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Preparation and luminescence properties of *in situ* formed lanthanide complexes covalently grafted to a silica network†

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Lanthanide-doped sol-gel-derived materials are an attractive type of luminescent materials that can be processed at ambient temperatures. However, the solubility of the lanthanide complexes in the matrix is a problem and it is difficult to obtain a uniform distribution of the complexes. Fortunately, these problems can be solved by covalently linking the lanthanide complex to the sol-gel-derived matrix. In this study, luminescent Eu^{3+} and Tb^{3+} bipyridine complexes were immobilized on sol-gel-derived silica. FT-IR, DTA-TG and luminescence spectra, as well as luminescence decay analysis, were used to characterize the obtained hybrid materials. The organic groups from the bipyridine-Si moiety were mostly destroyed between 220 and 600 °C. The luminescence properties of lanthanide bipyridine complexes anchored to the backbone of the silica network and the corresponding pure complexes were comparatively investigated, which indicates that the lanthanide bipyridine complex was formed during the hydrolysis and co-condensation of TEOS and modified bipyridine. Excitation at the ligand absorption wavelength (336 nm for the hybrid materials and 350 nm for the pure complexes) resulted in strong emission of the lanthanide ions: Eu^{3+} $^5D_0$–^7F_J ($J = 0, 1, 2, 3, 4$) and Tb^{3+} $^5D_4$–^7F_J ($J = 6, 5, 4, 3$) emission lines due to efficient energy transfer from the ligands to the lanthanide ions.

Introduction

Complexes between lanthanides and organic ligands (especially Eu^{3+} diketonate and Tb^{3+} heterocyclic complexes) have long been known to give intense emission lines upon UV light irradiation because of the effective intramolecular energy transfer from the ligands to the central lanthanide ions. The importance of lanthanide ions is related to the particularities of their luminescence, that is, long decay times and narrow-band emission. The organic ligand not only protects the metal ions from vibrational coupling but also increases the light absorption cross section by the "antenna effect".[1–5] The luminescence properties of lanthanide complexes in a variety of solutions have been investigated extensively; these studies have demonstrated that lanthanide complexes have superior fluorescence properties with respect to simple salts in solutions.[6–10] However, materials made for practical uses are limited to inorganic solids and metal complexes are excluded, despite their high luminescence efficiency, because of their limited thermal stability. Recently, there has been considerable interest in the optical properties of luminescent species in sol-gel-derived siloxane hybrid materials for photonic applications due to the fact that they potentially combine the optical quality of silica, its thermal stability and its mechanical strength together with the optical characteristics of active species.[11–15] Apart from organic dyes, many experiments have demonstrated that incorporating lanthanide complexes into sol-gel-derived materials can improve the luminescence properties of the corresponding lanthanide complexes.[16–23]

The sol-gel method employed, which has been proven to be a suitable approach for the preparation of such materials, is based on the hydrolysis and condensation of molecular precursors. One advantage of this method is its low-temperature processing, allowing the incorporation into the networks of organic moieties that cannot withstand high temperatures.[24,25] Typically, these materials were obtained by doping silica gel with the lanthanide complexes (class I hybrid materials), where only weak interactions exist between the organic and inorganic parts. Consequently, the clustering of emitting species is difficult to prevent by this method. Inhomogeneous dispersion of both components and leaching of dopants are observed in class I hybrid materials for which the concentration of organic species is also limited. Another approach that can result in a homogeneous dispersion of the lanthanide cations within the hybrid materials consists of the hydrolysis and polycondensation of rare earth complexes with ligands bearing hydrolyzable $Si(OR)_3$ groups. This method affords monophasic organic-inorganic nanostructured hybrid materials[26–29] (class II) in which the organic ligand is covalently linked to the silica framework. Up to now and to the best of our knowledge, very few papers concerning the preparation of materials incorporating lanthanide ions by this route have been reported.

In this paper, we describe the preparation of luminescent materials obtained by grafting the lanthanide bipyridine complexes to a silica sol-gel glass *via* Si–C covalent bonds. These class II hybrid materials containing covalently linked lanthanide organic complexes were prepared using bipyridine-Si as one of the precursors, which reacted with the tetraethoxysilane (TEOS) by hydrolysis and co-condensation in the presence of lanthanide ions. Bipyridine-Si was synthesized using 2,2′-bipyridine-4,4′-dicarboxylic acid chloride as the starting reagent and (3-aminopropyl)triethoxysilane as the coupling reagent.

