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Near-Infrared Luminescence of Lanthanide Calcein and Lanthanide Dipicolinate Complexes Doped into a Silica−PEG Hybrid Material

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The near-infrared luminescence of lanthanide complexes of 4′,5′-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]fluorescein (calcein) and pyridine-2,6-dicarboxylic acid (dipicolinic acid, dpa) doped in a hybrid sol−gel material was investigated. The silica−poly(ethylene glycol) (silica−PEG) inorganic−organic materials were prepared at a neutral pH. The lanthanide ions are well shielded from the environment by the calcein and dpa ligands, and the complexes are stable in the sol−gel matrix after preparation. The dysprosium and neodymium dipicolinate complexes showed near-infrared luminescence (NIR-luminescence) by direct excitation to the 4f-levels. The ytterbium dipicolinate complex doped in the sol−gel showed NIR-luminescence by excitation of the ligand in the UV region. All other tested lanthanide ions (Ln = Pr, Sm, Er, Ho) did not show luminescence. Neodymium and ytterbium complexes with calcein show intense NIR-luminescence when the ligand is excited by visible light. The corresponding erbium complex doped in the silica-PEG matrix also showed NIR-luminescence at 1525 nm. No NIR-luminescence could be detected for the other lanthanide complexes doped in the matrix (Ln = Pr, Sm, Dy, Ho).

Introduction

The sol−gel process allows the preparation of silica-based or siloxane-based materials at ambient temperatures. Pure silica glasses doped with lanthanide complexes can be made by hydrolysis and polymerization of silicon alkoxides.[1,2] The resulting glasses are transparent and have good mechanical properties. However, these materials have some drawbacks, such as the low solubility of lanthanide complexes in the sol−gel matrix at the low pH needed for the hydrolysis reaction.[2,3] One way to overcome these solubility problems is to neutralize the solution after hydrolysis and to introduce organic components in the material. The properties of the inorganic−organic hybrid materials depend on the chemical nature of the different constituents.[4,5] Poly(ethylene glycol) (PEG) can be introduced in a silica matrix by simply mixing PEG with the silica precursors, but no covalent bonds are formed between the PEG chains and the silica backbone.[6,7] The solubility of lanthanide complexes can be improved by performing the sol−gel synthesis in a buffered solution.[8]

Recently, much attention has been paid to near-infrared luminescence (NIR-luminescence) of trivalent lanthanide ions, because several lanthanides show luminescence in the telecommunication low-loss NIR-regions of silica.[9,10] Candidates for luminescence in these spectral regions are the trivalent ions of neodymium, praseodymium, samarium, dysprosium, holmium, erbium, and ytterbium. The observation of NIR-luminescence by lanthanide ions in silica sol−gel glasses is hampered by quenching of the excited states via vibronic coupling with the hydroxyl group vibrations (in Si−OH and H_2O).[11] The concentration of hydroxyl groups is high in wet xerogels. The most common method to decrease the degree of quenching is to calcine the sol−gel materials at high temperatures (>900 °C). This method has successfully been demonstrated for sol−gel-processed glasses, optical fibers, and thin films.[12−14] Different glass compositions (e.g. SiO_2, $SiO_2{-}TiO_2$, $SiO_2{-}Al_2O_3$, $SiO_2{-}TiO_2{-}P_2O_5$) in addition to silica have been used in attempts to enhance the luminescence.[11,15−17] A disadvantage of such lanthanide-doped

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glasses is the low absorbance of the lanthanides.[18] The antenna effect of organic ligands cannot be used, because the sensitizers decompose at the high calcination temperatures.

