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Optical properties of lissamine functionalized Nd³⁺ complexes in polymer waveguides and solution

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Abstract

Lissamine functionalized terphenyl-based Nd complexes are synthesized, and incorporated in deuterated dimethylsulfoxide solutions and partially fluorinated planar polymer waveguides. Optical excitation of the lissamine sensitizer around 500 nm, followed by intramolecular energy transfer to the Nd³⁺ ion, causes near-infrared photoluminescence (890, 1060, 1340 nm) due to intra-4f transitions in the Nd³⁺ ion. The intramolecular energy transfer rate is larger than 10⁷ s⁻¹. Due to the large absorption cross-section of the sensitizer (>10⁻¹⁷ cm² around 500 nm), the Nd³⁺ is excited 10⁴ times more efficiently than in a pure complex, without sensitizer. The Nd³⁺ luminescence lifetime is relatively short, both in solution (2.2 μs) and in a polymer host (0.8 μs), which is attributed to coupling to vibrational states of nearby C–H and O–H groups. Spincoated fluorinated polymer planar waveguides, doped with these sensitized organic Nd complexes show excellent waveguide properties. Upon continued illumination, photodegradation is observed in the doped polymer films. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Trivalent rare earth ions are well known for their special optical properties [1]. The 4f-shell of these ions is not completely filled and shielded from the surroundings by filled 5s and 5p shells. This shielding minimizes the effect of the crystal field of the host material on the energy levels of the 4f-shell and as a result the absorption and emission bands remain rather sharp. The small influence of the crystal field induces mixing of wave functions with opposite parity within the 4f-shell, making

the parity forbidden transitions slightly allowed. The lifetimes of these transitions are therefore relatively long.

These properties make the rare earth ions useful for applications in integrated optics. The rare earths erbium (Er) and neodymium (Nd) are commonly used in optical fiber amplifiers [2–5] due to their intra-4f transitions at 1550 nm (Er, ⁴I_{13/2} → ⁴I_{15/2}) and 1340 nm (Nd, ⁴I_{3/2} → ⁴I_{11/2}), two standard telecommunication wavelengths. A lot of research has focused on rare earth-doped solid-state planar optical amplifiers for integrated optics applications, and working planar amplifiers have been reported for rare earth ions in silica, Al₂O₃, phosphate glasses, and LiNbO₃ [6,7]. The

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growing importance of polymer thin films in integrated optics technology makes it interesting to study rare earth doped polymer waveguides, and see if polymer optical amplifiers can be made [8,9]. These polymer waveguide amplifiers could then be integrated with existing polymer devices such as splitters, switches, and multiplexers [10].

Rare earth ions cannot be dissolved directly into a polymer film. Therefore, the ions have to be encapsulated by an organic ligand to form a complex, which can be dissolved in the polymer matrix. Previously, we have shown that optically active Er-doped polydentate cage complexes can be synthesized, and show room temperature photoluminescence at 1.535 μm when optically excited either directly into an Er level, or indirectly via the cage which also acts as a chromophore [11]. We found that the luminescence lifetime of these complexes is rather short (0.8 μs), which was attributed to energy transfer of the excited state of the Er^{3+} ion to $-\text{OH}$ and $-\text{CH}$ vibrational states of the complex or of the solvent molecules [12,13]. Deuteration of $-\text{CH}$ and $-\text{OH}$ bonds reduces some of these quenching paths [14].

Obviously these non-radiative quenching processes are a disadvantage of the use of organic cage complexes. On the other hand, an advantage is that highly absorbing antenna chromophores can be incorporated in the organic complex. Once this chromophore is excited it can transfer its excitation energy to the rare earth ion. If the energy transfer from chromophore to rare earth ion is efficient, this process strongly enhances the excitation efficiency of the rare earth ion.

