Sensitized near-infrared luminescence from polydentate triphenylene-functionalized Nd^{3+}, Yb^{3+}, and Er^{3+} complexes

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Hexa-deutero dimethylsulfoxide (DMSO-d_6) solutions of terphenyl-based Nd^{3+}, Yb^{3+}, and Er^{3+} complexes functionalized with a triphenylene antenna chromophore exhibit room temperature near-infrared luminescence at wavelengths of interest for the optical telecommunication network (~1330 and ~1550 nm). The sensitizing process takes place through the triplet state of triphenylene as can be concluded from the oxygen dependence of the sensitized luminescence. A significant fraction of the excited triphenylene triplet state is quenched by oxygen, instead of contributing to the population of the luminescent state of the lanthanide ion. The luminescence lifetimes of the triphenylene-functionalized lanthanide complexes (**(2)**Ln) are in the range of microseconds with a lifetime of 18.6 μs for **(2)**Yb, 3.4 μs for **(2)**Er, and 2.5 μs for **(2)**Nd in DMSO-d_6. These luminescence lifetimes seem almost completely dominated by the vibrational quenching by the organic groups in the polydentate ligand and solvent molecules, which leads to low overall luminescence quantum yields. © *1999 American Institute of Physics.* [S0021-8979(99)07615-X]

I. INTRODUCTION

The trivalent rare earth or lanthanide ions are known for their unique optical properties such as line-like emission spectra and long luminescence lifetimes.[1] Because of their intrinsically low absorption cross sections, the indirect excitation of lanthanide ions via an antenna chromophore has been studied in detail for europium (Eu^{3+}) and terbium (Tb^{3+}) luminescence.[1,2] The transfer of the excitation energy to the lanthanide ion is generally considered to take place through the triplet state of the antenna chromophore via an electron-exchange mechanism.[3] Recently, there has been a growing interest in polydentate complexes of the near-infrared (NIR) emitting lanthanide ions erbium (Er^{3+}), ytterbium (Yb^{3+}), and neodymium (Nd^{3+}) for applications in fluoroimmuno assays,[4,5] laser systems,[6] and optical amplification.[7] However, only a few studies have been reported on the sensitized emission of Nd^{3+} and Yb^{3+},[5,8] and even fewer studies on Er^{3+}.[4,7,9]

In the optical telecommunication network an optical transition of Er^{3+}, doped into an inorganic matrix such as silica, is used for amplification of light around 1550 nm.[10] An optical transition of praseodymium (Pr^{3+}) is used for the amplification of light around 1300 nm.[11] The ultimate goal of our research is the development of a polymer-based optical amplifier in which overall neutral organic lanthanide complexes are incorporated into polymer waveguides. In order to achieve an efficient population of the lanthanide luminescent state, these complexes will be functionalized with an antenna chromophore. We have reported the synthesis and photophysical properties of terphenyl-based Nd^{3+} and Er^{3+} complexes.[9,12] Recently, a polymeric waveguide doped with the neodymium chloride salt has been shown to amplify light of 1060 nm.[13]

In the present article we report novel sensitizer-functionalized Nd^{3+}, Yb^{3+}, and Er^{3+} complexes, and their sensitized NIR luminescence. The terphenyl-based ligand **(1)**H_3 and its triphenylene-functionalized derivative **(2)**H_3 were designed to provide eight oxygen donor atoms for the encapsulation of the lanthanide ion: three ether oxygens, three carboxylate oxygens, and two amide carbonyl oxygens (See Fig. 1).

The triphenylene antenna chromophore was incorporated into ligand **(2)**H_3, because it allows excitation up to 350 nm and it has a high intersystem crossing quantum yield (0.89).[2] This is favorable since the sensitized excitation of the lanthanide ion occurs via the triplet state of the chromophore.[3] The antenna chromophore will be positioned in close proximity to the lanthanide ion because of the coordination of the amide carbonyl (*vide infra*).

