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Photofunctional Eu³⁺/Tb³⁺ hybrids through sulfoxide linkages: coordination bonds construction, characterization and luminescence[†]

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New kinds of organic–inorganic hybrid materials consisting of rare earth (Eu³⁺, Tb³⁺) complexes covalently bonded to a silica-based network have been obtained by a sol–gel approach. Three novel versatile molecular building blocks containing sulfoxide organic units have been synthesized by methylene modification reaction, which are used as the ligands of rare earth ions and also as siloxane network precursors. The obtained hybrids are characterized by chemical analysis and spectroscopic methods such as FTIR and UV; XRD and SEM. Photoluminescence measurements on the prepared hybrids were performed showing the intra-4fⁿ emission in the visible (Eu³⁺, Tb³⁺) region and in all the cases being sensitized by the sulfoxide ligands. The emission quantum efficiency and the Judd–Ofelt intensity parameters of Eu³⁺ hybrid materials were also investigated in detail.

Introduction

Rare earth ions are well known as an important class of emitting centers in luminescent materials for their sharp and intense emission bands based on f-f electronic transitions and a wide range of lifetimes suitable for various applications, which are due to the fact that the emitting excited state and the ground state have the same f^n electronic configuration, and the shielding of the 4f electrons from interaction with their surrounding by the filled 5s² and 5p⁶ orbitals.¹ However, the direct RE³⁺ photoexcitation is not very efficient, limiting the light output. This can be improved with the consequent increase of the RE³⁺ luminescence intensity through the design of rare earth complexes, in which the ligands incorporate organic chromophores strongly bonded to the 4f metal center. RE3+ ions form complexes with various organic ligands, such as aromatic carboxylic acids, β -diketonates, calixarenes and heterocyclic ligands, emitting efficiently in the near-UV (Ce³⁺ and Gd³⁺), visible (Sm³⁺, Eu³⁺, Tb³⁺ and Dy³⁺), and NIR (Nd³⁺, Er³⁺, Tm³⁺ and Yb³⁺) spectral regions. These organic ligands typically present effective absorption cross-sections 10⁴-10⁵ times higher and over a much broader spectral range than the RE^{3+} corresponding ones, and the energy they absorb can be transferred to nearby RE3+ ions, which in turn undergo a radiative

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emitting process. In analogy to light-harvesting molecules found in natural photosynthetic systems, this process is called rare earth luminescence sensitization, or *antenna* effect,² and such complexes may be seen as efficient light-conversion molecular devices (LCMDs).³ The β -diketonate complexes are the most popular and the most intensively investigated luminescent rare earth coordination complexes.⁴ Their popularity is partially because many different β -diketones are commercially available and the synthesis of the corresponding rare earth complexes is relatively easy, but also because of their excellent luminescence properties.

During the past years, there has been growing interest in the development of new rare earth-based luminescent hybrid materials that combine good mechanical, thermal, and chemical stability in air with high room-temperature emission quantum yields.⁵ These organic-inorganic hybrids processed by the sol-gel method are considered to be good candidates to assemble such properties, lending themselves to applications in displays and lighting devices. The concept of organic-inorganic hybrids emerged in the last three decades, with the advent of "soft" inorganic chemistry processes, in particular the sol-gel route. However, the conventional and simple doping method is unable to solve the problem of the quenching effect of luminescent centers because only weak interactions (such as hydrogen bonding, van der Waals forces, or weak static effects) exist between organic and inorganic moieties. So another appealing method has emerged which concerns covalently bonded hybrids. The covalent bonding of rare earth complexes to the inorganic matrix reduces the risk of leaching the complex out from the matrix, and in general higher doping concentrations can be reached such that the luminescent hybrid materials have a better homogeneity.6 The design of new luminescent hybrid systems based on covalently bonded rare earth complexes is at present a very active research field.7

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[†] Electronic supplementary information (ESI) available: Figures of infrared spectra of europium hybrid materials, phosphorescence spectra of PPS and precursor PPSSi, ultraviolet-visible diffuse reflection absorption spectra of the europium hybrid materials, and the emission decay curves and the fit curves of the hybrid materials. Tables of assignments of the main infrared absorption bands for organic ligands, silyated precursors and corresponding hybrid materials, and triple state energies of organic ligands and their energy transfer with rare earth ions. See DOI: 10.1039/c0dt01793k

In the present work we aim at gaining a deeper understanding of the RE3+-based covalently bonded hybrids, especially the construction of different functional bridges as the molecular building blocks, which can display dual functions of both coordinating to rare earth ions and allowing sol-gel processes to constitute a covalent Si-O network.8 In this article, as a continuation of our efforts to investigate the effects of new functional bridge molecular and photoluminescent properties of such rare earth hybrids, we report herein three novel sulfoxide functional bridge ligands and the properties of the corresponding hybrids. Such sulfoxide ligands are attractive because their flexibility and analogy to the structure of the β -diketonate may offer good chelating groups to coordinate with the rare earth ions, and can effectively sensitize the luminescence of rare earth ions. This work provides an effective pathway towards the design and construction of the novel hybrids, and enriches the family of functional bridge structures by incorporation of the different organic sulfoxide ligands.

Experimental section

Materials

The purity of rare earth oxide exceeds 99.99%. Rare earth nitrates hexahydrate were prepared by dissolving the corresponding oxides in dilute nitric acid, then heating the solution appropriately. All of the other reagents were analytically pure and solvents were purified according to literature procedures.⁹

Synthetic procedures

Synthesis of 2-(methylsulfinyl) acetophenone (MSAP). To slurry of 3.7 g potassium *tert*-butoxide in 20 mL of dimethyl sulfoxide (DMSO) was added 5.0 g of ethyl benzoate dropwise. The mixture was stirred vigorously at 70 °C for 2 h and then poured into ice water containing excess HCl. Product was extracted into chloroform and recrystallized from ether-CHC1₃. Yield: 65%. mp: 84–85 °C. Anal. Calcd. For C₉H₁₀O₂S (%): C 59.3, H 5.53; Found: C 59.1, H 5.68. ¹H NMR (CDCl₃, 400 MHz): δ 2.77 (s, 3H, *CH*₃), 4.32 (m, 2H, *CH*₂), 7.49 (t, 2H, *m*-C₆H₅), 7.62 (t, 1H, *p*-C₆H₅), 7.97 (d, 2H, *o*-C₆H₅). ¹³C NMR (CDCl₃, 100 MHz): δ 39.7 (CH₃), 62.3 (CH₂), 129.0 (*m*-C₆H₅), 129.1 (*o*-C₆H₅), 134.6 (*p*-C₆H₅), 136.1 (CC=O), 192.1 (C=O).

