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Photofunctional Eu³⁺/Tb³⁺ hybrid material with inorganic silica covalently linking polymer chain through their double functionalization

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ABSTRACT

In the context, 2-thiosalicylic acid (TSA) is modified with two crosslinking reagents (3-chloropropyltrimethoxysilane (CTPMS), 3-(triethoxysilyl)-propyl isocyanate (TESPIC)) to achieve two kinds of sulfide bridges (abbreviated as TSA-CSi and TSA-TSi, respectively). And two organic polymers (poly acrylamide (PAM) and poly ethylene glycol (PEG)) are also functionalized with TESPIC to form their polymeric silane derivatives PAMSi and PEGSi. Then series of multi-component Eu³⁺/Tb³⁺ hybrid material have been assembled with inorganic silica covalently linking organic polymer through the sulfide bridges after co-hydrolysis and co-polycondensation with the above inorganic or organic alkoxyl compounds (TSA-CSi(TSi), PAMSi(PEGSi)) and tetraethoxysilane (TEOS). These hybrid material are characterized in details to compare with the binary hybrid material without organic polymer unit, whose results reveal that the photoluminescence properties of the hybrid system are improved with the introduction of the polymer unit.

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1. Introduction

Photofunctional Eu³⁺ and Tb³⁺ coordination compounds are readily to achieve the ideal luminescence behavior such as narrow emission bands to obtain high color purity, wide spectral and lifetime range for extensive application, etc. [1-3]. In order to improve the thermal or optical stabilities of Eu³⁺ and Tb³⁺ complex systems, the common popular method is to incorporate them into inorganic silica host gel or organic polymer matrix to construct organic/inorganic hybrid material [4-10]. To presence, the study are mainly focused on the chemically bonding assembly of component unit to obtain the hybrid systems which can overcome the inhomogeneity and leaching or clustering of the photoactive center by conventional doping methods for these kinds of hybrid material belong to the complicated molecular-scale network [4-10]. The critical step to construct the chemically bonded hybrid material is to design functional molecular bridge as covalent linkage both coordinating to Eu³⁺ or Tb³⁺ and bonding with host. There are many kinds of modifying routes of organic ligands to the building block to assemble hybrid material, which are based on the functional group of them [11–24]. Among most work are focused on the organically modified silica hybrid material for that silane precursors are abundant to be easily functionalized.

In addition, luminescent Eu³⁺ or Tb³⁺ polymeric hybrid systems also have been investigated for their potential applications in luminescence and laser fields [25–27]. The hybrid material with

the simply doping of luminescent Eu³⁺ or Tb³⁺ complexes in polymers possess improved processing ability, chemical stability, and mechanical strength, due to the nature of polymer [28]. It has been testified that if a rare-earth ion is chemically bonded to the chains of polymer, the content of rare-earth ion, the type of chemical interaction between the rare-earth ion and polymer chain, and the distribution of rare-earth ion along the polymer chains, etc. will strongly influence the luminescent properties of the final materials [29-32]. With the same content of rare-earth complex, a dispersion of smaller-sized particles of the complex leads to a higher transparency of the hybrid material and a larger interfacial region between the dispersed complex particles and the polymer matrix, both of which will improve the efficiency of excitation [33-36]. So the tendency for rare earth hybrid materials is to assemble inorganic polymeric Si-O network and organic polymeric chain into one hybrid system to integrate their functions together effectively [37–40]. While these hybrid materials are mainly based on the direct coordination between rare earth ions and the organic polymer chain unit [41,29,42].

Herein, we put forward another path to synthesize the rare earth hybrid materials, whose organic chain unit is covalently bonded with inorganic silica through Si–O network while not coordinating to rare earth ions. 2-Thiosalicylic acid (TSA) can be functionalized with crosslinking reagents to achieve two kinds of sulfide bridges [17]. At the same time, organic polymers (poly acrylamide (PAM) and poly ethylene glycol (PEG)) can also be modified to form alkoxyl groups along the polymer chain. So the hybrid material of organically bonded silica/polymer can be prepared through the cohydrolysis and copolycondensation reaction, and Eu³⁺ or Tb³⁺ ions can be introduced within the hybrid system





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through the coordination bonding to sulfide linkage. The physical characterization and especially the photophysical property have been compared to study in details.

