1**]aza and [(Eu)**1**]phen samples with 0.44 (since only this fraction of antennas is coordinated to the Eu^{3+} ion), and to use this value as A_u in eq 1.

Titration Experiments. To 2.5 mL of a 1.05 × 10^{-5} M solution of tetraazatriphenylene in CH$_2$Cl$_2$, 25-μL aliquots of a (Eu)**1** solution (5.2 × 10^{-4} M) were added. The antenna was excited at 330 nm and the intensity of Eu^{3+} ^{5}D$_0$→^{7}F$_2$ emission around 615 nm was monitored as a function of added amounts of (Eu)**1**. In a similar way the formation of [(Eu)**1**]bfa was monitored. In this experiment the antenna was excited at 340 nm. To 2.6 mL of a 3.05 × 10^{-5} M solution of (deprotonated) bfa in CH$_2$Cl$_2$, 25-μL aliquots of a (Eu)**1** solution (5.08 × 10^{-4} M) were added. The bfa stock solution was prepared by mixing in CH$_2$Cl$_2$ (10 mL), bfa (13.18 mg, 6.10 × 10^{-2} mmol) with 65 μL (6.5 × 10^{-2} mmol) of a 1 M solution of NBu$_4$OH in methanol. The solvents were removed in vacuo, subsequently dichloromethane was added (10 mL) and the mixture was concentrated to dryness. This was repeated twice. Finally, the deprotonated bfa antenna was redissolved in CH$_2$Cl$_2$ to a concentration of 1.85 × 10^{-6} M.

Results and Discussion

Nature of the Complex. The formation of the ternary complexes was studied by monitoring the sensitized luminescence intensity as a function of the concentration of the Eu^{3+}
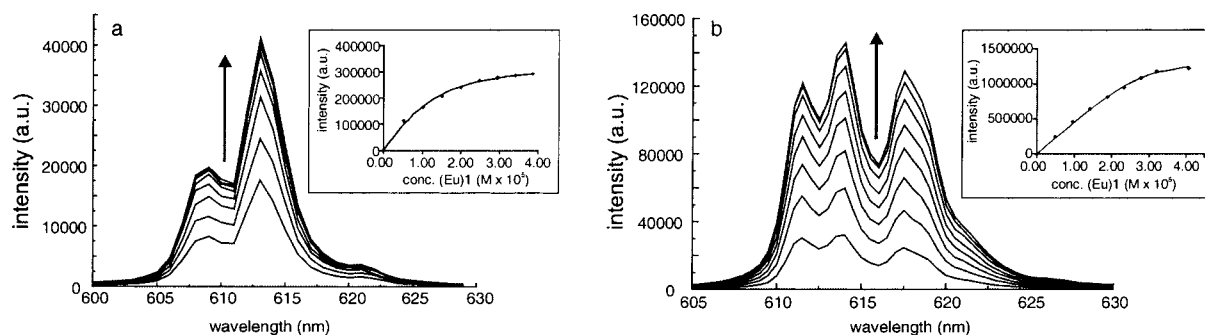
Figure 2. The increase in the sensitized $^5D_0 \rightarrow {}^7F_2$ emission band around 615 nm upon the addition of increasing concentrations of (Eu)**1** to the aza (a) and bfa (b) antenna chromophores in dichloromethane. The insets show the formation of the ternary complexes as a function of the sensitized luminescence intensity. The solid lines are the theoretical curves for a 1:1 complex with K = 1.4 ± 0.1 × 10^5 M^{-1} for [(Eu)**1**]aza and K = 3.8 ± 0.2 × 10^7 M^{-1} for [(Eu)**1**]bfa, respectively.
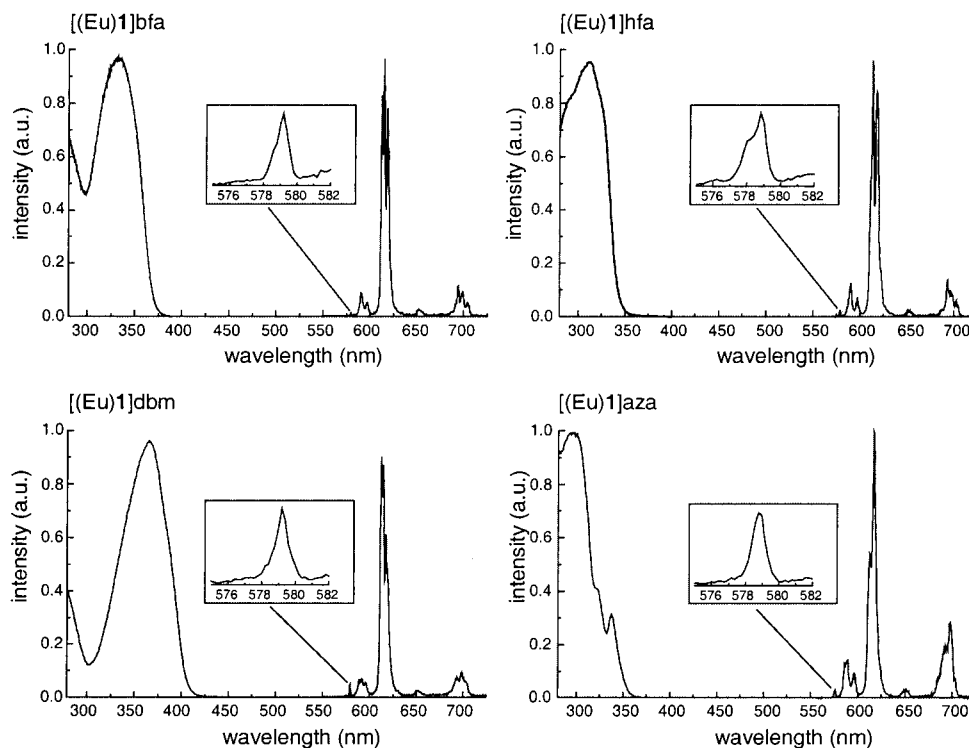
Figure 3. The corrected (and normalized) excitation (λ_{em} 615 nm) and emission spectra (λ_{exc} 330 nm) of [(Eu)**1**]bfa, [(Eu)**1**]hfa, [(Eu)**1**]dbm, and [(Eu)**1**]aza in dichloromethane (10^{-5} M). The inset shows a magnification of the $^5D_0 \rightarrow {}^7F_0$ emission at 579 nm. The spectra were taken with a spectral bandwidth of 0.2 nm.