Another method to avoid quenching of the excited state is to shield the lanthanide ion from the deactivating groups by a shell of organic ligands.[19] Luminescence of neodymium in sol−gel monoliths processed at room temperature was demonstrated by Lai et al. for the tris(dipicolinato)neodymate(III) complex $[Nd(dpa)_3]^{3-}$.[20] Another benefit of using organic ligands is that energy absorbed by a ligand containing a chromophoric group, can be transferred to the lanthanide(III) ion. This mechanism is called the *antenna effect*.[21] Calcein (4′,5′-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]fluorescein) has been successfully used as a water-soluble sensitizer for NIR-luminescent lanthanide ions.[22] The triplet levels are situated around 600 nm, whereas those of the dipicolinate ligand are situated much higher at around 350 nm. The ytterbium(III)−calcein complex has been used as a NIR-luminescent label in fluoroimmunoassay.[23] Silica sol−gel coatings doped with calcein, but without lanthanide ions, were prepared by Garcia et al. for use as a pH sensor.[24]

In this paper, the preparation of silica−PEG hybrid materials doped with lanthanide calcein and lanthanide dipicolinate complexes and the NIR-luminescence properties of these materials are described. This type of matrix was chosen because it provides a type of sol−gel glass that can be prepared under conditions at which the lanthanide complexes are stable and soluble in the matrix.

Experimental Section

The preparation of the dipicolinate complexes $[Ln(dpa)_3]^{3-}$ and their incorporation in the silica−PEG sol−gels was reported previously.[8] Silica−PEG sol−gels containing complexes of Pr(III), Nd(III), Sm(III), Dy(III), Er(III), Ho(III), and Yb(III) were prepared. The concentration of the complex in the silica−PEG sol−gel was varied between 5.0×10^{-2} and 5.0×10^{-4} mol/L.

Freshly made solutions containing an exact amount of 4′,5′-bis[*N*,*N*-bis(carboxymethyl) aminomethyl]fluorescein (calcein, calc45) and the lanthanide ion were prepared by dissolving equimolar amounts of the ligand and the lanthanide ion in a solution containing triethylammonium acetate (TEAAc) buffer. The concentration of the lanthanide complex was 1.0×10^{-3} mol/L. The TEAAc concentration was 0.1 mol/L and the pH was 8. Adding the metal ion to the solution quenches the ligand luminescence as the complex is formed. Complexes of Pr(III), Nd(III), Sm(III), Dy(III), Er(III), Ho(III), and Yb(III) were prepared. The silica−PEG sol−gels were synthesized by hydrolysis and polymerization of the monomeric precursor tetramethyl orthosilicate (TMOS) with water and PEG-200.[6,8] First, a solution A was made by mixing 8 mL of TMOS with 2 mL of water containing hydrochloric acid or nitric acid to obtain pH = 2. This solution was stirred for 1 h. For solution B, 8.00 g of PEG-200 was mixed with 0.50 mL of the buffered complex solution and 1.50 mL of distilled water. The final solution C was prepared by mixing 1 mL of solution A with 5 mL of solution B. Stirring was continued for 20 min. Then 2 mL portions of solution C were poured in disposable PMMA (poly(methyl methacrylate)) UV-microcuvettes. All volumes were exactly pipetted. The cuvettes were sealed with aluminum foil and were placed in an oven (50°C). The solutions gelled after a few hours and were further dried for 3 weeks. The concentration of the calcein complex in the dried silica−PEG sol−gel is around 5.0×10^{-5} mol/L.

The NIR-luminescence spectra and decay curves of all the samples were measured at room temperature after gelling, and a second measurement was recorded after drying for 3 weeks in an oven. The luminescence spectra were recorded on an Edinburgh Instruments FS-920P spectrofluorimeter equipped with a xenon arc lamp (450 W), a Continuum Minilite II Nd:YAG pumped dye-laser (Coumarin 153, Coumarin 120 and Rhodamine 6G), a double excitation monochromator from Edinburgh Instruments, and a Hamamatsu R5509-72 NIR-photomultiplier (600−1700 nm). Absorption spectra have been measured on a Varian Cary 5000 spectrophotometer.

Calcein was purchased from Molecular Probes Inc. Tetramethyl orthosilicate (TMOS) and PEG-200 were purchased from Fluka. All other chemicals were obtained from Aldrich or ACROS.

Results and Discussion

A major problem of most strongly luminescent lanthanide complexes is that they do not dissolve well in water and in most starting solutions for the synthesis of sol−gel glasses. On the other hand, dipicolinate and calcein lanthanide complexes are well-studied, water-soluble lanthanide complexes. These lanthanide complexes are only stable in a small pH region. At a pH lower than 5, the ligands will be protonated and do not bind to the metal ion. At a pH higher than 9, lanthanide hydroxides can precipitate. The calcein complex did not dissolve sufficiently in pure silica sol−gel glasses prepared by hydrolysis and condensation of pure TMOS, or the resulting glasses showed cracks.

