Lanthanide-Doped Nanoparticles with Excellent Luminescent Properties in Organic Media

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Surface-coated nanoparticles of LaF₃ and LaPO₄ doped with the luminescent trivalent lanthanide ions Eu³⁺, Nd³⁺, Er³⁺, Pr³⁺, Ho³⁺, and Yb³⁺ have been prepared. These ions emit in the visible and in the near-infrared part of the electromagnetic spectrum. The ions Nd³⁺, Er³⁺, Pr³⁺, and Ho³⁺ are the main focus in this research because they show emissions in telecommunication windows. The Yb³⁺ ion is of interest because it can be used as a sensitizer for Er³⁺. The Eu³⁺ ion has been used as a probe for the structural environment of the luminescent ion. It is shown that these lanthanide ions are incorporated in the inorganic host of the particles and that the particles are dispersable in organic solvents. The luminescent lifetimes of the ions are increased by orders of magnitude compared to organic complexes, with values ranging from several microseconds for Pr³⁺ and Ho³⁺, up to about 200 μs for Nd³⁺, and 1 ms for Er³⁺. This increase in the luminescence lifetime is indicative of an effective shielding of the lanthanide ions from nonradiative decay of the excited state by the high-energy vibrations of the solvents and the coordinated organic ligands. A model is proposed to describe the nonexponential behavior of the luminescence decay by quenching from outside the particle. It uses two fit parameters, kᵣ, a parameter describing the luminescence decay rate in the absence of surface quenching, and C, a parameter describing the sensitivity toward quenching. Using this model, the luminescence decays can be fitted very well, and factors influencing the luminescence lifetime like concentration quenching and solvent effects can be described accurately.

Introduction

Nanoparticles coated with organic surfactants are an interesting new class of materials that emerged over the past decade.¹,² The surfactant coating protects the particles against aggregation, controls the growth of the particles, and gives them dispersability in organic solvents. Luminescent nanoparticles are an important class of these nanoparticles because they open a way to use the luminescence of inorganic compounds in an organic environment. Inorganic compounds doped with lanthanide ions are widely used as the luminescent material in lighting and displays,³ optical amplifiers,⁴ and lasers.⁵ The luminescence of trivalent lanthanide ions is a result of transitions within the partially filled 4f shell of the ions. These transitions are parity forbidden leading to low molar absorption coefficients in the order of 10 cm⁻¹ and long luminescent lifetimes, up to several milliseconds. These long luminescent lifetimes are advantageous in applications in which population inversions have to be created, such as lasers and optical amplifiers, and for excited state absorption processes, such as up-conversion. There is a growing interest in making optical components in polymer materials because of the easy processing of polymer materials by spin-coating and photolithography.⁶ However, in organic media the long-lived excited state of the lanthanide ions is quenched very effectively by the high-energy vibrations of closely spaced organic groups.⁷ This is in particular true for the lanthanide ions that emit in the near-infrared, like Er³⁺ and Nd³⁺, because the energy gap between the luminescent excited state and the ground state is small.⁸ Due to this quenching, the pump power has to be very high to reach population inversion. One way of protecting the lanthanide ion from the organic environment is by doping the ions in the core of inorganic nanoparticles. These nanoparticles have

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organic groups on the surface and therefore are dispersable in organic solvents, but the ion itself is in an inorganic matrix leading to long luminescent lifetimes. A lot of nanoparticles doped with lanthanide ions have been reported, but most of these particles are made in high temperature processes leading to particles without been reported, but most of these particles are made in high temperature processes leading to particles without any general consensus. A lot of nanoparticles doped with lanthanide ions have been reported that are dispersable in organic solvents, and the luminescence lifetimes of the ions are long compared to these ions in solution or in organic complexes. A difference between the two particles is the phonon energy of the host matrix. For LaPO₄, the highest phonon energy is around 1050 cm⁻¹ while for LaF₃ this is only 350 cm⁻¹. The lower phonon energies of the LaF₃ particles could in principle lead to longer luminescent lifetimes, and this material has been used extensively for a variety of NIR emitting lanthanide-doped nanoparticles that have been reported that are dispersable in organic solvents, but the NIR emitting ions such as Nd³⁺, Er³⁺, and Pr³⁺ have been used extensively for a variety of NIR emitting lanthanide-doped nanoparticles in the form of crystals and thin films. The ligand ammonium dioctadecylidithiophosphate used in the synthesis of the LaF₃ particles was prepared by heating a solution of 614 mg (0.95 mmol) of ammonium di-n-octadecylidithiophosphate and 126 mg (1 mmol) of NaF in 35 mL of ethanol/water at 75 °C. A solution of La(NO₃)₃·6H₂O and Eu(NO₃)₃·6H₂O (1.33 mmol total) in 2 mL of water was added dropwise, and the solution was stirred at 75 °C for 2 h and then cooled to room temperature. The precipitate was separated by centrifugation and was washed subsequently with water and ethanol. The particles were further purified by dispersing in dichloromethane and precipitating by addition of ethanol. After separation by centrifugation, the particles were dried in a vacuum over P₂O₅ for 2 days. After drying the particles, they are soluble in apolar solvents such as chloroform, dichloromethane, and toluene.

**Experimental Section**

All chemicals were used as received without further purification. The lanthanide salts were purchased from Aldrich or Acros in the highest purity available (at least 99.9%). Octadecanediol (99%), Sodium fluoride (99%), and tris(ethylenedimine)phosphate (98%) were purchased from Fluka, phosphorus pentasulfide (99%) from Aldrich, and trioctylamine (98%) from Acros. LaPO₄ particles were synthesized using a procedure described before. Briefly, 1 mmol of the hydrated LnCl₃ (Ln = La³⁺, Eu³⁺, Nd³⁺, or Pr³⁺) was dissolved in 10 mL of dichloromethane, and a drop of a diluted particle dispersion, in methanol in the case of LaF₃, in dichloromethane in the case of LaPO₄ and dichloromethane in the case of LaF₃ particles, was added. The reaction mixture was heated at 200 °C under argon. After 40 h, the solution was cooled to room temperature, and methanol was added to precipitate the nanoparticles. The particles were separated by centrifugation and washed two times with methanol. The particles were soluble in methanol by the addition of tetramethylammonium hydroxide. The particles could be precipitated by the addition of ethyl acetate and separated by centrifugation. Particles precipitated in this way were surface coated with tetramethylammonium hydroxide sodium, and an ammonium was bubbled through this solution. The resulting precipitate was separated by filtration, washed with hexane, and dried. The NMR (DMSO-d₆): δ 7.2–6.9 (broad, 4H), δ 3.7 (d, J = 8.1, 6.6 Hz, 4H), δ 1.5–1.4 (m, 4H), δ 1.35–1.1 (m, 60H), δ 0.84 (t, J = 6.2 Hz, 6H). MS (MALDI-TOF) m/z = 634.0 (1147, 104), calculated for C₆H₅NO₃P₃: 633.5. Anal. Calc'd for C₆H₅NO₃P₃: C, 66.31; H, 12.16; N, 2.15; S, 9.83. Found: C, 66.50; H, 12.24; N, 2.27; S, 9.56.