complex in solution during a titration experiment. In this way, the formation of the two ternary complexes [(Eu)**1**]aza and [(Eu)**1**]bfa in dichloromethane was examined in more detail. Figure 2 shows the titration experiments, in which small amounts of a (Eu)**1** stock solution were added to a solution of tetraazatriphenylene or (deprotonated) bfa. The complexes were excited in the absorption bands of the antenna chromophores, at a wavelength (i.e. $\lambda_{exc.}$ 330 nm) where the (Eu)**1** complex itself has no absorption bands.[25,26] Upon addition of increasing concentrations of (Eu)**1** to the antenna chromophores, the sensitized Eu^{3+} emission increased (see Figure 2).

During the titration experiment, the absorption bands of the antenna chromophores above 300 nm did not change, indicating that upon coordination to (Eu)1 the singlet excited states of the antenna chromophores are not affected significantly by the Eu^{3+} ion. Analysis of the titration data yields formation constants of the 1:1 ((Eu)**1**:antenna) complexes, $K = 1.4 \pm 0.1 \times 10^5$ M^{-1} for [(Eu)**1**]aza and $K = 3.8 \pm 0.2 \times 10^7$ M^{-1} for [(Eu)**1**]bfa, respectively.

**Preparation of the Complexes.** The [(Eu)**1**]β-diketonate complexes were prepared by mixing one equivalent of the tetrabutylammonium salt of the appropriate β-diketonate and one equivalent of (Eu)**1** in dichloromethane, and subsequent removal of the solvent. The neutral tetraazatriphenylene and phenanthroline complexes were prepared in a similar way. The ternary complexes have been characterized by mass spectrometry (FAB) and IR spectroscopy (see the Experimental Section). The mass spectra show the expected 1:1:1 stoichiometry (ligand: Eu^{3+} : sensitizer) of the ternary complexes.

The Steady-State Luminescence Spectra of the Ternary Complexes. Upon excitation of the antennas ($\lambda_{exc.}$ 330 nm) of the corresponding ternary complexes in dichloromethane (10^{-5} M), the steady-state luminescence spectra show the narrow Eu^{3+} emission bands that correspond to the $^5D_0 \rightarrow {}^7F_J$ transitions (see Figure 3). The insets of Figure 3 show a magnification of the 580 nm emission band corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition. The excitation spectra of the complexes closely follow the absorption spectra of the coordinated sensitizers (not depicted),
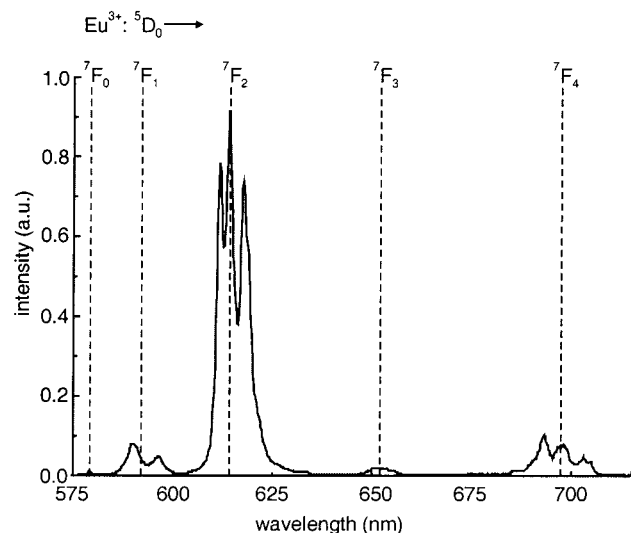
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Figure 4. Magnification of the normalized emission spectrum (λ_{exc} 330 nm) of [(Eu)1]bfa in dichloromethane (10^{-5} M). The emission bands have been assigned to the appropriate $^5D_0 \rightarrow {}^7F_n$ transitions. The spectrum was recorded with a spectral bandwidth of 0.2 nm.

