



## New luminescent lanthanide centered Si–O–Ti organic–inorganic hybrid material using sulfoxide linkage

Lei Guo, Bing Yan\*

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China

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### ABSTRACT

A new sort of chemically bonded lanthanide organic–inorganic hybrid material has been constructed through the bifunctional sulfoxide molecular bridge (MSAPSi, which is functionalized 2-(methylsulfinyl) acetophenone (MSAP) by 3-(triethoxysilyl)-propyl isocyanate (TESPIC)) linking Si–O–Ti–O inorganic networks. The results suggest that the obtained hybrid materials are totally amorphous without phase separation phenomenon and exhibit the characteristic luminescence of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions. Furthermore, the decay times and emission quantum efficiency of  $\text{Eu}^{3+}$  hybrid material are also determined.

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Lanthanide organic–inorganic hybrid materials have attracted much attention for about one decade. In general, these hybrid materials have superior mechanical properties and have a better processability than the pure molecular lanthanide complexes. Moreover, embedding a lanthanide complex in a hybrid matrix is also beneficial for its thermal stability and luminescence output [1–4]. Following the classification by Sanchez and Ribot [5], the organic–inorganic hybrids can be classified according to the interaction established between the organic and inorganic components. While in Class I hybrids organic molecules are entrapped within the inorganic network, which only has the weak interactions (such as hydrogen bonding, van der Waals force or weak static effect) between organic and inorganic components, in Class II materials the organic and inorganic counterparts are covalently linked. On the basis of the former work [6–10], the design of new luminescent hybrid systems based on covalently bonded lanthanide complexes (Class II) is at the present a very active research field. The key procedure to construct this kind of materials is to design a functional bridge molecule by the grafting reaction, which has double functions of coordinating to lanthanide ions and forming a covalent Si–O network in sol–gel processing.

In this report, we modified a novel sulfoxide ligand and used it as the bifunctional molecular bridge to be introduced into Ti–O inorganic network and expected to assemble the hybrids with Si–Ti composite inorganic network. The resultant organic–inorganic hybrid materials display excellent homogeneousness; the organic and inorganic parts are joined together and coordinated to the lan-

thanide ions. Finally, the photophysical properties of the resulting hybrid materials were discussed in detail.

The bifunctional molecular bridges MSAPSi (MSAP = 2-(methylsulfinyl) acetophenone) was modified by 3-(triethoxysilyl)-propyl isocyanate (TESPIC). The typical procedure was described in the literature [11]. Representative spectroscopic data for MSAPSi ( $\text{C}_{29}\text{H}_{52}\text{N}_2\text{O}_{10}\text{SSi}_2$ ):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.61 (t, 4H,  $\text{CH}_2\text{Si}$ ), 1.21 (m, 18H,  $\text{CH}_3$ ), 1.60 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 3.13 (m, 4H,  $\text{NHCH}_2$ ), 3.80 (m, 12H,  $\text{SiOCH}_2$ ), 7.45 (t, 2H, m- $\text{C}_6\text{H}_5$ ), 7.64 (t, 1H, p- $\text{C}_6\text{H}_5$ ), 7.95 (d, 2H, o- $\text{C}_6\text{H}_5$ ), 8.58 (d, 2H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  7.3 ( $\text{CH}_2\text{Si}$ ), 18.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 23.3 ( $\text{CH}_2\text{CH}_3$ ), 42.7 ( $\text{NHCH}_2$ ), 58.2 ( $\text{CH}_2\text{CH}_3$ ), 123.4 ( $\text{C}=\text{O}$ ), 128.3 (m- $\text{C}_6\text{H}_5$ ), 128.5 (o- $\text{C}_6\text{H}_5$ ), 128.6 (p- $\text{C}_6\text{H}_5$ ), 135.7 ( $\text{C}=\text{O}$ ), 150.0 ( $\text{C}=\text{O}$ ). The final hybrids (denoted LnM) were prepared by MSAPSi reacting with tetrabutyl titanate (TBT). The mole ratio of  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}/\text{MSAPSi}/\text{TBT}/\text{H}_2\text{O}$  was 1:3:6:24. The mixture was agitated magnetically to achieve a single phase after two days, and then, it was aged at 65 °C until the onset of gelation in about 5 days. The gels were collected as monolithic bulks and were ground into the powder materials for photophysical studies. The concentration of lanthanide ions in final materials were measured under the traditional titration method that determined by EDTA titration using xylenol-orange as an indicator. The contents of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions in final materials were 5.02% and 5.11%, respectively, which were in agreement with the stoichiometry  $[\text{Ln}(\text{MSAPSi})_3](\text{NO}_3)_3 \cdot 6\text{TiO}_2 \cdot 3\text{H}_2\text{O}$  (Anal. Calcd: 5.24 for Eu; 5.46 for Tb).