The LaPO₄ nanoparticles were prepared by heating a solution of tritycylamine in 3 mL of tris(ethylhexyl)phosphate was added, and the reaction mixture was heated at 200 °C under argon. After 40 h, the solution was cooled to room temperature, and methanol was added to precipitate the nanoparticles. The particles were separated by centrifugation and washed two times with methanol. The particles were soluble in methanol by the addition of tetramethylammonium hydroxide. The particles could be precipitated by the addition of ethyl acetate and separated by centrifugation. Particles precipitated in this way were surface coated with tetramethylammonium hydroxide sodium, and an ammonium was bubbled through this solution. The resulting precipitate was separated by filtration, washed with hexane, and dried. The NMR (DMSO-d₆): δ 7.2–6.9 (broad, 4H), δ 3.7 (d, J = 8.1, 6.6 Hz, 4H), δ 1.5–1.4 (m, 4H), δ 1.35–1.1 (m, 60H), δ 0.84 (t, J = 6.2 Hz, 6H). MS (MALDI-TOF) m/z = 634.0 (1147, 104), calculated for C₆H₅NO₃P₃: 633.5. Anal. Calc'd for C₆H₅NO₃P₃: C, 66.31; H, 12.16; N, 2.15; S, 9.83. Found: C, 66.50; H, 12.24; N, 2.27; S, 9.56.

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TEM images were collected on a Philips CM 30 Twint TEM, operating at 300 keV. Samples were prepared by evaporating a drop of a diluted particle dispersion, in methanol in the case of LaPO₄ and dichloromethane in the case of LaF₃ particles, on a carbon coated 200 mesh copper grid. H NMR spectra were recorded at 25 °C on a Varian Inova 300 NMR spectrometer. Element analyses were carried out with a model 1106 Carlo Erba Strumentazione element analyzer. X-ray fluorescence was carried out on a Philips PW 1489 spectrometer using LaF₃, Li₃PO₄, Eu₂O₃, Nd₂O₃, Er₂O₃, Pr₂O₃, and Ho₂O₃ as the standards. Infrared spectra were recorded on a FT-IR Perkin-Elmer Spectrum BX spectrometer. Mass spectra were recorded using a Perkin-Elmer time-of-flight mass spectrometer. Phosphorus NMR measurements in the visible were done with an Edinburgh Instruments FS/FL instrument with a 450 W Xe arc lamp and a red sensitive Peltier element cooled Hamamatsu R955 PMT. The emission spectra were corrected for the detector response, and the excitation spectra were corrected for the lamp intensity. The NIR spectrum of Ho³⁺ was measured with the same instrument using a liquid nitrogen cooled Ge detector. The other NIR spectra were measured by exciting the samples with a CW Ar⁺ ion laser operating at 488 nm (Er³⁺), 476 nm (Pr³⁺), and 514 nm (Nd³⁺). The continuous light was modulated with an acousto-optic modulator and focused on the sample in 1 x 1 cm² quartz cuvettes. The signal was focused with a 20 cm lens on a monochromator and detected at the monochromator exit with a liquid nitrogen cooled Ge detector (Northcoast) or a PMT (AgOCS) for the spectral region between 700 and 1000 nm. The signal of the detector was fed to a lock-in amplifier. The spectra of the near-infrared emitting ions were measured with a resolution of 6 nm and of the visible emitting ions with a resolution of 0.9 nm.

Luminescence quantum yields were determined by comparing the luminescence intensity of a particle solution with a solution of quinine bisulfate in 1 M H₂SO₄ with approximately 20% T.
the same absorption at the excitation wavelength of 274 nm. The quantum yield was calculated from the equation \( \Phi_{\text{sample}} = \left( \frac{n_{\text{sample}}}{n_{\text{ref}}} \right)^2 \frac{A_{\text{ref}}}{A_{\text{sample}}} \Phi_{\text{ref}} \), with \( n \) the refractive index, \( A \) the absorption, and \( I \) the emission intensity and taking the quantum yield of quinine bisulfate as 54.4\%.

Results and Discussion

Characterization. The doping concentration in all particles was 5% of the luminescent ion compared to the total concentration of lanthanide ions, to give a molar ratio of \( \text{La}^{3+}/\text{Ln}^{3+} \) of 19/1, unless stated otherwise. Particles of LaPO_4 were synthesized using a literature procedure\(^{10} \) from the hydrated LnCl_3 salts and phosphoric acid. The growth of the particles is controlled by the coordinating solvent tris(ethylhexyl)phosphate and protonated trioctylamine. During the reaction, some of the solvent is hydrolyzed, and the resulting bis(ethylhexyl)phosphate binds to the surface as can be seen by \(^1\text{H} \) NMR spectroscopy. The LaF_3 nanoparticles were synthesized using ammonium diocadecyldithiophosphate as ligand. To a solution of this ligand and NaF in a water/ethanol mixture was added dropwise a solution of the Ln(NO_3)_3 salts in water. The dithiophosphate headgroup of the ligand coordinates weakly to the lanthanide ions allowing the growth of the nanoparticles but coordinates strongly enough to keep the particles from aggregating.\(^{17} \) The particles were characterized using TEM by evaporating a drop of particle dispersion on a carbon coated copper grid. Typical pictures for LaF_3:Ln and LaPO_4:Ln (Ln = Eu\(^{3+} \) and Nd\(^{3+} \)) are shown in Figure 1.

The morphologies of both particles are independent of the dopant ion. The high crystallinity of the particles can clearly be seen, despite the fact that the particles were synthesized at relatively low temperatures, i.e., below 200 °C. The LaPO_4 particles with an average size of 4.3 nm are somewhat smaller in size than the LaF_3 particles with an average size of 6.3 nm. In addition, the size distribution of 15% for the LaPO_4 particles is lower than the size distribution of the LaF_3 particles, which is 28%. The LaF_3 particles are less spherical in shape with aspect ratios between 1 and 3. The spherical and elongated particles both consist of one crystal domain, so the elongated particles are not formed by the aggregation of multiple particles. In the size distribution histograms, the sizes of the elongated particles were determined by averaging the long and the short axes. The sizes of both particles are sufficiently small to prevent scattering when the particles are incorporated in a polymer matrix.\(^{18} \)

The elemental composition of the particles was determined using X-ray fluorescence (XRF) and combustion elemental analysis. The results are summarized in Table 1.