TABLE 2: The Photophysical Data of the Ternary Eu^{3+} Complexes in Dichloromethane (10^{-5} M)

complex	I_{7F2}/I_{7F1}[a]	ϕ_{SE}[b]	$^5D_0 \tau$ (ms)[c]	$^5D_1 \tau$ (μs)[d]	$^5D_0 \tau_0$ (ms)[e]	$^5D_0 \tau/\tau_0$[f]
[(Eu)1]hfa	9.0	0.26	1.27	1.51	2.0	0.6
[(Eu)1]bfa	11.4	0.29	1.08	1.53	1.6	0.7
[(Eu)1]dbm	10.1	0.034	0.38	0.36	1.7	0.2
[(Eu)1]phen	4.9	0.10	0.93	n.d.	2.9	0.3
[(Eu)1]aza	5.4	0.062	0.71	2.97	2.7	0.3

[a] Intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ emission and the $^5D_0 \rightarrow {}^7F_1$ emission (error $\pm$ 0.5, from triplo measurements). [b] The overall quantum yield of the sensitized Eu^{3+} emission (error $\pm$ 5%). [c] Luminescence lifetime of the $^5D_0$ emission (error $\pm$ 5%). [d] Luminescence lifetime of the $^5D_1$ emission (error $\pm$ 5%); [b–d]Errors were determined by duplo measurements (see also ref 23). [e] Calculated radiative lifetimes of the $^5D_0$ emission using eq 3. [f] Calculated luminescence quantum yield of the Eu^{3+} ion.

and thus prove that the Eu^{3+} luminescent state is populated via the antenna. From the excitation spectra it can be seen that the dbm antenna allows the longest wavelength excitation of up to 425 nm.

The emission spectra of the ternary complexes will be discussed in more detail using the spectrum of [(Eu)**1**]bfa as an example. Figure 4 shows an enlarged spectrum of the [(Eu)**1**]-bfa complex in which the emission bands have been assigned. The spectrum has been recorded using a bandwidth of 0.2 nm. The relatively high resolution was used to make sure that the bands of the individual $^5D_0 \rightarrow {}^7F_J$ transitions are well separated.

The radiative transitions within the [Xe]4f^6 configuration of Eu^{3+} are parity forbidden and consist mainly of weak magnetic dipole (MD) and induced electric dipole (ED) transitions. The emission bands of Eu^{3+} remain narrow even in an organic matrix and in solution due to the fact that the partially filled 4f orbitals are shielded from the environment by the filled 5s and 5p orbitals. The probabilities of MD transitions are independent of the chemical environment of the ion, in contrast to those of the ED transitions. The Judd-Ofelt theory has been very successful in understanding and predicting the spectral intensities of the induced ED transitions, especially for ions in glasses and crystals.[27]

The $^5D_0 \rightarrow {}^7F_{0,3}$ transitions at 579 and 650 nm, respectively, are very weak (see Figure 4). In fact these transitions cannot be accounted for by either the MD mechanism or the Judd-Ofelt theory. A more detailed analysis has indicated that these transitions 'borrow' intensity from the $^5D_0 \rightarrow {}^7F_2$ transition through higher order perturbations by the ligand field.[28] The $^5D_0 \rightarrow {}^7F_1$ emission around 593 nm is a pure MD transition. The strongest emission is observed around 615 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition. The intensities of some ED transitions are extremely sensitive to the nature and symmetry of the coordinating environment, and the $^5D_0 \rightarrow {}^7F_2$ transition is an example of such a *hypersensitive* transition. The spectrum shows splitting of the $^5D_0 \rightarrow {}^7F_1$ and the $^5D_0 \rightarrow {}^7F_2$ emission bands in the order of $100-200$ cm^{-1} caused by the ligand field. The $^7F_0$ state is nondegenerate, and therefore the $^5D_0 \rightarrow {}^7F_0$ emission band does not exhibit ligand field splitting. The single peak at 579 nm in the emission spectrum therefore indicates that there is only one (time-averaged) luminescent Eu^{3+} species in solution. Since the