Synthesis of phenylphenacylsulfoxide (PPS). The thiophenol was added to an ethanol solution of sodium hydroxide and stirred at room temperature for one hour. Then the amount of α -bromo acetophenone was added, and the mixture was stirred overnight at room temperature. The mixture was poured into water and extracted with ether and then, upon ethanol recrystallization, white crystals were obtained. Yield: 80%. mp: 53 °C. Phenylphenacyl sulfide was dissolved in acetone, and then 30% hydrogen peroxide was added to it at once. The mixture was stirred continuously at room temperature for 24 h. After the reaction stopped, the mixture was extracted with ether. Then a white solid was precipitated, filtered and dried in vacuum. yield: 80%. mp: 70-71 °C. Anal. Calcd. For C₁₄H₁₂O₂S (%): C 68.8, H 4.95; Found: C 68.8, H 5.10. ¹H NMR (CDCl₃, 400 MHz): δ 4.34 (d, 2H, CH₂), 7.48 (t, 4H, m- C_6H_5), 7.58 (t, 2H, p- C_6H_5), 7.89 (d, 4H, o- C_6H_5). ¹³C NMR (CDC1₃, 100 MHz): δ 65.8 (CH₂), 124.1 (*m*-C₆H₅), $129.1 (o-C_6H_5), 131.4 (p-C_6H_5), 133.9 (CC=O), 191.0 (C=O).$

Synthesis of bis(benzoylmethyl) sulfoxide (BBMS). Bis(benzoylmethyl) sulfoxide was synthesized according to the method of Ref. 10. Yield: 90%. mp: 110–111 °C. Anal. Calcd. For C₁₆H₁₄O₃S (%): C 67.1, H 4.93; Found: C 66.8, H 4.68. ¹H NMR (CDCl₃, 400 MHz): δ 4.43 (d, 2H, *CH*₂), 4.77 (d, 2H, *CH*₂), 7.50 (t, 4H, *m*-C₆H₅), 7.63 (t, 2H, *p*-C₆H₅), 7.99 (d, 4H, *o*-C₆H₅). ¹³C NMR (CDCl₃, 100 MHz): δ 59.3 (CH₂), 128.8 (*m*-C₆H₅), 128.9 (*o*-C₆H₅), 134.4 (*p*-C₆H₅), 136.1 (*CC*=O), 192.4 (*C*=O).

Synthesis of the precursors MSAPSi, PPSSi and BBMSSi. To a solution of MSAP (4 mmol) in 10 mL of pyridine was added 8 mmol of NaH. Two hours later, TESPIC (8 mmol) dissolved in 10 mL of pyridine was added dropwise with stirring, then the mixture was refluxed at 70 °C for approximately 24 h under argon in a covered flask. The solvent was removed in vacuum, and the residue was obtained in a 90% yield.11: Anal. Calcd. For MSAPSi (C₂₉H₅₂N₂O₁₀SSi₂) (%): C 51.5, H 7.74, N 4.10; Found: C 50.8, H 7.48, N 4.02. ¹H NMR (CDCl₃, 400 MHz): δ 0.61 (t, 4H, CH₂Si), 1.21 (m, 18H, CH₃), 1.60 (m, 4H, CH₂CH₂CH₂), 3.13 (m, 4H, NHCH₂), 3.80 (m, 12H, SiOCH₂), 7.45 (t, 2H, m-C₆H₅), 7.64 (t, 1H, p-C₆H₅), 7.95 (d, 2H, o-C₆H₅), 8.58 (d, 2H, NH). ¹³C NMR (CDC1₃, 100 MHz): δ 7.3 (CH₂Si), 18.0 (CH₂CH₂CH₂), 23.3 (CH₂CH₃), 42.7 (NHCH₂), 58.2 (CH₂CH₃), 123.4 (CS=O), 128.3 $(m-C_6H_5)$, 128.5 $(o-C_6H_5)$, 128.6 $(p-C_6H_5)$, 135.7 (CC=0), 150.0 (C=O). The other precursor PPSSi and BBMSSi were synthesized by the same manner from the reaction between TESPIC with PPS and BBMS. Anal. Calcd. For PPSSi (C₃₄H₅₄N₂O₁₀SSi₂) (%): C 55.3, H 7.36, N 3.81; Found: C 55.0, H 7.13, N 3.59. ¹H NMR (CDCl₃, 400 MHz): δ 0.63 (t, 4H, CH₂Si), 1.21 (m, 18H, CH₃), 1.85 (m, 4H, CH₂CH₂CH₂), 3.11 (m, 4H, NHCH₂), 3.73 (m, 12H, SiOCH₂), 7.29 (t, 4H, m-C₆H₅), 7.33 (t, 2H, p-C₆H₅), 7.52 (d, 4H, $o-C_6H_5$), 8.42 (d, 2H, NH). ¹³C NMR (CDC1₃, 100 MHz): δ 7.5 (CH₂Si), 17.3 (CH₂CH₂CH₂), 23.0 (CH₂CH₃), 42.3 (NHCH₂), 58.3 (CH_2CH_3), 119.2 (CS=O), 124.3 ($m-C_6H_5$), 128.7 ($o-C_6H_5$), 130.6 (*p*-*C*₆*H*₅), 133.2 (*CC*=O), 152.8 (*C*=O). Anal. Calcd. For BBMSSi (C₅₆H₉₈N₄O₁₉SSi₄) (%): C 52.7, H 7.68, N 4.42; Found: C 52.5, H 7.40, N 4.25. ¹H NMR (CDCl₃, 400 MHz): δ 0.62 (t, 8H, CH₂Si), 1.21 (t, 36H, CH₃), 1.62 (m, 8H, CH₂CH₂CH₂), 3.16 $(m, 8H, NHCH_2), 3.79 (q, 24H, SiOCH_2), 7.43 (t, 4H, m-C_6H_5),$ 7.66 (t, 2H, $p-C_6H_5$), 7.93(d, 4H, $o-C_6H_5$), 8.62 (t, 4H, NH). ¹³C NMR (CDC1₃, 100 MHz) δ 7.6 (*CH*₂Si), 18.3 (CH₂*CH*₂CH₂), 23.6 (CH_2CH_3) , 43.0 $(NHCH_2)$, 58.5 (CH_2CH_3) , 93.8 (CS=0), 128.3 $(m-C_6H_5)$, 128.6 $(o-C_6H_5)$, 133.1 $(p-C_6H_5)$, 136.0 (CC=O), 149.9 (C=O).