2. Experimental

2.1. Materials

Europium and terbium nitrates are obtained by dissolving corresponding oxides (Eu_2O_3, Tb_4O_7) in concentrated nitric acid. The silane crosslinking reagents, 3-chloropropyltrimethoxysilane (CPTMS) and 3-(triethoxysilyl)-propyl isocyanate (TESPIC) are provided by Alfa company and Lancaster Synthesis Ltd., respectively. Tetraethoxysilane (TEOS) and 2-thiosalicylic acid (TSA) are supplied by Aldrich. The normal solvents are purchased from China National Medicine Group (A.P.). Other starting reagents are used as received.

2.2. Synthesis of molecular bridge as covalent linkages [17]

2.2.1. TSA-CSi

One millimole of TSA (0.231 g, 1.5 mmol) is first dissolved in 10 mL of *N*,*N*-dimethyl formamide (DMF). CPTMS (0.299 g, 1.5 mmol) is then added to the solution by drops while stirring. K₂CO₃ (0.08 g) is added as catalyst. The whole mixture is refluxing at 80 °C for 3 h. After cooling, the solvent is removed by using a rotary vacuum evaporator, and then the yellow oil-like products are obtained. Yield: 78%. *Anal.* Calc. for C₁₃H₂₀O₅SSi: C, 49.34; H, 6.37. Found: C, 49.03; H, 6.10%. ¹H NMR (CDC1₃, 400 MHz): δ

0.78(2H, t), 1.88(2H, m), 3.16(2H, t), 3.58(9H, s), 7.15(1H, q), 7.32(1H, d), 7.78(1H, q), 8.08(1H, d), 11.2(1H, s).

2.2.2. TSA-TSi

TSA (0.231 g, 1.5 mmol) is first dissolved in 10 mL of pyridine and then TESPIC (0.371 g, 1.5 mmol) is added by drops. The whole solution is maintained at 80 °C for 3 h. The solvent is removed by a rotary vacuum evaporator, and then the yellow oil-like products are obtained. Yield: 81%. *Anal.* Calc. for $C_{17}H_{27}O_6NSSi$: C, 50.85; H, 6.78; N, 3.49. Found: C, 50.61; H, 6.49; N, 3.30%. ¹H NMR (CDC1₃, 400 MHz): δ 0.64(2H, t), 1.25(9H, t), 1.56(2H, m), 3.23(2H, t), 3.78(6H, q), 7.33(1H, q), 7.43(1H, t), 7.72(1H, d), 7.90(1H, q), 8.76(1H, d), 11.1(1H, s).

2.3. Synthesis of the polymer functionalized silane (PAM-Si, PEG-Si)

2.3.1. PAM-Si

Acrylamide (3 mmol, 0.213 g) is first dissolved in absolute alcohol, and then CP (3 mmol, 0.597 g) is added by drops. The whole mixture is refluxing under nitrogen for 12 h. After removing the solvent, a pale yellow solid is obtained (AM-Si). The resulting products are obtained the yield 92%. *Anal.* Calc. for C₉H₁₉O₄NSi: C, 46.33; H, 8.21; N, 6.00. Found: C, 46.17; H, 8.04; N, 5.83%. ¹H NMR (DMSO-d⁶, 400 MHz): δ 6.7(1H, t), 6.30(1H, t), 6.24(1H, t), 5.70(1H, t), 3.62(9H, t), 2.24(2H, m), 1.23(2H, m), 0.25(2H, t). AM-Si is subsequently dissolved in 10 mL DMF, and the initiator benzoyl peroxide (0.02 g) is added to the solution to proceed the polymerization reaction under nitrogen. The temperature is



Fig. 1. The selected scheme for the synthesis and predicted composition of ternary europium and terbium polymeric hybrid material (A) RE-TSA-CSi-PAM, (B) RE-TSA-TSi-PAM, (C) RE-TSA-CSi-PEG, and (D) RE-TSA-TSi-PEG.

maintained at 60 $^{\circ}$ C for 3 h. The solvent DMF is removed using a rotary vacuum evaporator, and the crude product obtained is washed with 20 mL of hexane. At last, the pure product PAM-Si is obtained (see Fig. 1).

