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Novel, covalently bonded hybrid materials of europium (terbium) complexes with silica

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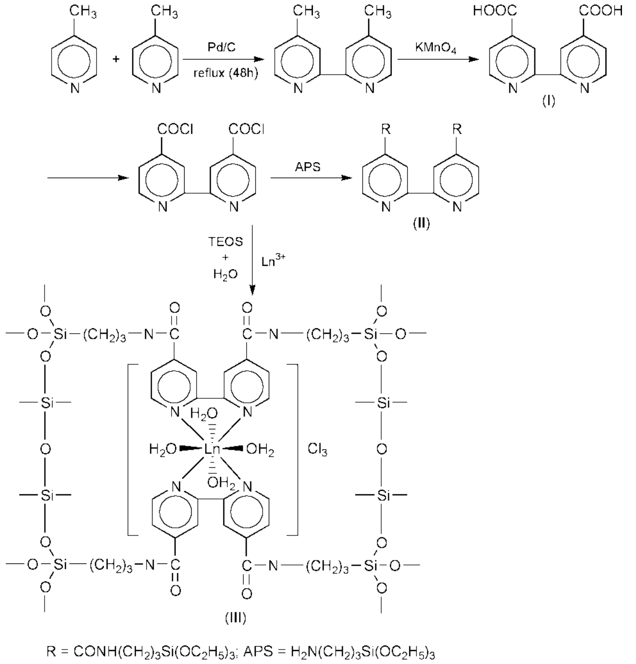
New kinds of hybrid materials containing covalently bonded Eu^{3+} (Tb^{3+}) bipyridine complexes in a silica network have been prepared and their luminescence properties reported.

The sol–gel method has been proven to be a suitable approach for the preparation of hybrid materials. One advantage of this method is its low processing temperature, allowing the incorporation of organic moieties that cannot withstand high temperatures into the networks.[1,2] Unfortunately, there are significant drawbacks in using these systems, which include inhomogeneous distribution of both components, leaching of dopants and limitations on the concentrations of dopants used. Covalent grafting of ligands on to the backbone of networks *via* Si–C bonds can greatly overcome the above-mentioned shortcomings.[3,4]

Herein, we present a new compound (denoted as bipyridine–Si) for sol–gelcontaining bipyridine, which plays a double role, *i.e.* as a ligand for lanthanide ions and as a sol–gel precursor. The hybrid luminescent materials were prepared using bipyridine–Si as one of the precursors, which reacted with the tetraethoxysilane (TEOS) by hydrolysis and condensation in the presence of lanthanide ions (see Scheme 1).

The IR spectra for 2,2′-bipyridine-4,4′-dicarboxylic acid (**I**), bipyridine–Si (**II**) and the hybrid material doped with Eu^{3+} (**III**) are shown in Fig. 1(A, B, C), respectively.‡ The absorption band at 1713 cm^{-1} in Fig. 1A corresponds to the asymmetric carbonyl stretch of carboxylic acid. This band is replaced by bands at 1653 and 1638 cm^{-1} due to the absorption of amide groups (CONH) in Fig. 1B and Fig. 1C, respectively, indicating that (3-aminopropyl)triethoxysilane (APS) has been successfully grafted on to 2,2′-bipyridine. Further evidence for this is the presence of the stretching ν(NH, 3379 cm^{-1}) and bending δ(NH, 1542 cm^{-1}) vibration modes, together with the stretching vibration of Si–O at 1094 cm^{-1} and the bending vibration of Si–O at 462 cm^{-1} (from APS) in Fig. 1B. The addition of Eu^{3+}, TEOS and water to bipyridine–Si (**II**) is also responsible for changes in the IR spectra (*cf.* Fig. 1C and Fig. 1B) due to hydrolysis/condensation of TEOS and bipyridine–Si (**II**) together with formation of a complex between Eu^{3+} and bipyridine–Si (**II**). The ν(Si–C) vibration located at 1198 cm^{-1} is still observed in the IR spectra of hybrid materials (Fig. 1C), which is consistent with the fact that no (Si–C) bond cleavage occurs during hydrolysis/condensation reactions. Furthermore, in Fig. 1C the broad absorption band at 1087 cm^{-1}, ν(Si–O–Si), indicates the formation of siloxane bonds.



R = CONH(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$; APS = H$_2$N(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$

Scheme 1 Synthesis procedure of bipyridine–Si and the predicted structure of hybrid materials.