Table 1. Elemental Composition of the Particles (wt %)

<table>
<thead>
<tr>
<th>particle</th>
<th>La</th>
<th>Ln</th>
<th>P</th>
<th>C</th>
<th>N</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPO_4:Na</td>
<td>41.97</td>
<td>2.42</td>
<td>12.19</td>
<td>6.33</td>
<td>1.01</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>LaPO_4:Er</td>
<td>41.80</td>
<td>2.36</td>
<td>12.56</td>
<td>5.57</td>
<td>1.20</td>
<td>2.63</td>
<td>0.0</td>
</tr>
<tr>
<td>LaPO_4:Pr</td>
<td>43.30</td>
<td>2.35</td>
<td>12.52</td>
<td>6.30</td>
<td>1.01</td>
<td>2.17</td>
<td>0.0</td>
</tr>
<tr>
<td>LaF_3:Na</td>
<td>17.81</td>
<td>0.86</td>
<td>11.23</td>
<td>42.49</td>
<td>7.76</td>
<td>5.76</td>
<td>0.0</td>
</tr>
<tr>
<td>LaF_3:Er</td>
<td>17.41</td>
<td>0.81</td>
<td>11.25</td>
<td>43.59</td>
<td>7.62</td>
<td>6.48</td>
<td>0.0</td>
</tr>
<tr>
<td>LaF_3:Ho</td>
<td>25.47</td>
<td>1.17</td>
<td>9.50</td>
<td>33.07</td>
<td>5.88</td>
<td>5.72</td>
<td>0.0</td>
</tr>
</tbody>
</table>

a XRF, b Combustion elemental analysis.

The same ratio of lanthanide ions as applied in the synthesis was found in the particles reflecting the similar reactivity of the lanthanide ions. The rest consists of organic groups on the outside of the particles such as tetramethylammonium ions and ethylhexyl chains for the LaPO_4 particles and the coordinated dithiophosphate ligands for the LaF_3 particles. The surfaces of the LaPO_4 nanoparticles consist of deprotonated phosphate groups coordinated to ammonium ions and some of the solvent and hydrolyzed products of the solvent. The coordination of the organic molecules can be seen from the broadened signals in the \(^1\text{H} \) NMR and the ratio of Ln/P, that is smaller than one, indicates that...
phosphate groups are at the surface and not the lanthanide ions. For the LaF₃ particles, it is likely that phosphate groups are at the surface and not the surface of the particles can be seen from the broadened signals of the ligand in the ¹H NMR spectrum. Fluoride could not be detected using both these analysis techniques so no information could be obtained about the amount of F in the LaF₃ particles. The amount of ligand measured with elemental analysis on the LaF₃ particles is not always constant. For the Nd³⁺ and Er³⁺ doped particles, the amount of carbon and hydrogen measured is the same, but the amount of sulfur is slightly lower for the Nd³⁺ particles. A deviation in the amount of sulfur could be caused by oxidation of the ligand after prolonged exposure to air, as found by mass spectrometry. This oxidation leads to a ligand with a phosphate headgroup, which binds more strongly to the particles and would therefore lead to even more stable particles. For the Ho³⁺ doped particles, the amount of carbon and hydrogen is lower than for the other two ions. The particle size and size distribution is the same as for the other two batches, so apparently there is less ligand coordinated to the Ho³⁺ doped particles. For all these particles, no free ligand is present because no nitrogen was detected and because only broadened signals are present in the ¹H NMR spectra proving the coordination of the ligand to the particle surface. Surface properties of nanoparticles usually play an important role in the luminescence properties, and it is therefore important to know which molecules are coordinated to the surface.

**Luminescence of Eu³⁺-Doped Particles.** The Eu³⁺ ion was used as a probe for the crystal environment in which the ion is located. Typical Eu³⁺ emission originating from the ⁵D₀ and ⁵D₁ levels was observed after direct excitation of the ion at 397 nm for LaF₃:Eu and 260 nm for LaPO₄:Eu (Figure 2).

In LaPO₄, the Eu³⁺ can be excited at 260 nm because of a charge transfer band. This charge transfer band is visible in more phosphors in which Eu³⁺ is coordinated to oxygen and is caused by an electron transfer in the Eu³⁺−O²⁻ bond. Deactivation of the charge transfer state leads to an excited Eu³⁺ ion. Due to the low reduction potential of Eu³⁺, this band occurs at wavelengths above 200 nm. In the emission spectrum, the ratio of the different peaks of the ⁵D₀ → ⁷Fⱼ (j = 1, 2) transition gives information about the symmetry of the crystal site in which the ion is located. This confirms that the dopant ion is present in a La³⁺ crystal site giving the Eu³⁺ ion C₁ symmetry in LaPO₄ and C₂ symmetry in LaF₃ particles, the same as for the bulk materials. In the LaF₃:Eu particles, emission from the ⁵D₁ level at 524, 534, 554, and 582 nm can clearly be observed as well. Emission from this level also occurs in the LaPO₄:Eu particles only with much less intensity. This large difference in emission from the ⁵D₁ level is caused by the difference in phonon energies of the host materials. The ⁵D₁ level lies only 1750 cm⁻¹ above the ⁵D₀ level, and thus, the ⁵D₁ level can be depopulated very fast to the ⁵D₀ level by multi-phonon emission in LaPO₄. In the LaF₃ host, the maximum phonon energies are so low that multi-phonon emission becomes inefficient. The different symmetry sites of Eu³⁺ in these particles can clearly be observed from the different emission spectra. The Eu³⁺ ion can also be used as a probe for more similar crystal structures as is illustrated in LnPO₄ nanoparticles with Ln = La, Gd, Y, and Lu, synthesized using the same procedure described for LaPO₄ particles. The crystal structure of these phosphates is dependent on the size of the lanthanide ion. A monazite type is found for the larger lanthanide ions (Ln = La³⁺−Gd³⁺) and xenotime for the smaller lanthanide ions (Ln = Tb³⁺−Lu³⁺). The excitation and emission spectra for LnPO₄:Eu (Ln = La³⁺, Gd³⁺, Y³⁺, Lu³⁺) nanoparticles are shown in Figure 3.