Synthesis of the hybrid materials. The precursor was dissolved in N,N-dimethyl formamide (DMF) solvent, and a stoichiometric amount of RE(NO₃)₃·6H₂O was added into the solution with stirring. After three hours, a stoichiometric amount of TEOS and H₂O was added into the mixed solution after the coordination reaction was completed between precursors and rare earth ions. Then one drop of dilute hydrochloric acid was added to promote hydrolysis. The molar ratio of RE(NO₃)₃·6H₂O : precursor : TEOS : H₂O was 1:3:6:24. The mixture was agitated magnetically to achieve a single phase after two days, and then it was aged at 70 °C until the onset of gelation in about one week. The gels were collected as monolithic bulks and were ground into powdered materials for the photophysical studies. The obtained hybrid materials are denoted as MSAPSi–RE, PPSSi–RE and BBMSSi–RE (RE = Eu^{3+} and Tb^{3+}), respectively.

Physical measurements

Melting points were measured on a XT4-100XA apparatus. ¹H NMR and ¹³C NMR spectra were measured by a Bruker AVANCE-400 spectrometer with tetramethylsilane (TMS) as internal reference (CDCl₃ as solvent). Fourier transform infrared spectra were recorded on KBr disk using Nicolet model 5SXC spectrometer in 4000-400 cm⁻¹ region. The ultraviolet absorption spectra (ethanol solution) and the ultraviolet-visible diffuse reflection spectra of the powder samples were recorded by an Agilent 8453 spectrophotometer and a BWS003 spectrophotometer, respectively. The X-ray diffraction (XRD) measurements were carried out on powdered samples via a BRUKER D8 diffractometer (40 mA/40kV), using monochromated Cu-K α_1 radiation $(\lambda = 1.54 \text{ Å})$ over the 2θ range of 10° to 70° . Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed on a NETZSCH STA 449C with a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Scanning electron microscope (SEM) images were obtained with a Philips XL-30. Phosphorescent spectra (ethanol solution) of these ligands and precursors were determined with a Perkin-Elmer LS-55 spectrophotometer at 77 K. Luminescence excitation and emission spectra were obtained on a SHIMADZU RF-5301 spectrofluorimeter at room temperature. The slit width of excitation and emission spectra were 3.0 nm. Luminescent lifetimes were determined on an Edinburgh Instruments FLS 920 phosphorimeter, using a 450 W xenon lamp as the excitation source (pulse width, 3 µs) with high dispersion, low stray light excitation and emission 300 mm monochromators of the Czerny-Turner Configuration and a detector of single photon counting photomultiplier. The excitation and emission wavelength for time decay curves were selected from the corresponding luminescent spectra. The excitation wavelength was selected by means of Andover Corporation optical bandpass filters $(10 \pm 2 \text{ nm})$.

Results and discussion

Chemical Characterizations of the Functional Sulfoxide Molecular Bridges and Hybrid Materials

The synthetic scheme of the hybrid materials *via* the functional sulfoxide molecular bridges covalently grafted to the inorganic Si–O networks is shown in Fig. 1. The precursors are prepared by the extraction of the methylene in sulfoxide ligands with the electrophilic reagent 3-TESPIC.¹² And ¹H NMR and ¹³C NMR spectra relative to the precursors are in full agreement with the proposed structures. However, the exact structure of this kind of non-crystalline hybrid materials is very difficult to prove and it is hardly possible to solve the coordination behavior of rare earth ions. But it can be predicted the main composition and coordination effect of them according to the principle of rare earth coordination chemistry and the functional groups of organic ligands. These predictions have also been confirmed by infrared spectra.

Fig. 2 shows the IR spectra of three sulfoxide ligands and their corresponding precursors, and the assignments of the main



Fig. 1 Schemes of synthesis of the functional sulfoxide molecular bridges and the predicted structure of the hybrid materials.



Fig. 2 Infrared spectra of organic sulfoxide ligands and their corresponding silylated precursors.

infrared absorption bands are shown in Table S1 (ESI[†]). For the IR spectra of the precursors, the vibration absorption band of the isocyanate group cannot be observed, indicating the completion of the modification reactions of sulfoxide and TESPIC.¹³ The vibrations of $-CH_2$ - at around 2950 cm⁻¹ are taken place by a strong broadband located at around 2975–2882 cm⁻¹, which can be designated to the methylene groups of TESPIC. At the same time, the occurrence of peak corresponding to the stretching vibration of grafted -NH group is also evidenced by the band located at about 3340 cm⁻¹.¹⁴