intensity of the MD $^5D_0 \rightarrow {}^7F_1$ transition is independent of the coordination sphere and the $^5D_0 \rightarrow {}^7F_2$ transition is a hypersensitive transition, the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition and the $^5D_0 \rightarrow {}^7F_1$ transition (I_{7F2}/I_{7F1}) is a good measure of the nature and symmetry of the first coordination sphere.[28,27] In a centrosymmetric environment the MD $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} is dominating, whereas distortion of the symmetry around the ion causes an intensity enhancement of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. For the 'bare' (Eu)**1** complex in dichloromethane, I_{7F2}/I_{7F1} is 3.5, which is comparable to the ratio of 4 that was found for this complex in methanol. For the β-diketonate ternary complexes [(Eu)**1**]bfa, [(Eu)**1**]hfa, and [(Eu)**1**]dbm, these ratios are significantly higher with values around 10 (see Table 2). This is the photophysical confirmation of the difference in the structure of the first coordination sphere of (Eu)1 and the ternary complexes. The domination of the $^5D_0 \rightarrow {}^7F_2$ transition in the emission spectrum is a typical feature of Eu-tris(β-diketonate) complexes and the high I_{7F2}/I_{7F1} ratios of the ternary complexes are in line with reported literature values for Eu-tris(β-diketonate) complexes.[28] As we will discuss later, by introducing a β-diketonate in the first coordination sphere of (Eu)**1** the probability of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition has been increased significantly and consequently the radiative rate of the complexed Eu^{3+} ion. By increasing the radiative rate, the Eu excited state will become less sensitive to deactivation processes, ultimately resulting in a more efficiently emitting Eu^{3+} complex.

The coordination of aza and phen causes a much smaller increase of the hypersensitive transition, with I_{7F2}/I_{7F1} ratios of approximately 5. Judd already reported that the symmetry of the coordination sphere and the *polarizability* of the coordinating groups play a role in the hypersensitivity of certain lanthanide-(III) transitions.[29] The coordinating carbonyl groups of β-diketonates are more polarizable[30] than the nitrogen donor atoms of phen and aza resulting in a larger increase in the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition.

Time-Evolution of the Sensitized Eu^{3+} Luminescence. By monitoring the early stages of the lanthanide luminescence using pulsed laser excitation ($\lambda_{exc.} = 337$ nm) and a streak camera,[31] the population of the $^5D_1$ and $^5D_0$ states of Eu^{3+} was studied. Upon pulsed excitation of the antenna, the lanthanide luminescence intensity is expected to rise with a rate equal to the decay rate of the donating state, assuming an immediate population of the donating state (for example the triplet state) and an energy transfer rate that exceeds the decay rate of the lanthanide luminescent state ($k_{Ln} < k_{ET}$). This latter assumption is easily valid for Eu^{3+}, because of its long-lived excited state, which is in the order of milliseconds.
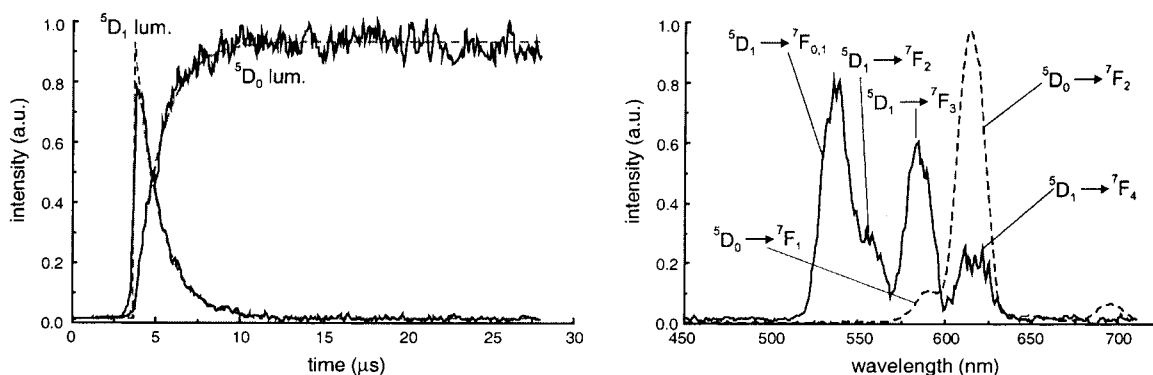
Figure 5. The temporal and spectral curves belonging to the two emissive states of Eu^{3+} in [(Eu)**1**]bfa, reconstructed from the streak image recorded upon pulsed laser excitation. Left: Time-evolution of the $^5D_1$ and $^5D_0$ states. The solid lines are the reconstructed profiles, the dashed lines are the fitted curves. Right: The emission spectra associated with the two states, the solid line corresponds to the $^5D_1$ emission and the dashed line corresponds to the $^5D_0$ emission.

