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Letter

Luminescent film with terbium-complex-bridged polysilsesquioxanes†

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A luminescent film with terbium-complex-bridged polysilsesquioxanes has been prepared by sol-gel processing of a new bifunctional monomer that combines the role of a sol-gel molecular precursor with a Tb^{3+} ion coordinate donor. The emission from Tb^{3+} ion due to ligand-to-metal energy transfer was observed by UV excitation.

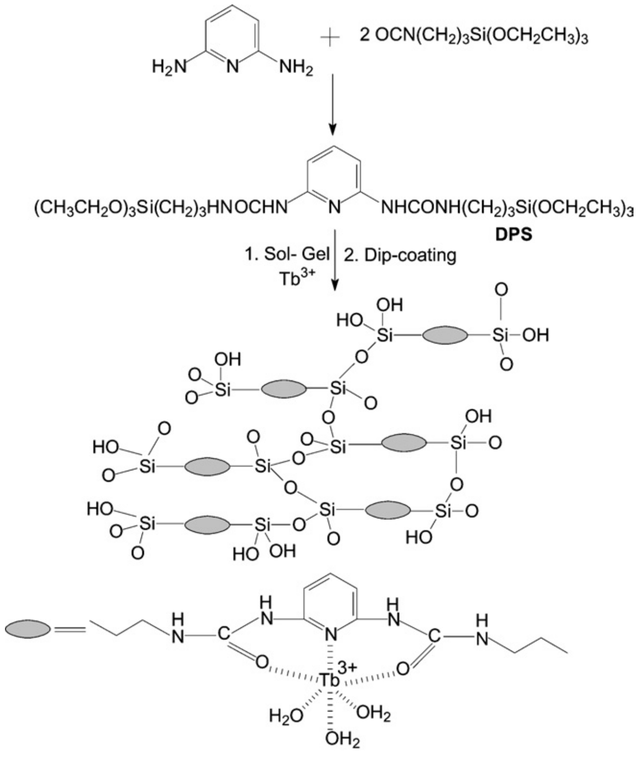
Hybrid materials have attracted much interest in the field of materials science due to their unique properties as they combine the respective characteristics of organic and inorganic components.[1–3] Bridged polysilsesquioxanes are a class of hybrid organic-inorganic materials prepared by sol-gel processing of monomers that contain a variable organic bridging group and trifunctional silyl groups.[4–6] The organic group is covalently anchored to the trifunctional silicon groups through Si–C bonds. This makes the organic group an integral part of the materials. The very large choice for the organic groups offers the opportunity to prepare materials with various compositions and therefore with tailored properties. Thus, a fine degree of control over the chemical and physical properties of the materials is achievable by varying the properties of the organic bridging group, such as length, rigidity, geometry of substitution, and functionality. The easy preparation of these materials, that is a "one-pot" synthesis, is another tremendous advantage. In addition, polysilsesquioxanes can be prepared as gels, films, or fibers due to the convenient routes available for the preparation of such hybrid materials.

To date much research has been carried out on optical applications of bridged polysilsesquioxanes by incorporating various chromophores in the bridging organic groups.[7–11] The use of dye molecules as bridging groups offers a high loading of chromophores and avoids the leaching or phase separation of the dye molecule. Some of these bridged polysilsesquioxanes are promising candidates as waveguides and nonlinear optical materials.[12,13] However, there are relatively few studies on the preparation of luminescent films based on polysilsesquioxanes with lanthanide complexes as the bridging group. Many studies concerning hybrid luminescent materials containing rare earth complexes use entrapping of rare earth complexes in a sol-gel derived host.[14,15] Since there is only weak interactions between the organic and inorganic parts in these materials, it is difficult to prevent aggregation of the emitting species and the dispersion of both components is inhomogeneous. Therefore, attention has been paid to grafting the ligands covalently to the silica backbone to overcome the above-mentioned limitations.[16,17]

In this paper, we present a new monomer (2,6-bis(propyltriethoxysilylureylene)pyridine, denoted as DPS) containing the ligand of Tb^{3+} ion in the organic bridging group. The preparation and the luminescence properties of the terbium complex-bridged polysilsesquioxanes are reported herein.

DPS was prepared easily by reaction of isocyanatopropyltriethoxysilane (ICPTES) with 2,6-diaminopyridine. Terbium complex-bridged polysilsesquioxanes were prepared by the sol-gel method at room temperature, involving hydrolysis and condensation of DPS in the presence of Tb^{3+} ion. The hybrid luminescent film was obtained by a dip-coating process (see Scheme 1).