The excitation spectra are scaled to the 393 nm peak of Eu³⁺, and all show a charge transfer band, but the excitation maximum is blue shifted upon a decrease in ion size. The excitation spectra of LuPO₄ and YPO₄ exhibit a sharp cutoff around 220 nm, which is caused by the absorption of the excitation light by the solvent. The blue shift of the charge transfer band upon decreasing the ion size can be explained by a stronger binding of the phosphate groups to the smaller trivalent ions and by the smaller crystal site the Eu³⁺ ion has in the LuPO₄ and YPO₄ lattices. This makes the phosphates more difficult to oxidize and the reduction of Eu³⁺ to Eu²⁺ less favorable. The sharp lines in the GdPO₄ host at 273, 276, and 278 nm and some smaller peaks around 310 nm are due to the excitation of Gd³⁺ (⁸S₇/₂ → ⁶D₁, ⁶P₁, J = ⁵/₂, ⁷/₂, and ⁹/₂) and subsequent energy transfer to the Eu³⁺ excited states. The emission spectra of all four LnPO₄:Eu materials exhibit the characteristic Eu³⁺ emission lines for the ⁵D₀ → ⁷Fⱼ (j = 0–4) transitions. Some differences are observed in the emission spectra of the two host materials with the larger ions (La³⁺ and Gd³⁺) compared to the host materials with the smaller ions (Y³⁺ and Lu³⁺). The relative intensities of the ⁵D₀ → ⁷F₂ transition are different: 0.30, 0.30, 0.43, and 0.50 for the doped LaPO₄, GdPO₄, LuPO₄, and YPO₄, respectively. These values correspond to a crystal site with a high degree of inversion symmetry and more inversion symmetry for the La and Gd phosphates than for the Lu and Y phosphates. Furthermore, a number of extra references are provided in the text.
peaks are found in the $^5D_0 \rightarrow ^7F_4$ transition, all consistent with the difference in crystal structure between the LaPO$_4$, GdPO$_4$ and the LuPO$_4$ and YPO$_4$ particles.

The luminescence decay of the ion gives information on the influence of quenching from the organic solvent and ligand outside the particle and quenching by impurities from inside the particle. An example of the decays of LaF$_3$:Eu and LaPO$_4$:Eu particles is given in Figure 4a.

Excitation occurs in the higher lying Eu$^{3+}$ levels followed by a rapid decay to the luminescent $^5D_0$ level. For the LaPO$_4$:Eu particles, the luminescence of the $^5D_0$ level shows a short rise with a time constant of 24 $\mu$s. This is similar to the decay time of the $^5D_1$ level of 23 $\mu$s showing that the $^5D_0$ level is partially populated through the $^5D_1$ level. After this short rise in the LaPO$_4$: Eu luminescence, both decays are clearly not monoexponential, so not all ions in the particles have the same probability of decay. An acceptable fit was obtained when two exponentials were used. However, there is no physical reason to use just two exponentials. Quenching by groups close to or at the surface of the nanoparticle should lead to a gradual change of quenching efficiency of the lanthanide ion from the surface to the core of the particle. Assuming a random distribution of the dopant lanthanide ion over the nanoparticle and that all ions are in the same crystal site, there is no physical justification for fitting the decay curve with just two exponentials, which suggests two populations. A random distribution of the doping ions is reasonable because of the high similarity in cation size, charge, and reactivity between the lanthanide ions. It was possible to check if all the ions are in the same crystal site. First of all, the emission of the $^5D_0 \rightarrow ^7F_0$ transition gives information on the amount of crystal sites the ion is doped in. This is a transition between two nondegenerate levels, so if all the ions are in the same crystal site, only one emission peak for this transition is present around 578 nm. In both Eu$^{3+}$ doped particles of LaF$_3$ and LaPO$_4$, we indeed see just one peak for this transition, measured at a resolution of 0.1 nm (inset Figure 2), indicating that all ions are in the same crystal site. Time-resolved spectroscopy is another method giving information on different crystal sites. Ions doped in different crystal sites have a different symmetry leading to a difference in emission spectrum and a difference in luminescent lifetime. An emission spectrum taken directly after an excitation pulse is caused.
by emission from both types of ions, but an emission spectrum at the end of the decay is the emission from ions with the longest lifetime. When all ions are in the same crystal site, no differences in emission spectrum should be observed. Figure 5 shows the emission spectra of LaPO₄:Eu in methanol 0.2 ms after an excitation pulse and 29 ms after an excitation pulse.

Although the intensity at the end of the decay is much lower, the shape of the emission spectrum is essentially the same as in the early stages of the decay, thereby confirming that Eu³⁺ is doped in one single crystal site.

**Modeling the Luminescence Decay.** When it is assumed that most of the quenching of the excited state is located close to the surface, a model can be designed taking into account these surface effects. Ions in the core of the particles will have the longest lifetime, and going to the outside the lifetime will decrease. When a particle is divided into a number of shells, the lifetime of one shell can be related to the lifetime in another shell by an effective radiative lifetime and a quenching factor that is dependent on the distance to the surface. The luminescence decay can thus be described using eq 1.

\[
l_t = l_0 \sum_{i=1}^{n} \frac{1}{n} e^{-k_it} = k_R + C \times f_{qi}
\]  

(1)

In this equation, \(l_t\) is the luminescence intensity at time \(t\), \(l_0\) the intensity at \(t = 0\), \(n\) the number of shells, \(k_i = 1/\tau_i\) the rate constant in shell \(i\), with \(\tau_i\) the luminescence lifetime of this shell, \(C\) the quenching constant. The value of \(k_R\) is an apparent decay rate, because it only takes into account quenching from the surface. All other quenching processes inside the nanoparticle, like concentration quenching and quenching by impurities inside the nanoparticle, can also be present. The constant \(C\) is a fit parameter that is dependent on the individual ion, the size and size distribution of the particles, and on the strength of the quenching. The size and size distribution are still in the quenching constant, because at this moment no size dependent decays are available. The relative quenching factor \(f_{qi}\) takes into account the distance of a shell to the surface and the distance dependence of the quenching. When quenching is assumed to take place via a dipole–dipole mechanism, the quenching has a distance dependence of \(r^{-6}\). The total quenching then has to be integrated over the total volume outside the particle. Integration over the total volume gives the total quenching factor \(f_{qi}\) (eq 2).

\[
f_{qi}(a_i) = \int_V r^{-6} \, dV
\]  

(2)

This equation was solved for a particle shell \(i\), with \(a_i = A_i/R_i\) as the center of each shell, by varying the radius \(r\) (Figure 6). Three domains can be defined. The first domain is totally inside the particle ranging from \(r = 0\) to \(r = (R - A)\), so for this domain no quenching is taken into account. In the second domain, the volume fraction \(d[V(r, \phi)]\) is dependent on both the radius and the angle \(\phi\) (part of the shell is inside the particle with no quenching and part is outside the shell, but with quenching). This domain ranges from \(r = (R - A)\) to \(r = (R + A)\) (Figure 6).