Since the streak camera enables the simultaneous detection of the wavelength and time-dependence of the luminescence signals, the two time-resolved spectra corresponding to the $^5D_1 \rightarrow {}^7F_J$ and $^5D_0 \rightarrow {}^7F_J$ emissions could be deconvoluted by using a mathematical procedure involving singular value decomposition.[32] For example, Figure 5 shows the reconstructed temporal (left) and spectral (right) curves[33] belonging to the two emissive states of Eu^{3+} in [(Eu)**1**]bfa. It should be noted that the temporal curve of the $^5D_0$ emission does *not* represent the behavior of the $^5D_0$ emission at a particular wavelength, but in fact that it represents the relative concentration of all Eu^{3+} species emitting from its $^5D_0$ state. In other words, all the observed $^5D_0 \rightarrow {}^7F_J$ emissions of [(Eu)**1**]bfa exhibit the same rise and decay kinetics. Although the emission spectra corresponding to the $^5D_0 \rightarrow {}^7F_J$ transitions are well documented, hardly any spectra corresponding to the $^5D_1 \rightarrow {}^7F_J$ transitions of organic Eu^{3+} complexes have been reported to date. Comparison of the spectral curves with the available $^5D_1$ emission spectra of $Eu(bfa)_4$ in acetonitrile,[5] shows that the assignment of the bands are in agreement. It is apparent from Figure 5 that the $^5D_0 \rightarrow {}^7F_J$ and $^5D_1 \rightarrow {}^7F_J$ emissions have significant overlap, which is important to realize when one measures the rise-time of the $^5D_0$ emission (vide infra).

In the measurements it was found that immediately after the laser pulse, the Eu^{3+} complexes exhibited emission from the $^5D_1$ state as is illustrated by the temporal spectrum of [(Eu)1]-bfa in Figure 5. The rise-time of the $^5D_1$ luminescence is shorter than the instrument response time, i.e., $\tau_{rise} < 50$ ns, indicative of a fast energy transfer ($k_{ET} > 10^8$ s^{-1}). The $^5D_1$ luminescence is expected to rise with a rate equal to the decay rate of the triplet state, because the triplet state is immediately populated ($k_{ISC} = \sim 10^{11}$ s^{-1}).[34] Furthermore, since it is likely that the energy transfer process will be dominating the triplet state decay, the rise-time represents the energy transfer rate.[10]

Subsequently, the $^5D_1$ state decayed with a time-constant in the order of microseconds (see Table 2), being converted radiatively to the ^7F_J manifold, e.g. the 530 nm emission ($^5D_1 \rightarrow {}^7F_1$ transition), and nonradiatively to the $^5D_0$ state. The $^5D_0$ luminescence exhibited a rise-time in the order of microseconds, after which it decayed with a much slower time-constant of ms. The rise-time of the $^5D_0$ emission is monoexponential and corresponds to the decay time of the $^5D_1$ state, indicating that the $^5D_0$ state is populated via the $^5D_1$ state. The subsequent decay times of the $^5D_0$ luminescence were also monoexponential with lifetimes of 1.27 ms for [(Eu)**1**]hfa and 1.08 ms for [(Eu)**1**]bfa, and slightly lower lifetimes of 0.93 ms for [(Eu)**1**]phen and 0.71 ms for [(Eu)**1**]aza (see Table 2). Compared to these complexes, [(Eu)**1**]dbm has a relatively short

lifetime of 0.38 ms (vide infra). These lifetimes are comparable to the lifetime of (Eu)**1** in methanol (0.80 ms).

A striking observation of the time-resolved spectra is that in all of the investigated ternary complexes there is no *direct* energy transfer from the antenna triplet to the $^5D_0$ level: the Eu^{3+} $^5D_0$ state is only populated via the $^5D_1$ state. This does not seem to be in agreement with what has previously been reported in the literature concerning the sensitization of Eu^{3+} by energy transfer from β-diketonates. For example, Watson *et al.*[35] reported that in $Eu(dbm)_3$ the energy transfer takes place to both the $^5D_1$ and $^5D_0$ states. They have based the conclusion that the $^5D_0$ state is populated by a fast direct and a slower indirect energy transfer (via the $^5D_1$ state), on their observation that the $^5D_0 \rightarrow {}^7F_2$ emission exhibited a rapid initial rise (faster than the instrument response time) followed by a slow rise with rise time in the microsecond region. An explanation for the discrepancy with our findings may be that Watson et al. have overlooked the overlap of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_4$ emission bands around 615 nm, and that, in fact, this 'hidden' $^5D_1 \rightarrow {}^7F_4$ emission is responsible for the observed rapid initial rise.