In addition, the complexation of RE3+ with the organic sulfoxide ligands in all of the hybrids can be shown by infrared spectra (Figure S1, ESI[†]). Compared with the IR spectra of the precursors, the IR bands for v(C=0) vibrations of hybrids are shifted to lower frequency. This is ascribed to the complexation of the RE³⁺ ion with the oxygen atom of the C=O. However, as most of the peaks around 1000 cm⁻¹ are rather broad, the assignment of the S=O group stretching modes can not be proved. Considering the structure of these sulfoxide ligands and the principle of rare earth coordination chemistry, we can infer that oxygen atom of the S=O group also takes part in the rare earth ions coordinative environment.¹⁵ Besides, the spectra of hybrid materials show a peak at 1384 cm⁻¹ in the NO₂ stretching region (1650–1250 cm⁻¹), suggesting the presence of nitrate ions. Furthermore, the spectra of hybrid materials are dominated by the broad absorption band at about 1040 cm⁻¹ (ν (Si–O–Si)), which indicated the formation of siloxane bonds. The v(Si-C) vibration located in the 1200 cm⁻¹ in the IR spectra of hybrid materials is consistent with the fact that no (Si–C) bond cleavage occurred during the hydrolysis and condensation reactions.¹⁶

The UV-visible absorption spectra (Fig. 3) of the organic sulfoxide ligands and precursors were measured from their ethanol solution. The accomplishment of the grafting reaction between the ligand and the TESPIC can also be proved by the ultraviolet spectra. From the spectra, the peak at about 250 nm is assigned to the π - π * electronic transition of the aromatic rings in the sulfoxide ligands, and there is a red shift between the organic ligands and the precursors. This indicates that the conjugating system is influenced by the introduction of the carbonyl group in TESPIC.¹⁷



Fig. 3 Ultraviolet absorption spectra of organic sulfoxide ligands and their corresponding silylated precursors.

As determined by XRD patterns (Fig. 4) of the obtained hybrids, all the materials with $10^{\circ} \le 2\theta \le 70^{\circ}$ are totally amorphous. All diffraction curves exhibit a single broad peak at about 22° , which is known as 'amorphous hump'. According to the literature,¹⁸ for the curve of hybrid materials with Si–O network, we can calculate that the structural unit distance by Bragg's law:

$$2d\sin\theta = n\lambda \tag{1}$$

where *d* is the distance in the real space between the structural units, λ the wavelength of X-ray radiation (1.54 Å), *n* is the diffraction series. Using the above equation, it is estimated that the structural unit distance is approximately 4.04 Å. This value is similar to those reported for vitreous SiO₂, *i.e.*, 4.2 Å. Therefore, these materials obtained are amorphous and free of any crystalline regions. In addition, none of the hybrid materials contains measurable amounts of phases corresponding to the pure



Fig. 4 Selected XRD patterns of europium hybrid materials.

organic ligand or free RE nitrate, which is an indication of the formation of true covalently-bonded molecular hybrid materials.

The thermal behavior of the material MSAPSi-Eu is examined by TG and DSC (Fig. 5). A typical TG trace showed that the obtained material has a good thermal stability, and there are no weight losses up to 150 °C, showing a moderately improved thermal stability compared with organic ligand MSAP whose melting point is only 84 °C. The material decomposes in three main steps between 25 °C and 1000 °C, leaving a residual mass of 53.58%. From the beginning to 150 °C, is possibly associated with the loss of the coordinated H_2O .¹⁹ The mass loss of 1.37% for this thermal event is revealed by the TGA curve, and it is calculated that there are approximately two molecular H₂O in one complex. The last two steps occurring in the range of 200-1000 °C are attributed to the thermal degradation of the organosilicate framework, involving Si-C, C-C, and C-N bond cleavage.²⁰ Correspondingly, the curves of DSC show the endothermic and exothermic peak corresponding with the curve of TGA. At 196.8 °C, 463.6 °C, there are obviously endothermic processes which are attributed to the decomposition of precursor. Generally, the higher thermal stability of the organic species in the hybrid is consistent with the successful encapsulation of the ligand within the rigid silica matrix.



Fig. 5 Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of hybrid materials MSAPSi–Eu.

The scanning electron micrographs for the hybrid materials prove that a homogeneous system is obtained. Because the rare earth complexes are covalently linked into inorganic networks by the strong Si-C bonds and a complicated huge molecule is formed, they are composed quite uniformly via a self-assembly process during the hydrolysis/polycondensation process so that the inorganic and the organic phases can exhibit their distinct properties together and no phase separation occurs.²¹ Fig. 6 shows the micrographs for (A) MSAPSi-Eu, (B) MSAPSi-Tb, (C) PPSSi-Eu, (D) PPSSi-Tb, (E) BBMSSi-Eu, and (F) BBMSSi-Tb, respectively. On the surface of those hybrids many similar linear stripes can be observed, which are mostly owing to the sol-gel treatment. Different hybrids derived from different sulfoxide linkages and rare earth ions have little influence on the micromorphology in this hybrid system. Besides, there are some branches at the end of every linear stripe and the stripes will continue to grow according to the directions of these branches. In the formation of the whole hybrid systems, there exist two main reaction processes, one is the cohydrolysis and copolycondensation reactions between sulfoxide linkage organically modified silica





Fig. 6 Scanning electron micrograph (SEM) images for the hybrids: (A) MSAPSi–Eu, (B) MSAPSi–Tb, (C) PPSSi–Eu, (D) PPSSi–Tb, (E) BBMSSi–Eu, and (F) BBMSSi–Tb.

and TEOS, the other is the coordination reaction of rare earth ions and ligands (sulfoxide linkage organically modified Si–O network). The competition between the two reactions jointly determines the microstructure of the final hybrid materials. Certainly, the tendency to form a polymeric Si–O–Si network in the cohydrolysis and copolycondensation reactions of sulfoxide linkage organically modified silica and TEOS become the primary tendency.

