Concentration effects in the photodegradation of lissamine-functionalized neodymium complexes in polymer waveguides

L. H. Slooff and A. Polman

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

S. I. Klink, L. Grave, and F. C. J. M. van Veggel

Supramolecular Chemistry and Technology and MESA$^+$ Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

J. W. Hofstraat

Philips Research, Dept. of Polymers and Organic Chemistry, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

The photodegradation of lissamine-functionalized Nd complexes doped at a concentration of 10 wt. % in a fluorinated polycarbonate waveguide has been studied.   On illumination at 458 nm and at 488 nm, the luminescence spectrum of the lissamine sensitizer shifts to shorter wavelengths, while the luminescence intensity first increases and then decreases.   The spectral shape of the Nd luminescence does not change on illumination, and the luminescence intensity shows a gradual decrease as a function of time.   The difference in response between the lissamine and the Nd luminescence can be described by a model that assumes the existence of two different types of complex.   One type exhibits energy transfer from the lissamine to the neodymium ion, with a large lissamine intersystem crossing rate, and hence low sensitivity to concentration quenching.   The other type does not show energy transfer to Nd, and does experience concentration quenching.   © 2001 Optical Society of America

OCIS codes: 160.5690, 250.4480, 250.5460, 150.3130, 250.5230, 160.2540.

1. INTRODUCTION

Trivalent rare-earth ions are often used in optical telecommunication technology because of their special optical properties.   The intra-$4f$ shell of the rare-earth ions is shielded by the $5s$ and $5d$ shells, making the energy levels of the $4f$ shell almost independent of the surrounding host material.   The transitions within the $4f$ shell are parity forbidden, which results in a long intrinsic luminescence lifetime of the order of milliseconds.   The neodymium (Nd) ion is often used because it has an intra-$4f$ transition at 1.34 μm, which coincides with the low-dispersion window of standard optical fibers.

Neodymium-doped lasers and amplifiers have been achieved in inorganic hosts such as silica,[1]   YAG,[2] yttrium lithium fluoride,[3] and LiNbO$_3$.[4,5]   Recently, research has also focused on rare-earth doped polymer-based materials.[6,7]   The rare-earth ions cannot be directly dissolved into the polymer matrix, because they tend to cluster.   To overcome this problem, organic complexes were designed to encapsulate the rare-earth ions so that they can be dissolved in the polymer matrix.[8]   However, the luminescence of the Nd^{3+} ions exhibits strong quenching caused by coupling of the excited state to vibrational modes of molecular bonds in both the complex and the polymer host.   Consequently, high pump powers are required for creating a population inversion in a Nd-doped polymer optical waveguide amplifier.   The attachment of a strongly absorbing antenna group to the organic complex can increase the pumping efficiency by 4 orders of magnitude.   Previously, we reported an efficient energy transfer (at a rate $> 10^7 \, \mathrm{s}^{-1}$) from a highly absorbing lissamine sensitizer to a Nd-doped terphenyl-based organic complex.[9]   We also found that on optical excitation the emission from Nd strongly decreased over time, which was attributed to photodegradation of the lissamine sensitizer.   This is an important limiting effect for the use of such complexes in optical amplifiers.   In this paper we report this effect in more detail, using time-dependent measurements of the luminescence and absorption of both the lissamine sensitizer and the Nd^{3+} ion.   The observations can be explained by a model that assumes that there are two types of complex: one in which the lissamine sensitizer can transfer the excitation energy to the Nd^{3+} ion and in which concentration quenching does not play an important role, and one in which the lissamine cannot transfer the energy to the Nd^{3+} ion and in which concentration quenching is present.

2. EXPERIMENT

Lissamine (sulfo-rhodamine-B) functionalized terphenyl-based Nd^{3+} complexes were synthesized by using the pro-
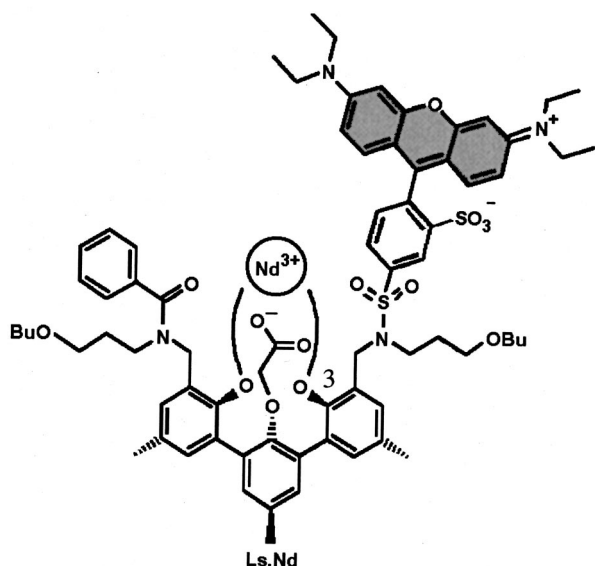
Fig. 1. Two-dimensional representation of lissamine–Nd^{3+} complex.