The third domain lies totally out of the particle and is from \(r = (R + A)\) to \(\infty\). The fraction of a shell in the second domain that is outside the particle equals \(2\pi r^2(1 - \cos \phi)dr\). The volume fraction \(dV\) of a shell in the third domain is \(4\pi r^2 dr\). Multiplying this with \(r^{-6}\) results in the following integral (eq 3), that was numerically solved for a particle consisting of 10 shells of equal volume. Assuming that the ions are randomly distributed in the particle will give all ions the same weight in the fit.

\[
f_{qi}(A, \phi) = \int_V r^{-6} \, dV = \int_{R - A}^{R + A} \frac{1}{r^6} 2\pi r^2(1 - \cos \phi)dr + \int_{R + A}^{\infty} \frac{1}{r^6} 4\pi r^2 dr
\]  

(3)

(23) In this approach, we neglect the \(5D_{2}\) emission from Eu³⁺ (typical lifetime of this level in LaF₃:Eu is 2.5 ms and 25 μs in LaPO₄:Eu). The contribution to the total emission is about 5% in the case of LaF₃:Eu and close to zero in the case of LaPO₄:Eu.


(25) The choice to take 10 shells is an arbitrary choice. Fitting with 6 shells gave the same results, but more shells could increase the accuracy of the fit.
This results in relative quenching factors for the different shells as shown in Table 2.

Using these values for the quenching factors, the decays of the particles can be fitted by varying the values for the apparent radiative lifetime $\tau_R$ and C. Good fits were obtained for LaPO$_4$:Eu and LaF$_3$:Eu particles (Figure 4a, --). In these fits, the luminescence of the $5d_1$ level is not taken into account. Emission from this level contributes only very little to the total emission, but it could have a small influence on the obtained values.

For LaPO$_4$:Eu particles in methanol, the value for $\tau_R$ is 7.0 ms with a quenching constant of $4.1 \times 10^{-2}$ s$^{-1}$. In the case of LaF$_3$:Eu particles in dichloromethane, the $\tau_R$ is 7.7 ms with a quenching constant of $2.9 \times 10^{-1}$ s$^{-1}$. These results show that the apparent radiative lifetime of Eu$^{3+}$ in LaF$_3$ is longer than that in LaPO$_4$ from the literature, but that the ion is quenched more strongly in the LaF$_3$ particles than in the LaPO$_4$ particles. The difference in solvent does not explain the difference in quenching strength, because methanol is a stronger quenching solvent than dichloromethane due to the presence of an O–H bond. The different termination of the surface could be the reason for a different quenching strength. The LaPO$_4$ particles are terminated with phosphate groups, but the LaF$_3$ particles are terminated with Ln$^{3+}$ groups. This means that in the case of LaF$_3$ particles the luminescent ion can directly coordinate to a quenching group of the organic environment or the ligand, which is not the case for the LaPO$_4$ particles. One other possible source of quenching is the coordination of water to the surface of the particles. It has been shown that the lifetime of LaF$_3$:Eu particles is longer when the particles are synthesized in deuterated solvents demonstrating that residual OH groups are present after the synthesis and act as quenchers. When this product was stirred in a water/methanol mixture, the lifetime of Eu$^{3+}$ went back to the value for particles synthesized in nondeuterated solvent, proving that the OH groups are at the surface of the particles and accessible to the solvent. The LaPO$_4$ particles are synthesized under near water free conditions, and any water present will be used in the hydrolysis of the solvent, so contamination with water is probably less important. The apparent radiative lifetimes ($\tau_R = 1/k_R$) do not necessarily relate to the real radiative lifetime, because quenching inside the particle is not taken into account in this model. However, the high values do indicate that quenching inside the particle is not significant. The size dispersity of the particles is in the quenching constant C, so the values of C for LaF$_3$ and LaPO$_4$ particles cannot be compared directly with each other. Figure 4b shows the variation of the lifetime $\tau_i$ in the different particle shells. As expected, the longest lifetimes are observed in the core of the particles, and going to the surface of the particles the lifetime decreases consistent with quenching by the solvent. Because the total luminescence is the area under the decay curve, an average lifetime of these 10 values can be calculated using eq 4.

$$\tau_{av} = \sum \frac{A_i \tau_i^2}{\sum A_i \tau_i}$$

For LaF$_3$:Eu, an average lifetime of 6.5 ms is calculated, and for LaPO$_4$:Eu particles, an average lifetime of 6.6 ms. The values for these materials are close to the radiative lifetimes calculated and measured previously for the bulk materials, but unfortunately, it is not possible to compare them directly to these radiative lifetimes, because the nanoparticles are in another solvent. However, they do indicate a high quantum yield.

Quantum Yield. A quantum yield of these lanthanide-doped particles can be determined using Ce$^{3+}$-doped particles. Ce$^{3+}$ has a high absorption between 200 and 300 nm because of an allowed 4f–5d transition. It is known that Ce$^{3+}$ shows efficient energy transfer to Tb$^{3+}$, which emits in the visible and from particles doped with both these ions, it is possible to determine the quantum yield by comparison with a dye. We determined the quantum yield by using quinine bisulfate dye. For La$_{0.4}$Ce$_{0.45}$Tb$_{0.15}$, a quantum yield of 10% in methanol was found, lower than the value of 24% found by Haase and co-workers. The value found by Haase et al. was measured using Rodamine 6G, and when we used this dye, a quantum yield of 21% was found, which is within the experimental error of about 2% (absolute). The value found using quinine bisulfate is probably more reliable, because this dye is more suitable for excitation in the UV, and it has a low absorption at the excitation wavelength and much overlap between emission and absorption, so at higher concentration, reabsorption of emission could occur leading to an overestimation of the quantum yield. The emission and absorption of quinine bisulfate have very little overlap so self-quenching at higher concentrations does not take place. It was also possible to synthesize La$_{0.4}$Ce$_{0.45}$F$_3$:Tb$_{0.15}$ particles, and the emission spectrum is shown in Figure 7 together with the emission spectrum of quinine bisulfate.