2.3.2. PEG-Si

PEG400 (3 mmol) and TESPIC (6 mmol, 1.482 g) are added to 20 mL of DMF. After refluxing at 80 °C for 10 h, the whole solution is concentrated to remove solvent using a rotary vacuum evaporator. The residue is washed three times with hexane, and then the pure yellow liquid is obtained. ¹H NMR (DMSO-d⁶, 400 MHz): δ 0.64(4H, t), 1.28(18H, t), 1.66(4H, t), 3.18(4H, m), 3.56(12H, q), 3.78(20H, t), 3.86(4H, t), 3.93(4H, t), 4.08(4H, t), 4.39(4H, t), 7.32(2H, t) (see Fig. 1).

2.4. Synthesis of the binary (ternary) Eu^{3+} and Tb^{3+} polymeric hybrid materials

2.4.1. Binary hybrid material

The synthesis of binary hybrid material is for comparison with the procedure as Ref. [17]. TSA-CSi/TSA-TSi is first dissolved in DMF, then a stoichiometric amount of Eu(NO₃)₃·6H₂O/ Tb(NO₃)₃·6H₂O is added into the solution by drops. After stirring for 5 h, a stoichiometric amount of TEOS and one drop of diluted hydrochloric acid are added to the whole mixture to promote hydrolysis. The molar ratio of Eu(NO₃)₃·6H₂O/Tb(NO₃)₃·6H₂O:TSA-CSi/TSA-TSi:TEOS:H₂O is 1:3:6:24. After the treatment of hydrolysis, an appropriate amount of hexamethylenetetramine is added to adjust the pH 6–7. The mixture is agitated magnetically to achieve a single phase, and then it is aged at 65 °C until the sample is solidified.

2.4.2. Ternary hybrid material

The method is similar to that of the binary hybrid materials. TSA-CSi/TSA-TSi is first dissolved in DMF, then a stoichiometric amount of $Eu(NO_3)_3 \cdot 6H_2O/Tb(NO_3)_3 \cdot 6H_2O$ is added into the solution by drops. After stirring for 5 h, a stoichiometric amount of TEOS, PEG-Si/PAM-Si and one drop of diluted hydrochloric acid are added to the mixture. The molar ratio of $Eu(NO_3)_3 \cdot 6H_2O/Tb(NO_3)_3 \cdot 6H_2O$. PEG-Si/PAM-Si:TSA-CSi/TSA-TSi:TEOS:H₂O is 1:1:3:6:24. Then an appropriate amount of hexamethylenetetramine is added to adjust the pH 6–7. The mixture is agitated magnetically to achieve a single phase, and then it is aged at 65 °C until the sample is solidified.

The final hybrid material samples are dissolved in nitric acid, then titrated with EDTA solution, using a buffer (pH 5.8) and xylenol-orange as indicator. The contents of rare earth ions (Eu³⁺, Tb³⁺) in the hybrid material are determined by complexometric titrations. For Eu³⁺, 7.40% (Eu-TSA-CSi), 7.25% (Eu-TSA-TSi), 7.02% (Eu-TSA-CSi-PAM); 6.82% (Eu-TSA-CSi), 7.25% (Eu-TSA-TSi), 7.02% (Eu-TSA-CSi-PAM); 6.82% (Eu-TSA-TSi-PAM), 6.92% (Eu-TSA-CSi-PEG), 6.76% (Eu-TSA-TSi-PEG). For Tb³⁺, 7.27% (Tb-TSA-CSi), 7.30% (Tb-TSA-TSi), 6.79% (Tb-TSA-CSi-PAM); 6.90% (Tb-TSA-TSi-PAM), 6.88% TSA-CSi-PEG), 7.01% (Tb-TSA-TSi-PEG). In fact, the sol-gel reaction cannot be guaranteed to be completely [43,44] and so it is difficult to determine the exact composition of the TSA-CSi(TSi)-PAM(PEG) networks within the complicated hybrid system not like small molecule complex.