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† Electronic supplementary information (ESI) available: color photograph of organic-inorganic hybrid materials containing Eu^{3+} ions and Tb^{3+} ions. See http://www.rsc.org/suppdata/nj/b4/b401673d/

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The *in situ* formation of the lanthanide complexes was verified by the luminescent features of the hybrid material.

Experimental

Tetraethoxysilane (TEOS, C. P.) and (3-aminopropyl)triethoxysilane (APS, Aldrich) were used as received. The solvent DMF was used after distillation in vacuum. Europium and terbium nitrates were obtained from the corresponding oxides, Eu_2O_3 (99.99%) and Tb_4O_7 (99.99%).

2,2′-Bipyridine-4, 4′-dicarboxylic acid was prepared according to the literature procedure.[30] Anal. calcd for $C_{12}H_8N_2O_4$: C, 59.0; H, 3.30; N, 11.50. Found: C, 59.12; H, 2.14; N 11.52.

Alkoxysilane-modified bipyridine was synthesized by modification of a literature procedure.[26] The pure byrpidine europium complex was prepared according to a previous report.[31] Anal. calcd for $Eu(Dipy)_2Cl_3 \cdot 2H_2O$: C 24.68, H 3.31, N 5.76, determined: 24.44, 3.10, 5.71.

Sol-gel-derived hybrid materials doped with lanthanide ions were prepared as follows: bipyridine-Si was dissolved in 4 mL of ethanol, TEOS and H_2O (pH = 2) was added to it with the molar ratio 1 : 4 : 16 (bipyridine-Si : TEOS : H_2O) under stirring. $EuCl_3$ ($TbCl_3$) was added to the resulting mixture, the ratio of bipyridine-Si to lanthanide ions being 2 : 1. The mixture was agitated magnetically to achieve a single phase and then transferred into cuvettes; thermal curing was performed at 70 °C and continued for 2 weeks until the sample solidified (see Scheme 1).

Fluorescence excitation and emission spectra were recorded at room temperature on a SPEX Fluorolog-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetime measurements were carried out on a Signal Detection and Analysis System (Model 4400, EG&G) using nitrogen laser radiation (337.1 nm) as the excitation source. Infrared (IR) spectra were measured within the 4000–400 cm^{-1} region using a Perkin–Elmer model 580B infrared spectrophotometer with the KBr pellet technique. TG-DTA analysis was performed on a Shimadzu analyzer from 25 to 1000 °C under nitrogen atmosphere.