For La$_{0.4}$Ce$_{0.45}$F$_3$:Tb$_{0.15}$ in dichloromethane, a quantum yield of 19% was found. When $D_2$O was added to a dichloromethane solution of LaCeF$_3$:Tb particles, an increase in quantum yield to 38% was observed. This confirms the hypothesis of a small amount of water to the surface of the particles leading to a change in the excited state of the lanthanide ions. The high-energy

### Table 2. Quenching Factor $f_{aq}$ for 10 Shells

<table>
<thead>
<tr>
<th>shell $i$</th>
<th>$a_i$</th>
<th>$f_{aq}(a_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>0.52</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>0.63</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>0.70</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>0.77</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>0.82</td>
<td>121</td>
</tr>
<tr>
<td>7</td>
<td>0.87</td>
<td>$3.0 \times 10^2$</td>
</tr>
<tr>
<td>8</td>
<td>0.91</td>
<td>$8.6 \times 10^2$</td>
</tr>
<tr>
<td>9</td>
<td>0.95</td>
<td>$4.9 \times 10^3$</td>
</tr>
<tr>
<td>10</td>
<td>0.98</td>
<td>$7.7 \times 10^4$</td>
</tr>
</tbody>
</table>

(28) Due to the low absorption of the lanthanide ions, it is difficult to determine the optical density of a particle solution, and it is therefore not possible to compare the emission with the emission of a dye with a known quantum yield.
emission is observed at 980 nm of the $^4\!_{11/2} \rightarrow ^4\!_{15/2}$ transition, which is not visible in the LaF$_3$ host, probably because of symmetry reasons. The excitation spectra are very similar for both particles, showing small differences in peak intensities caused by symmetry differences. For the Pr$^{3+}$ ion, luminescence can originate from different levels depending on the crystal field and on the quenching mechanisms. Luminescence originating from the $^1\!D_2$ level was observed in LaPO$_4$: Pr particles by excitation with the 476 nm line of an Ar$^+$ laser. When the LaF$_3$:Pr particles were excited using the same laser line, no emission was observed, although it is known that the Pr$^{3+}$ ion can emit very efficiently in this host matrix. It is possible that Pr$^{3+}$ does not absorb at this wavelength in the LaF$_3$ host or that the Pr$^{3+}$ ion is very sensitive to the small amount of water present at the surface of the LaF$_3$. Under excitation with an Xe arc lamp at 443 nm, the emission of LaPO$_4$:Pr could also be detected, but only weak emission was observed for LaF$_3$:Pr particles. For the Ho$^{3+}$ ion, emission could be detected in the LaF$_3$:Ho particles at 960 and 1460 nm from the $^5\!F_5 \rightarrow ^5\!I_8$ and $^5\!F_5 \rightarrow ^5\!I_7$ transitions. In the visible, an emission of the $^5\!F_5 \rightarrow ^5\!I_8$ transition at 640 nm was also observed (not shown). In this host, Ho$^{3+}$ luminescence is known to occur from a variety of levels. The dominant luminescence found in the bulk material is from the $^5\!S_2$ level at 540 nm, which is, however, not observed in our nanoparticles. A reason for this can be that this level lies approximately 3000 cm$^{-1}$ above the $^5\!F_5$ level which corresponds to the vibrational energy of a CH bond. The presence of the ligands on the surface of the particle could lead to a fast nonradiative decay of the $^5\!S_2$ level to the $^5\!F_5$ level from which luminescence occurs. The LaPO$_4$:Ho particles did not show any luminescence at all. Ho$^{3+}$ emission in LaPO$_4$ crystals is not reported in the literature probably because the phonon energies in LaPO$_4$ are too high, leading to relatively inefficient nonradiative processes. NIR emission of Pr$^{3+}$ and Ho$^{3+}$ in an organic environment has not been reported till now, proving the good shielding against the organic groups when they are doped in the nanoparticles. Using these ions the spectral window between 1300 and 1600 nm, which is of interest to telecommunication purposes, can be covered completely.

Yb$^{3+}$ as a Sensitizer. To increase the effective absorption of the Er$^{3+}$ ion, codoping with Yb$^{3+}$ is often used. Yb$^{3+}$ has a higher absorption at 980 nm than Er$^{3+}$, and it is able to transfer energy to the Er$^{3+}$ ion. The 980 nm wavelength is commonly used for pumping Er$^{3+}$ ions because at this wavelength a large variety of cheap semiconductor pump lasers are available. Yb$^{3+}$ also has a low reduction potential leading to charge transfer bands in phosphates, similar to Eu$^{3+}$, so the possibility of a charge transfer in LaPO$_4$ particles was investigated. The emission and excitation spectra of a sample of LaPO$_4$:Yb in methanol are shown in Figure 9.

References:

In the excitation spectrum, a broad band peaking at 250 nm observed. Excitation of the sample at this wavelength leads to typical Yb$^{3+}$ emission peaking at 980 nm. The only excited 4f level of Yb$^{3+}$ is the 2F$_{5/2}$ level, so the broad band at 250 nm is caused by charge transfer excitation. The peak of this charge transfer emission is blue shifted compared to Eu$^{3+}$ reflecting the higher reduction potential of Yb$^{3+}$ compared to Eu$^{3+}$.39

Figure 8. Emission (left) and excitation (right) spectra of (A) LaF$_3$:Nd (--), LaPO$_4$:Nd (--); (B) LaF$_3$:Er (--), LaPO$_4$:Er (--); (C) LaPO$_4$:Pr; and (D) LaF$_3$:Ho. The LaF$_3$ particles were dissolved in CH$_2$Cl$_2$ and the LaPO$_4$ particles in methanol-d$_4$. The emission spectra of the Nd$^{3+}$ doped particles were collected after excitation at 514 nm and the excitation spectra by collecting the emission at 1060 nm. The Er$^{3+}$ doped particles were excited at 488 nm, and the emission was measured at 1530 nm. For Pr$^{3+}$ and Ho$^{3+}$, the excitation was at 476 and 448 nm, respectively, and the emission at 730 and 966 nm, respectively.

The emission and excitation spectra of LaPO$_4$ particles co-doped with Yb$^{3+}$ and Er$^{3+}$ both at 5% are shown in Figure 10.

