Near-IR Luminescent Rare Earth Ion–Sensitizer Complexes

J. W. Hofstraat,[1,4,5] **M. P. Oude Wolbers,**[2,3] **F. C. J. M. van Veggel,**[2] **D. N. Reinhoudt,**[2] **M. H. V. Werts,**[4] **and J. W. Verhoeven**[4]

Rare earth ions, with relatively long luminescence lifetimes, have significant advantages for application in fields as varied as diagnostics and optical amplification. In diagnostics the long luminescence lifetimes allow for extremely sensitive time-gated detection, where the difference in temporal behavior of scatter and background fluorescence and the long-lived rare earth luminescence is utilized. In optical amplification the long excited-state lifetime makes it easier to obtain population inversion, a requirement for effective stimulated emission. Unfortunately the absorption cross section of rare earth ion transitions is extremely low. However, via sensitized excitation by means of a suitable organic molecule, efficient excitation is obtained. It is shown that excitation in the visible part of the spectrum can be used to excite rare earth ions which luminesce in the near-IR, such as ytterbium, neodymium, and erbium, via a fluorescein-derivative as sensitizer. The advantages of this approach are manifold. Low-cost light sources are available for the visible part of the spectrum, and interferences from the matrix (scatter, absorption) are minimal. Detection in the near-IR is almost interference-free. For optical amplification the wavelength regions around 1300 and 1550 nm, which can be covered with the neodymium and erbium complexes, respectively, are the most important for applications in optical telecommunication.

INTRODUCTION

Generally, attention in the literature is focused on the rare earth ions europium(III) and terbium(III). These two ions show efficient emission in the red and green part of the optical spectrum and may give extremely long luminescence lifetimes, up to several milliseconds.

[1] Akzo Nobel Central Research, Department RGL, P.O. Box 9300, NL-6800 SB Arnhem, The Netherlands.
[2] University Twente, Department of Supramolecular Chemistry and Technology, NL-7500 AE Enschede, The Netherlands.
[3] Present address: University Twente, Department of Inorganic Materials Science, P.O. Box 217, NL-7500 AE Enschede, The Netherlands.
[4] University of Amsterdam, Laboratory of Organic Chemistry, Nieuwe Achtergracht 129, NL-1018 WS Amsterdam, The Netherlands.
[5] To whom correspondence should be addressed at Philips Research, Prof. Holstlaan 4, NL-5656 AA Eindhoven, The Netherlands.

These properties make these rare earth ions attractive for diagnostic applications, where the long luminescence lifetimes are employed to obtain background-free time-gated detection. One important disadvantage of the rare earth ions is that they have extremely small absorption cross sections, so that significant emission intensity may be attained only by bringing them in close proximity to a suitable organic sensitizer molecule. Moreover, due to energetic constraints the sensitizer has to be excited in the UV, which results in more background signals and possible radiation-induced damage to the biological sample. Nevertheless, a variety of such rare earth ion-sensitizer complexes for diagnostic applications has been reported [1–5].

Recently, rare earth ions have also received attention for application in optical telecommunication. In particular erbium-doped fiber amplifiers (EDFAs) are used

to compensate for signal losses in optical fibers [6–8]. For this application also the long lifetime of the excited state is important, since it facilitates the inversion of the population between the excited state and the ground state, which is essential for effective amplification by stimulated emission of photons. For applications in optical telecommunication, in particular, the two optical transmission windows, around 1300 and 1550 nm, are of interest. The fiber amplifiers which have been currently reported are all based on inorganic materials doped with erbium ions (for the 1550-nm window) and praseodymium (for the 1300-nm window). Due to the high sensitivity of the latter ion to phonon-mediated deactivation of the excited state, an effective signal gain could be obtained only in low-phonon glasses, such as ZBLAN and chalcogenide-based materials [9–11]. Here, also, the low-absorption cross sections of the rare earth ions require high-intensity lasers for excitation.

In this paper a new concept is discussed which, in principle, would allow both the sensitive detection of analytes in diagnostic applications and the effective excitation of rare earth ions for optical amplification. The concept is based on the use of near-IR luminescent rare earth ions in combination with efficient organic sensitizer molecules. Such sensitizers may be excited in the visible part of the spectrum due to the relatively low energy of the excited state of the rare earth ion which needs to be populated. The use of organic molecule-based rare earth ion complexes is particularly interesting because of their compatibility with polymer-based optical components, which have many advantages for application in optical telecommunication [12–14].