II. EXPERIMENT

The synthesis of the ligands **(1)**H_3 and **(2)**H_3 is depicted in Fig. 2. Full details of the synthesis will be reported in a forthcoming publication. The key step is the asymmetric functionalization of **4**. Reaction of bis(amine) **4** with 1.3 equivalents of benzoyl chloride gave the mono(amide) **5** in

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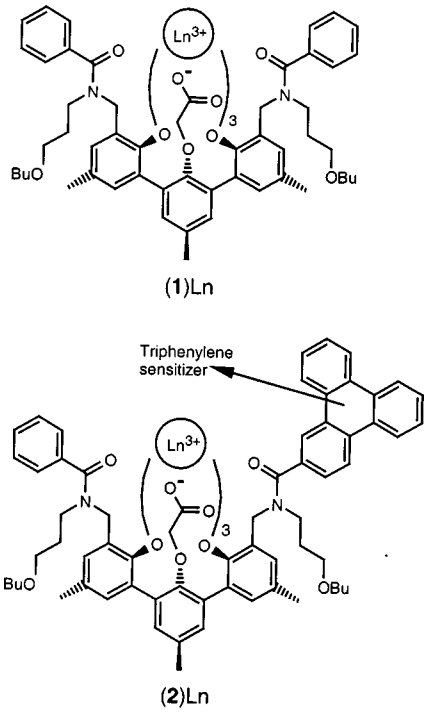

FIG. 1. Schematical representation of the terphenyl-based complex (**1**)Ln and its triphenylene-functionalized derivative (**2**)Ln.

20% yield and bis(amide) **7** in 50% yield. The mono(amide) **5** was reacted with triphenylene carboxylic acid chloride yielding **6** in 70% yield. After hydrolysis of the *tert*-butylesters of **6** and **7** with trifluoroacetic acid, the corresponding complexes were readily formed upon addition of the lanthanide nitrate salts to the ligands in the presence of Et_3N as a base.

Fast atom bombardment mass spectrometry indicated that the complexes have a 1:1 stoichiometry.[14] The IR spectra showed that all carboxylic acid groups are deprotonated and that the amide carbonyls are also coordinated to the lanthanide ion.[15]

Steady state photoluminescence measurements in the NIR region were performed using the 351.1/363.8 nm lines of an Ar ion pump laser at a power of 60 mW for excitation. The laser beam was modulated with an acousto-optic modulator at a frequency of 40 Hz. The luminescence signal was focused into a monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques. The spectral resolution was 6 nm. When a Xe lamp was used as the excitation source, the steady state measurements were performed according to Ref. 12. Luminescence lifetime measurements were performed by monitoring the luminescence decay after excitation with a 0.5 ns pulse of a N_2 laser ($\lambda_{exc}=337$ nm, pulse energy 20 μJ, 10 Hz repetition rate). Decay signals were recorded using a liquid-nitrogen-cooled Ge detector with a time resolution of 0.3 μs. The signals were averaged using a digitizing oscilloscope. All decay curves were analyzed by deconvolution of the measured detector response.