Recently, de Sa et al.[30] derived some selection rules for the energy transfer from an antenna triplet to the excited states of Eu^{3+} via electron-exchange and multipolar interactions. According to these rules, direct energy transfer to the $^5D_0$ level is not allowed, while the $^5D_1$ level is an excellent receiving energy level for energy transfer via an electron-exchange mechanism. Our experimental observations are in agreement with these rules. However, De Sa et al. further reported that the rule that forbids a direct energy transfer to the $^5D_0$ state is relaxed due to J-mixing effects (which obscures the assignment of the J-states) and thermal population of the $^7F_1$ level (an energy transfer to the $^5D_0$ state is allowed when it involves a $^5D_0 \leftarrow {}^7F_1$ transition instead of the 'forbidden' $^5D_0 \leftarrow {}^7F_0$ transition). This is in line with the observation that in systems where the antenna triplet energy lies between the $^5D_0$ and $^5D_1$ state, a direct energy transfer takes place to the $^5D_0$ state.[36]

The Quantum Yield of the Overall Process. The overall quantum yields of the ternary complexes were determined relative to a reference solution of quinine sulfate in 1 M H_2SO_4 ($\phi = 0.546$) and corrected for the refractive index of the solvent.[37] All quantum yields were measured with aerated solutions. The results have been summarized in Table 2 and show that the bfa antenna is clearly the most efficient sensitizer for Eu^{3+} with a quantum yield of 0.29, followed by the hfa antenna with a quantum yield of 0.26. These values compare favorably with quantum yields of Eu^{3+} complexes reported in the literature.[5,22,36] The process is less efficient in [(Eu)**1**]dbm

Synergistic Complexation of Eu^{3+}

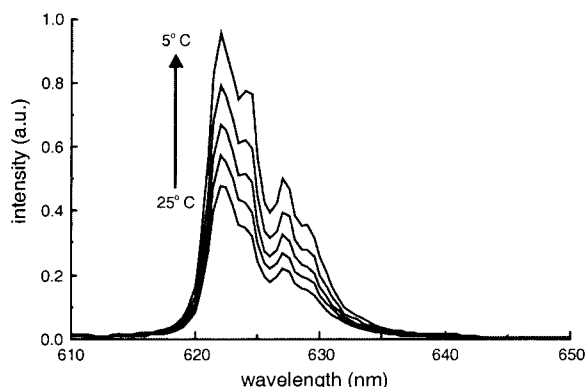*J. Phys. Chem. A, Vol. 106, No. 15, 2002* **3687**

Figure 6. Increase of the luminescence intensity of [(Eu)**1**]dbm upon lowering the temperature from 25 °C to 5 °C.

and rather unexpectedly, also in [(Eu)**1**]aza with luminescence quantum yields of only 0.034 and 0.062, respectively.

The differences in the luminescence quantum yields for the β-diketonate complexes can be explained qualitatively in terms of the antenna triplet state energies, since the intersystem crossing yields as well as the antenna-lanthanide distances in these three complexes are comparable. Since the $^5D_1$ level is the receiving energy level, we will focus on the difference in energy between the antenna triplet and this level. Sato and Wada found that in Eu-tris(β-diketonate) complexes, the triplet energy level of the donating β-diketonate ligand should be approximately 2000 cm^{-1} above the $^5D_1$ level of Eu^{3+} (at ~19,-000 cm^{-1}) in order to obtain the highest luminescence quantum yields.[5] A larger energy difference decreases the luminescence quantum yield, because the overlap between the energy levels of the donor and acceptor becomes smaller. On the other hand, a smaller energy difference reduces the quantum yield because of a thermally activated energy back-transfer process. For the hfa and bfa antenna chromophores the energy difference with the $^5D_1$ state is approximately 3000 and 2400 cm^{-1}, respectively, resulting in a slightly higher quantum yield for [(Eu)**1**]bfa than for [(Eu)**1**]hfa. The much lower luminescence quantum yield of [(Eu)**1**]dbm is explained by a thermally activated energy back-transfer process. The energy gap is only 1600 cm^{-1}, which allows for a significant energy back-transfer within the millisecond lifetime of the lanthanide luminescence. This is corroborated by the observation that the luminescence quantum yield of [(Eu)**1**]dbm increases from 0.03 to 0.06 by decreasing the temperature from 25 °C to 5 °C (see Figure 6), whereas the luminescence quantum yield of [(Eu)**1**]bfa is constant in this temperature region. Such behavior has also been reported for the corresponding Eu(dbm)$_4$ and Eu(bfa)$_4$ complexes.[5,35] The relatively short lifetimes of the $^5D_0$ and $^5D_1$ states of [(Eu)**1**]-dbm further indicate the occurrence of an energy back-transfer (see Table 2). Since the $^5D_0$ state does not have a strong interaction with the dbm triplet state, the $^5D_0$ is depopulated via the $^5D_1$ state and subsequent energy back-transfer to the dbm antenna (see Figure 6).