In this paper, we will report the optical properties of terphenyl-based Nd^{3+} complexes with and without a highly absorbing lissamine antenna chromophore. Complexes were dissolved either in hexadeutero-dimethylsulfoxide (DMSO- d_6) solutions or in partially fluorinated polycarbonate planar waveguides. In complexes without lissamine, excitation of the Nd^{3+} ion at a wavelength of 515 nm leads to population of the ${}^4\text{G}_{7/2}$ level, from where it decays to the ${}^4\text{F}_{3/2}$ level (see Fig. 1). Decay from this level leads to the characteristic Nd^{3+} luminescence at 890, 1060 and 1340 nm due to transitions to the ${}^4\text{I}_{9/2}$, ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$ levels, respectively. In complexes with the lissamine sensi-

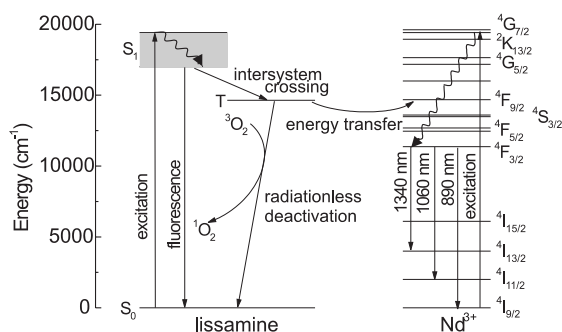


Fig. 1. Schematic energy level diagram of the lissamine- Nd^{3+} complex. The arrows indicate the excitation mechanisms of the Nd^{3+} ion: either directly into the ${}^4\text{G}_{7/2}$ level by pumping at 515 nm, or through the lissamine sensitizer ($\text{S}_0 \rightarrow \text{S}_1$ transition followed by intersystem crossing and energy transfer).

tizer, the 515 nm light is mainly absorbed by the high absorbing lissamine, which becomes excited into the singlet state (S_1). This is followed by intersystem crossing to the triplet state (T , $E_{\text{T}} = 14600 \text{ cm}^{-1}$) (see Fig. 1). From the triplet state energy transfer to the Nd^{3+} ion can occur, which results in excitation of the Nd^{3+} ion into the ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels. After relaxation to the ${}^4\text{F}_{3/2}$ level the 890, 1060 and 1340 nm luminescence can be observed. The luminescence intensities, lifetimes, excitation mechanisms, waveguide properties, and photostability of these complexes will be discussed.

2. Experimental

Terphenyl-based Nd^{3+} complexes were synthesized [15] using the procedure described in Ref. [15]. Some complexes were functionalized with lissamine, a Rhodamine-B derivative [16]. Fig. 2 shows a schematic picture of the structure of the terphenyl-based Nd^{3+} complexes (a) with two benzoyl side-groups (Bz.Nd) and (b) with one benzoyl side-group and a lissamine sensitizer (Ls.Nd). Both complexes have a cage-like configuration, encapsulating the Nd^{3+} ion. The complexes were dissolved in DMSO- d_6 to a concentration of 10^{-2} M for Bz.Nd and 10^{-6} M for Ls.Nd, or dissolved in partially fluorinated polycarbonate [17] waveguides at a concentration of

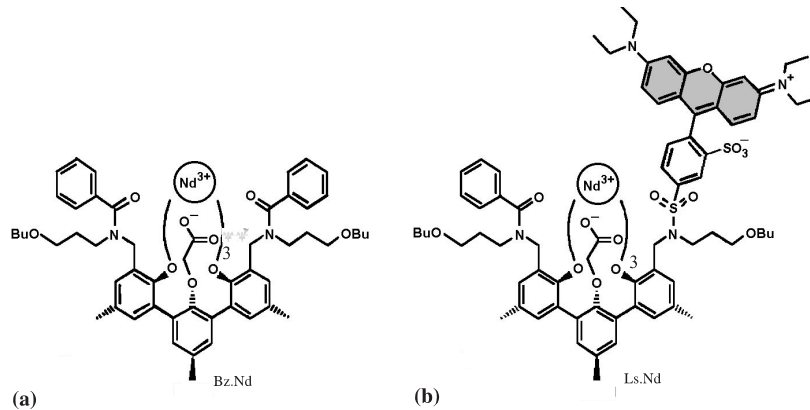


Fig. 2. Schematic picture of (a) benzoyl- Nd^{3+} complex (Bz.Nd) and (b) lissamine functionalized Nd^{3+} complex (Ls.Nd).

3 wt% (complex). The polycarbonate waveguides were made by spincoating a cyclohexylacetate solution of polycarbonate and complex onto a Si substrate covered with a 3 μm thick thermally grown SiO_2 layer. The spincoating was performed for 30 s at a spinrate of 3000 s^{-1} and followed by thermal annealing at 190°C (in vacuum) for 1 h. The thickness of the polymer layer was 3.55 μm .