EXPERIMENTAL

Instrumental

Steady-state luminescence measurements were done with a modified Photon Technology International (PTI) Alphascan spectrofluorimeter. For excitation either the light from a 75-W quartz–tungsten–halogen lamp was focused into a SPEX 1680 double monochromator and subsequently onto the sample or the light from an Argon-ion laser (488 nm) was applied. The excitation light was modulated by a mechanical chopper at 35–70 Hz. The emitted light was collected under an angle of 90°, separated by a PTI 0.25-m monochromator and detected with a NorthCoast 817L liquid nitrogen-cooled Germanium detector coupled to a Stanford Research SRS 530 lock-in amplifier.

Time-resolved luminescence measurements were done with an Edinburgh Instruments LP900 system, using a Laser Technik Berlin LTB nitrogen laser/dye laser for excitation and a NorthCoast 817P liquid nitrogen-cooled Germanium detector coupled to a Tektronix fast digital oscilloscope for detection. The pulse width of the nitrogen laser is about 500 ps; the response of the detector is 250 ns and, therefore, determines the attainable lifetime resolution. The shortest lifetime which can be determined with reasonable accuracy (<10%) with this setup is 100 ns. The instrument response function was obtained by recording the evolution of the signal of the near-IR emitting dye IR140 in ethanol. The fluorescence lifetime of this dye is shorter than 1 ns, which is significantly shorter than the time scale set by the instrument response.

Materials

The preparation of the complexes has been described in detail in separate papers [15,16]. The preparation of the water-soluble diethylenetriamine pentaacetic anhydride (DTPA) complex was based on direct reaction of the anhydride with 5-aminofluorescein, followed by chromatographic purification of the reaction mixture [15]. The chelate was prepared by adding an aqueous solution of the rare earth ion and excess ion was washed away using a solid-phase extraction column to hold the chelate. The calix[4]arene-based complexes were conceived so that they are soluble in apolar solvents and, thus, more suitable for application in polymer matrices. The monofunctionalized calix[4]arenetriethylester, containing a primary (propyl- or hexyl-) amine group, is reacted with fluoresceinisothiocyanate; subsequently the triacid is obtained by hydrolysis with potassiumhydroxide in methanol under reflux conditions. The rare earth ion complex was obtained by adding the ions to the triacid dissolved in a THF solution containing 4 equiv of triethylamine as a base [16]. The two types of complexes are shown in Fig. 1.

The photophysical properties of the complexes were characterized in solution. As solvents D_2O (99.9%), Tris-d_{11} buffer, and DCl (as a 35% solution in D_2O) from Aldrich were used. Methanol and DMSO were acquired from Baker; methanol-d_4 was from Cambridge Isotopes. Experiments were done on 10^{-6} M, or less concentrated, to prevent intermolecular or photophysical interferences.

RESULTS AND DISCUSSION

Two types of complexes were prepared, based on the same basic structure, i.e., the combination of a flu-
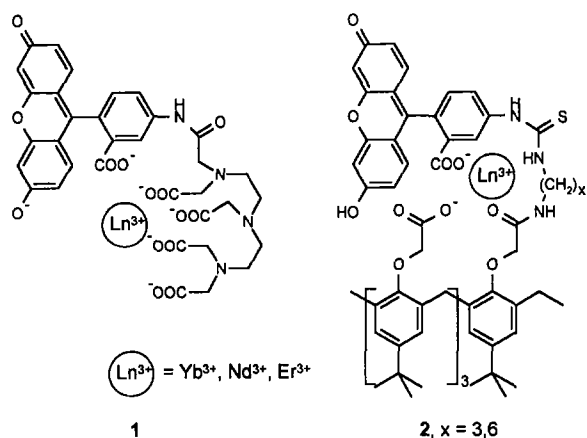
Fig. 1. Structures of the DTPA–fluorescein chelate (**1**) and the Calix[4]arene–fluorescein complex (**2**).

orescein derivative as organic sensitizer molecule and a separate, ionic, structure for complexation of the rare earth ion (see Fig. 1). For diagnostic application, however, the complex should be water soluble, and for application in an optical amplifier, the complex preferentially should dissolve in an organic solvent and be compatible with a polymer matrix. Obviously, these conditions require the use of different structures to bind the ions.