Photoluminescence studies

The low-temperature phosphorescence spectra of organic sulfoxide ligand PPS and precursor PPSSi are recorded in Figure S2 (ESI[†]). The lowest triplet state energy levels and energy differences (ΔE) between the triplet state energy levels and the resonant emitting energy levels of the central RE^{3+} (RE = Eu, Tb) are shown in Table S2 (ESI[†]). From the Figure S2, a broad phosphorescence band, which corresponds to the triplet state emission of the ligand and precursor, is observed and the blue shift occurs between PPS and PPSSi. According to the energy transfer and intramolecular energy mechanism,¹⁹ the intramolecular energy transfer efficiency from organic ligands to the central RE³⁺ is the most important factor to determine the luminescence properties of rare earth complexes. This process is referred to as luminescence sensitization or antenna effect and is quite intricate since several mechanisms may be involved:²² One is from the triplet state energy of organic ligands to the resonant energy level by Dexter's resonant exchange interaction theory:23

$$P_{\rm da} = (2\pi Z^2 / R) \int F_{\rm d}(E) E_{\rm a}(E) \, \mathrm{d}E \tag{2}$$

$$k_{\rm ET} = K P_{\rm da} \exp(-2 R_{\rm da}/L) = K' F_{\rm d}(E) E_{\rm a}(E) dE$$
(3)

and the other is the inverse energy transition by thermal deactivation mechanism.²²

$$k(T) = A \exp(-\Delta E/RT)$$
(4)

 $P_{\rm da}$ is the transition probability by the resonant exchange interaction, and $k_{\rm ET}$ is the rate constant of the intramolecular energy transfer. $2\pi Z^2/R$ is a constant relative to the specific mutual distance between the central RE³⁺ ion and its coordinated atoms (oxygen or nitrogen). $F_{d}(E)$ and $E_{a}(E)$ are the experimental luminescence spectrum of energy donor (ligands) and the experimental absorption spectrum of energy acceptor (RE^{3+}), respectively, so both of them represent the overlap spectrum of RE³⁺ cations. R_{da} is the intramolecular distance between donor atoms and acceptor atoms, and L is the van der Waals radius. Both R_{da} and L may be considered to be constant in intramolecular transfer processes, so k_{ET} is proportional to the overlap of F_{d} (E) and E_{a} (E). With the decrease of the energy difference between the triplet state of organic ligands and RE³⁺ excited levels, the overlap of $F_{d}(E)$ and E_a (E) is increased. On the other hand, the activation energy ΔE is equal to the energy difference ΔE (Tr-RE³⁺) whereas from the formula the inverse energy transfer rate constant k(T) increased with decreasing ΔE (Tr-RE³⁺). Energy is usually transferred onto RE^{3+} levels with higher energy than the emissive level; otherwise, back energy transfer occurs, resulting in low quantum yields and short, temperature-dependent lifetimes.^{6,24} From the Table S2 (ESI[†]), the triplet state energy of the precursors with different sulfoxide ligands are similar, and we estimate the efficiency of the energy transfer for all the hybrids of both series are similar too, with respect to the value of the quantum efficiency. It also can be deduced that sulfoxide ligands can sensitize the Eu³⁺ and Tb³⁺ ions.

UV-visible diffuse reflection absorption spectra are performed on powdered hybrid materials. Figure S3 (ESI[†]) shows the spectra of Eu³⁺ hybrid materials. It exhibits a broad absorption band in the 200–500 nm region, which belongs to the whole near-UV range. This absorption band corresponds to transition from the ground state of the organic ligand to the first excited state. It is more specifically attributed to π - π * transition of the aromatic ring. Besides, it is also observed that the broad bands overlap with the luminescence excitation spectra completely. It can be predicted that the energy match between organic ligand and RE³⁺ is appropriate so that the organic ligand can absorb energy in the ultraviolet–visible range to transfer the energy to the corresponding hybrid materials. This speculation has been confirmed by the phosphorescence spectra and luminescence spectra of these materials.

The luminescence properties of the hybrids have been investigated at room temperature. The organic–inorganic hybrids containing rare earth ions give out a bright red (for Eu³⁺) or green (for Tb³⁺) emission when irradiated under a UV lamp. The excitation and emission spectra of the obtained hybrids are shown in Fig. 7 and 8, respectively. For the europium hybrid materials, the excitation spectrum exhibits a broad band ranging from 250 to 400 nm and no f–f transitions could be observed. The broad band can be mainly ascribed to transitions involving the π – π * states of the chelate ring of the organic ligand.²³ The higher relative



Fig. 7 Excitation and emission spectra of the europium hybrids.



Fig. 8 Excitation and emission spectra of the terbium hybrids.

intensity of the ligand excited state reveals that the rare earth sensitization process is the more efficient excitation path for the hybrid material.²⁵ The typical photoluminescence spectra of the europium hybrids recorded by excitation at 366 nm are shown in Fig. 7. All of the spectra show the characteristic narrow band emission of Eu³⁺ ions, which indicates that the surrounding ligands absorb and transfer energy efficiently to the chelated rare earth ions. Five narrow emission peaks centered at 577, 590, 614, 649, and 695 nm, of Eu³⁺. ${}^{5}D_{0}-{}^{7}F_{J}$ (J = 0-4) are observed, with the hypersensitive transition ${}^{5}D_{0}-{}^{7}F_{2}$ as the most prominent group. This also indicated that the Eu³⁺ local environment is characterized by a low symmetry group without an inversion centre. Further evidence of a single Eu³⁺ local environment is given by the presence of a single line for the non-degenerate ${}^{5}D_{0}-{}^{7}F_{0}$ transition. Fig. 8 illustrates typical photoluminescence spectra of the terbium hybrid materials. Similarly to the luminescent features of Eu³⁺ hybrids, the excitation spectrum monitored with the Tb³⁺. The ${}^{5}D_{4}-{}^{7}F_{5}$ (545 nm) emission exclusively consists of a broad excited band, indicating an energy transfer from the ligands to the central Tb³⁺ ions. The emission spectrum obtained after excitation at 324 nm contains four characteristic emission bands at 488 (${}^{5}D_{4}-{}^{7}F_{6}$), 543 $({}^{5}D_{4}-{}^{7}F_{5})$, 581 $({}^{5}D_{4}-{}^{7}F_{4})$, and 619 $({}^{5}D_{4}-{}^{7}F_{3})$ nm, with the ${}^{5}D_{4}-{}^{7}F_{5}$ green emission as the most prominent peak.