Fig. 1 presents the scheme of synthesis process and the predicted structure of the hybrid materials. To presence, it is very difficult to prove exact structure of these non-crystalline hybrid materials and even it is hardly possible to solve the coordination

\* Corresponding author. Tel.: +86 21 65984663; fax: +86 21 65982287.  
E-mail address: [byan@tongji.edu.cn](mailto:byan@tongji.edu.cn) (B. Yan).

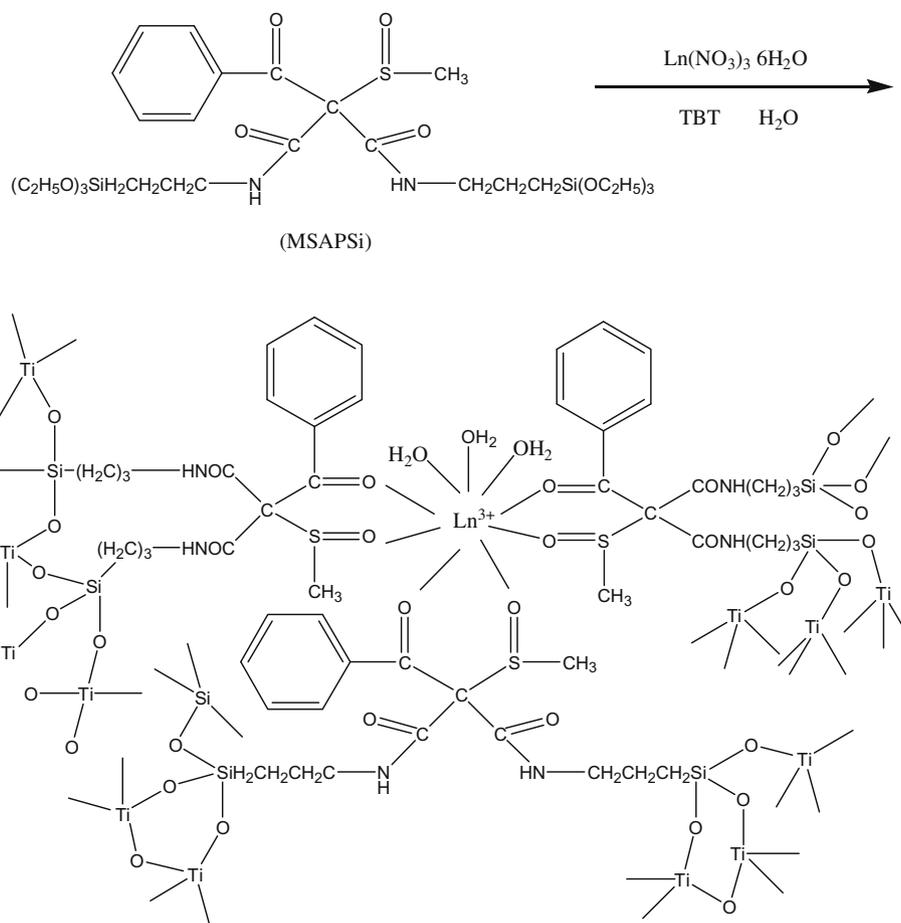


Fig. 1. Schemes of synthesis processes and the predicted structure of the hybrid materials.

behavior of lanthanide ions. But it can be predicted the main composition and coordination effect of them according to the lanthanide coordination chemistry principle and the functional groups of organic unit. The coordination number of obtained hybrids is six which originate from three bifunctional molecular MSAPSi, but taking into account the common coordination number of the lanthanide ion, there may exist about three water molecules in these hybrid system. This number of water molecules is also according to the calculated value that is calculated by Horrocks' previous research [12].