The efficiency of the sensitization process is quite moderate for the [(Eu)1]aza ($\phi_{SE} = 0.07$) and [(Eu)**1**]phen complexes ($\phi_{SE} = 0.09$), especially when these results are compared to other systems involving the same tetraazatriphenylene antenna with quantum yields of 0.41 and 0.67 for the Eu^{3+} and Tb^{3+} complex, respectively.[22] To obtain more insight into the factors governing the efficiency of tetrazatriphenylene as an antenna chromophore in our complexes, we have also synthesized the [(Tb)**1**]aza complex and have determined its luminescence lifetime and quantum yield. Also, the overall luminescence quantum yield

of [(Tb)**1**]aza is moderate ($\phi_{SE} = 0.15$). The luminescence lifetimes of [(Eu)**1**]aza (0.73 ms), [(Tb)**1**]aza (2.08 ms), and [(Eu)**1**]phen (0.93 ms) are similar to the lifetimes of the 'bare' complexes in methanol (~0.80 ms), and therefore a deactivation process of the lanthanide luminescent state is apparently not the problem. Dissolved oxygen may be competing with the lanthanide ion as an alternative acceptor of the excitation energy from the antenna triplet, if the energy transfer rate is slower or in the same order of magnitude as the oxygen quenching rate.[38] Deoxygenation of the samples did not increase the sensitized luminescence intensity of both [(Eu)**1**]aza and [(Tb)**1**]aza.[39] This is in agreement with the time-resolved measurements which show that the energy transfer rate exceeds 10^8 s^{-1}. A competing process that has frequently been encountered in the search of efficient sensitizers for Eu^{3+} is deactivation via a low-lying Eu^{3+} to antenna charge-transfer state.[2,40] However, such a process does not occur in the case of Tb^{3+}, and this mechanism does not explain the relatively low luminescence quantum yield of [(Tb)**1**]aza.

Influencing the Radiative Rate of Eu^{3+}. Besides the good sensitizing capabilities of the β-diketonates (in this case bfa and hfa), these antennas also contribute positively to the overall luminescence quantum yield (ϕ_{SE}) by increasing the intrinsic luminescence quantum yield of the Eu^{3+} ion (ϕ_{Ln}). The Eu^{3+} luminescence quantum yield (ϕ_{Ln}) is the ratio of the observed lifetime (τ) and the radiative lifetime (τ_0) of the Eu^{3+} luminescence (eq 2).

$$\phi_{Ln} = \tau/\tau_0 \qquad (2)$$

In the previous section it was shown that upon coordination to the Eu^{3+} ion, the probability (oscillator strength) of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition increases. Since the pure radiative lifetime of the Eu^{3+} luminescence is related to the weighted sum of the oscillator strengths of the individual $^5D_0 \rightarrow {}^7F_J$ transitions, this increase will influence the radiative lifetime. Assuming that both the energy of the MD $^5D_0 \rightarrow {}^7F_1$ transition and its dipole strength are constant, Equation 3 provides a means to calculate the radiative lifetime directly from the corrected emission spectrum without the intervention of the Judd-Ofelt theory.[41]

$$1/\tau_0 = A_{MD,0}\,n^3(I_{tot}/I_{MD}) \qquad (3)$$

In this equation, n is the refractive index of the solvent, $A_{MD,0}$ is the spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition in vacuo, and I_{tot}/I_{MD} the total area of the (corrected) Eu^{3+} emission spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ band. It was theoretically calculated and experimentally verified that $A_{MD,0}$ has a value of 14.65 s^{-1}.[41] Using Equation 3, the radiative lifetimes of the Eu^{3+} complexes in dichloromethane ($n = 1.4242$) have been calculated from the corresponding emission spectra (see Figure 4) and they are tabulated in Table 2. The ternary β-diketonate complexes have significantly shorter radiative lifetimes than the ternary aza and phen complexes. As a result, the balance between the radiative and nonradiative decay of the ternary β-diketonate complexes is shifted in favor of the radiative decay, resulting in a value of ϕ_{Ln} that is twice as high compared to the ternary aza and phen complexes.