FTIR experiments were performed on monomer DPS as well as on the hybrid thin film. The ν(Si–C) and ν(Si–OEt) absorption bands characteristic of trialkoxysilyl functions appear at 1194 and 1080 cm^{-1}, respectively. The sharp bands located at 1682, 1652, 1562 cm^{-1} corresponding to the urea NH–CO–NH function provide strong evidence that ICPTES has been successfully added to 2,6-diaminopyridine. After complexation with Tb^{3+} ion, the ν(C=O) vibration is shifted



Scheme 1 Preparation of DPS and the proposed structure of the hybrid film.

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† Electronic supplementary information (ESI) available: IR, UV-Vis and excitation spectra and decay curves. See http://www.rsc.org/suppdata/nj/b2/b206815j/

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to lower frequency ($\Delta v = 20$ cm^{-1}). It is also noticed that the complexation induces a shift of the δ(NH) absorption band to higher frequency ($\Delta\delta = 7$ cm^{-1}) [see Electronic supplementary information ESI)].

The UV-Vis absorption spectrum of DPS shows two broad absorption bands centered at 265 and 310 nm, respectively. The band at 265 nm can be attributed to a π-π* transition based on the conjugated double bonds of the pyridine ligand and the band at 310 nm is assigned to the conjugated system between pyridine and urea bonds. An obvious red shift is observed in the spectrum of hybrid film owing to the complexation of the ligand to the Tb^{3+} ion (see ESI).

The excitation spectra of the Tb-DPS complex and the corresponding hybrid film were recorded by monitoring the $^5D_4 \rightarrow {}^7F_5$ transition at 545 nm (see ESI). The spectrum of the Tb complex is dominated by two broad bands centered at 282 and 340 nm, respectively, which are assigned to the absorption of the ligand. Compared with the spectrum of the Tb complex, the excitation spectrum of the hybrid film also shows two broad bands (centered at 269 and 324 nm), but with a shift to higher energy. The emission spectra of the hybrid thin film and pure organic Tb complex (Fig. 1) were recorded at room temperature by direct excitation of the ligand at 269 nm. They look somewhat similar, which shows that the Tb^{3+} ion has been coordinated to the ligand in the hybrid thin film. Also, a green emission was observed in their emission spectra, indicating that the energy is absorbed by the surrounding ligand and transferred to the chelated Tb^{3+} ion. The narrow band emissions of Tb^{3+} were assigned to transitions from the $^5D_4$ level to the ^7F_j($j = 6, 5, 4, 3$) levels at 486, 545, 584, 621 nm, respectively, with the transition $^5D_4 \rightarrow {}^7F_5$ (545 nm) as the most prominent band. Compared to the results obtained by Zambon *et al.*,[18] this shows that silylated ligands based on pyridine are efficient sensitizers for the luminescence of lanthanide ions. It is also evidenced that by choosing appropriate precursors hybrid luminescent materials with the desired properties can be prepared easily.

The luminescence decay curve of the hybrid thin film can be described by a single exponential, showing that the Tb^{3+} ion lies in the same average chemical environment. The fluorescence lifetime obtained through the least squares method was 1.39 ms. However, it appears that the lifetime in the hybrid material is lower than that in the pure organic complex (1.81 ms; see ESI). This can be attributed to a possible quenching by silanol groups.

In order to investigate the number of coordinated water molecules (n_w) in the hybrid thin film, we replaced Tb^{3+} ion with Eu^{3+} ion to measure the emission spectrum and the decay time of Eu^{3+} in the hybrid thin film since measurements on Eu^{3+} provide a more sensitive means of determining the number of coordinated water molecules. Horrocks' equation or its modified form is widely used to evaluate n_w.[19–21] In our experiment, the following empirical formula

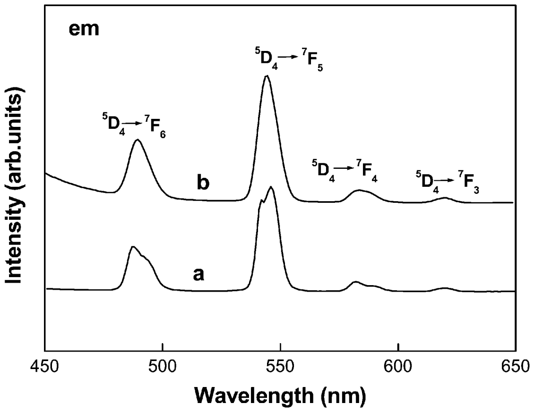

Fig. 1 Emission spectra of (a) the hybrid film and (b) the pure Tb-DPS complex in DMF (excited at 269 nm).