The real and imaginary parts of the refractive index of the polymer waveguide were measured using a variable angle spectroscopic ellipsometer. The optical losses were measured using the sliding prism method [18]. Diiodomethane was used as an index matching liquid for optimum output coupling. A white light source as well as lasers operating at 633, 838, 1305 and 1565 nm were used.

Photoluminescence (PL) measurements were performed using various lines of an Ar-ion laser as an excitation source. The complexes in DMSO- d_6 solution were analyzed in square quartz cells. The power on the cell was 60 mW, at a spot diameter of 1 mm. The beam was modulated using an acousto-optic modulator, operating at different frequencies. 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. Absorption measurements were performed using a spectrophotometer. Measurements on waveguide films were performed by pumping the waveguide (total length about 25 mm) with a rectangular spot (5 \times 15 mm) from the top near

the entrance facet of the waveguide. The luminescence was collected at the output facet, using a multi-mode optical fiber. The fiber was led to an objective in front of the monochromator. The spectral resolution ranged from 0.2 to 6 nm. Photoluminescence decay curves were measured using a photomultiplier tube and a photon counting system. The time resolution of the system was about 100 ns.

3. Results and discussion

Fig. 3 shows the PL intensities at 1060 nm for a 10^{-2} M solution of Bz.Nd and a 10^{-6} M solution of Ls.Nd (lissamine sensitized), both in DMSO- d_6 , at different excitation wavelengths as available from the Ar-ion laser. The absorption spectrum measured for the same solutions is also included in the figure. The pump power for excitation was 60 mW for all excitation wavelengths. The excitation spectrum for the complex without sensitizer (Bz.Nd) shows some structure, which is roughly similar to that found in the absorption measurement, and is consistent with the absorption bands of the Nd^{3+} ion around 475 and 513 nm. The excitation spectrum for the complex with sensitizer (Ls.Nd) shows a completely different behavior: the 1060 nm emission intensity increases strongly with excitation wavelength, again very similar to what is found for the absorption spectrum. Given the fact that the lissamine complex shows a broad

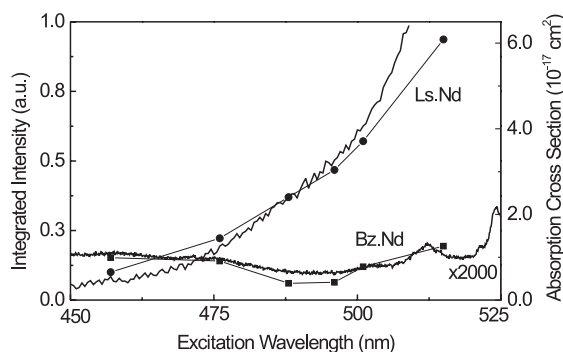


Fig. 3. Photoluminescence at 1060 nm as a function of excitation wavelength for Bz.Nd (10^{-2} M, squares) and Ls.Nd (10^{-6} M, circles) in DMSO-d6 solutions. The absorption spectra of Bz.Nd and Ls.Nd are also shown (drawn lines). The absorption data for the Bz.Nd solution are multiplied by a factor of 2000.

absorption band around 580 nm, this clearly indicates that the excitation of Nd^{3+} around 500 nm takes place via the sensitizer. The absorption of the lissamine occurs at the xanthene unit (i.e. the gray part in the structure for Ls.Nd in Fig. 2(b)). Note that the measured absorption cross-section is in the 10^{-17} cm^2 range, which is four orders of magnitude above the typical Nd^{3+} intra-4f transition cross-section.

Fig. 4 shows the room-temperature PL spectra for 10^{-2} M Bz.Nd and 10^{-6} M Ls.Nd in DMSO-d6, recorded using excitation at 515 nm at a pump power of 60 mW. The complexes show room-

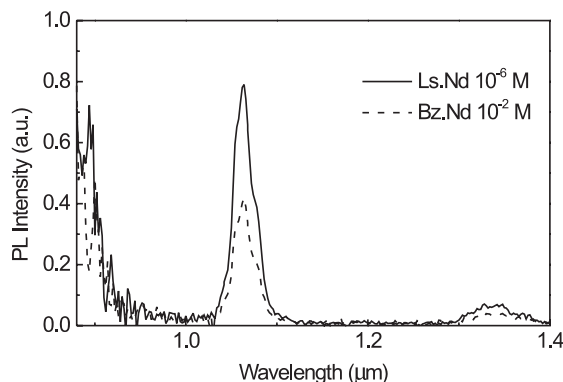


Fig. 4. Photoluminescence spectra of Ls.Nd (10^{-6} M) and Bz.Nd (10^{-2} M) in DMSO-d6 solutions. The excitation wavelength is 515 nm at a pump power of 60 mW.