The excitation spectrum monitored using the Eu^{3+} $^5D_0$–$^7F_2$ transition at 614 nm is dominated by a broad band centered at 336 nm, which is the characteristic absorption of the ligands due to their efficient $\pi \rightarrow \pi^*$ transition. This indicates that an energy transfer occurs from the ligands to the central Eu^{3+}. Upon excitation at the ligands (336 nm), only the emission lines of Eu^{3+} $^5D_0$–^7F_J (J = 0,1,2,3,4) were observed with the hypersensitive transition $^5D_0$–$^7F_2$ (614 nm) as the most prominent group; no emission from the ligands was detected, suggesting that the energy transfer from the ligands to Eu^{3+} is efficient in the hybrid sample. However, when the excitation is at 396 nm (*i.e.* at the $^7F_0$–$^5L_6$ absorption band of Eu^{3+}), the obtained emission spectrum contains not only the emission of Eu^{3+}, but also a broad emission band in the blue region with a maximum at 458 nm. Apparently, the red emission of Eu^{3+} produced in

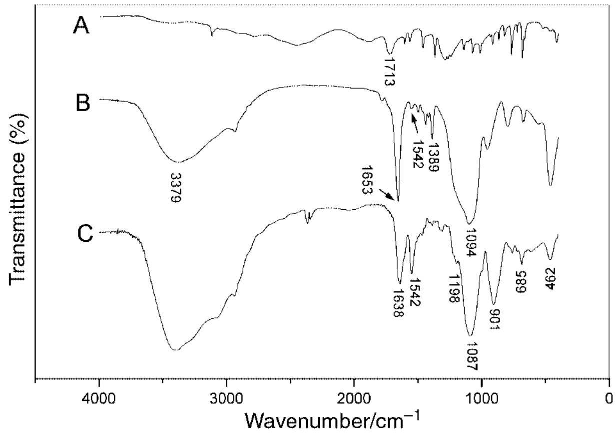


Fig. 1 IR spectra for 2,2′-bipyridine-4,4′-dicarboxylic acid (A), bipyridine–Si (B) and hybrid materials doped with Eu^{3+} (C).

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† Electronic supplementary information (ESI) available: Excitation (A) and emission (B, C) spectra of hybrid materials in Scheme 1 (Ln = Eu). See http://www.rsc.org/suppdata/cc/b1/b102160p/

this case results from direct excitation into Eu^{3+}. Here it is interesting from the appearance of the broad blue band, which can have no other cause than the excitation of the complex. Because the ligands can by no means be excited at 396 nm, it is obvious that the blue emission originates from an intracomplex due to metal-to-ligand energy transfer, possibly by charge transfer. A similar situation has been reported for Eu^{3+} in bipyridine and PEG200 by Bekiari and Lianos.[5] It can be concluded that both the red and blue emissions originate mainly from an intracomplex energy transfer process because the Eu^{3+} ion does not absorb at 336 nm and the ligand does not absorb at 396 nm, further pointing out the formation of a complex between Eu^{3+} and the ligands in bipyridine–Si.

The decay curve of the hybrid material with Eu^{3+} was singly exponential, confirming that the chemical environment of Eu^{3+} is uniform in the hybrid material, from which the luminescence lifetime was determined to be 123.6 μs. This value is much shorter than that of Eu^{3+} in inorganic solid host lattices (generally in the millisecond range),[6] indicating an important quenching by the OH groups (from the coordinated H_2O) or silanol (Si–OH) groups in the hybrid materials (see Scheme 1).

Very similar results were obtained when the Eu^{3+} was replaced by Tb^{3+} in the hybrid materials, *i.e.* the excitation spectrum was identical to that of Eu^{3+}, and the emission consisted of $^5D_4$–^7F_J (J = 3,4,5,6) transitions of Tb^{3+}, with the $^5D_4$–$^7F_5$ (543 nm) green emission as the most prominent group.

In conclusion, modification of 2,2′-bipyridine with APS results in the formation of a hybrid compound, which can act as both the ligand of lanthanide ions and as a sol–gel precursor.

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Notes and references

‡ *Experimental*: Compound **I** was prepared according to the literature procedure.[7] Anal. Calc. for $C_{12}H_8N_2O_4$: C, 59.10; H, 3.30; N, 11.50. Found: C, 59.12; H, 2.14; N, 11.52%. Compound **II** was synthesized according to the literature procedure.[3] Hybrid materials **III** were prepared as follows: bipyridine–Si was dissolved in 4 mL ethanol; TEOS and H_2O (pH 2) were added to it in the molar ratio 1:4:16 (bipyridine–Si:TEOS:H_2O) with stirring. $EuCl_3$ (or $TbCl_3$) was added to the resulting mixture with the molar ratio of bipyridine–Si : Eu^{3+} (or Tb^{3+}) of 2:1. The mixture was agitated magnetically to achieve a single phase and then transferred into cuvettes. A thermal curing was performed at 40 °C and was continued for three weeks until the sample solidified.

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