The dipicolinate ligands form with lanthanides a complex of D_3-symmetry.[25−27] The coordination sphere can be described as a distorted tricapped trigonal prism. The three tridentate dipicolinate molecules allow the lanthanide ion to obtain coordination number 9 and to saturate the first coordination sphere without the need of additional water molecules. The dipicolinate ligands shield the lanthanide ions from PEG and water molecules. The Judd−Ofelt theory has been used to compare the intensities of lanthanide dipicolinate complexes $[Ln(dpa)_3]^{3-}$ in sol−gel materials.[8] Lai et al. published the luminescence of the neodymium(III) complex in a pure silica glass.[20] This ion has a strong luminescence at 1064 nm.

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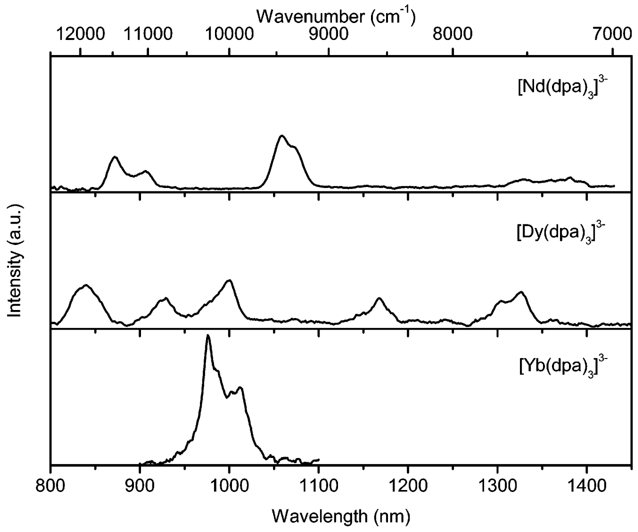

Figure 1. Room-temperature NIR-luminescence spectrum of $[Nd(dpa)_3]^{3-}$, $[Dy(dpa)_3]^{3-}$, and $[Yb(dpa)_3]^{3-}$ in a silica−PEG hybrid matrix. The excitation wavelengths are 580, 390, and 290 nm, respectively.

The luminescence of $Na_3[Ln(dpa)_3]$ (with Ln = Pr, Nd, Sm, Dy, Er, Ho, and Yb) was studied. The silica−PEG samples gelled in a few hours, were dried for one month, and were not degassed prior to the measurement. No antenna effect was observed, and NIR-luminescence could only be detected for the $Na_3[Nd(dpa)_3]$ and $Na_3[Dy(dpa)_3]$ complexes at a relatively at high concentration (5.0×10^{-2} mol/L). The spectra are presented in Figure 1. Because direct excitation of the neodymium(III) and dysprosium(III) ions by the xenon arc lamp was used (580 and 390 nm, respectively) the luminescence intensity was low. The luminescence of neodymium(III) at 880, 1064, and 1320 nm can be assigned to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions, respectively. The luminescence of dysprosium(III) in the NIR region at 840, 930, 1000, 1180, and 1330 nm can be assigned to the f−f transitions $^4F_{9/2} \rightarrow {}^6H_{5/2}$, $^4F_{9/2} \rightarrow {}^6F_{7/2}$, $^4F_{9/2} \rightarrow {}^6F_{5/2}$, and $^4F_{9/2} \rightarrow {}^6F_{3/2}$, $^6F_{1/2}$.

Intense luminescence was observed for $Na_3[Yb(dpa)_3]$ by excitation at 290 nm in the absorption bands of the dipicolinate ligands. Ytterbium(III) is a special case among the NIR-emitting lanthanide ions. The ytterbium(III) ion has only one absorption peak around 977 nm, the $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition. The luminescence is also observed at 977 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, resonance luminescence, no Stokes shift). Photosensitized near-infrared luminescence of ytterbium(III) occurs mainly via an internal redox process.[28] Ytterbium(III) has a low reduction potential, −1.05 V versus the normal hydrogen electrode, compared to an average of −3 V for most other lanthanides. If there is ligand-to-metal charge transfer (LMCT), the charge recombination (ligand$^+$−Yb(II) to ligand−Yb(III)*) leaves ytterbium(III) in an excited state.