temperature PL of Nd^{3+} at 890, 1060, and 1340 nm. Although the concentration of Ls.Nd is 10^4 times lower than the concentration of Bz.Nd, the PL intensity is two times higher. Optical absorption measurements at 515 nm for both solutions show an almost equal absorption: 0.033 cm^{-1} for 10^{-2} M Bz.Nd and 0.031 cm^{-1} for 10^{-6} M Ls.Nd. The fact that the sensitized complex shows higher luminescence than the complex without a sensitizer, even though the measured absorption was the same, indicates that the internal energy transfer efficiency within the sensitized complex is quite high. The factor 2 difference can be due to the fact, that upon direct excitation into the higher lying state of the Nd^{3+} ion, the Nd^{3+} ion can also decay radiatively to the ground level (indeed, 524 nm luminescence has been observed, resulting from the transition from the ${}^2\text{K}_{13/2} \rightarrow {}^4\text{I}_{9/2}$ transition), leading to a lower quantum yield for the near-infrared transitions in the case of direct optical excitation of the Nd^{3+} at 515 nm. The measured luminescence lifetime (not shown) at 1060 nm for the Bz.Nd complex in DMSO-d6 is 2.5 μs , and for the sensitized Ls.Nd complex it is 2.2 μs . The luminescence lifetime of Nd^{3+} in inorganic materials can be as high as 250 μs [19]. The low quantum yield in the organic complexes is attributed to quenching of the Nd^{3+} excited state by coupling to overtones of nearby C–H and O–H vibrational states.

Fig. 5(a) shows the measured (dashed line) and simulated (solid line) ellipsometry parameter Δ as a function of wavelength for a partially fluorinated polycarbonate planar polymer waveguide doped with 3 wt% Ls.Nd. The interference structure is caused by reflections at the air/polymer, polymer/ SiO_2 , and SiO_2/Si interface. A clear dip in Δ is observed around 580 nm, which is caused by the high absorption of the lissamine. The simulated data are based on a Lorentz oscillator model and correspond well with the measured data. From the simulation parameters, the real (n) and imaginary (k) part of the refractive index of the Nd-doped polymer waveguide layer can be calculated and they are shown in Fig. 5(b). Also shown is the measured refractive index of an undoped reference polymer. Outside the resonance region, the refractive index of the Nd-doped waveguide layer is

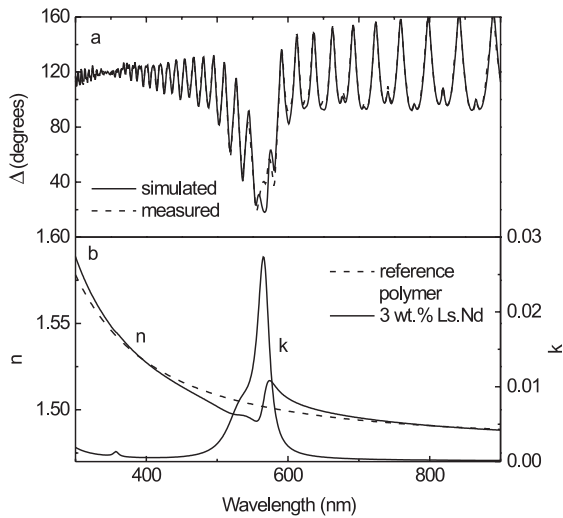


Fig. 5. (a) Measured and calculated ellipsometric parameter Δ as a function of wavelength for a 3 wt% Ls.Nd-doped partially fluorinated polycarbonate waveguide. (b) Real (n) and imaginary (k) part of the refractive index derived from the simulation data indicated by the solid line in (a). The real index for an undoped reference waveguide is shown for reference (dashed line in (b)).

very similar to that of the undoped layer, indicating that the spincoating technique leads to Nd-doped waveguide layers with similar density as pure waveguide layers. The maximum value of k is 0.027 at 580 nm which corresponds to an absorption cross-section of $4.5 \times 10^{-16} \text{ cm}^2$, which is roughly 2–3 times higher than the literature value for Rhodamine-B [14]. It is clearly seen that the high absorption of the lissamine causes a change in the real part of the refractive index around 580 nm as described by Kramers–Kronig theory.