In order to further quantify the different photoluminescence features of the hybrids, the lifetime values of the ${}^{5}D_{0}$ (Eu³⁺) and ${}^{5}D_{4}$ (Tb³⁺) excited states were measured on the basis of the emission decay curves monitored within the more intense Eu³⁺ (${}^{5}D_{0}-{}^{7}F_{2}$) and Tb³⁺ (${}^{5}D_{4}-{}^{7}F_{5}$) transitions, respectively. Both of the decay curves (Figure S4 and Figure S5†) can be well-fitted

Table 1 Lifetime $(\tau, \mu s)$, quantum efficiency (η) , radiative $(A_{n\tau}, s^{-1})$ and nonradiative $(A_{n\tau}, s^{-1})$ transition probabilities of the ⁵D₀ level and number of water molecules coordinated to the Eu³⁺ ion (n_w) for europium hybrid materials

Hybrids	MSAPSi–Eu	PPSSi–Eu	BBMSSi–Eu
τ (us)	386.0	400.8	572.4
I_{02}/I_{01}	3.45	3.88	2.43
$A_{\rm r} ({\rm s}^{-1})$	252.4	276.2	220.9
$A_{\rm nr}$ (s ⁻¹)	2338.3	2218.8	1526.1
η (%)	11.0	11.1	12.6
n _w	~2	~2	~1.5
$\Omega_{2} (\times 10^{-20} \text{ cm}^{2})$	5.21	5.85	3.66
$\Omega_{4} (\times 10^{-20} \text{ cm}^{2})$	0.35	0.35	0.61

by a single exponential function: $\ln[S(t)/S_0] = -k_1t = -t/\tau$, which corroborates that all the rare earth ions occupy the same average local environment within each of the hybrids. From the emission spectra, it can be suggested that there exist weak emission bands for the residual emission of the aromatic groups of organically modified silane host, so we have tried fitting the curves to a double exponential decay, but there is no improvement in fit when a double exponential is applied. The resulting lifetime data of europium hybrids are given in Table 1. For the Tb³⁺-containing materials, the obtained lifetime values are 334.9, 325.0, 437.4 µs for MSAPSi–Tb, PPSSi–Tb, BBMSSi–Tb, respectively.

Further, the radiative (A_r) and nonradiative (A_{nr}) transition rates of the ${}^5\mathrm{D}_0$ level and the quantum efficiency (\eta) of the europium hybrids, $\eta = A_r/(A_r + A_{nr})$ are estimated by using a procedure based on the room temperature emission spectrum and ⁵D₀ lifetime values.²⁶ The radiative contribution may be calculated from the relative intensities of the ${}^{5}D_{0}$ - ${}^{7}F_{0-4}$ transitions (the ${}^{5}D_{0}$ - $^7\mathrm{F}_{5,6}$ branching ratios are neglected due to their poor relative intensity with respect to that of the remaining ${}^{5}D_{0}-{}^{7}F_{0-4}$ lines). The ${}^{5}D_{0}-F_{1}$ transition does not depend on the local ligand field and thus may be used as a reference for the whole spectrum, in vacuo $A_{01} \approx 50 \text{ s}^{-1}$.²⁷ The values found for η , A_r and A_{nr} of Eu³⁺ hybrids are gathered in Table 1. From the Table 1, is can be seen that similar η (⁵D₀) values for different functional sulfoxide precursor are observed. Comparing the η (⁵D₀) values of the Eu³⁺ hybrids with those previously reported in our work, the quantum efficiencies of functional sulfoxide hybrid systems are much higher than the hybrid materials with functional calix[4]arene organic ingredients (below 5%),²⁷ or those with functionalized triazole (below 4.5%).²⁷ On the basis of these results, we may presume that the functional sulfoxide precursor can sensitize luminescence of rare earth ions and easily provide stable and efficient hybrid materials.

Moreover, the variations in the η and $A_{\rm nr}$ values may be rationalized in terms of the number of water molecules coordinated to the Eu³⁺ ions ($n_{\rm w}$) based on the empirical formula $n_{\rm w} = 1.11 \times (A_{\rm nr}-0.31)$.²⁸ The results obtained for hybrids indicate about 2 water molecules in the first Eu³⁺ coordination sphere, which is in agreement with the result of the thermogravimetric analysis. However, the coordinated water molecules produce severe vibration of the hydroxyl group, resulting in the large nonradiative transition and decreasing the luminescence efficiency.

From the emission spectra shown in Fig. 6, we have determined the Judd–Ofelt Parameters for the Eu^{3+} hybrids. In the case of Eu^{3+} , the pure magnetic dipole transition ${}^{5}D_{0}-{}^{7}F_{1}$ does not

depend on the host environment (and can thus be used as an intensity standard for comparison of spectra) while the ${}^{5}D_{0}{}^{-7}F_{2,4,6}$ induced electric dipole transitions depend only on the corresponding doubly reduced matrix elements.²⁹ So, the Ω_2 , Ω_4 and Ω_6 parameters for the ${}^{5}D_0{}^{-7}F_{2,4,6}$ transitions, representing the square of the charge displacement due to the induced electric dipole transition, may be regarded as phenomenological parameters that characterise the radiative transition probabilities within the ground state configuration.

The spontaneous emission probability, A, of the transition is related to its dipole strength according to eqn (5).

$$4 = [64\pi^4 \gamma^3 / 3h(2J+1)][n(n^2+2)^2 S_{\rm ED} / 9 + n^3 S_{\rm MD}]$$
(5)

where γ is the average transition energy in cm⁻¹, *h* is Planck's constant (6.63 × 10⁻²⁷ erg s), 2*J*+1 is the degeneracy of the initial state (1 for ⁵D₀). *S*_{ED} and *S*_{MD} are the electric and magnetic dipole strengths (in esu² cm²), respectively. *n*(*n*²+2)²/9 is the Lorentz local field correction term and the average refractive index *n* = 1.5.