2.5. Physical measurements

All measurements are performed at room temperature. Infrared spectra are recorded on a Nexus 912 AO439 FT-IR spectrophotometer. We mixed the compound with the dried potassium bromide (KBr) and then pressed into pellets. The spectra are collected over the range 4000–400 cm⁻¹ by averaging 32 scans at a maximum resolution of 8 cm⁻¹. ¹H NMR spectra are recorded in CDCl₃ on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS)

as an internal reference. The UV-Vis diffuse reflection spectra of the powder samples are recorded by a BWS003 spectrophotometer. X-ray powder diffraction patterns are recorded using a Rigaku Dmax-rB diffractometer system equipped with a Cu anode in a 2θ range from 10° to 70°. The luminescence spectra are obtained on a RF-5301 spectrofluorimeter equipped with a stable spec-xenon lamp (450 W) as the light source. Luminescent lifetimes are recorded on an Edinburgh FLS 920 phosphorimeter, using a 450 W xenon lamp as the excitation source (pulse width, 3 µs). The outer luminescent quantum efficiency is determined using an integrating sphere (150 mm diameter, BaSO₄ coating) from Edinburgh FLS920 phosphorimeter. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal. The absorption intensity is calculated by subtracting the integrated intensity of the light source with the sample in the integrating sphere from the integrated intensity of the light source with a blank sample in the integrating sphere. All above measurements are completed under room temperature. The microstructures are checked by scanning electronic microscopy (SEM, Philips XL-30).

3. Results and discussion

The Fourier transform infrared spectra of TSA and the two modified linkages are presented in Fig. 2(A). It can be clearly observed that there exists absorption band centered at around 2950 and 2875 cm⁻¹ in the three precursors, corresponding to the asymmetric stretching vibration and symmetric stretching vibration for the methylene (-CH₂-) of the coupling reagents. The vanishing of the v(S-H) at around 2520 cm⁻¹ suggests the modification of the coupling reagent. The broad band at about 3440 cm⁻¹ and the low absorption peak at 920 cm⁻¹ in the IR spectra of the three precursors are ascribed to the stretching vibration and the out-of-plain bending vibration of OH group. The disappearance of the stretch vibration of the v(C-Cl) at 800 cm⁻¹ for TSA-CSi and (N=C=O) at 2250–2275 cm⁻¹ for TSA-TSi indicates the coupling reagent is grafted onto the TSA. Besides, the existence of stretching vibration of Si–C, located at 1200 cm⁻¹ and the stretching vibration of Si–O at 1100 and 1050 cm^{-1} suggest the formation of the siloxane bonds. Fig. 2(B) shows the UV absorption spectra of TSA and linkages (TSA-CSi and TSA-TSi). The absorption bands corresponding to the $\pi \rightarrow \pi^*$ electronic transition of aromatic carboxylic acids all locate at 253 and 265 nm. But the absorption peaks corresponded to the $n \rightarrow \pi^*$ electronic transition of sulfide group locate at different wavelength. There is a red shift of the $n \to \pi^*$ electronic transitions (from 293 to 305 nm) by comparing the precursors to TSA. As well there is a change of molar absorbance at around 300 nm. All these facts indicate the modification of the sulfide linkage influence the energy difference levels among electron transitions.