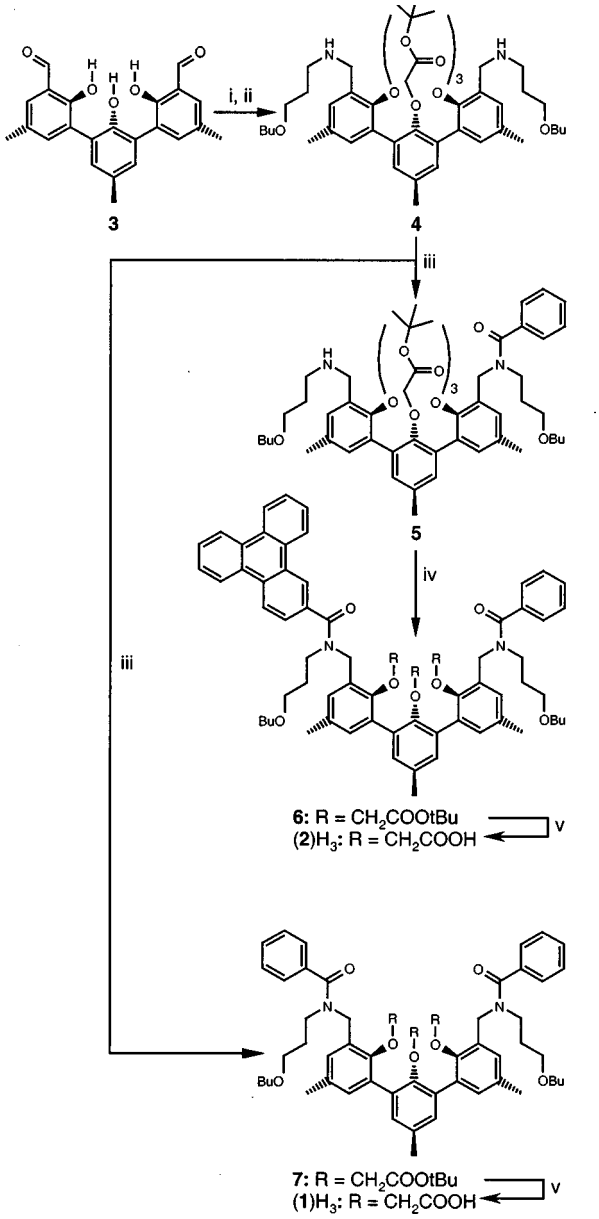

FIG. 2. Reagents and conditions: (i) *tert*-butyl bromoacetate, K_2CO_3, CH_3CN, reflux (80% yield); (ii) 3-butoxypropylamine, H_2, Pd/C (cat.), EtOH (100% yield); (iii) benzoyl chloride, Et_3N, CH_2Cl_2, room temp., 12 h: **5** (20% yield) and **7** (50%, yield); (iv) triphenylene carboxylic acid chloride, Et_3N, CH_2Cl_2, room temp., 12 h (70% yield); (v) TFA, room temp., 12 h, (100% yield).

III. RESULTS AND DISCUSSION

The processes that follow the excitation of the antenna chromophore into its singlet excited state are intersystem crossing to the triplet state, energy transfer to the lanthanide ion, and subsequent lanthanide luminescence (See Fig. 3). The overall quantum yield of sensitized emission ϕ_{se} is therefore the product of the triplet yield ϕ_{isc}, the energy transfer yield ϕ_{et}, and the intrinsic luminescence quantum yield ϕ_{lum}, hence:

$$\phi_{se}=\phi_{isc}\phi_{et}\phi_{lum}. \tag{1}$$

Hexa-deutero dimethylsulfoxide (DMSO-d_6) solutions of the NIR emitting (**2**)Ln complexes (1 mM) exhibit the

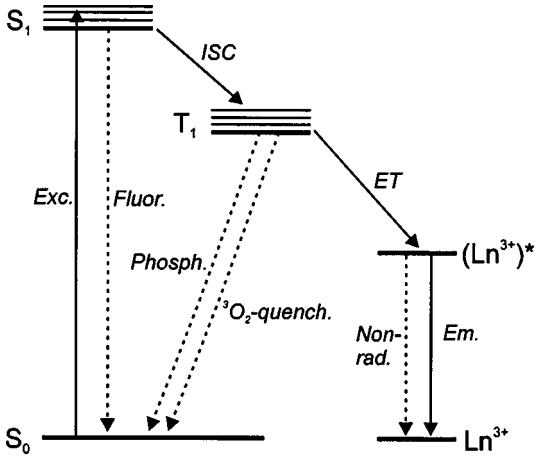

FIG. 3. Photophysical model describing the main pathways in the sensitization process.

typical line-like lanthanide emission upon excitation of the triphenylene antenna chromophore. At room temperature sensitized emission at 1540 nm ($^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition) is observed for **(2)**Er, at 880, 1060, and 1330 nm ($^4F_{3/2}\rightarrow{}^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ transition, respectively) for **(2)**Nd, and at 980 nm ($^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition) for **(2)**Yb (See Fig. 4).