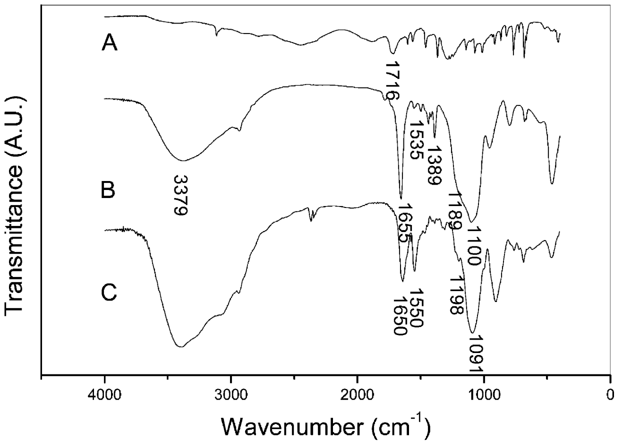
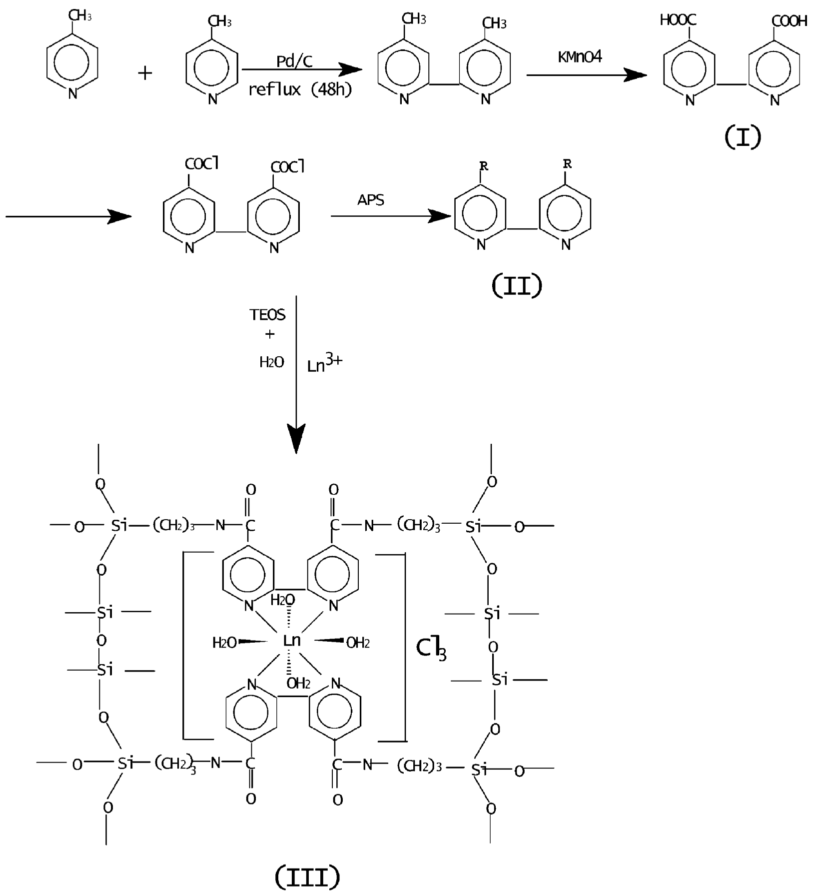


Fig. 1 IR spectra for 2,2′-bipyridine-4, 4′-dicarboxylic acid (trace A), bipyridine–Si (trace B) and hybrid material doped with Eu^{3+} (trace C).

Results and discussion

The IR spectra for 2,2′-bipyridine-4, 4′-dicarboxylic acid, bipyridine-Si and hybrid material doped with Eu^{3+} ions are shown in Fig. 1. The spectra are dominated by the υ(Si–OEt/ Si–O–Si) absorption bands. The grafting reaction is evidenced by the sharp band located at 1680–1640 cm^{-1}, corresponding to amide groups. From Fig. 1, we can observe that the CO group from amide functions do not participate in the Ln environment. No absorption bands characteristic of the carboxylic



Scheme 1 Synthetic procedure for formation of the bipyridine-Si hybrid materials and their predicted structure.

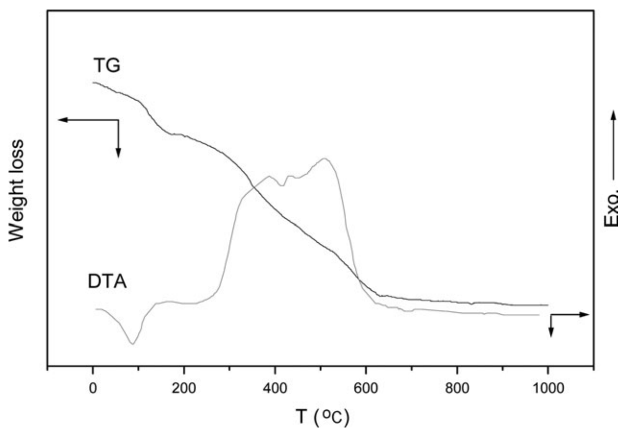


Fig. 2 TG and DTA curves of hybrid materials doped with Eu^{3+} ions.

acid chloride or carboxylic acid functions are detected in the 1760–1710 cm^{-1} range, which is a further proof of the completion of reaction. The stretching υ(NH) and bending δ(NH) vibrational modes located near 3380 and 1550 cm^{-1}, respectively, are also clearly observed in the IR spectra. The υ(Si–C) vibration located in the 1188–1193 cm^{-1} range is also observed in the IR spectra of the hybrid materials, which is consistent with the fact that there is not a great extent of Si–C bond cleavage occurring during the hydrolysis/condensation reactions. The broad absorption band at 1120–1000 cm^{-1} [υ(Si–O–Si)] indicates the formation of siloxane bonds.