Fig. 3(A) and (B) shows the FT-IR spectra of the europium and terbium hybrid materials through the TSA-CSi or TSA-TSi linkages, both of which present the similar feature for the identical modified TSA Si-O network and the introduction of polymer chain has no apparent influence on the IR spectra. Because the large content of Si-O network and polymer chain, the organic groups of the TSA-CSi or TSA-TSi framework cannot be clearly to be distinguished in their IR spectra. The absorption peaks at around 2925 cm⁻¹ can be ascribed to the -CH₂ vibration and the broad absorption bands at the range of $3000-3750 \text{ cm}^{-1}$ are corresponded to the X–H groups (X = O, N, S). The stretching vibration of C=O group at 1730 cm^{-1} disappears after coordination with Eu³⁺ or Tb³⁺ ions and new absorption band at 1680 and 1560 cm⁻¹ appears, which is attributed to the symmetric vibration and asymmetric vibration of the carbonyl groups belonging to the amide groups, respectively. The absorption peak at around 1370 cm^{-1} is attributed to the



Fig. 2. The FT-IR spectra (A) and ultraviolet absorption spectra (B) of the TSA, TSA-CSi, TSA-TSi.



Fig. 3. The FT-IR spectra of the binary and ternary europium and terbium polymeric hybrid material with TSA-CSi bridge (A) and TSA-TSi bridge (B).

nitrate group in the hybrid system. In addition, the weak absorption at about 440 cm⁻¹ is ascribed to the RE–O vibration. The broad absorption bands at 1200–1100 cm⁻¹ ($v_{Si-O-Si(R)}$) indicate the formation of siloxane bonds. The containing of the organic groups by the silicate inorganic host which occurred in the hydrolysis and condensation process caused the decrease of other peaks' intensities. The infrared spectroscopy can also prove the coordination of RE³⁺ ions by the ligands. The $v(COO^-)$ vibrations is shifted to lower frequencies ($\Delta v = 40-70$ cm⁻¹) after coordination to the metallic ion with the oxygen atom of the carbonyl group.

The X-ray diffraction (from 10° to 70°) spectra of the hybrid materials show they are amorphous. All the materials exhibit the similar XRD patterns with a broad peak centered at around 23° which is the characteristic diffraction of amorphous siliceous backbone material [45,46]. Moreover, there is no new diffraction peaks for the ternary hybrid material with the introduction of polymer chain, which reveals that the polymer chain in the hybrid system has not changed the disordered silicon skeleton. Fig. 4 shows the micrographs of the selected europium hybrid materials: A, B, C for the hybrid material with TSA-CSi linkage and D, E, F for those with TSA-TSi linkage. It can be seen from the images of all hybrid material that homogeneous, molecular based system is formed without any phase separation phenomenon, which demonstrate that covalent bonds are constructed between the organic and inorganic phases with functional bridge molecule as covalent linkage. Comparing the SEM images of the binary and the ternary europium hybrid materials through TSA-CSi linkage, it can be found that there exist apparent differences of their micromorphology. For the binary hybrid material Eu-TSA-CSi, it forms the uniform tissue network microstructure. While for the ternary hybrid material Eu-TSA-CSi-PAM(PEG), the stripe microstructure are shown and especially Eu-TSA-CSi-PEG shows the dendrite with ordered

morphology on the surface. The similar features are shown in the SEM images for the binary and ternary europium hybrid material with TSA-TSi linkage series. These results verify that the organic polymer chain plays an important role in the formation of the ultimate complicated hybrid system (Fig. 4(B), (C), (E), and (F)). Comparing the SEM images of the two binary europium hybrid material with two different linkages (Fig. 4(A) and (D)), it can be found they are very different texture microstructure. And the ternary hybrid material with the polymer chain units show the similar microstructure (Fig. 4(B), (C), (E), and (F)), suggesting the similar effect from the same polymer chain PAM or PEG. These interesting morphologies can be explained from the formation process of the binary and ternary hybrid system. It is considered that the coordination reaction and hydrolysis-condensation process are the critical factor on ultimate morphology of the hybrid material. For binary hybrid material, europium ions are chelated by small bridge molecule TSA-CSi(TSi) in the initial stage to generate the luminescent center. When TEOS is added, the cohydrolysis and copolycondensation reactions occur between the terminal silanol groups of TSA-CSi(TSi) and OH groups of hydrolyzed TEOS. At the beginning of the reaction, the individual hydrolysis of TSA-CSi(TSi) and TEOS are predominant. Then the condensation reaction is performed between hydroxyl groups of both TSA-CSi(TSi) and TEOS. This cohydrolysis and copolycondensation process are carried out by encircling the luminescent center without directivity because of the structure of the luminescent center is non-rigid and easily changed in the surrounding micro-environment, which lead to the forming disordered and irregular micromorphology. Furtherly, the coordination reaction between Eu³⁺ and TSA-CSi(TSi) unit group also have influence on the morphology of the final hybrid material, which is related to the ligand group of TSA-CSi and TSA-TSi. TSA-TSi is provided with one new C=O of amide group