Optical loss measurements were performed on an undoped partially fluorinated polycarbonate waveguide using the prism coupling technique. The result is shown in Fig. 6. The peak around 1650 nm is due to overtone absorption by C–H bonds. The band around 1400 nm is attributed to absorption by C–H bonds and O–H bonds in the polymer. The two peaks around 1150 nm arise from second overtone absorption by aromatic and aliphatic C–H bonds. The background loss at the Nd^{3+} emission wavelengths is $<0.05 \text{ dB/cm}$ at 1060 nm and 0.08 dB/cm at 1305 nm. This indicates that

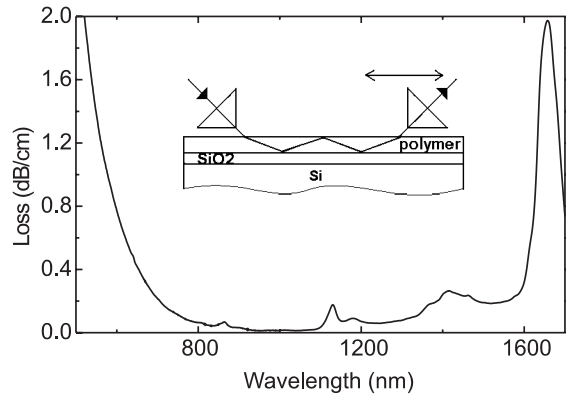


Fig. 6. Optical loss spectrum of an undoped partially fluorinated polycarbonate waveguide, also shown is the measurement configuration.

these polycarbonate waveguides are ideally suited for planar waveguide applications.

Fig. 7 shows the PL intensity of a 3 wt% Ls.Nd doped fluorinated polycarbonate waveguide after excitation at a wavelength of 515 nm. The dashed line shows the luminescence measured after excitation and collection of the light from the top of the sample ($P = 40 \text{ mW}$). The 890 and 1060 nm luminescence of the Nd^{3+} ion are clearly seen.

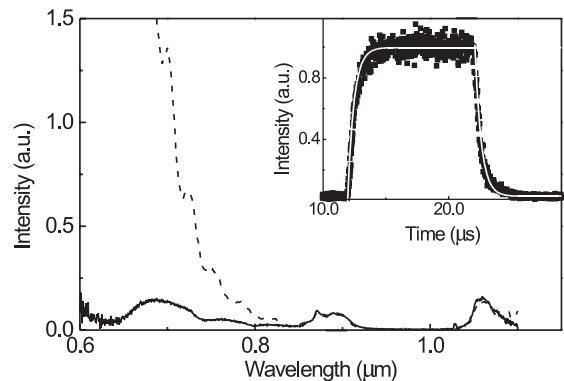


Fig. 7. Photoluminescence spectra of a 3 wt% Ls.Nd-doped polymer waveguide. The dashed line indicates the spectrum collected from the top of the waveguide after excitation at 515 nm at a power of 40 mW. The solid line indicates the spectrum after excitation at 515 nm at a power of 140 mW and collected from the output face of the waveguide using a multimode optical fiber. The inset shows the time dependence of the 1060 nm luminescence upon pulsed excitation.

Spectra taken in the near-infrared region (not shown) also show the 1340 nm luminescence. The emission observed in the lower wavelength region is due to luminescence of the lissamine, which has a peak emission wavelength ($S_1 \rightarrow S_0$ transition) at 580 nm. The small peaks at the shoulder of the lissamine luminescence are attributed to an interference effect between the waveguide layers. The solid line in Fig. 7 is the spectrum observed for excitation from the top and collecting from the output facet of the waveguide ($P = 140$ mW, spot 5×15 mm²). Again the 890 and 1060 nm luminescence are observed, but here the luminescence of the lissamine is strongly decreased, which is attributed to re-absorption by the lissamine itself. This indicates that self-absorption should be taken into account when designing waveguide devices.

The inset of Fig. 7 shows the time dependence of the 1060 nm PL signal after switching the 515 nm pump on and off. An exponential fit through the decay part results in a PL lifetime of 0.8 μ s. This is significantly lower than the decay measured for complexes in DMSO-d₆ solution (2.2 μ s), which indicates that quenching by C–H and O–H groups in the polymer matrix also contributes to the radiationless deactivation of the Nd³⁺.