The thermal analysis profiles are shown in Fig. 2. The weight loss between 25 and 220 °C is possibly associated with the removal of solvents and water trapped within the pore system or with partial dehydroxylation.[32] The weight loss occurring between 220 and 600 °C is attributed to thermal degradation of the organosilicate framework, involving Si–C, C–C, and C–N bond cleavage.[24] The thermal analysis profiles also suggests that the bipyridine-Si moiety is destroyed between 220 and 600 °C and the remaining organics are destroyed above 600 °C. This is supported by FT-IR spectroscopy of the hybrid material treated at specified temperatures, as shown in Fig. 3. The bands centered at 1655, 1552, 1439, 1380 and 680 cm^{-1} due to bipyridine-Si diminish in intensity at 250 °C and disappear at 600 °C. Furthermore, the band located at 960 cm^{-1}, which is attributed to the stretching of terminal Si–OH groups on the silica surface, decreases with increasing treatment temperature because the Si–OH group has undergone condensation to form Si–O–Si networks. Nevertheless, even at 600 °C, bands at 3450 and 1639 cm^{-1} still exist. This can be attributed to rehydration of the silica surface.

The luminescence properties of the hybrid materials have been investigated at room temperature. The organic-inorganic hybrid materials containing lanthanide ions give out a bright red (for Eu^{3+}) or green (for Tb^{3+}) emission when irradiated under a UV lamp. Figs 4(a) and (b) show the excitation spectra of the pure europium bipyridine complex and the sample doped with Eu^{3+} ions, respectively; both were monitored at the Eu^{3+} $^5D_0$–$^7F_2$ transition. For the Eu^{3+} ion doped hybrid material, the excitation spectrum exhibits a broad band ranging from 250 to 380 nm ($\lambda_{max} = 336$ nm), which can be assigned to the absorption of the bipyridine ligand anchored to the silica; this indicates that an energy transfer occurs between the organic ligand and Eu^{3+} ions. In contrast, a broad band centered at 350 nm, due to the absorption of the bipyridine ligand, and also narrow transitions at 395 and 466 nm can be observed in the pure complex; these are attributed to the Eu^{3+} $^4f_6$ intrashell $^7F_0$–$^5L_6$ and $^7F_0$–$^5D_2$ excitation transitions, respectively. These transitions are weak compared to that of the ligand, which proves that luminescence sensitization *via* excitation of ligands is much more efficient than direct excitation of the Eu^{3+} ion's absorption levels. Moreover, the maximum of the broad band shifts towards the high-energy region for the hybrid material. The difference indicates that the ligand environment has changed in the hybrid materials. Furthermore, it means that the siloxo part of the structure affects the energy transfer.[33]

Strong photoluminescence emission spectra recorded by excitation at 350 nm (the pure complex) and 336 nm (the hybrid material doped with Eu^{3+} ions) are also shown in Fig. 4.