Fig. 4. The selected SEM images of binary and ternary europium polymeric hybrid material (A) Eu-TSA-CSi, (B) Eu-TSA-CSi-PAM, (C) Eu-TSA-CSi-PEG, (D) Eu-TSA-TSi, (E) Eu-TSA-TSi-PAM, and (F) Eu-TSA-TSi-PEG.

besides the COO group of TSA molecules, so it is easily to form the bidentate chelation to Eu³⁺ and oxygen atoms of hydroxyl group are left to produce the bridging effect for the formation of the chain or strip structure, resulting in the long stripe morphology for Eu-TSA-TSi hybrid material (Fig. 4(D)). While TSA-CSi linkage has not the C=O group and only the COO group of TSA unit take part in the coordination to Eu³⁺ and easily to form the chelated structure for the formation of tissue morphology. For ternary hybrid material, the polymer chain (PAM or PEG) of PAMSi or PEGSi are introduced into the sol-gel process for the modification of siliane and so the cohydrolysis and copolycondensation processes are engaged among three components (TEOS, TSA-CSi(TSi) and PAM-Si(PEGSi)) and become more complicated than the binary hybrid material. Therefore, it is worthy pointing out that the polymer chain of PAM or PEG has the macromolecular template effect to induce the whole hybrid system to be more stripe microstructure. Moreover, the apparent distinction of the morphology of ternary hybrid material depends on the different polymer chain unit of PAM or PEG, which may be due to the composition of them. PEGSi provides double ester group and two amide groups while the PAM-Si only possesses the amide groups, so the template effect of PEG may be more complicated than PAM, which results in the long dendritic or stripe-shaped morphology of Eu-TSA-CSi(TSi)-PEG hybrid

material. Therefore, it can be drawn a conclusion that the more ordered and regular microstructure is achieved with the introduction of the polymer.

Fig. 5 exhibits the UV–Vis diffuse reflection absorption spectroscopy of the selected hybrid materials: the hybrid material of TSA-CSi linkage for A and the hybrid material of TSA-TSi linkage for B, respectively. There is a large broad absorption band in each hybrid which is attributed to the π – π * electronic transition of the aromatic ring in the hybrid system. Among the ternary europium and terbium hybrid material with PAM chain present the more half band width and longer absorption side than other hybrid systems, revealing that the introduction of PAM polymer unit is favorable for the energy absorption of the whole hybrid systems. This can be verified from the luminescent spectra of europium and terbium hybrid material in Figs. 6 and 7.

Figs. 6 and 7 show the excitation and emission spectra of europium and terbium hybrid materials. For the excitation spectra of europium hybrid material (Fig. 6), two kinds of excitation bands can be observed. Firstly, a series of sharp lines appear at the range of 300–450 nm, which can be ascribed to f–f transitions of Eu³⁺ ion (326 nm, $^{7}F_{0} \rightarrow ^{5}H_{6}$; 375 nm, $^{7}F_{0} \rightarrow ^{5}D_{4}$; 383 nm, $^{7}F_{0} \rightarrow ^{5}G_{2}$; 394 nm, $^{7}F_{0} \rightarrow ^{5}L_{6}$, strongest; 417 nm, $^{7}F_{0} \rightarrow ^{5}D_{3}$) [47]. Secondly, broad bands ranging from 280 to 350 nm arise from the π – π^{*}



Fig. 5. The UV–Vis diffuse reflectance spectra of the binary and ternary europium and terbium polymeric hybrid material with TSA-CSi bridge (A) and TSA-TSi bridge (B).