The luminescence intensity is enhanced by 35% for **(2)**Nd, 120% for **(2)**Er, and 90% for **(2)**Yb upon deoxygenation of the samples, indicating that oxygen quenching of the triplet state of triphenylene is competing with the energy transfer to the encapsulated lanthanide ion. The energy transfer rate can be estimated from this oxygen dependence by using the Stern–Volmer equation[16] for the diffussion-controlled oxygen quenching of the triplet state of triphenylene:

$$I_0/I = 1 + k_{\text{diff}}\tau_T[\text{O}_2], \tag{2}$$

where I_0 and I are the lanthanide luminescence intensities in the absence and presence of oxygen, respectively, k_{diff} is the diffusion-controlled quenching rate constant, τ_T is the lifetime of the triplet state of triphenylene, and $[\text{O}_2]$ is the oxygen concentration in DMSO at room temperature. In the deoxygenated solutions the triphenylene triplet state lifetime is mainly governed by the energy transfer rate constant k_{et},[17] and thus

$$k_{\text{et}} = 1/\tau_T. \tag{3}$$

If k_{diff} is taken as $10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$ and $[\text{O}_2]$ is taken as 0.46 mM,[18] the triphenylene triplet state lifetime and energy transfer rate constants in the different complexes can be calculated (see Table I).

The results show that the energy transfer rate is in the same order of magnitude as the oxygen quenching rate, which is equal to the product of k_{diff} and $[\text{O}_2]$. Since the energy transfer process and the oxygen quenching are considered to be the only processes that depopulate the triplet state,[17] the quantum yield of the energy transfer ϕ_{et} can be calculated from

$$\phi_{\text{et}} = k_{\text{et}}/(k_{\text{et}} + k_{\text{diff}}.[\text{O}_2]). \tag{4}$$

For an energy transfer to the lanthanide ion with a efficiency near unity, k_{et} must be at least $10^8\,\text{s}^{-1}$, or else the triplet state will partially be depopulated by molecular oxygen. The slow energy transfer rate can be attributed to two factors in our system. First, there is a distance of approximately 5 Å between the center of the sensitizer and the lanthanide ion.[19] Second, there is a large energy difference between the triplet state of triphenylene ($22\,900\ \text{cm}^{-1}$)[20] and the luminescent state of especially Yb^{3+}. The lanthanide-sensitizer distance and the energy difference between the triplet state and the lanthanide luminescent state are known to strongly influence the energy transfer process in the sensitized emission of Eu^{3+} and Tb^{3+}.[2,3]

Recently, an internal redox mechanism was proposed for the sensitized Yb^{3+} luminescence that takes place through the singlet state of the antenna chromophore.[8] Since such an internal redox energy transfer mechanism takes place through the triphenylene singlet state, the triphenylene fluorescence of **(2)**Yb must not only be competing with intersystem crossing, but also with the redox energy transfer mechanism. However, the intensity of the triphenylene fluorescence of **(2)**Yb and **(2)**Nd (the internal redox energy transfer mechanism does not take place in the latter complex) is the same. Furthermore, the overall sensitized luminescence is oxygen dependent. These observations strongly indicate that the energy transfer pathway takes place through the triplet state of triphenylene.

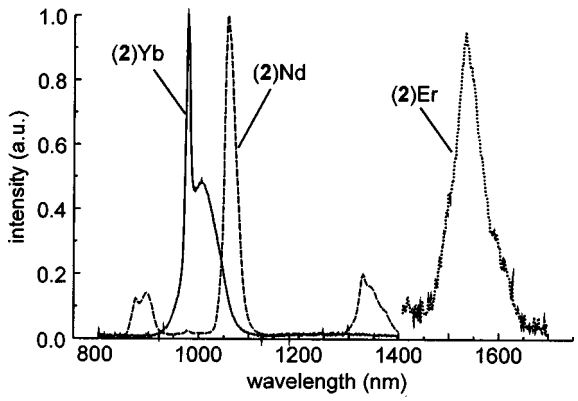

FIG. 4. Photoluminescence spectra of (**2**)Yb, (**2**)Er, and (**2**)Nd in DMSO-d_6 (1 mM) upon excitation of the triphenylene antenna chromophore (351.1/363.8 nm lines of an Ar ion pump laser).