Fig. 2 exhibits the IR spectra of MSAPSi (A), EuM (B) and TbM (C), respectively. The vibrations of  $-\text{CH}_2-$  at around 2974, 2927 and  $2887\text{ cm}^{-1}$  designates the three methylene groups of TESPIC. The stretching vibration of grafted  $-\text{NH}$  group is located at  $3348\text{ cm}^{-1}$  [13]. Compared with the IR spectra of the silylated precursors, the IR bands for  $\nu(\text{C}=\text{O})$  vibrations of hybrids are shifted to lower frequency. This is ascribed to the complexation of the  $\text{Ln}^{3+}$  ion with the oxygen atom of the  $\text{C}=\text{O}$ . However, as most of the peak about  $1000\text{ cm}^{-1}$  are rather broad, the assignment of the  $\text{S}=\text{O}$  group stretching modes cannot be proved by IR measurements. Considering the structure of MSAPSi, we can infer that oxygen atom of the  $\text{S}=\text{O}$  group also takes part in lanthanide ions coordinative environment [14,15]. In addition, the quite broad band locating at the range of  $520\text{--}689\text{ cm}^{-1}$  is ascribed to the characteristic absorption of  $\text{Ti}-\text{O}$  stretching and  $\text{Ti}-\text{O}-\text{Ti}$  bridging stretching modes [16]. A broad peak in the FTIR spectra of EuM and TbM occurs at around  $897\text{ cm}^{-1}$ , which is ascribed to the vibration involving a  $\text{SiO}_4$  tetrahedron bonded to a titanium atom through  $\text{Si}-\text{O}-\text{Ti}$  bonds [17,18]. The  $\nu(\text{O}-\text{H})$  vibration at around  $3400\text{ cm}^{-1}$  can also be observed, which means the existence of the  $\text{H}_2\text{O}$  molecule.

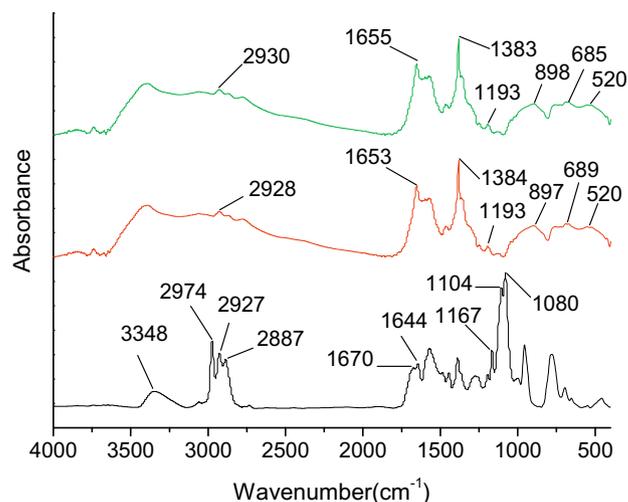


Fig. 2. Infrared spectra of (A) MSAPSi, hybrid materials EuM (B) and TbM (C).

Ultraviolet-visible diffuse reflection absorption spectra performed on powder hybrid materials are shown in Fig. S1. It exhibits a broad absorption band in the range of  $200\text{--}500\text{ nm}$ , which belongs to the whole near-UV range. As determined by XRD patterns (Fig. S2) of the obtained hybrids with  $10^\circ \leq 2\theta \leq 70^\circ$ , all the materials are totally amorphous. All diffraction curves exhibit a single broad peak at about  $22^\circ$ , which is known as 'amorphous hump' [19]. TG analyses in Fig. S3 show that grafting the organic components to a  $\text{Ti}-\text{O}$  network enables a better thermal stability.

The scanning electron micrographs (Fig. S4) for hybrid materials LnM show that homogeneous materials are obtained and no phase separation is observed. Because the organic components are covalently linked into inorganic networks 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 happened [20,21].