DTPA-Based Complexes

The stable binding of a rare earth ion in a water-soluble macromolecule requires a very strong binding chelate, since the water molecules themselves bind strongly to the ion. Such a chelate is, for instance, DTPA, a polyaminocarboxylic acid, which offers—after coupling to the sensitizer molecule—four carboxylic acid groups for binding the lanthanide ion.

Once the three near-IR emitting rare earth ions have been brought into contact with the chelate, the typical emission is detected: for neodymium(III) luminescence is observed at 876 nm (from the $^4I_{9/2} \leftarrow\ ^4F_{3/2}$ transition), at 1064 nm ($^4I_{11/2} \leftarrow\ ^4F_{3/2}$), and at 1337 nm ($^4I_{13/2} \leftarrow\ ^4F_{3/2}$); for the ytterbium(III) chelate, at 981 nm ($^2F_{7/2} \leftarrow\ ^2F_{5/2}$); and for the erbium(III) chelate, at 1522 nm ($^4I_{15/2} \leftarrow\ ^4I_{13/2}$). For all three complexes the same excitation spectrum was recorded, which shows a maximum at 491 nm. The excitation spectrum exactly matches the absorption spectrum of the fluorescein-derivative attached to the DTPA unit. At the absorption maximum the sensitizer has an extinction coefficient of $5.10^4\ M^{-1}\ cm^{-1}$, which is more than 4 orders of magnitude higher than the extinction coefficients for direct excitation of the

near-IR transitions of the rare earth ions themselves. Sensitized excitation hence provides a much more efficient pathway to obtain excited rare earth ions than direct excitation. The excitation spectra corroborate this observation, since no evidence of direct excitation [e.g., the 580-nm absorption band for neodymium(III) or the 540-nm band for erbium (III), bands with extinction coefficients of 6 and 2.5 M^{-1} cm^{-1}, respectively [17]] is visible in the spectra. The emission spectra obtained for all three ions and the excitation spectrum for the ytterbium(III)-containing chelate (the spectra for the two other chelates are exactly the same) are depicted in Fig. 2.

The total yield of sensitized luminescence is determined by three factors (see also Fig. 3):

$$\Phi_{total} = \Phi_{isc} \cdot \Phi_{ET} \cdot \Phi_{Ln} \tag{1}$$

where Φ_{isc} represents the triplet yield of the sensitizer, which is determined by two processes: (1) the rate of intersystem crossing from the excited singlet state of the sensitizer to its triplet state and (2) the rate of population of the excited singlet state of the sensitizer (since the triplet state of the sensitizer and the accepting state of the lanthanide ion may be long-lived, population bottlenecks may occur somewhere in the system, so that nonlinear effects may play a role). Φ_{ET} is the efficiency of energy transfer from the triplet state of the sensitizer to the excited state of the rare earth ion, which is determined by the effectiveness of competing deactivating pathways of the triplet state; in solution this is predominantly oxygen-induced quenching. Φ_{Ln} is the efficiency of luminescence from the excited rare earth ion. For near-IR luminescent rare earth ions the quenching of the excited state of the ion by high-energy vibrational modes of nearby groups (from the chelate or from the solvent) is predominant; in particular, O–H vibrations (with a vibrational energy of about 3400 cm^{-1}) and N–H vibrations (at 3200 cm^{-1}) are very efficient. But for the near-IR luminescent ions with low-energy excited states, also quenching by the abundant C–H vibrations (at 3000 cm^{-1}) may also play a role. To gain insight into the efficiency of the luminescence obtained from the chelates, two types of experiments were done. First, the effect of deoxygenation on the luminescence intensity was examined by comparing the luminescence intensity before and after purging of the solution with argon, which gives direct information on Φ_{ET}. Second, the luminescence lifetime of the rare earth ions was determined, which is a direct reflection of Φ_{Ln}. Under the applied experimental conditions, no nonlinear effects were observed when the intensity of the exciting radiation was varied, so the triplet yield is determined by the sensitizer
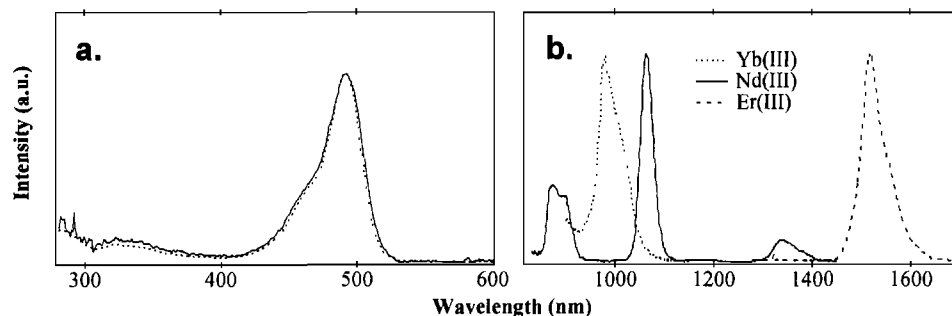
Fig. 2. Luminescence emission and excitation spectra of the near-IR luminescent rare earth ion chelates of DTPA–fluorescein (1).
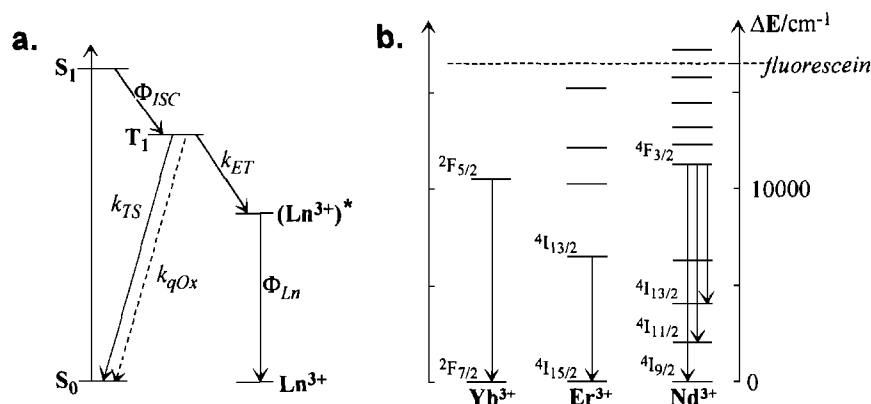