The absorption lines of Er$^{3+}$ and a broad band peaking at 250 nm are visible in the excitation spectrum. The presence of this broad band is caused by charge transfer excitation of Yb$^{3+}$ followed by energy transfer to Er$^{3+}$. When the sample was excited in the broad band at 250
nm, emission at 980 nm from Yb$^{3+}$ and at 1530 nm from Er$^{3+}$ was observed. The appearance of Yb$^{3+}$ emission means that energy transfer is not complete. The direct excitation of Er$^{3+}$ at 378 nm leads to Er$^{3+}$ emission at 1530 nm as expected, but also Yb$^{3+}$ emission at 980 nm is observed, showing that energy transfer from Er$^{3+}$ to Yb$^{3+}$ is also possible. This reverse process needs phonon energy from the surroundings because the $^4I_{11/2}$ energy level of Er$^{3+}$ lies a bit lower in energy than the $^2F_{5/2}$ level of Yb$^{3+}$. In LaF$_3$ particles, energy transfer between Yb$^{3+}$ and Er$^{3+}$ is also observed after direct excitation of Yb$^{3+}$ into the $^2F_{5/2}$ level around 980 nm. In this matrix, no charge transfer band is observed, similar to Eu$^{3+}$.

Particles of LaF$_3$ codoped with various amounts of Yb$^{3+}$ and 5% of Er$^{3+}$ were synthesized, and the luminescence properties were determined in order to optimize the energy transfer.

The emission spectra of LaF$_3$ particles doped with a varying amount of Yb$^{3+}$ and 5% Er$^{3+}$ excited at 940 nm are shown in Figure 11. The emission spectra are normalized to the Yb$^{3+}$ emission. Excitation at 940 nm was chosen because Er$^{3+}$ has no absorption at this wavelength, so all emission from Er$^{3+}$ is formed through sensitized emission by Yb$^{3+}$. At 1530 nm, Er$^{3+}$ emission is clearly observed, proving the energy transfer between the ions. The Yb$^{3+}$ emission at 980 nm is still dominating, so energy transfer is not complete. By increasing the amount of Yb$^{3+}$, the relative Er$^{3+}$ emission increases, so the energy transfer becomes more efficient up to a doping concentration of 20% Yb$^{3+}$, where the maximum energy transfer is reached. Increasing the concentration of Yb$^{3+}$ above 25% does not increase the energy transfer further. At increasing Yb$^{3+}$ concentration, the energy transfer becomes more efficient because the average distance between the ions decreases. It levels off when all the Er$^{3+}$ ions have at least one Yb$^{3+}$ ion as the nearest neighbor. The excitation spectra of Er$^{3+}$ luminescence at 1530 nm for samples doped with
different amounts of Yb$^{3+}$ are also shown in Figure 11. The excitation spectra are scaled to the Er$^{3+}$ absorption peak at 650 nm, because the amount of Er$^{3+}$ in the sample is constant. It can be seen that the excitation peak of Er$^{3+}$ in the sample without Yb$^{3+}$ around 980 nm is very low and that it can be increased by codoping with Yb$^{3+}$. Increasing the amount of Yb$^{3+}$ leads to a linear increase of the Yb$^{3+}$ peak compared to the Er$^{3+}$ peak, because more energy is absorbed by Yb$^{3+}$ ions. It was reported in the literature that energy transfer from Yb$^{3+}$ to Er$^{3+}$ in Y$_2$O$_2$S nanoparticles is less efficient than in bulk material, because of the absence of low energy phonons. These low energy phonons are required to take up the small energy released when the excitation energy is transferred from Yb$^{3+}$ to Er$^{3+}$. In the present case, in which the nanoparticles are capped with organic molecules, these low energy phonons are present in the form of vibrational and rotational energies, thus facilitating a more efficient energy transfer.

Decays of Near-Infrared Emitting Ions. Luminescence decays of NIR emitting ions could also be fitted using the described model. Some decays with fits are shown in Figure 12, and Table 3 gives the values of the fit constants $\tau_R$ and $C$.

The luminescence lifetimes reported for Er$^{3+}$ and Nd$^{3+}$ are very long compared to values reported previously in an organic environment. An increase in the luminescence lifetime by a factor of 10–1000 is observed. For Nd$^{3+}$, the values of the average lifetime and $\tau_R$ are higher for LaF$_3$ than for LaPO$_4$, reflecting the difference in the phonon energies of the matrices. This is the other way around for Er$^{3+}$. Both the value of $\tau_R$ and the average lifetimes are lower for the LaF$_3$:Er particles compared to the LaPO$_4$:Er particles. Not only the quenching is stronger, but the lower $\tau_R$ indicates that there are more quenching possibilities for Er$^{3+}$ remaining inside the particles. This could be a result of the higher reaction temperature for the LaPO$_4$ particles, which functions as a better annealing step compared to the LaF$_3$ particles. The average lifetimes of Pr$^{3+}$ and Ho$^{3+}$ are in the microsecond range reflecting the shorter radiative lifetimes of these ions. For Pr$^{3+}$ in a phosphate host, a lifetime of 70 $\mu$s for the 5D$_0$ level was reported in the literature, and for Ho$^{3+}$ in LaF$_3$, a lifetime of the 5F$_5$ level of 780 $\mu$s was calculated.

Using the described model, different factors influencing the luminescence lifetimes of these particles were investigated. Er$^{3+}$ usually shows a large dependence on the doping concentration, and when the particles are doped with different concentrations of Er$^{3+}$, this is indeed reflected in the values of $\tau_R$ and $C$ (Table 4). A decrease in Er$^{3+}$ concentration should not change the quenching constant $C$ because the Er$^{3+}$ ions are still in the same crystal site and at the same average distance to the surface. The value of $\tau_R$ should increase with decreasing doping concentration because quenching processes such as cross-relaxation and up-conversion become less important. This is clearly observed in the fitted values for LaF$_3$:Er with different Er$^{3+}$ concentrations. A pronounced increase in $\tau_R$ is observed when the concentration is lowered, while $C$ stays about the same for the concentrations used here. For the LaPO$_4$:Er particles, the constant $C$ does change and becomes lower at a lower doping concentration. The different surface termination of the particles can play a role here. One quenching path is the transfer of the excitation energy of ions in the core of the particles to ions closer to the surface followed by quenching. This process is dependent on the concentration of the doping ion, because energy transfer becomes more efficient at higher doping concentrations, but also on the surface termination. In the LaF$_3$ particles, lanthanide ions are coordinated directly to the ligand and other possible quenchers, but in the case of the LaPO$_4$ particles, PO$_4$ groups are at the surface.

In addition, quenching by solvents with a different quenching strength can be described using this model. Fit values obtained for LaPO$_4$:Nd and LaPO$_4$:Eu in...
methanol with a different degree of deuteration are given in Table 5.