cedure described in Ref. 10. A two-dimensional representation of the structure of the complex is shown in Fig. 1. The strongly absorbing lissamine moiety is indicated in gray. The complexes were dissolved in partially fluorinated polycarbonate[11] waveguides at a concentration of 10 wt. % (complex). The waveguides were made by spin coating a cyclohexylacetate solution containing both polycarbonate and lissamine complex onto a microscope glass slide. The spin coating was performed for 30 s at a spin rate of 3000 rpm followed by thermal annealing at 190 °C (in vacuum) for 1 h. The thickness of the polymer layer was 1 μm as measured by ellipsometry.

Luminescence measurements were performed at an excitation wavelength of 488, or 515 nm with an Ar-ion laser as an excitation source. The power on the sample was 1 W, with a Gaussian spatial-intensity distribution and a full width at half-maximum varying between 1 and 5 mm. For each measurement a fresh spot was taken on the sample. The beam was modulated with an acousto-optic modulator operating at 12.5 Hz. The emitted luminescence was focused into a monochromator and detected with a photomultiplier tube or a liquid-nitrogen-cooled Ge detector. All spectra were corrected for the detector response. The light intensity transmitted through the sample was monitored with a Si photodiode positioned behind the sample, and changes in transmission were converted to absorption coefficients through use of the known film thickness and Lambert–Beer's law. Absorption spectra were measured before and after laser illumination with a variable-angle spectroscopic ellipsometer.

Luminescence lifetime measurements were performed under excitation at a wavelength of 337 nm with a 1.5-ns pulsed N_2 laser with a pulse energy of 20 μJ. The luminescence signal was detected by a Hamamatsu streak camera system. The time resolution of the system was ~300 ps.

3. RESULTS AND DISCUSSIONS

Figure 2 shows the schematic energy-level diagram of the lissamine–Nd system. The lissamine is excited from the singlet ground state (S_0) into the excited singlet state (S_1) at a pump rate W_p. From there it can decay back to the ground state at a rate W_{s1} or decay via intersystem crossing (W_{isc}) to the triplet state. From the triplet state it can decay to the ground state (W_t) or transfer its energy to the Nd^{3+} ion (W_{et}), in which case it also returns to the singlet ground state. After energy transfer from the lissamine sensitizer, the Nd^{3+} is excited into the $^4F_{9/2}$ and $^4S_{3/2}$ level, from which it will decay rapidly to the luminescent $^4F_{3/2}$ state. In our experiment direct absorption by the Nd^{3+} ion can be neglected, because its direct absorption cross section is 4 orders of magnitude smaller than that of the lissamine. Figure 2 also shows the energy diagram of a lissamine complex not coupled to Nd, which is discussed below.

Figure 3 (top) shows the luminescence spectra of a lissamine–Nd-complex-doped polymer film excited at an excitation wavelength of 488 nm at a pump power of 1 W and a spot diameter of 5 mm. The emission is attributed to the lissamine sensitizer (W_{s1} in Fig. 2). The time to take each spectrum was 6 min, and the time given in the figure is the total elapsed time at the end of the measurement. As can be seen from the spectra, continued illumination results in a small blueshift of the peak luminescence from the lissamine sensitizer, as is also shown in the inset of Fig. 3 (top). The integrated luminescence intensity initially increases and then decreases.