Calcein is a ligand combining a fluorescein group and an EDTA group. Two isomers are commercial available: 4′,5′-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-fluorescein (noted as calc45, Figure 2) and 2′,7′-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]fluorescein. Calc45 has more favorable complexation behavior toward lanthanide ions than when the *N*,*N*-bis(carboxymethyl)-aminomethyl groups are situated in the 2′- and 7′-positions. Calcein is used as a fluorescent indicator for calcium ions, hence its name. The ionic radius of the calcium(II) ion resembles those of the trivalent lanthanide ions. Calcein forms water-soluble 1:1 complexes with trivalent lanthanides (Figure 2). The binding site for the lanthanide ion is closely situated to the fluorescein chromophore. Formation constants of the 1:1 complexes at pH = 8 are around 1.0×10^{12}.[29]

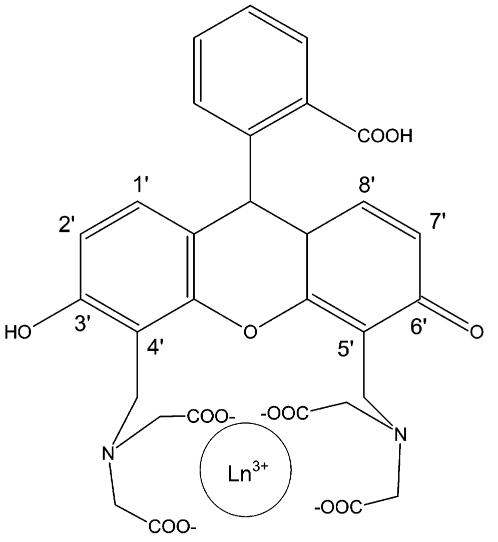

Figure 2. Structure of a lanthanide(III) complex of 4′,5′-bis-[*N*,*N*-bis(carboxymethyl) aminomethyl]fluorescein (calcein, calc45).

Addition of trivalent lanthanide ions to a solution containing calcein quenches the calcein fluorescence. This is due to enhancement of the intersystem crossing by the paramagnetic and the heavy atom effects (enhanced spin−orbit coupling).[30,31] Due to the larger spin−orbit coupling, the wave functions of the ligand singlet and triplet levels do not remain pure singlet or triplet wave functions. A part of the singlet wave functions is mixed into that of the triplet wave function and vice versa; therefore, the triplet level achieve some singlet character. The enhanced intersystem crossing leads to an enhanced energy transfer from the ligand via the triplet levels to the lanthanide ion. The absorption spectra of the complexes are slightly different for each lanthanide ion.[22] The absorption spectrum of a [Nd(calc45)]-doped silica−PEG hybrid material is shown in Figure 3.

The intense absorption band is from the calcein ligand.[29] The position of the $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition of neodymium(III) is indicated by the arrow in Figure 3. This is the most intense neodymium(III) transition in the absorption spectrum. The absorption cross-section of the Laporte forbidden f−f transitions is very low.[18] NIR-luminescence spectra were recorded after excitation of the ligand at 480 nm with a xenon arc lamp. The luminescence spectrum of the [Nd(calc45)] complex