The energy transfer from the lissamine to the Nd³⁺ ion occurs via the triplet state of the lissamine. However, the triplet state can also be quenched by e.g. O₂, that is, always present in solution or in a polymer film. In order to investigate this, we measured the Nd³⁺ luminescence intensity of Ls.Nd in DMSO-d₆ solutions before and after degassing (not shown). The Nd³⁺ PL intensities were similar, indicating that quenching by O₂ does not play a role in the DMSO-d₆ solutions. As it is known that the quenching rate by O₂ is about 10^7 s⁻¹, it can be estimated that the intramolecular energy transfer rate to the Nd³⁺ ion has to be $>10^7$ s⁻¹. This transfer rate is of the same order of magnitude as for triphenylene sensitized Eu³⁺ in acetonitrile solutions [20]. A space filling model of Ls.Nd, in which all atoms are represented by their van der Waals radius, shows that the distance between lissamine and the Nd³⁺ ion is 7–8 Å, whereas the effective average Bohr radius for the excited lissamine and the unexcited Nd³⁺ ion is

about 2.5 Å. According to Dexter [21], this means that 3% of the maximum possible energy transfer rate is reached. This could be improved by reducing the distance between the lissamine and the Nd³⁺ ion by changing the configuration of attachment of the lissamine. Another possibility to increase the energy transfer rate is to improve the spectral overlap between the sensitizer and the Nd³⁺ ion [22]. In the present case, the energy of the triplet state of lissamine matches with the 14 600 cm⁻¹ band of Nd³⁺ which shows weak absorption. If a sensitizer could be used that matches the strong 13 600 cm⁻¹ absorption band, the energy transfer rate could be increased.

Finally, photo-degradation measurements of the 580 nm lissamine luminescence were performed on polymer waveguides doped with 3 wt% (complex) and are shown in Fig. 8(a) for normal incidence irradiation at three different pump powers. The luminescence signal was detected normal to the waveguide. For a pump power of 4 mW the luminescence intensity slowly rises to a maximum and then decreases again. At higher pump powers the same effect is observed, but both the increase and the decrease processes occur faster. The photo-degradation process may be the result of oxygen induced quenching. Another possibility is that upon photo-excitation, radicals are formed which react with the sensitizer [23]. Further research is

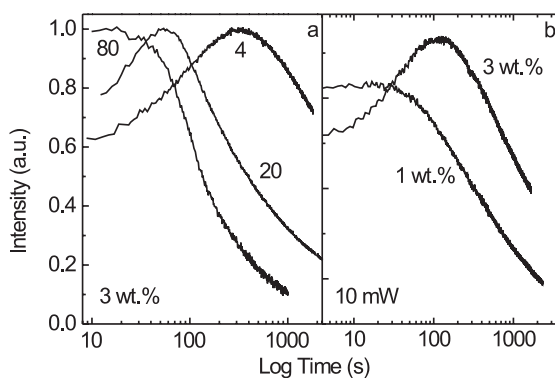


Fig. 8. (a) 580 nm lissamine photoluminescence of a 3 wt% Ls.Nd-doped waveguide at pump powers of 4, 20 and 80 mW. (b) Similar measurements on a 3 and 1 wt% Ls.Nd-doped waveguide at a pump power of 10 mW. As can be seen, the 1 wt% luminescence does not show the initial increase in the intensity.

going on to determine the exact nature of the photo-degradation.

4. Conclusions

Room-temperature photoluminescence of Nd³⁺ complexes in DMSO-d6 solution and partially fluorinated polycarbonate waveguides has been observed for both direct excitation of the Nd³⁺ ion into a higher excited state, and excitation via a highly absorbing sensitizer (lissamine). It is shown that the excitation efficiency upon excitation via the sensitizer is 10⁴ times higher than for direct excitation. The intramolecular transfer rate from the sensitizer to the Nd³⁺ ion is >10⁷ s⁻¹. The luminescence lifetime is relatively short, both in DMSO-d6 (2.2 μs) and in the partially fluorinated polycarbonate waveguide (0.8 μs), which is attributed to coupling to O–H and C–H vibrations of the complex and the host material. Good quality optical waveguides can be spincoated with optical losses for the undoped polycarbonate waveguide of <0.05 dB/cm at 1060 nm and 0.08 dB/cm at 1340 nm. Strong photo-degradation is observed that might be due to the presence of oxygen in the polymer film or due to radicals, which are formed upon photo-excitation.

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