The transitions from ${}^{5}D_{0}$ to ${}^{7}F_{0.3.5}$ (J = 0, 3, 5) are forbidden both in magnetic and induced electric dipole schemes (S_{ED} and S_{MD} are zero). The transition to ${}^{7}F_{1}$ (J = 1) is the only magnetic dipole transition, and has no electric dipole contribution. As is already mentioned, magnetic dipole transitions in rare earth ions are practically independent of the ion's surroundings, and can be well calculated by theory ($S_{MD} = 9.6 \times 10^{-42} \text{ esu}^2 \text{ cm}^2 = 9.6 \times 10^{-6} \text{ debye}^2$).³⁰ The remaining transitions (J = 2, 4, 6) are purely of induced electric dipole nature. According to the Judd–Ofelt theory, the strength of all induced dipole transitions (absorption and emission) of a rare earth ion in a certain matrix can be calculated on basis of only three parameters Ω_{λ} , using eqn (6).

$$S_{\rm ED} = e^2 \Sigma \Omega_{\lambda} |\langle J || U^{(\lambda)} || J' \rangle |^2$$
(6)

where *e* is the electronic charge, and $\langle J || U^{(\lambda)} || |J' \rangle|^2$ values are the square reduced matrix elements whose values are 0.0032 and 0.0023 for J = 2 and 4,³¹ respectively. Besides, the ${}^{5}D_{0} - {}^{7}F_{6}$ transition could not be experimentally detected, and it is not necessary to determine its J–O parameter. So, we only need to estimate the two parameters (Ω_2 , Ω_4) related to the two purely induced electric dipole transitions ${}^{5}D_{0} - {}^{7}F_{2}$, 4.

On the basis of this analysis, the Ω_2 and Ω_4 values obtained for Eu³⁺ hybrid materials are shown in Table 1. It is known that the parameter Ω_2 is associated with short-range coordination effects and its value increases with the basic character of the ligand, increasing coordination number, decreasing site symmetry and decreasing metal–ligand bond lengths.³² In these results the relatively higher value of the Ω_2 intensity parameter of MSAPSi– Eu and PPSSi–Eu than that of BBMSSi–Eu. This might be interpreted as a consequence of the hypersensitive behavior of the ${}^5D_0-{}^7F_2$ transition, suggesting that the dynamic coupling mechanism is quite operative and that the chemical environment is highly polarizable.³³ The deep relationship between the different hybrid materials and the luminescence behavior needs to be fundamentally investigated further.

Conclusions

In this work we were able to synthesize new organic-inorganic hybrid materials composed of rare earths and modified silica networks that provide coordinating groups. The three novel sulfoxide functional bridge ligands, prepared by the extraction of the methylene in sulfoxide ligands with the electrophilic reagent TESPIC, were used as the ligands of rare earth ions and also as the siloxane network precursors. The chemical characterizations and photoluminescence properties of the hybrids are studied. The hybrids exhibit the characteristic luminescence of Eu^{3+} and Tb^{3+} ions, in all the cases being sensitized by the sulfoxide ligands. The distinction of the luminescent intensity parameters for the obtained hybrids with different sulfoxide precursors is not apparent. Furthermore, the current molecular design method can be conveniently applied to other ligands and to different modified alkoxysilanes, and the desired properties can be tailored by an appropriate choice of the different precursors.

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References

- J. C. G. Bunzli, S. Comby, A. S. Chauvin and C. D. B. Vandevyver, J. Rare Earths, 2007, 25, 257–274; G. Blasse, B. C. Grabmaier, Luminescent Materials, Springer, Berlin, Germany, 1994.
- 2 J. M. Lehn, Angew. Chem., Int. Ed. Engl., 1990, 29, 1304-1319.
- 3 G. F. de Sa, O. L. Malta, C. D. Donega, A. M. Simas, R. L. Longo, P. A. Santa-Cruz and E. F. da Silva, *Coord. Chem. Rev.*, 2000, **196**, 165–195; N. Sabbatini, M. Guardigli, J. M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201–228.
- 4 P. A. Vigato, V. Peruzzo and S. Tamburini, *Coord. Chem. Rev.*, 2009, 253, 1099–1201.
- W. H. Green, K. P. Le, J. Grey, T. T. Au and M. J. Sailor, *Science*, 1997, **276**, 1826–1828; P. C. R. Soares-Santos, H. I. S. Nogueira, V. Felix, M. G. B. Drew, R. A. Sá Ferreira, L. D. Carlos and T. Trindade, *Chem. Mater.*, 2003, **15**, 100–108; L. D. Carlos, R. A. S. Ferreira, V. D. Bermudez and S. J. L. Ribeiro, *Adv. Funct. Mater.*, 2001, **11**, 111–115; L. D. Carlos, V. D. Bermudez, R. A. S. Ferreira, L. Marques and M. Assuncao, *Chem. Mater.*, 1999, **11**, 581–588; L. D. Carlos, R. A. S. Ferreira, V. D. Bermudez and S. J. L. Ribeiro, *Adv. Mater.*, 2009, **21**, 509–534.
- 6 K. Binnemans, Chem. Rev., 2009, 109, 4283-4374.
- 7 N. N. Lin, H. R. Li, Y. G. Wang, Y. Feng, D. S. Qin, Q. Y. Gan and S. D. Chen, *Eur. J. Inorg. Chem.*, 2008, **30**, 4781–4785; B. H. Tong, S. J. Wang, H. Hao, F. R. Ling, Y. Z. Meng and B. Wang, *J. Photochem. Photobiol.*, *A*, 2007, **191**, 74–79; P. Lenaerts, A. Storms, J. Mullens, J. D'Haen, C. Gorller-Walrand, K. Binnemans and K. Driesen, *Chem. Mater.*, 2005, **17**, 5194–5201.
- 8 J. L. Liu and B. Yan, J. Phys. Chem. B, 2008, **112**, 10898–10907; H. F. Lu, B. Yan and J. L. Liu, *Inorg. Chem.*, 2009, **48**, 3966–3975; J. L. Liu, B. Yan and L. Guo, *Eur. J. Inorg. Chem.*, 2010, 2290–2296; B. Yan and H. F. Lu, *Inorg. Chem.*, 2008, **47**, 5601–5611.
- 9 D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, U.K., 1980.
- 10 W. X. Li, L. Guo, L. J. Chen and X. Y. Shi, J. Fluoresc., 2008, 18, 1043–1049.
- 11 L. Guo and B. Yan, *Inorg. Chem. Commun.*, 2010, **13**, 358–360; L. Guo, B. Yan, J. L. Liu, K. Sheng and X. L. Wang, *Dalton Trans.*, 2011, **40**, 632–638.
- (a) B. Yan and Q. M. Wang, Cryst. Growth Des., 2008, 8, 1484–1489;
 Y. Li, B. Yan and H. Yang, J. Phys. Chem. C, 2008, 112, 3659–3968;
 (b) B. Yan and Y. Li, Dalton Trans., 2010, 39, 1480–1487.
- 13 K. Binnemans, P. Lenaerts, K. Driesen and C. Gorller-Walrand, J. Mater. Chem., 2004, 14, 191–195.
- 14 H. R. Li, J. Lin, H. J. Zhang, L. S. Fu, Q. G. Meng and S. B. Wang, *Chem. Mater.*, 2002, 14, 3651–3655.
- 15 J. R. Li, X. H. Bu and R. H. Zhang, *Inorg. Chem.*, 2004, **43**, 237–244; J. R. Li, X. H. Bu and R. H. Zhang, *Eur. J. Inorg. Chem.*, 2004, 1701–1704.