Fig. 3. Energy scheme, illustrating the sensitization of the rare earth ion by the fluorescein derivative and showing the competing deactivation pathways.

Table I. Change in Luminescence Intensity Due to Deaeration and Luminescence Lifetimes of Near-IR Luminescent Rare Earth Ions Complexed with DTPA-Based Chelates

Ion	I_{deaer}/I_{aer}	$\Phi_{flu,\ sens}{}^a$	τ_{lum} (μs)
Nd^{3+}	1.2	0.10	0.6
Yb^{3+}	5.8	0.26	8.5
Er^{3+}	1.1	0.13	1.0

^{a} The quantum yield of the sensitizer has been determined with reference to free fluorescein in 0.01 M NaOH (pH = 12), with Φ_{flu} = 0.92[19]. The quantum yield of the aminofluoresceine–DTPA compound, without rare earth ion, in this solution is 0.75.

and its direct environment. The intrinsic triplet yield of fluorescein is low (Φ_{ISC} = 0.02 [18]), but the presence of the rare earth ion will result in an enhancement of the intersystem crossing rate due to the heavy atom effect. The triplet yield of the chelate could not be determined yet, but the increase in triplet yield is demonstrated by the reduction of the fluorescence of the sensitizer after

chelation of the rare earth ion. For complexes with the three near-IR luminescent rare earth ions the reduction amounts to 65–85% (see Table I). Since the absorption spectrum shows only minor changes upon chelation, the reduction of the fluorescence must be due mainly to enhanced intersystem crossing.