The absorption spectra of the lissamine–Nd-complexdoped polymer film for different illumination times are shown in Fig. 3 (bottom). As can be seen, the spectral shape of the absorption spectrum remains the same, but the absorption decreases upon illumination. The blueshift and the increase in the intensity of the luminescence spectra could in principle be explained by the bleaching of dimers or aggregates of complexes that may be present at the high concentrations applied,[12–14] because these species have a different emission spectrum than monomers as a result of the electronic interaction between the molecules. However, this interaction should also result in a change in the shape of the absorption spectrum upon
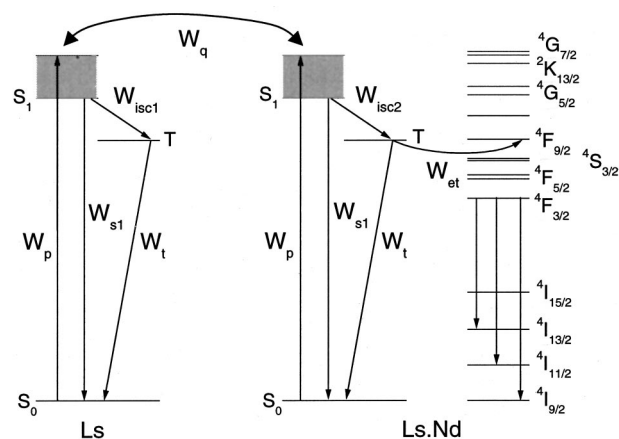

Fig. 2. Schematic energy-level diagram of the lissamine–Nd^{3+} complex. The arrows indicate the excitation and decay mechanisms. Complexes with and without energy transfer to Nd are shown, and the interaction between the two types is indicated by W_q.
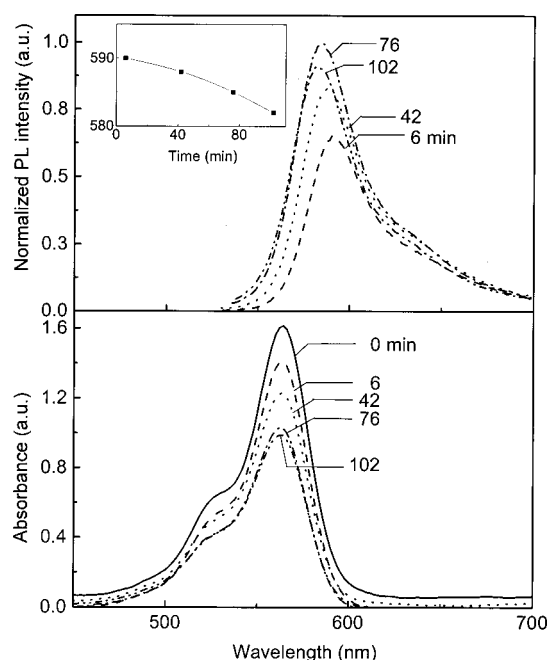
Fig. 3. Luminescence (top) and absorption (bottom) spectra of the lissamine sensitizer for different illumination times. The excitation wavelength was 488 nm at a pump power of 1 W in a 5-mm spot. The inset shows the peak position in nanometers as a function of the illumination time.
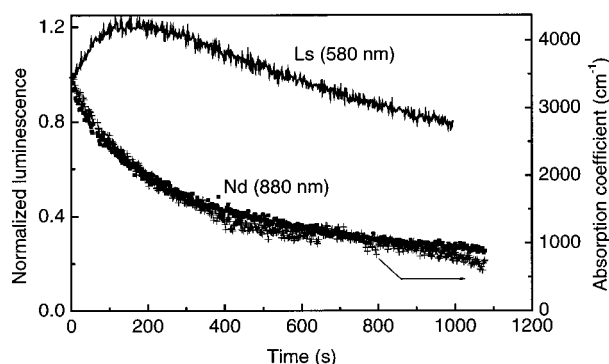

Fig. 4. Lissamine luminescence intensity (580 nm, solid curve) and Nd^{3+} luminescence intensity (880 nm, solid squares) as a function of illumination time. Also shown is the absorption coefficient of the film measured at 515 nm during illumination (crosses). A pump excitation wavelength of 515 nm at a power of 1 W and a 1-mm-diameter spot was used.

bleaching, which is not observed in Fig. 3 (bottom), so that this dimer bleaching model may be excluded. Alternatively, the blueshift can be explained by a change in self-absorption as the density of optically active lissamine decreases upon illumination [as seen in Fig. 3 (bottom)]. Figure 3 shows that the absorption and emission spectra of lissamine strongly overlap. The absorption cross section of lissamine is 4×10^{-16} cm^2 at 580 nm, and the concentration in the 1-μm-thick film is 5×10^{19} cm^{-3}, which results in an absorption depth of roughly 0.5 μm. This means that a rather large fraction of the lissamine luminescence is reabsorbed by the surrounding lissamine molecules. As the concentration of optically active lissamine

is reduced due to photobleaching upon illumination, the self-absorption is reduced, and as a result the collected luminescence intensity can increase in the region where the absorption and emission spectra overlap. This results in an apparent blueshift of the luminescence spectrum, as is observed in Fig. 3 (top).[15] Note that the pump absorption depth at 488 nm is 6.6 μm, so that the lissamine causes no significant depletion of the pump intensity through the film.