For all particles, the same \( R \) is found in agreement with the fact that the particle itself does not change. The \( C \) constants are different, as expected. A small quenching constant is found for the Eu\(^{3+}\) ions, because the energy gap of Eu\(^{3+}\) is relatively large and it is therefore less sensitive to quenching. In nondeuterated methanol, the strongest quencher is the OH group, and replacing this with an OD group leads to a large decrease in \( C \). Replacement of the CH group by CD leads to another small decrease in quenching in the case of Nd\(^{3+}\), but in the case of Eu\(^{3+}\), the effect is negligible, consistent with the larger energy gap between the excited state and the ground state for Eu\(^{3+}\).

One factor not included in the model is the difference in refractive index between the core and the surrounding solvent. The radiative lifetime of the lanthanide ion is dependent on the refractive index of the surroundings, and it was previously found that particles in solvents with a different refractive index show a different luminescence lifetime.\(^{12,45}\) The average lifetime for LaF\(_3\):Eu particles dissolved in different solvents increased

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**Table 3. Fit Parameters for the NIR Emitting Ions in the Two Different Particles**

<table>
<thead>
<tr>
<th>particle</th>
<th>solvent</th>
<th>( R ) (( \mu s ))</th>
<th>( C ) (s(^{-1}))</th>
<th>( \bar{R} ) (( \mu s ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPO(_4):Nd</td>
<td>CD(_3)OD</td>
<td>90</td>
<td>107</td>
<td>68</td>
</tr>
<tr>
<td>LaPO(_4):Nd</td>
<td>CH(_2)Cl(_2)</td>
<td>347</td>
<td>23.5</td>
<td>265</td>
</tr>
<tr>
<td>LaPO(_4):Er</td>
<td>CD(_3)OD</td>
<td>315</td>
<td>4.66</td>
<td>304</td>
</tr>
<tr>
<td>LaPO(_4):Er</td>
<td>CH(_2)Cl(_2)</td>
<td>326</td>
<td>3.29</td>
<td>226</td>
</tr>
<tr>
<td>LaPO(_4):Pr</td>
<td>CD(_3)OD</td>
<td>4.0</td>
<td>57.3</td>
<td>3.7</td>
</tr>
<tr>
<td>LaF(_3):Ho</td>
<td>CH(_2)Cl(_2)</td>
<td>35</td>
<td>27</td>
<td>31</td>
</tr>
</tbody>
</table>

\(^a\) All doping concentrations were 5%. The errors in \( R \) are \( \approx 3\%)\) and in \( C \) \( \approx 10\%)\) determined from duplicate measurements.

---

**Table 4. Fit Parameters for LaF\(_3\):Er and LaPO\(_4\):Er at Different Doping Concentrations**

<table>
<thead>
<tr>
<th>concentration</th>
<th>LaF(_3):Er</th>
<th>LaPO(_4):Er</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R ) (( \mu s ))</td>
<td>( C ) (s(^{-1}))</td>
</tr>
<tr>
<td>5%</td>
<td>236</td>
<td>3.29</td>
</tr>
<tr>
<td>2%</td>
<td>332</td>
<td>3.73</td>
</tr>
<tr>
<td>1%</td>
<td>465</td>
<td>3.54</td>
</tr>
</tbody>
</table>

\(^a\) The errors in \( R \) are \( \approx 3\%)\) and in \( C \) \( \approx 10\%)\) determined from duplicate measurements.

---

**Table 5. Fit Parameters for LaPO\(_4\):Nd and LaPO\(_4\):Eu in Methanol with Different Degrees of Deuteration**

<table>
<thead>
<tr>
<th>solvent</th>
<th>Nd(^{3+})</th>
<th>Eu(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R ) (( \mu s ))</td>
<td>( C ) (s(^{-1}))</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>87</td>
<td>733</td>
</tr>
<tr>
<td>CH(_3)OD</td>
<td>91</td>
<td>214</td>
</tr>
<tr>
<td>CD(_3)OD</td>
<td>90</td>
<td>107</td>
</tr>
</tbody>
</table>

\(^a\) The errors in \( R \) are \( \approx 3\%)\) and in \( C \) \( \approx 10\%)\) determined from duplicate measurements.

---

Figure 12. Luminescence decay curves of (A) LaF\(_3\):Nd, (B) LaF\(_3\):Er, (C) LaPO\(_4\):Nd, and (D) LaPO\(_4\):Er particles dissolved in CH\(_2\)Cl\(_2\). The Nd\(^{3+}\) doped particles were excited with the 514 nm line of an Ar\(^{+}\) laser, and the emission was collected at 1060 nm. The Er\(^{3+}\) doped particles were excited with the 488 nm line of an Ar\(^{+}\) laser, and the emission was collected at 1530 nm. The solid lines represent the fits using the model described in the text.

---

from 6.1 ms in a refractive index of 1.525 to an average lifetime of 7.3 ms in a solvent with a refractive index of 1.352. The effect of the refractive index on the luminescence lifetimes of a biexponential fit was primarily seen on the long component of the two lifetimes, not on the short one. The short component is mostly determined by surface quenching, and for this reason, the effect of the refractive index on the results of the model will be small, except for changing the $r_R$.

Another refinement of the model will be to take into account the size and size distribution of the particles. The size and size distribution are currently taken up by the constant $C$, averaging all the sizes in one batch. By taking into account the size and size distribution, we could look systematically at the effect of different particle sizes on the luminescent lifetime.

**Conclusions**

Nanoparticles of LaF$_3$ and LaPO$_4$ doped with luminescent trivalent lanthanide ions that are dispersable in organic solvents were prepared. These nanoparticles show typical lanthanide luminescence characteristic of the ions doped in the respective bulk material. The luminescence lifetimes of the ions are somewhat lower than for the bulk material, but the lifetimes are much longer compared to lanthanide ions previously measured in solution and in organic complexes. The increase in the luminescence lifetimes shows the effective shielding from the organic environment by the particle. Due to this increase in luminescence lifetime, they are promising materials for applications where population inversion is required like lasers and optical amplifiers, or where excited state absorption is required in processes such as up-conversion. The luminescence lifetimes are not monoexponential, and a model has been proposed to explain this in terms of quenching by groups outside the particles. With this model, factors influencing the luminescence lifetime, like concentration quenching, and quenching by the solvent, can be described. With the model, the deviation from monoexponential behavior is described in terms of surface quenching and not in terms of two distinct populations, which is the case for a biexponential fit.

**Acknowledgment.** This research is supported by the Council of Chemical Sciences of The Netherlands Organization for Scientific Research (NWO-CW). CM034495D