The results of the deaeration and the luminescence lifetime experiments are assembled in Table 1. The deaeration experiment clearly shows a significant increase in the luminescence intensity of the rare earth ion luminescence upon the removal of oxygen. The effect is most important for ytterbium(III), which has the largest energy gap between the accepting level and the sensitizing triplet state. The large oxygen quenching effects suggest that the Φ_{ET} is less than 1, and for ytterbium(III), even much less than 1. In some cases even emission signals from $^1O_2$ at 1275 nm may be observed; this reactive oxygen species is formed as a result of the triplet–triplet annihilation process taking place when the triplet state of the sensitizer molecule and molecular oxygen
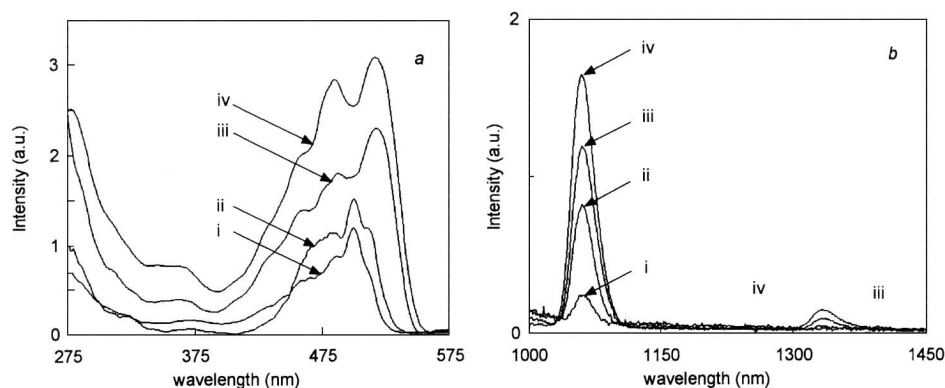
Fig. 4. Luminescence emission and excitation spectra for $5\cdot10^{-5}$ M solutions of the Nd^{3+}–calix[4]arene-propyl-fluoresceine and –hexylfluoresceine complexes in methanol-d_4 and in DMSO. (a) Excitation spectra of (i) 2–C6–Nd^{3+} in methanol-d_4, (ii) 2–C3–Nd^{3+} in methanol-d_4, (iii) 2–C6–Nd^{3+} in DMSO, and (iv) 2–C3–Nd^{3+} in DMSO, detected at 1060 nm. (b) Emission spectra of DMSO solutions of (i) 2–C6–Nd^{3+} excited at 310 nm, (ii) 2–C3–Nd^{3+} excited at 310 nm, (iii) 2–C6–Nd^{3+} excited at 515 nm, and (iv) 2–C3–Nd^{3+} excited at 515 nm.

interact [19]. The quenching by oxygen is a collision-induced one; the quenching rate is therefore determined by the product of the quenchers and the diffusion rate ($k_{O_2} = k_q \cdot [O_2]$); for aqueous solutions $k_q \sim 3 \cdot 10^{10}$ M^{-1} s^{-1} [20], and $[O_2] \sim 1.3 \cdot 10^{-3}$ M [21], so that the oxygen-induced quenching rate is of the order of $k_{O_2} = 4 \cdot 10^7$ s^{-1}. The energy transfer rate from the triplet state of the sensitizer to the accepting state of the rare earth ion therefore is, at most, of the same order of magnitude as the radiationless quenching rate.

Luminescence lifetime measurements indicate that strong quenching of the excited states of the rare earth ions takes place. The lifetimes are all in the microsecond range, being significantly longer for ytterbium(III) than for neodymium(III) and erbium(III). Comparison to data for these ions in inorganic glasses, where high-energy vibrational modes are absent, indicates that the vibrational quenching in organic solution is substantial. For instance, erbium(III) in QE-7 phosphate glass has a luminescence lifetime of 8 ms and neodymium(III) in Q-88 phosphate glass has a lifetime of 0.3 ms [22]. A radiative lifetime of 22 ms was derived for erbium(III)-doped soda–lime glass by extrapolation to extremely dilute solid solutions, in order to remove concentration quenching effects [23]. Therefore the main factor determining the overall efficiency of the luminescence originating from the near-IR luminescent rare earth ion chelate is the quenching due to the direct environment of the ion. Comparison of the luminescence lifetimes suggests that the luminescence yield of the organic complex in solution is about 10^{-3} of that of the ion in an inorganic environment, but the loss in luminescence

yield is amply compensated by the increase in excitation efficiency due to the use of the organic sensitizer.

Calix[4]arene-Based Complexes

The calix[4]arene-based complexes were designed in such a way that they dissolve in nonaqueous solvents. Such solvents are more suited for preparation of thin polymer films, which is preferentially done by spin coating [12–14]. The calix[4]arene-based complexes contain three carboxylic acid groups, so that the final rare earth ion-containing ligand is electrically neutral; the presence of the carboxylic acid moiety in the sensitizer may result in additional shielding of the ion and will improve the (distance-dependent; see above) energy transfer efficiency. The complex thus obtained has advantages not only in terms of improved solubility in apolar solvents, which are preferred to reduce the water content, but also for use in active optical components where electric fields are applied across the polymer layer [14].