Figure 4 shows measurements of the lissamine luminescence at 580 nm as well as the Nd^{3+} luminescence at 880 nm as a function of illumination time. The pump power was 1 W at an excitation wavelength of 515 nm and a spot diameter of 1 mm. The Nd^{3+} emission spectrum does not show a spectral change upon illumination (not shown). The lissamine luminescence first increases and then decreases as was also seen in Fig. 3 (top). Also depicted is the absorption coefficient measured at 515 nm during illumination (crosses), which shows that the concentration of optically active lissamine is gradually decreasing. Without self-absorption the lissamine luminescence intensity would scale with the absorption coefficient, but at high lissamine concentration (short illumination time) the self-absorption reduces the detected luminescence intensity. This would result in a more constant intensity for short times, but it cannot explain the initial increase in the luminescence intensity as observed in Fig. 4.

The increase may be explained by a concentration quenching model: at the high lissamine concentration used (10 wt. %), the lissamine molecules are spaced by only a few nanometers, so that excitations can easily transfer from one lissamine to another by a Förster energy transfer mechanism. In this way the excitation can migrate through the film until it reaches a quenching center and hence is lost. In such a quenching model, the luminescence quantum efficiency increases with decreasing lissamine concentration. So, if the active lissamine concentration is reduced as a result of illumination, the quantum efficiency increases. This additional reduction of the luminescence intensity for high concentration can describe the initial increase in the luminescence intensity with time. For a lower intrinsic lissamine concentration in the film, one would expect the initial increase to be smaller or even absent. Indeed, this has been seen for a 1 wt. % doped polymer film.[9] We can use the combined effect of self-absorption and concentration quenching to describe the data of Fig. 4 qualitatively. A quantitative description is not possible because of several unknown effects, like, e.g., changes in the refractive index as a result of the photobleaching, changes in the active lissamine depth profile within the layer due to the gradient of the pump power in the film, and the effect of the standing-wave pattern in the pump intensity throughout the film, which results from multiple reflections at the interfaces of the layers.

As can be seen in Fig. 4, the Nd^{3+} luminescence intensity shows a completely different time dependence than the lissamine luminescence. It precisely follows the decrease in the absorption coefficient due to the decreasing active lissamine concentration. As the excitation of the Nd^{3+} ion occurs via the triplet state of the lissamine, one

would also expect an initial increase in the Nd^{3+} luminescence. However, this is not observed. One way to explain the different behavior of the lissamine and Nd^{3+} intensities is by assuming that two types of complex exist in the polymer film (see Fig. 2). One complex shows the lissamine behavior as observed in Fig. 4, explained by concentration quenching, and does not couple to the Nd^{3+} ion (denoted Ls); the other complex couples to the Nd^{3+} ion but does not show concentration quenching (denoted Ls.Nd). The presence of two types of complex has been observed previously for a similar complex in solution.[16] The fact that no concentration quenching would be observed for complexes that couple to the Nd^{3+} ion could be explained by the heavy-atom effect.[17,18] The presence of a heavy atom such as Nd^{3+} increases the intersystem crossing rate within the lissamine.[10,19] If the intersystem crossing rate would be larger than the effective quenching rate that is due to concentration quenching ($\sim 10^8 \text{ s}^{-1}$, on the order of the luminescence decay rate), quenching would not be observed.