TABLE I. The ratio of the sensitized lanthanide luminescence intensities in the absence and presence of oxygen (1 mM DMSO-d_6 solutions), as well as the calculated energy transfer rate constants k_{et} using the Stern–Volmer equation (Xe lamp: $\lambda_{\text{exc.}}$ 320 nm).

Complex	I_0/I	τ_T (ns)[a]	k_{et} ($10^7\ \text{s}^{-1}$)[b]	ϕ_{et}[c]
(**2**)Yb	1.90	196	0.51	0.53
(**2**)Er	2.20	261	0.38	0.45
(**2**)Nd	1.35	76	1.32	0.74

[a] $\tau_T = (I_0/I - 1)/(k_{\text{diff}}[\text{O}_2])$, $k_{\text{diff}} = 10^{10}\ \text{s}^{-1}\,\text{M}^{-1}$, $[\text{O}_2] = 0.46$ mM.
[b] $k_{\text{et}} = 1/\tau_T$.
[c] $\phi_{\text{et}} = k_{\text{et}}/(k_{\text{et}} + k_{\text{diff}}[\text{O}_2])$.

TABLE II. The luminescence lifetimes of the terphenyl-based complexes in DMSO-d_6 (τ_d) and DMSO-h_6 (τ_h), the calculated luminescence quenching rates by the CH_3 groups of DMSO-h_6 (k_q), as well as the calculated lanthanide luminescence quantum yield (N_2 laser: $\lambda_{exc.}$ 337 nm; 1 mM solutions).

Complex	τ_d (μs)	τ_h (μs)	k_q (10^4 s^{-1})[a]	ϕ_{lum} (DMSO-d_6)	ϕ_{lum} (DMSO-h_6)
(**1**)Yb	19.9	9.1	6.0	0.01	0.005
(**2**)Yb	18.6	9.4	5.3	0.009	0.005
(**1**)Er	3.3	2.1	17.3	0.0002	0.0002
(**2**)Er	3.4	2.4	12.3	0.0002	0.0002
(**1**)Nd	2.5	1.2	43.3	0.01	0.005
(**2**)Nd	2.5	1.4	31.4	0.01	0.006

[a] $k_q = 1/\tau_h - 1/\tau_d$.

Time-resolved luminescence measurements showed that the observed luminescence lifetimes of the complexes in DMSO-d_6 are in the range of microseconds (See Table II), with the Yb^{3+} complexes having the longest lifetimes and the Nd^{3+} complexes the shortest. Our present results compare favorably with the recently published luminescence lifetimes of Nd^{3+} and Yb^{3+} complexes,[5,21] and our previously published lifetimes of Er^{3+}.[7,12] In DMSO-h_6 the luminescence lifetimes are decreased significantly due to the fact that the methyl groups ($-CH_3$) of DMSO-h_6 are more efficient quenchers of the lanthanide excited state than the deutero methyl groups ($-CD_3$) groups of DMSO-d_6. Our observation that the rate constants of the quenching by the methyl groups of the solvent DMSO-h_6 is the largest for Nd^{3+} and the smallest for Yb^{3+} (See Table II) is in agreement with the energy gap law, as is the case for the well-documented quenching by hydroxyl groups (–OH) of Eu^{3+} and Tb^{3+} luminescence.[22] According to the energy gap law the smaller the harmonic number of vibrational quanta that is required to match the energy gap between the lowest luminescent state and the highest nonluminescent state of the lanthanide ion, the more effective the vibronic quenching will be. For the C–H vibration, which has vibrational quanta of 2950 cm^{-1}, the number of harmonics needed to match the energy gap is largest for Yb^{3+}, and smallest for Nd^{3+} (see Fig. 5).