Neodymium(III) and erbium(III) complexes were prepared, which are both of interest for application in optical telecommunication (for the 1300- and for the 1550-nm wavelength region, respectively). A praseodymium(III) complex was prepared as well, but no emission could be detected in the near-IR. Spectra obtained for both types of complexes have been recorded in methanol-d_4 and in DMSO. Emission and excitation spectra for the neodymium(III) complexes are shown in Fig. 4; those for the erbium(III) complexes, in Fig. 5. The fluorescein-based sensitizer has been connected to the calix[4]arene via a propyl or a hexyl bridge. As has
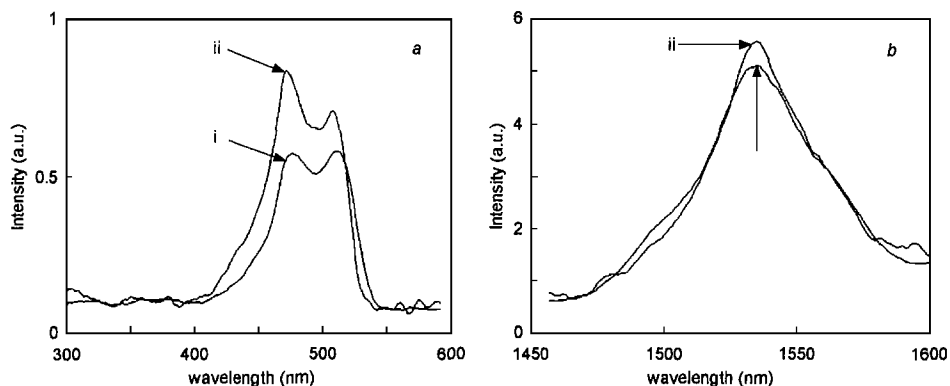
Fig. 5. Luminescence emission and excitation spectra for $5 \cdot 10^{-5}$ *M* solutions of the Er^{3+}–calix[4]arene-propylfluoresceine and–hexylfluoresceine complexes in DMSO. (a) Excitation spectra detected at 1535 nm and (b) relative emission spectra after excitation at 515 nm, both of DMSO solutions of (i) 2–C6-Er^{3+} and (ii) 2–C3-Er^{3+}.

Table II. Luminescence Lifetimes (μs) of Neodymium(III) and Erbium(III) Ions Complexed with Calix[4]arene-Based Complexes

Solvent	C6–Nd^{3+}	C3–Nd^{3+}	C6–Er^{3+}	C3–Er^{3+}
Methanol-d_4	0.9	0.8	0.8	0.9
DMSO	1.2	1.3	1.7	1.6

been discussed for DTPA-based chelates, calix[4]arene complexes also show clear evidence of near-IR rare earth ion emission sensitized by the fluorescein moiety. The excitation spectra clearly show the features of the fluorescein chromophore, with a maximum at about 500 nm. The excitation spectra obtained for the calix[4]arene-complexes in methanol-d_4 and, in particular, in DMSO are significantly red-shifted compared to the excitation spectra obtained for the DTPA-based chelates. The emission spectra are very similar for the two types of complexes, the neodymium(III) complex showing emission with a maximum at 1350 nm, and the erbium(III) complex at 1535 nm.

The same experiments as described above for the DTPA chelates to elucidate the luminescence efficiency, by examination of the luminescence lifetime and of oxygen quenching effects, were done for the calix[4]arene complexes. Deaeration did not lead to a significant change in luminescence intensity of the calix[4]arene-based complexes, which indicates that the energy transfer from the sensitizer to the rare earth ion is much more efficient in these complexes than in the DTPA-based ones. Since the energy transfer efficiency is strongly dependent on the distance between sensitizer and acceptor, this would imply that there is a stronger interaction between sensitizer and rare earth ion in the calix[4]arene-

based complexes than in the DTPA-based chelates. This is also suggested by the observed red shift of the fluorescein sensitizer in the former type of complexes. The fluorescence intensity of the sensitizer is reduced upon complexation, which is in line with the observed interaction of the sensitizer with the rare earth ion, pointing to an increased singlet-to-triplet intersystem crossing rate due to the heavy atom effect. The rate of energy transfer from sensitizer to rare earth ion in the calix[4]arene complexes must be significantly faster than $3 \cdot 10^8$ s^{-1}, the oxygen quenching rate in the two solvents applied (the solubility of oxygen in methanol and DMSO is approximately one order of magnitude higher than in water) [21].