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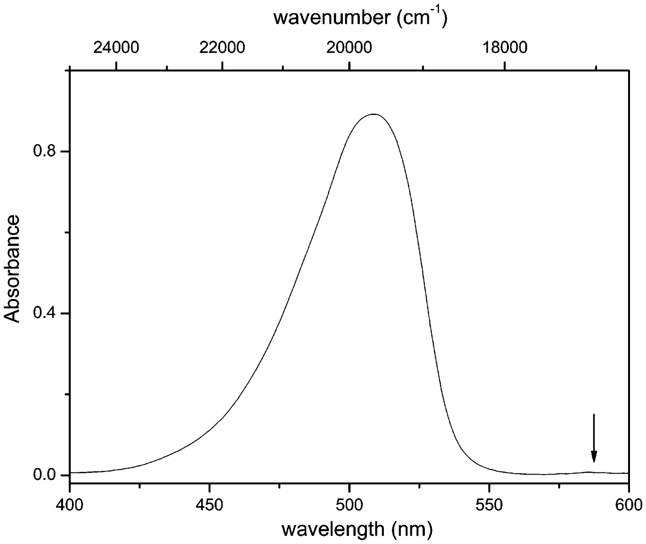

Figure 3. Room-temperature absorption spectrum of [Nd(calc45)] in a silica−PEG hybrid matrix. The position of the $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition of neodymium(III) is indicated by an arrow.

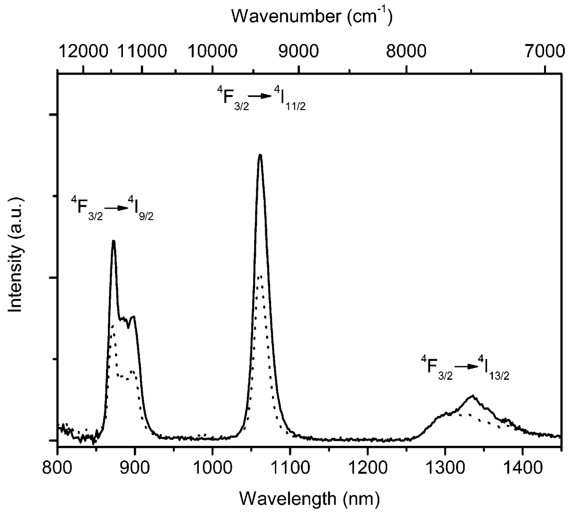

Figure 4. NIR-luminescence spectrum of [Nd(calc45)] in a silica−PEG hybrid matrix at room temperature. The excitation wavelength is 480 nm. The dotted and full lines indicate the spectrum before and after drying, respectively.

before and after drying for 3 weeks in an oven is shown in Figure 4. The transitions are intense despite the low concentration of the neodymium(III) ion. The energy absorbed by the ligand is transferred to the neodymium(III) ion (antenna effect). No luminescence was detected by direct excitation of a neodymium(III) absorption band such as the $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition shown in Figure 3, because the lanthanide concentration was too low (5×10^{-5} mol/L). Room-temperature infrared emission in neodymium(III)-doped organic−inorganic hybrids analogous to the materials described here was demonstrated by Sá Ferreira et al.[32] In this paper the energy transfer of the matrix to the lanthanide ion was demonstrated for samples with concentrations of neodymium(III) larger than 1.5% (w/w) neodymium(III) versus sol−gel matrix. Here the concentration is below 0.01% (w/w).

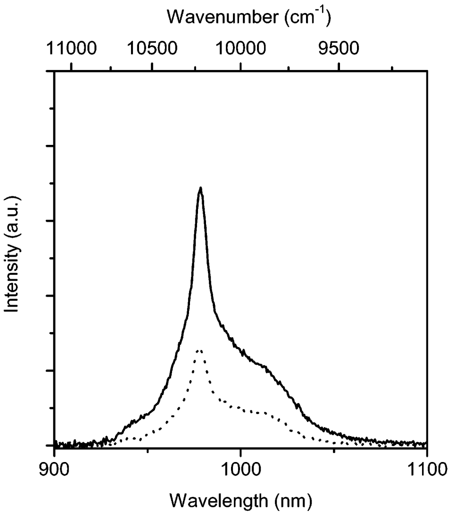

Figure 5. Room-temperature NIR-luminescence spectrum of [Yb(calc45)] in a silica−PEG hybrid matrix at 977 nm. The excitation wavelength is 480 nm. The luminescence band corresponds to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. The dotted and full lines indicate the spectrum before and after drying, respectively.