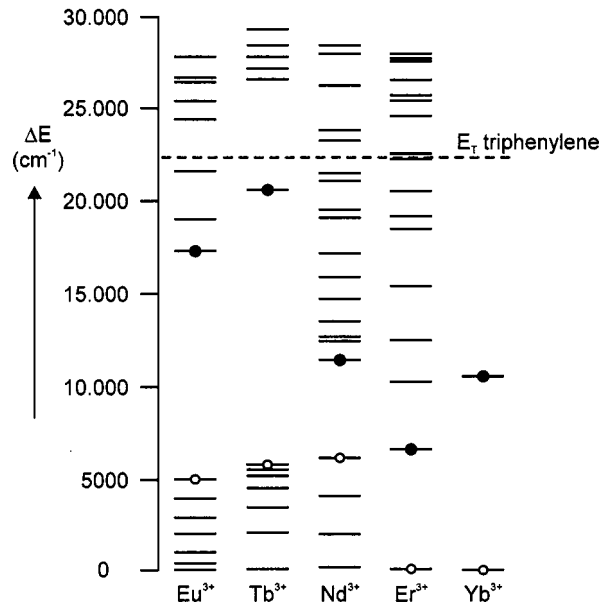

FIG. 5. Energy diagram of the $4f$ levels responsible for the lanthanide luminescence (a filled circle denotes the lowest luminescent state, an open circle denotes the highest nonluminescent state). Adapted from Ref. 21.

The natural lifetimes τ_0 of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} and the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} have been calculated from the absorption spectra of these transitions[23] to be 14 ms for (**1**)Er and 2 ms for (**1**)Yb. The natural lifetime of Nd^{3+} cannot be determined in this way, since the 1060 and 1330 nm emissions do not involve a transition back to the ground state. Instead a literature value of 0.25 ms was taken for Nd^{3+}.[24] The intrinsic luminescence quantum yield ϕ_{lum} of the complexed ions follows

$$\phi_{lum} = k_0/k = k_0/(k_0 + k_{nrad}) = \tau/\tau_0, \tag{5}$$

where k_0 is the natural radiative decay rate, k is the observed radiative decay rate, k_{nrad} the nonradiative decay rate, τ is the observed lifetime, and τ_0 is the natural lifetime. The calculated intrinsic luminescence quantum yields are summarized in Table II. This value of ϕ_{lum} is also the upper limit of the overall quantum yield of sensitized emission ϕ_{se}, because this is the product of the triplet yield ϕ_{isc}, the energy transfer yield ϕ_{eh}, and the intrinsic luminescence quantum yield ϕ_{lum}. This means that, even when ϕ_{isc} and ϕ_{et} are close to unity, the overall quantum yield is low, because the transferred energy is lost mainly via nonradiative processes involving the luminescent states of the lanthanide ions. High-frequency oscillators such as C–H vibrations in the ligand and the solvent molecules, provide a very efficient nonradiative pathway for relaxation of the luminescent state of the NIR emitting lanthanide ions via vibronic coupling.

IV. CONCLUSIONS

In summary, these novel sensitizer functionalized Er^{3+}, Nd^{3+}, and Yb^{3+} complexes exhibit sensitized NIR emission with luminescence lifetimes in the microsecond range. The energy transfer rate from the antenna chromophore to the lanthanide ion should be optimized by incorporating sensitizers with lower triplet energy states in even closer proximity of the lanthanide ion. Substitution of the CH groups in our ligand system for CD groups will further increase the overall luminescence quantum yield.