The luminescence lifetimes of the complexes are given in Table II. The luminescence lifetimes for the propylamine (C3) and hexylamine (C6) are similar and very short, approximately 3 orders of magnitude shorter than the lifetimes obtained in inorganic solids, which—again—points to quenching by the high-energy vibrational modes of the organic ligand. The luminescence lifetimes in DMSO solution are significantly longer than in deuterated methanol for both ions. DMSO forms a relatively strong complex with the rare earth ions via the sulfoxide groups. It is generally observed that rare earth ions in DMSO containing solvents show enhanced luminescence lifetimes [24]. The observed enhancement of the luminescence lifetimes in DMSO suggests that the solvent also contributes to the radiationless deactivation of the excited state of the lanthanide ion.

Comparison of the photophysical data of the DTPA-based chelates and the calix[4]arene-based complexes shows that the luminescence lifetimes are similar, suggesting that the deactivation of the excited rare earth

ions is about the same in the two types of organic complexes. The efficiency of the population of the excited state of the rare earth ion, however, appears to be more efficient for the calix[4]arene-based complex. These complexes do not show deaeration effects, even though the concentration of oxygen in the methanol and DMSO solutions is about one order of magnitude higher than in water. This difference may be due to the fact that the fluorescein—which does contain a deprotonated carboxylic acid group with complexating power—is able to fold toward the rare earth ion in calix[4]arene. The complexating ability of the chelate is higher than that of the modified calix[4]arene. Thus, in the latter complex, the lanthanide ion may be positioned between the calix[4]arene cavity and the fluorescein. This can explain both the more efficient energy transfer and the large effect of the solvent on the luminescence properties of the calix[4]arene-based complex. The effective distance of the sensitizer to the rare earth ion is crucial for the efficiency of the energy transfer process.

On the basis of the measured (extinction coefficient, luminescence lifetimes) and estimated (energy transfer rates, triplet yield) photophysical parameters for the erbium(III) complex, a rough calculation was made of the gain which may be reached using calix[4]arene-based material as the medium for an optical amplifier. This calculation indicates that the—more than 10^4-fold increased—excitation efficiency of the rare earth ion brought into contact with the organic sensitizer more than compensates for the reduced luminescence lifetime, compared to the free rare earth ion in an inorganic complex. Obviously, some loss in efficiency may be caused by inefficient population of the sensitizer triplet state or by inefficient energy transfer, represented by the factors Φ_{ISC} and Φ_{ET} in Eq. (1). For a 2-μm core waveguide doped with an erbium(III)–organic sensitizer complex, a 1.7-dB/cm gain should be obtainable when only a 1.4-mW pumping power is applied, which would mean a significant improvement over inorganic glass-based erbium-doped fiber amplifiers [25].

CONCLUSION

The organic dye fluorescein, with absorption in the green part of the spectrum, has been shown to be an efficient sensitizer for rare earth ions which luminesce in the near-IR. Two types of complexes, one based on the polyaminocarboxylate DTPA and one based on a tricarboxylate-calix[4]arene, were prepared with a fluorescein derivative covalently attached to it. Both show sensitized luminescence for neodymium(III), ytter-

bium(III), and erbium(III). The luminescence lifetimes which have been obtained are about three orders of magnitude shorter than those of rare earth ions in inorganic matrices, which demonstrates the effectiveness of high-energy vibrational modes in deactivation of the excited states of the ions. The loss in radiative lifetime, however, is amply compensated by the significant increase in excitation efficiency, which amounts to more than four orders of magnitude when fluorescein is applied. The total luminescence yield is not determined just by the efficiency of the excitation process and the radiative lifetime of the ions. Also, the triplet yield of the sensitizer and the efficiency of energy transfer from the sensitizer to the rare earth ion are important. The energy transfer efficiency is much higher in the calix[4]arene-based complex than in the DTPA-based complex, since a significant increase in luminescence intensity is observed upon deaeration in the latter compound.

The new classes of compounds described in this paper form the basis of new developments which hold promise for application both in diagnostics and in optical telecommunication. Remaining challenges are (1) the improvement of the energy transfer efficiency from sensitizer to rare earth ion; (2) the reduction of rapid deactivation pathways, in order to increase the radiative lifetime; and (3) a further shift of the excitation wavelength to the red, so that low-cost excitation sources may be applied.