To study the heavy-atom effect, we performed measurements of the luminescence lifetime of the lissamine singlet state at 580 nm on Ls and Ls.Nd complexes in dimethylsulfoxide (not shown) and found a luminescence lifetime of 2.6 ns for the free lissamine and 1.2 ns for the complex. The reduction in luminescence lifetime is the result of an increase in the intersystem crossing rate due to the presence of Nd^{3+}, which leads to an intersystem crossing rate in the presence of the Nd^{3+} ion of $4 \times 10^8 \text{ s}^{-1}$. Indeed, this is much higher than the intrinsic intersystem crossing rate of pure lissamine, which is known to be $8 \times 10^6 \text{ s}^{-1}$. Note that these measurements were performed in solution, where the equilibrium position of the sensitizer with respect to the Nd^{3+} ion can be substantially different than that in a polymer film, and hence the intersystem crossing rate determined here may not be representative for the polymer film. However, these data clearly indicate the possible effect of Nd on the intersystem crossing rate and hence, as argued above, on the concentration quenching. Streak images of the lissamine luminescence of a lissamine-complex-doped film were measured after excitation at 337 nm with a 1.5 ns-pulsed N_2 laser. The streak image displays the luminescence intensity versus time and wavelength. Figure 5 shows the
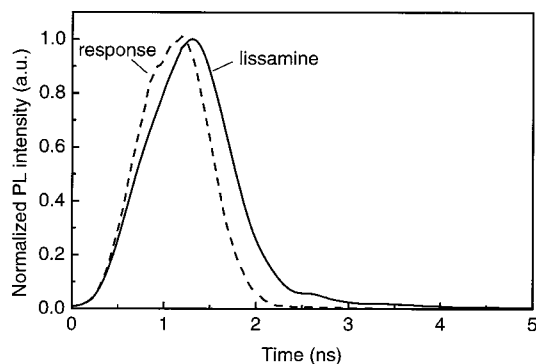

Fig. 5. Time-dependent luminescence trace at $\lambda = 580$ nm for a lissamine–neodymium doped polymer film (solid curve) after excitation with a 1.5 ns (FWHM) pulse at 337 nm and a pulse energy of 20 μJ. The dashed curve shows the system response after excitation.

luminescence intensity at 580 nm versus time as obtained from the measured streak image. Also shown is the system time response to the 337 nm laser pulse. A streak image is normally built up by luminescence spectra of different species in the sample with different luminescence lifetimes. Singular value decomposition[20] can be performed on the two-dimensional streak data set in order to derive the number of individual components that contribute to the streak image. Using singular value decomposition on the lissamine streak image, two contributions were found: one with a time component in the order of the system response (300 ps) and one with a time component of ~ 0.6 ns. The luminescence spectra corresponding to the two time components were identical to the lissamine luminescence spectrum, which is consistent with the above assumption of the existence of two different types of lissamine complex. In that case, the short time component of 300 ps can be related to the luminescence lifetime of a lissamine complex exhibiting energy transfer to the Nd^{3+} ion, which corresponds to an intersystem crossing rate of $> 1.6 \times 10^9 \text{ s}^{-1}$. This would indeed explain the absence of a concentration quenching effect for these complexes. The longer time component of 0.6 ns would then correspond to the lifetime of the lissamine complexes without energy transfer to the Nd^{3+} ion. That this lifetime is shorter than that measured for the same complexes in the solution (2.6 ns) is probably a result of the concentration quenching that reduces the luminescence lifetime.

4. CONCLUSIONS

Lissamine-functionalized terphenyl-based neodymium complexes were dissolved into a polycarbonate film at a concentration of 10 wt. %. On continuous laser illumination at 488 nm (~ 1 W), the lissamine sensitizer shows photobleaching, which results in a blueshift of the lissamine emission spectrum due to reduced self-absorption within the film. At a fixed wavelength the lissamine luminescence intensity first increases and then decreases during illumination, which is attributed to a reduction in self-absorption and concentration quenching as a result of the decreasing concentration, which increases the emission quantum efficiency. The Nd^{3+} luminescence intensity shows no initial increase, although it would be expected based on the fact that the neodymium is excited through the lissamine. This suggests that concentration quenching has no effect on the Nd^{3+} luminescence. The difference in behavior of the emission intensity with illumination time is explained by a model that assumes the presence of two different types of complex. One type exhibits rapid energy transfer to the Nd^{3+} ion, which increases the intersystem crossing rate within the lissamine and thereby reduces the influence of concentration quenching. The other type does not have energy transfer to the neodymium and shows concentration quenching. The lack of energy transfer might be explained by a larger distance between the sensitizer and the Nd^{3+} ion, which reduces the energy transfer rate.

REFERENCES

1. T. Kitagawa, K. Hattori, and Y. Hibino, "Neodymium-doped silica-based planar waveguide laser," J. Lightwave Technol. **12**, 436–442 (1994).

2. D. P. Shepherd, C. T. A. Brown, T. J. Warburton, D. C. Hanna, A. C. Tropper, and B. Ferrand, "A diode-pumped, high gain, planar waveguide $Nd:Y_3Al_5O_{12}$ amplifier," Appl. Phys. Lett. **71**, 876–878 (1997).

3. J. Hulliger, P. Rogin, and R. Burkhalter, "Waveguides in YLF grown by liquid-phase epitaxy," Laser Phys. **8**, 764–768 (1998).