Fig. 6. The excitation and emission spectra of binary and ternary europium hybrid material with TSA-CSi bridge (A) and TSA-TSi bridge (B).



Fig. 7. The excitation and emission spectra of binary and ternary terbium hybrid material with TSA-CSi bridge (A) and TSA-TSi bridge (B).

transition of the TSA organically modified Si–O network, whose wide bands are overlapped with some f–f transition peaks. As a result, the sharp emission peaks assigned to the ${}^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions can be seen at about 579, 591, 615, 653 and 697 nm, respectively for europium ions, indicating that conjugated systems have formed between the TSA group of organically modified Si–O network and europium ions and energy transfer have occurred in these hybrid materials. While the emission lines assigned to ${}^5D_0 \rightarrow {}^7F_2$ transitions are the most intense for the europium hybrid materials, indicating that the europium ion occupies a site without inversion symmetry [48]. Comparing the emission intensities of the europium hybrid materials of TSA-CSi (A) and TSA-TSi (B) linkages, it is observed that the relative emission intensities of the ternary hybrid material with PAM/PEG polymer chain are obviously stronger than those of the binary hybrid material

without polymer chain. This indicates that the introduction of PAM or PEG is benefit for the photoluminescence of the hybrid material, which may be due to the fact that the polymer chain unit can affect the microstructure of the whole hybrid systems to improve the luminescence.

Fig. 7 shows the excitation spectra of terbium hybrid material, which consist of the broad band appears at the ultraviolet region of 300–350 nm, corresponding to the absorption of TSA group of the organically bonded silica. The f–f transitions of Tb^{3+ 4}f₈ configuration in the longer ultraviolet region are too weak to be checked. The corresponding emission spectra are measured of the terbium hybrid materials present the sharp emission peaks assigned to the transitions ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (*J* = 6, 5, 4, 3) can be seen at 490, 545, 582 and 620 nm, respectively for terbium ions, indicating that conjugated systems have formed between the TSA group of organically

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Table 1

The photoluminescent lifetimes and quantum efficiencies data of rare earth hybrid materials.

Hybrids	I_{02}/I_{01}	$A_{\rm rad}~({\rm s}^{-1})$	$\tau (\mu s)^{a,b}$	η (%) ^c
Eu-TSA-CSi	3.0	218	365	2.3 (7.9)
Eu-TSA-CSi-PAM	3.3	232	456	3.4 (10.6)
Eu-TSA-CSi-PEG	3.3	235	454	3.7 (10.7)
Tb-TSA-CSi			875	7.1
Tb-TSA-CSi-PAM			428	3.5
Tb-TSA-CSi-PEG			617	5.3
Eu-TSA-TSi	2.9	214	376	2.4 (8.0)
Eu-TSA-TSi-PAM	3.4	239	466	3.5 (11.1)
Eu-TSA-TSi-PEG	3.6	246	385	2.7 (9.5)
Tb-TSA-TSi			745	6.2
Tb-TSA-TSi-PAM			492	3.6
Tb-TSA-TSi-PEG			804	6.5

 $^{a}~^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$ transition of Eu $^{3+}$

^b ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of Tb³⁺.

^c Calculated value in bracket from spectra and lifetime.

modified Si–O network and europium or terbium ions and energy transfer have occurred in these hybrid materials. For the terbium hybrid materials, the green emission assigned to the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transitions is the most striking.

The decay curves of all the europium and terbium hybrid materials are measured at room temperature, all of which can be described as a single exponential $(\ln[S(t)/S_0] = -k_1t = -t/\tau)$. The resulting luminescent lifetimes of europium hybrid material are detailed in Table 1. Furthermore, we selectively determined the emission quantum efficiency of 5D_0 Eu $^{3+}$ excited state for europium containing hybrid material on the basis of emission spectra and lifetimes of 5D_0 emitting level. Assuming that only nonradiative and radiative processes are essentially involved in the depopulation of the 5D_0 state, η can be defined as follows [49–53]:

$$\eta = A_{\rm r}/(A_{\rm r} + A_{\rm nr}) \tag{1}$$

Here, A_r and A_{nr} represent radiative and nonradiative transition rates, respectively. A_r can be obtained by summing over the radiative rates A_{0J} for each ${}^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions of Eu³⁺.