The excitation and emission spectra of the obtained hybrid materials are shown in Figs. 3 and 4. The excitation spectra were obtained by monitoring the emission of  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  at 614 or 545 nm and dominated by a series of broad bands centered at about 366 or 324 nm in the ultraviolet region. The emission lines of the hybrid material are assigned to the transitions from the  $^5\text{D}_0$ - $^7\text{F}_j$  ( $j = 0-4$ ) transitions at 576, 589, 612, 647 and 695 nm for europium ion and  $^5\text{D}_4$ - $^7\text{F}_6$ ,  $^5\text{D}_4$ - $^7\text{F}_5$ ,  $^5\text{D}_4$ - $^7\text{F}_4$ ,  $^5\text{D}_4$ - $^7\text{F}_3$  transitions at 491, 543, 581 and 620 nm for terbium ion, respectively. Among these emission peaks, the most striking red emissions ( $^5\text{D}_0$ - $^7\text{F}_2$ ) and green luminescence ( $^5\text{D}_4$ - $^7\text{F}_5$ ) are observed in their emission spectra which indicated that the energy transfer took place between the bifunctional molecular bridge MSAPSi and the chelated lanthanide ions. In addition, a broad band in the blue/green spectral region, which ascribed to the emitting levels of the hybrid host and already observed in similar organic-inorganic hybrids [22,23]. In order to further investigate photoluminescence properties of the hybrid materials, the typical decay curves of the  $\text{Eu}^{3+}$  hybrid materials were measured, and it can be described as a single exponential in the form  $\ln[S(t)/S_0] = -k_1t = -t/\tau$ . The lifetime value of  $\text{Eu}^{3+}$  hybrids is 265.9  $\mu\text{s}$ . Furthermore, we selectively determined the emission quantum efficiencies of the  $^5\text{D}_0$  europium ion excited state for  $\text{Eu}^{3+}$  hybrids on the basis of the emission spectra and lifetimes of the  $^5\text{D}_0$  emitting level according to Refs. [24–27], the calculated value of the luminescence quantum efficiency for  $\text{Eu}^{3+}$  hybrids is 6.0%. (The detail of calculation process of luminescence quantum efficiency can be seen in Supporting Information.)

In summary, a new functionalized luminescent lanthanide ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ) complex has been grafted to the Si-O-Ti-O composite networks via the sol-gel process of the ethoxy groups of both MSAPSi and TBT, which displayed the connection of organic/inorganic parts at a molecular level to acquire a synergetic composition of the properties typical of each constituent. The photophysical properties of them (luminescent spectra, lifetime and quantum efficiency) were studied. These results can be expected to provide a typical approach to design sulfoxide bifunctional molecular linkages and construct organic/inorganic hybrids.

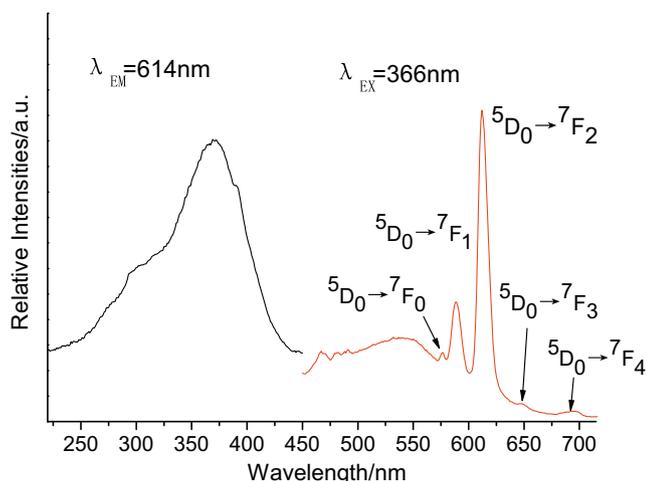


Fig. 3. Excitation and emission spectra of the europium hybrid material.

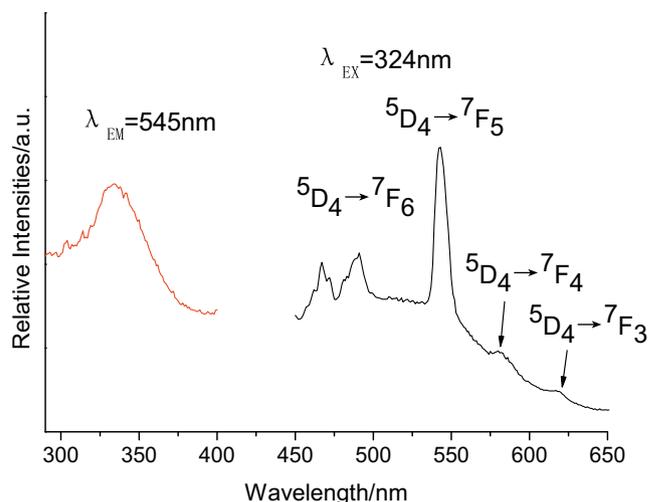


Fig. 4. Excitation and emission spectra of the terbium hybrid material.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.12.021.

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