REFERENCES

1. B. Alpha, J.-M. Lehn, and G. Mathis (1987) *Angew. Chem.* **99**, 259–261.
2. J. Coates, P. G. Sammes, and R. M. West (1996) *J. Chem. Soc. Perkin Trans.* **2**, 1275–1282, 1283–1287.
3. M. Li and P. R. Selvin (1995) *J. Am. Chem. Soc.* **117**, 8132–8138.
4. V.-M. Mukkala and J. Kankare (1992) *Helv. Chim. Acta* **75**, 1578–1592, 1621–1632.
5. S. Aime, M. Botta, D. Parker, and J. A. G. Williams (1996) *J. Chem. Soc. Dalton Trans.* 17–23.
6. B. J. Ainslie (1991) *J. Lightwave Technol.* **9**, 220–227.
7. W. J. Miniscalco (1991) *J. Lightwave Technol.* **9**, 234–250.
8. B. Pedersen, W. J. Miniscalco, and S. A. Zemon (1992) *J. Lightwave Technol.* **10**, 1041–1049.
9. Y. Osishi, T. Kanamori, T. Kitagawa, S. Takahashi, E. Snitzer, and G. H. Sigel, Jr. (1991) *Opt. Lett.* **16**, 1747–1749.
10. Y. Osishi, M. Yamada, A. Mori, T. Kanamori, M. Shimizu, and S. Sudo (1995) *Opt. Lett.* **20**, 383–385.
11. J. Lucas and J. L. Adam (1995) *Optronics* **167**, 121–126.
12. L. A. Hornak (1992), *Polymers for Lightwave and Integrated Optics: Technology and Applications*, Marcel Dekker, New York.
13. M. B. J. Diemeer, T. Boonstra, M. C. J. M. Donckers, A. M. van Haperen, B. H. M. Hams, T. H. Hoekstra, J. W. Hofstraat, J. C. Lamers, W. Y. Mertens, R. Ramsamoedj, M. van Rheede, F. M. M. Suijten, U. E. Wiersum, R. H. Woudenberg, B. Hendriksen,

W. H. G. Horsthuis, and H. M. M. Klein Koerkamp (1995) *SPIE Proc.* **2527**, 411–416.

14. M. C. Flipse, C. P. J. M. van der Vorst, J. W. Hofstraat, R. H. Woudenberg, R. A. P. van Gassel, J. C. Lamers, E. G. M. van der Linden, W. J. Veenis, and M. B. J. Diemeer (1996) Recent progress of polymer based electro-optic modulators: Materials and technology, in F. Kajzar, V. M. Agranovich, and C. Y.-C. Lee (Eds.), *Photoactive Organic Materials. Science and Applications. Proceedings of the NATO Advanced Research Workshop*, Kluwer Academic, Dordrecht, The Netherlands, pp. 227–246.

15. M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, and J. W. Verhoeven (1997) *Chem. Phys. Lett.* **276**, 196–201.

16. M. P. Oude Wolbers, J. W. Hofstraat, F. A. J. Geurts, F. C. J. M. van Veggel, and D. N. Reinhoudt (1998) *Chem. Eur. J.* **4**, 772.

17. K. A. Gschneider and L. Eyring (1979) *Handbook on the Chemistry and Physics of Rare Earths, Vol. 3*, North-Holland, Amsterdam.

18. S. L. Murov, I. Carmichael, and G. L. Hug (1993) *Handbook of Photochemistry*, 2nd ed., Marcel Dekker, New York.

19. N. J. Turro (1978) *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA.

20. J. B. Birks (1970) *Photophysics of Aromatic Molecules*, Wiley, New York.

21. H. Stephen and T. Stephen (1963) *Solubility of Inorganic and Organic Compounds*, Pergamon Press, Oxford.

22. Kigre, Inc. (1990) *Standards and Specifications of Kigre Laser Rods*.

23. A. Polman (1997) *Appl. Phys. Rev.* **82**, 1–39.

24. A. Beeby and S. Faulkner (1997) *Chem. Phys. Lett.* **266**, 116–122.

25. L. H. Slooff, A. Polman, M. P. Oude Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstraat (1998) *J. Appl. Phys.* **83**, 497–503.