The calculated values of τ_0 and ϕ_{Ln} of Eu^{3+} in the ternary β-diketonate complexes deserve two additional comments. First, although in aqueous solution τ_0 has been reported as 5.3 ms for Eu^{3+} ions,[42] τ_0 values for Eu^{3+} ions in organic ligands as low as 2 ms are not unprecedented. Some upper limits on τ_0, implied by quantum yields and lifetimes reported in recent

literature for organic complexes of Eu^{3+}, include 2.3 ms with a 4-(phenylethynyl)pyridine-2,6-dicarboxylic acid as a ligand[43] and 2.0 ms with a bisisoquinoline-*N*-oxide based cryptate.[44] Second, if we consider the overall quantum yield of [(Eu)**1**]bfa and [(Eu)**1**]hfa of approximately 0.3, then the calculated ϕ_{Ln} value of these complexes of approximately 0.7 implies that the product of the efficiencies of the two preceding steps, i.e. intersystem crossing from the antenna singlet to the triplet state and energy transfer from the triplet state to the Eu^{3+} ion, is only approximately 0.4. At first sight this is rather unexpected: a reported value for the intersystem crossing quantum yield of bfa in $Gd(bfa)_3$ is 0.84,[9] whereas the short antenna-Eu^{3+} distance would ensure a fast and complete energy transfer. As was mentioned earlier, a problem that has often been encountered in the sensitization of Eu^{3+} is a competing photon-induced electron-transfer process from the antenna to Eu^{3+},[45] due to the low reduction potential of Eu^{3+} in comparison with other trivalent lanthanide ions. In the case of [(Eu)**1**]bfa and [(Eu)-**1**]hfa the singlet and the triplet excited states of the antenna may be partially deactivated by an electron transfer to Eu^{3+},[46] instead of populating the triplet excited state and the Eu^{3+} ion excited states, respectively.[47]

Based on Equation 4[48] the driving force can be estimated for the charge transfer of the excited sensitizer to Eu^{3+}.

$$\Delta G_{CT} = E(sens^{\cdot}/sens^{-1}) - E(sens^{-1*}) - E(Eu^{3+}/Eu^{2+}) \quad (4)$$

With ΔG_{CT} the change in free energy of the electron transfer, $E(sens^{\cdot}/sens^{-1})$ the oxidation potential of the sensitizer, $E(sens^{-1*})$ the singlet or triplet energy of the sensitizer, and $E(Eu^{3+}/Eu^{2+})$ the reduction potential. Please note that in this paragraph we use $sens^{-1}$ for the β-diketonate and $sens^{\cdot}$ for the oxidized sensitizer, whereas in the rest of the article we follow the conventions in this field. With $E(sens^{\cdot}/sens^{-1})$ of 1.60 and 1.40 V (vs NHE) for bfa/bfa^{-1} and hfa/hfa^{-1}, respectively,[49] and the 1-electron reduction potential of Eu^{3+} equal to -0.36 V[50] this gives a driving force for bfa of -1.51 eV and -0.69 eV for energy transfer from the singlet and triplet excited state, respectively, and -1.83 eV and -0.97 eV for hfa. These estimates show that deactivation of the antenna seems thermodynamically feasible.[51]

Although the strategy discussed in this paragraph is not limited to Eu^{3+}, the radiative rate of Eu^{3+} is relatively easily influenced, because its emission spectrum contains a hypersensitive transition. Whereas the luminescence intensities of 'ordinary' ED transitions can vary by a factor of $2-3$ depending on the coordination sphere, a hypersensitive ED transition can increase by a factor of up to 200.[27] It is through this transition, that we have influenced the radiative rate of the complexed Eu^{3+} ion and thus ϕ_{Ln}.

Conclusion

The synergistic complexation of Eu^{3+} by the bidentate antenna and the polydentate ligand has led to the construction of efficiently emitting Eu^{3+} complexes. In these complexes the antenna-lanthanide ion distance has been minimized and the Eu^{3+} ion is completely shielded from the solvent. The ternary β-diketonate complexes combine high association constants (K) and high overall luminescence quantum yields (ϕ_{SE}), for example $K = 3.8 \pm 0.2 \times 10^7$ M^{-1} and $\phi_{SE} = 0.29$ for [(Eu)-**1**]bfa. The photophysical studies of the ternary complexes have shown that there is no direct energy transfer from the antenna triplet to the $^5D_0$ state, but that instead the $^5D_0$ state is populated via the $^5D_1$ state. It has been demonstrated that the overall

efficiency of the sensitized emission is not only determined by the distance from the antenna to the lanthanide ion, and by the requirements of the antenna triplet energy level, but also by the influence of the coordinated antenna on the radiative lifetime of the complexed Eu^{3+} ion.

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