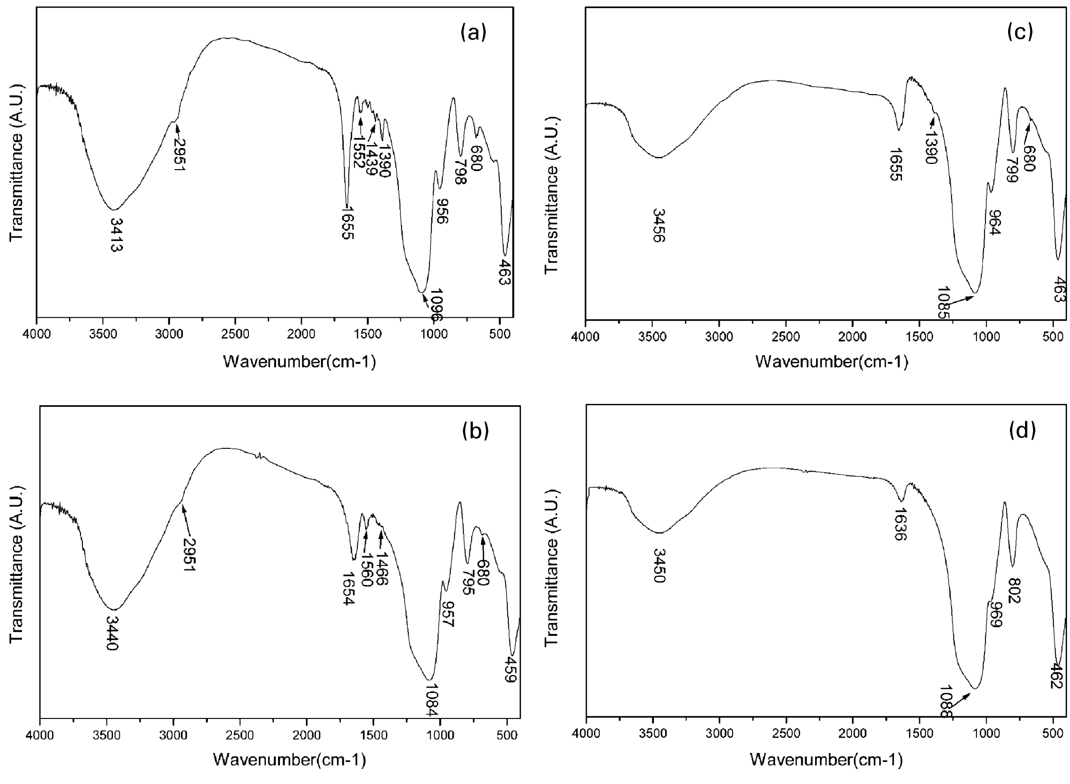


Fig. 3 IR spectra of hybrid materials doped with Eu^{3+} ions after thermal treatment at (a) 100, (b) 250, (c) 500 and (d) 600 °C.

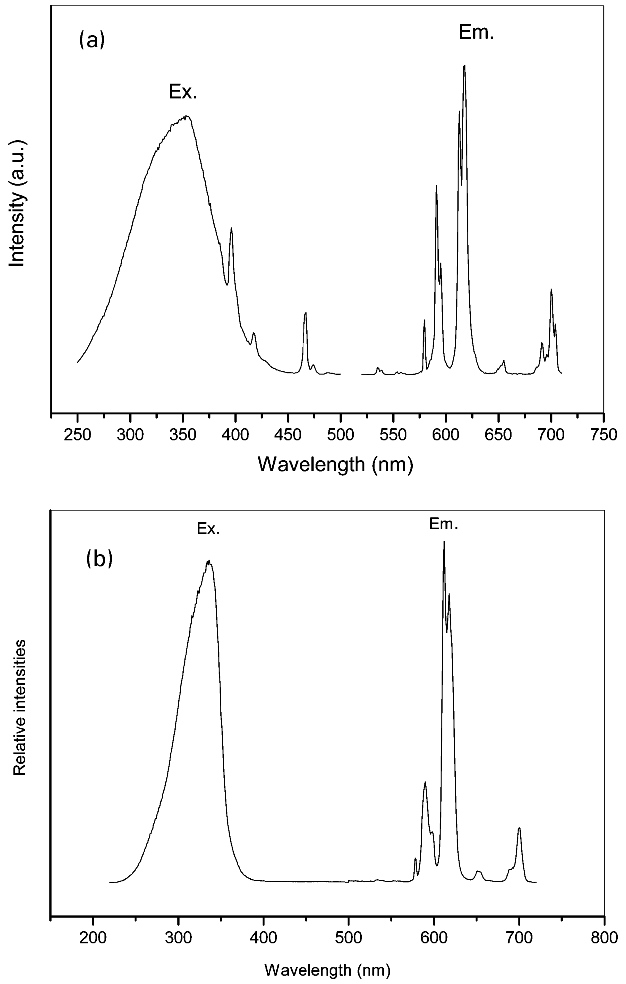


Fig. 4 Excitation spectra and emission spectra of (a) pure Eu complex and (b) organic-inorganic hybrid material containing Eu^{3+}.