Unreacted silanol groups and water molecules present in the matrix reduce the intensity strongly in the NIR region, and drying improves the luminescence. Drying almost doubles the intensity. The NIR-luminescence lifetime of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition at 1064 nm decay is 139 ± 4 ns before and 280 ± 4 ns after drying. The lifetime decay is single-exponential. The NIR-luminescence lifetime of this complex in pure water is of the same order (2.5×10^2 ns).[22]

The intense luminescence of the ytterbium(III)−calcein complex can be observed in the silica−PEG hybrid material (Figure 5). The intensity was found to increase by a factor 2 during drying. The NIR-luminescence lifetime of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition at 977 nm is 1.83 ± 0.02 μs before and 3.72 ± 0.02 μs after drying. To our best knowledge, no comparable data of NIR-luminescence of ytterbium(III) complexes in sol−gel materials were reported previously. The NIR-luminescence lifetime of this complex in aqueous solution is 1.9 μs.[22]

The most interesting lanthanide ion in NIR-luminenscence studies is erbium(III). The transition around 1540 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) is at the right position for telecom applications (erbium-doped fiber amplifiers). Although the intensity is low, a transition can be observed at 1530 nm. This illustrates the good complexing power of calc45. It is very remarkable that erbium(III) luminescence could be detected without using laser excitation and without using extensive drying of the matrix at high temperature. Here a xenon arc lamp was used to obtain the spectrum in Figure 6, although a low concentration ($<5 \times 10^{-5}$ mol/L) was used. With the same experimental setup, no luminescence could be detected for Er(calc45) in pure water. To our knowledge, this is the first time that an organic ligand is used to sensitize the NIR-luminescence of erbium(III) in a silica sol−gel material.

Poly(ethylene glycol), incorporated in the sol−gel matrix, can complex cations.[8] Ligands such as 1,10-phenanthroline or 2,2′-bipyridine are not strong enough to remove the water and PEG molecules out of the first

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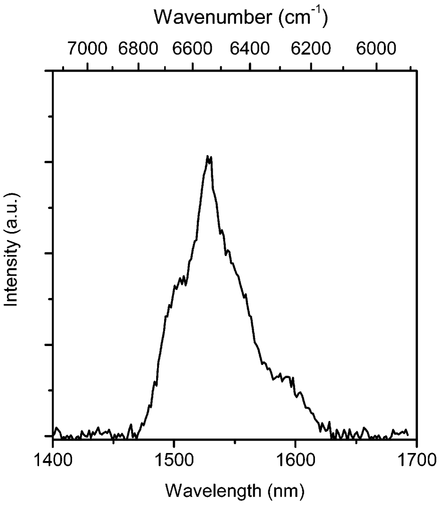

Figure 6. Typical NIR-luminescence of [Er(calc45)] in a silica−PEG hybrid matrix at 1530 nm. The excitation wavelength is around 480 nm. The luminescence band corresponds to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

coordination sphere of the lanthanide ions.[8] The good NIR-luminescence at the low concentration used in this study shows that the calcein ligands shield the lanthanide ions well from their surroundings. The samples are stable and the luminescence did not change after storing the sample for 2 weeks in an inert, moisture-free atmosphere.

The fluorescein chromophore group is able to efficiently transfer the absorbed energy to the neodymium(III), erbium(III), and ytterbium(III) ions. Other lanthanide complexes of calcein ([Ln(calc45)], with Ln = Pr, Sm, Dy, Ho) were tested, but no NIR-luminescence was observed. Sensitization by the calcein ligand does not occur for these lanthanide ions.

Conclusion

Silica−PEG hybrid materials containing NIR-luminescent lanthanide complexes were prepared via a sol−gel process. The lanthanide ions are well-shielded by three dipicolinate ligands or one calcein ligand and the complexes are stable in the sol−gel matrix after preparation. NIR-luminescence is detected for the dipicolinate complexes of neodymium(III), dysprosium(III), and ytterbium(III). The silica−PEG hybrid materials that contain calcein complexes with neodymium(III) and ytterbium(III) show intense NIR-luminescence after ligand excitation by a xenon arc lamp. It was also demonstrated that erbium(III) NIR-luminescence can be detected in sol−gel hybrid materials, without the need for using high drying temperatures in the preparation method.

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