- 16 A. C. Franville, D. Zambon, R. Mahiou and Y. Troin, *Chem. Mater.*, 2000, **12**, 428–435.
- X. F. Qiao and B. Yan, J. Phys. Chem. B, 2008, 112, 14742–14750; X.
 F. Qiao and B. Yan, Dalton Trans., 2009, 8509–8518; X. F. Qiao and B.
 Yan, Inorg. Chem., 2009, 48, 4714–4723.
- 18 M. C. Goncalves, Bermudez, V. D. Ferreira, R. A. S. Carlos, L. D. Ostrovskii and D. J. Rocha, *Chem. Mater.*, 2004, 16, 2530–2543.
- 19 S. M. Bruno, R. A. S. Ferreira, L. D. Carlos, M. Pillinger, P. Ribeiro-Claro and I. S. Goncalves, *Microporous Mesoporous Mater.*, 2008, 113, 453–462.
- 20 P. Tien and L. K. Chau, *Chem. Mater.*, 1999, **11**, 2141–2147; S. H. Bo, X. H. Liu and Z. Zhen, *J. Lumin.*, 2008, **128**, 1725–1730.
- Q. M. Wang and B. Yan, J. Photochem. Photobiol., A, 2006, 178, 70–75;
 B. Yan and F. F. Wang, J. Organomet. Chem., 2007, 692, 2395–2401.
- 22 S. Sato and M. Wada, *Bull. Chem. Soc. Jpn.*, 1970, 43, 1955–1962; D. L. Dexter, *J. Chem. Phys.*, 1953, 21, 836–850; C. R. S. Dean and T. M. Shepherd, *J. Chem. Soc., Faraday Trans.* 2, 1975, 71, 146–150; Q. M. Wang, B. Yan and X. H. Zhang, *J. Photochem. Photobiol.*, *A*, 2005, 174, 119–124.
- 23 B. Yan and B. Zhou, J. Photochem. Photobiol., A, 2005, 171, 181–186.
- 24 P. P. Lima, S. S. Nobre, R. O. Freire, S. A. Júniro, R. A. S. Ferreira, U. Pischel, O. L. Malta and L. D. Carlos, *J. Phys. Chem. C*, 2007, **111**, 17627–17634.
- 25 C. M. Granadeiro, R. A. S. Ferreira, P. C. R. Soares-Santos, L. D. Carlos and H. I. S. Nogueira, J. Alloys Compd., 2008, 451, 422–

425; C. M. Granadeiro, R. A. S. Ferreira, P. C. R. Soares-Santos, L. D. Carlos and H. I. S. Nogueira, *Eur. J. Inorg. Chem.*, 2009, 5088– 5095.

- 26 L. D. Carlos, Y. Messaddeq, H. F. Brito, R. A. S. Ferreira, V. D. Bermudez and S. J. L. Ribeiro, *Adv. Mater.*, 2000, **12**, 594–598; B. Yan, Q. M. Wang and D. J. Ma, *Inorg. Chem.*, 2009, **48**, 36–44.
- 27 J. C. Boyer, F. Vetrone, J. A. Capobianco, A. Speghini and M. Bettinelli, *J. Phys. Chem. B*, 2004, **108**, 20137–20144; S. J. L. Ribeiro, K. Dahmouche, C. A. Ribeiro, C. V. Santilli and S. H. J. Pulcinelli, *J. Sol-Gel Sci. Technol.*, 1998, **13**, 427–432; J. L. Liu and B. Yan, *J. Phys. Chem. C*, 2008, **112**, 14168–14178.
- 28 R. M. Supkowski and W. DeW. Horrocks Jr, *Inorg. Chim. Acta*, 2002, 340, 44–48.
- 29 R. Reisfeld, E. Greenberg, R. N. Brown, M. D. Drexhage and C. K. Jorgensen, *Chem. Phys. Lett.*, 1983, 95, 91–94.
- 30 M. J. Weber, T. E. Varitimos and B. H. Matsinger, *Phys. Rev. B: Solid State*, 1973, 8, 47–53.
- 31 K. Binnemans, K. Van Herck and C. Gorller-Walrand, *Chem. Phys. Lett.*, 1997, **266**, 297–302; W. Dew. Horrocks Jr and D. R. Sudnick, *J. Am. Chem. Soc.*, 1979, **101**, 334–340.
- 32 S. Moynihan, R. Van Deun, K. Binnemans and G. Redmond, *Opt. Mater.*, 2007, 29, 1821–1830.
- 33 S. S. Nobre, C. D. S. Brites, R. A. S. Ferreira, V. D. Bermudez, C. Carcel, J. J. E. Moreau, J. Rocha, C. M. Wong and L. D. Carlos, *J. Mater. Chem.*, 2008, **18**, 4172–4182.