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[1] (a) K. A. Gschneider and L. R. Eyring, *Handbook on the Physics and Chemistry of Rare Earths* (North Holland, Amsterdam, 1979); (b) N. Sabbatini, M. Guardigli, and J.-M. Lehn, Coord. Chem. Rev. **123**, 201 (1993), and references cited therein.
[2] F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. van der Tol, and J. W. Verhoeven, J. Am. Chem. Soc. **117**, 9408 (1995).
[3] S. Sato and M. Wada, Bull. Chem. Soc. Jpn. **43**, 1955 (1970).
[4] M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, and J. W. Verhoeven, Chem. Phys. Lett. **276**, 196 (1997).
[5] A. Beeby, R. S. Dickins, S. Faulkner, D. Parker, and J. A. G. Williams, Chem. Commun. (Cambridge) **1997**, 1401.
[6] (a) M. Iwamuro, Y. Hasegawa, Y. Wada, K. Murakoshi, T. Kitamura, N. Nakashima, T. Yamanaka and S. Yanagida, Chem. Lett. **1997**, 1067. Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka, and S. Yanagida, J. Phys. Chem. **100**, 10201 (1996).
[7] M. P. Oude Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, E. S. E. van Beelen, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, Chem.-Eur. J. **4**, 772 (1998).
[8] W. D. Horrocks, Jr., J. P. Bolender, W. D. Smith, and R. M. Supkowski, J. Am. Chem. Soc. **119**, 5972 (1996).
[9] L. H. Slooff, A. Polman, M. P. Oude Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstraat, J. Appl. Phys. **83**, 497 (1997).
[10] E. Desurvire, Phys. Today **97**, 20 (1994).
[11] Y. Oshishi, T. Kanamori, T. Kitagawa, S. Takashashi, E. Snitzer, and G. H. Sigel, Jr., Opt. Lett. **16**, 1747 (1991).
[12] (a) M. P. Oude Wolbers, F. C. J. M. van Veggel, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, J. Chem. Soc., Perkin Trans. 2 **1997**, 2275. (b) M. P. Oude Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruël, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, *ibid.* **1998**, 2141.
[13] D. An, Z. Yue, and R. T. Chen, Appl. Phys. Lett. **72**, 2806 (1998).
[14] Selected mass spectra (FAB): (**1**)Er:$m/z=1154.4$ $[(M+H)^+$, calcd 1154.4]; (**1**)Yb:$m/z=1160.2$ $[(M+H)^+$, calcd 1160.4]; (**1**)Nd:$m/z=1130.4$ $[(M+H)^+)$, calcd 1130.4]; (**2**)Er:$m/z=1304.5$; $[(M+H)^+$, calcd 1304.4]; (**2**)Yb:$m/z=1310.4$ $[(M+H)^+$, calcd 1310.4]; (**2**)Nd:$m/z=1280.3$ $[(M+H)^+$, calcd 1280.4].
[15] For all complexes: IR spectral data (KBr): $C{=}O_{amide}$: 1630–1635 cm^{-1}; COO^-: 1595–1600 cm^{-1} (sh.).
[16] A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry* (Blackwell Scientific, London, 1991).
[17] At room temperature, the contribution of phosphorescence ($\sim 10^{-2}\ s^{-1}$) and nonradiative processes ($\sim 10^{5}\ s^{-1}$) to the depopulation of the triphenylene triplet state is negligible compared to the contribution of the energy transfer ($\sim 10^{7}\ s^{-1}$) and oxygen quenching ($\sim 10^{7}\ s^{-1}$).
[18] S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry*, 2nd ed. (Marcel Dekker, New York, 1993).
[19] This value was estimated from the structure of (**1**)Eu that was minimized in the gas phase and subjected to molecular dynamics simulations in a cubic OPLS box of methanol, following the protocol reported in F. J. C. M. van Veggel and D. N. Reinhoudt, Recl. Trav. Chim. Pays-Bas. **114**, 387 (1995).
[20] The triplet energy level was determined by taking the 0–0 transition in the phosphorescence spectrum at 77 K.
[21] A. Beeby and S. Faulkner, Chem. Phys. Lett. **266**, 116 (1997).
[22] G. Stein and E. Würzberg, J. Chem. Phys. **62**, 208 (1975).
[23] W. J. Miniscalo, J. Lightwave Technol. **9**, 234 (1991).
[24] M. J. Weber, Phys. Rev. **171**, 283 (1968).