Table 1 Decay time τ, experimental (k_{exp}) and calculated radiative (k_r) and nonradiative (k_{nr}) $^5D_0$ decay rates, and the number of water molecules (n_w) coordinated to Eu^{3+} in the hybrid film

Parameter	Hybrid thin film containing Eu^{3+}
τ/ms	0.35
k_{exp}/ms^{-1}	2.86
k_r/ms^{-1}	0.27
k_{nr}/ms^{-1}	2.59
n_w	2.7

$$n_w = 1.05\ (k_{exp} - k_r) \tag{1}$$

$$k_{exp} = \tau_{exp}{}^{-1} = k_r + k_{nr} \tag{2}$$

are applied to determine n_w, where k_r and k_{nr} are the radiative and nonradiative probabilities, respectively.[22] The radiative contribution can be calculated from the relative intensities of the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions and can be expressed as[23]

$$k_r = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^{4} \frac{S_{0-J}}{E_{0-J}} \tag{3}$$

where A_{0-1} are Einstein's coefficient of spontaneous emission between the $^5D_0$ and $^7F_1$ levels (usually considered to be equal to 50 s^{-1}),[24,25] and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $^5D_0 \rightarrow {}^7F_J$ transitions, respectively. The parameters k_r, k_{nr} and n_w, obtained using eqn. (1–3), are reported in Table 1. From these results it is reasonable to assume that the number of water molecules coordinated to Eu^{3+}(Tb^{3+}) in the hybrid thin film is 3.

In summary, we have synthesized a new monomer (DPS) by reacting 2,6-diaminopyridine with ICPTES. The monomer incorporating the ligand of the rare earth ion in the organic bridging group also acts as a sol-gel molecular precursor. A luminescent organic-inorganic hybrid thin film has been prepared *via* a one-step method and characterized by FTIR and UV-Vis spectroscopy. Fluorescence spectra show clearly that the hybrid thin film possesses the luminescence characteristics of Tb^{3+}.

Experimental

DPS was prepared as follows: 5 mmol of 2,6-diaminopyridine was dissolved in 10 ml of dry chloroform. To this solution 10 mmol of ICPTES was then added and the resulting solution was refluxed for 5 h. Petroleum ether (60 ml) was then added and the white precipitate formed was filtered off and washed with petroleum ether. The monomer was confirmed by ^{1}H NMR and MS. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (2H, s, NH), 7.61 (2H, br s, NH), 7.50 (1H, t, PyH, $J = 5.6$ Hz), 6.92 (2H, d, PyH, $J = 5.6$ Hz), 3.85 (12H, q, OCH_2, $J = 6.8$ Hz), 3.35 (4H, t, NCH_2, $J = 6.4$ Hz), 1.70 (4H, quint, CH_2, $J = 8.0$ Hz), 1.23 [18H, t, CH_3(OEt), $J = 6.8$ Hz], 0.76 (4H, t, $SiCH_2$, $J = 6.8$ Hz). MS (ES) $m/z = 576.3$ $(M+H)^+$.

A typical procedure for the preparation of hybrid thin films was as follows. A solution of $TbCl_3$ in 4 ml *N*,*N*′-dimethylformide (DMF) and 0.5 ml deionized H_2O (acidified to 0.2 M HCl) was added to a DPS solution in DMF. The mixture was vigorously stirred at room temperature for 8 h and then allowed to stand for 4 days. The solution was dip-coated onto freshly cleaned quartz substrate at 10 cm min^{-1} to give a wet gel film. Finally, a transparent film was obtained after the wet gel was kept at 55 °C for 1 week. The molar ratio of Tb^{3+} ion to DPS is 1:1.

The excitation and emission spectra were obtained with a SPEX FL-2T2 spectrofluorimeter with a 0.8 mm slit and equipped with a 450 W lamp as the excitation source. Luminescence lifetimes were measured with a SPEX 1934D phosphorimeter using a 7 W xenon lamp as the excitation source with a 3 μs pulse width.

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