$$A_{\rm r} = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04} \tag{2}$$

The branching ratio for the ${}^{5}D_{0} \rightarrow {}^{7}F_{5,6}$ transitions can be neglected as they are not detected experimentally, whose influence can be ignored in the depopulation of the ${}^{5}D_{0}$ excited state. Since ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is an isolated magnetic dipole transition, it is practically independent of the chemical environments around the Eu³⁺ ion as an internal reference for the whole spectra, the experimental coefficients of spontaneous emission, A_{0j} can be calculated according to the equation [49–53].

$$A_{0J} = A_{01} (I_{0J} / I_{01}) (v_{01} / v_{0J})$$
(3)

Here, A_{0J} represents the experimental coefficients of spontaneous emission. A_{01} represents the Einstein's coefficient of spontaneous emission between the ${}^{5}D_{0}$ and ${}^{7}F_{1}$ energy levels. In vacuum, A_{01} as a value of 14.65 s^{-1} , when an average index of refraction *n* equal to 1.506 is considered, the value of A_{01} can be determined to be 50 s^{-1} approximately ($A_{01} = n^{3}A_{01(\text{vac})}$) [49–53]. I_{01} and I_{0J} are the integrated intensities of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ transitions (J = 0-4) with v_{01} and v_{0J} ($v_{0J} = 1/\lambda_{J}$) energy centers, respectively. Here v_{0J} refers to the energy barrier and can be determined with the emission bands of Eu^{3+*}s {}^{5}D_{0} \rightarrow {}^{7}F_{J} emission transitions.

On the basis of the above discussion, the quantum efficiencies of the europium hybrid materials can be determined, as shown in Table 1. Seen from the equation to calculate η , the value η mainly depends on the values of two factors: one is lifetimes and the other is I_{02}/I_{01} (red/orange ratio). If the lifetime and red/orange ratio are

large, the quantum efficiency must be high. As can be seen clearly from Table 1, the quantum efficiencies of the europium hybrid materials are determined in the order: Eu-TSA-CSi-PAM \approx Eu-TSA-CSi-PEG > Eu-TSA-CSi for the hybrid material with TSA-CSi linkage and Eu-TSA-TSi-PAM > Eu-TSA-TSi-PAM > Eu-TSA-TSi for the hybrid material with TSA-TSi one. Besides, the calculated value of luminescent quantum efficiencies for the europium hybrids are lower than the experimental measured value. This may be due to the fact there exist some errors in the measurement and calculation of spectral and lifetimes. For europium hybrid materials, the introduction of polymer chain are favorable for the luminescence of the whole system, while for terbium hybrid materials, the results become complicated. The introduction of PEG chain still improve the luminescent lifetimes and quantum efficiencies while it is contrary to the introduction of PAM chain. The results reveal that the introduction of the polymer chain is only the one factor influencing on the luminescence properties of the overall hybrid system. In addition, we compare the photoluminescent properties of them to the different hybrid materials with single sulfide without polymer unit and the hybrid materials without interaction between organically modified silica and polymer chain in our previous work [17,54]. It is found that these hybrid materials can display the matchable luminescent quantum efficiency with the other kinds of hybrid materials reported in [17,54], suggesting that the assembly path in the present work is a candidate technology to prepare the hybrid materials.

4. Conclusions

In summary, series ternary Eu³⁺/Tb³⁺ hybrid materials have been assembled with sulfide functionalized silica network (TSA-CSi(TSi)) covalently linking polymer chain (PAM(PEG)), whose physical characterization, microstructure and especially photophysical property are studied comparing with binary hybrid material without polymer chain. The results reveal that the ternary hybrid materials present more regular morphology, stronger luminescence intensity, longer lifetimes and higher quantum efficiency than the binary hybrid material, indicating that the introduction of the polymer can induce the occurrence of the self-assemble process of the microstructure and sensitize the luminescence of the hybrid materials.

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