4. R. Brinkmann, W. Sohler, H. Suche, and C. Wersig, "Fluorescence and laser operation in single-mode Ti-diffused $Nd:MgO:LiNbO_3$ waveguide structures," IEEE J. Quantum Electron. **28**, 466–470 (1992).

5. E. Lallier, J. P. Pocholle, M. Papuchon, M. De Micheli, M. J. Li, Q. He, D. B. Ostrowsky, C. Grezes-Besset, and E. Peletier, "$Nd:MgO:LiNbO_3$ channel waveguide laser devices," IEEE J. Quantum Electron. **27**, 618–625 (1991).

6. R. Gao, C. Koeppen, G. Zheng, and A. F. Garito, "Rare-earth-doped polymers for optical amplification and lasing," in *Rare-Earth-Doped Devices II*, S. Honkanen and S. Jiang, eds., Proc. SPIE **3280**, 14–22 (1998).

7. R. T. Chen, M. Li, S. Tang, and D. Gerald, "Rare-earth-ions-doped graded-index single-mode polymer waveguide amplifier," in *Technologies for Optical Fiber Communications*, G. J. Brown, D. J. Decoster, J. S. La Course, Y. Park, K. D. Pedrotti, and S. R. Sloan eds., Proc. SPIE **2149**, 77–78 (1994).

8. L. H. Slooff, A. Polman, M. P. Oude Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstraat, "Optical properties of erbium-doped organic polydentate cage complexes," J. Appl. Phys. **83**, 497–503 (1998).

9. L. H. Slooff, A. Polman, S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstraat, "Optical properties of lissamine functionalised Nd^{3+} complexes in polymer waveguides and solution," Opt. Mater. **14**, 101–107 (2000).

10. S. I. Klink, P. Oude Alink, L. Grave, F. G. A. Peters, J. W. Hofstraat, F. A. J. Geurts, and F. C. J. M. van Veggel, "Fluorescent dyes as efficient photosensitizers for near-infrared Nd^{3+}," J. Chem. Soc., Perkin Trans. 2 **2**, 363–372 (2001).

11. R. H. Woudenberg and T. O. Boonstra, "Polymers comprising a fluorinated carbonate moiety," International patent, deposited September 3, 1998, WO 9838237.

12. T. Förster, and E. Koning, "Absorptionsspektren und Fluoreszeneigenschaften konzentrierter Lösungen organischer Farbstoffe," Z. Elektrochem. **61**, 344–348 (1957).

13. E. G. McRae and M. Kasha, "Enhancement of phosphorescence ability upon aggregation of dye molecules," J. Chem. Phys. **28**, 721–722 (1958).

14. R. W. Chambers, T. Kijiwara, and D. R. Kearns, "Effect of dimer formation on the electronic absorption and emission spectra of ionic dyes," J. Phys. Chem. **78**, 380–385 (1974).

15. S. Ahmed, S-W. Zang, K. M. Yoo, M. A. Ali, and R. R. Alfano, "Effect of multiple light scattering and self-absorption on the fluorescence and excitation spectra of dyes in random media," Appl. Opt. **33**, 2746–2766 (1994).

16. S. I. Klink, L. Grave, D. N. Reinhoudt, F. C. J. M. van Veggel, M. H. V. Werts, F. A. J. Geurts, and J. W. Hofstraat, "A systematic study of the photophysical processes in polydentate triphenylene-functionalized Eu^{3+}, Tb^{3+}, Yb^{3+}, and Er^{3+} complexes," J. Phys. Chem. A **104**, 5457–5468 (2000).

17. S. Tobita, M. Arakawa, and I. Tanaka, "Electronic relaxation processes of rare-earth chelates of benzoyltrifluoroacetone," J. Phys. Chem. **88**, 2697–2702 (1984).

18. S. Tobita, M. Arakawa, and I. Tanaka, "The paramagnetic effect on the ligand localized S_1-T_1, intersystem crossing in the rare-earth-metal complexes with methyl salicylate," J. Phys. Chem. **89**, 5649–5654 (1985).

19. M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, and J. W. Verhoeven, "Fluorescein and eosin as sensitizing chromophores in near-infrared luminescent ytterbium(III), neodymium(III), and erbium(III) chelates," Chem. Phys. Lett. **276**, 196–201 (1997).

20. M. Kubista, J. Nygren, A. Elbergali, and R. Sjöback, "Making reference samples redundant," Crit. Rev. Anal. Chem. **29**, 1–28 (1999).