Both spectra show the characteristic narrow band emission of Eu^{3+} ions, which indicates that the surrounding ligands absorb and transfer energy efficiently to the chelated lanthanide ions. The emission spectra of the hybrid material doped with Eu^{3+} ions and pure complex look somewhat alike. They exhibit five main transitions between the Russell–Saunders multiplets $^5D_0$–^7F_J ($J = 0, 1, 2, 3, 4$). The typical red color of the europium emission is mostly attributed to the strongest transition ($^5D_0$–$^7F_2$), with its maximum intensity at 611–614 nm. The fine splitting of the $^5D_0$–$^7F_2$ transition is related to an ordered 'crystalline' rare-earth ion environment, rather than an amorphous one, which indicates that a rare-earth–bipyridine complex is formed during synthesis of the hybrid material.[34] From the spectra, it was observed that both the organic-inorganic hybrid material and the pure complex possess excellent luminescence characteristics, not only strong emission intensity but also narrow emission half width (below 15 nm). Compared to the spectrum of the pure complex, a loss of resolution in the hybrid material can be observed and this could be explained by site-to-site inhomogeneities and the porous microstructure of the matrix.

The lifetime of the Eu^{3+} first excited state, $\tau_{exp}(^5D_0)$, was measured at 614 nm (the most intense Eu^{3+} emission line) with an excitation wavelength of 336 nm for the hybrid material and 350 nm for the pure complex. Both of the decay curves can be well-fitted by a single exponential function: $I = I_0 + A\exp[-(t - t_0)/\tau]$ (A is constant, I_0 is the intensity at t_0). The luminescence lifetimes were determined to be 123 μs for Eu^{3+} ions in the hybrid material and 522 μs for the pure complex by the above fits, confirming that all the Eu^{3+} ions lie in the same average environment. In general, the radiative lifetime of the $^5D_0$ state falls in the millisecond range,[35] nevertheless, the experimental decay time is much shorter than the theoretically predicted one, indicating important quenching by the OH (from the coordinated H_2O, see Scheme 1) or silanol groups from the matrices.

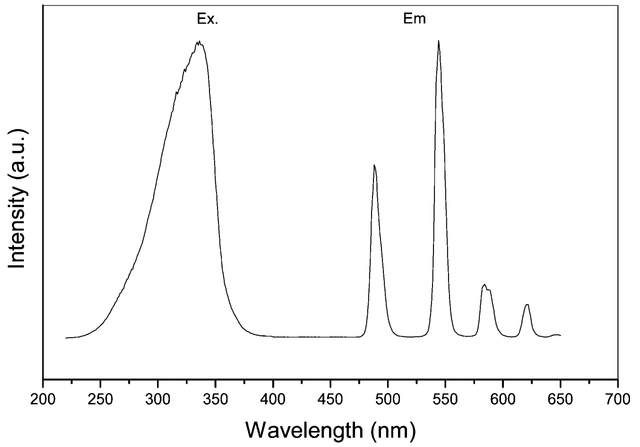


Fig. 5 Excitation ($\lambda_{em} = 545$ nm) and emission spectra for hybrid material doped with Tb^{3+} ions excited at 336 nm.

The behavior of Eu^{3+} has its special characteristics but is not unique. Similar behavior is also observed when Eu^{3+} is replaced by Tb^{3+} in the hybrid material. The excitation and emission spectra for the hybrid material doped with Tb^{3+} are exhibited in Fig. 5. Similarly to the optical features of Eu^{3+} doped hybrid materials, the excitation spectrum monitored with the Tb^{3+} $^5D_4$–$^7F_5$ (544 nm) emission exclusively consists of the excitation band of the ligands peaking at 336 nm, indicating an energy transfer from the ligands to the central Tb^{3+} ions. The emission spectrum obtained after excitation at 336 nm contains four intense emission lines of Tb^{3+}, peaking at 489 ($^5D_4 \rightarrow {}^7F_6$), 545 ($^5D_4 \rightarrow {}^7F_5$), 586 ($^5D_4 \rightarrow {}^7F_4$) and 620 ($^5D_4 \rightarrow {}^7F_3$) nm, with the $^5D_4 \rightarrow {}^7F_5$ green emission as the most prominent peak.

Conclusion

Grafting of lanthanide bipyridine complexes to the silica has been obtained by co-condensation of TEOS and bipyridine-Si in the presence of lanthanide ions. The luminescence of organic-inorganic hybrid materials shows the *in situ* formation of lanthanide bipyridine during the hydrolysis and condensation of TEOS and bipyridine-Si. As the method of synthesis can be easily applied to other ligands and to different modified alkoxysilanes, the desired properties can be tailored by an appropriate choice of the precursors. In this way, we might expect to obtain stable and efficient hybrid phosphors.

Acknowledgements

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