

Luminescent homo- and hetero-metallic hybrid molecular materials constructed by covalent grafting

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In this paper, 3-(triethoxysilyl)-propyl isocyanate (abbreviated as TESPIC) was modified by ethylparaben (EPB) to produce corresponding organic-inorganic monomers (EPB-TESPIC) with two components equipped with covalent bonds, which not only can coordinate to RE ions (Tb^{3+} and Eu^{3+}) but also act as a sol-gel precursor. Luminescent hybrid materials consisting of terbium-europium complex, covalently bonded to silica-based network, have been obtained in situ via a sol-gel approach. Proton nuclear magnetic resonance spectroscopy (1H NMR) and Fourier transform infrared spectroscopy (FT-IR) were applied to characterize the structure of EPB-TESPIC. UV-visible, phosphorescence, and luminescence spectra were obtained to characterize the photophysical properties of the obtained hybrid material. Through co-hydrolysis and polycondensation, Tb^{3+} and Eu^{3+} can be introduced into the same organic-inorganic hybrid monomer, forming Si-O backbones. The experimental results show that the strong luminescence of rare-earth ions substantiates the optimum energy match and effective intramolecular energy transfer between the triplet state energy of coordination complex and the emissive energy level of the rare-earth ions. The hybrid material systems are expected to have potential applications in photophysical sensors.

Keywords: *chemical modification; organic-inorganic hybrids; photoluminescence; sol-gel process*

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1. Introduction

Rare earth complexes have long been the subject of extensive research owing to their excellent luminescent characteristics due to the electronic transitions between the 4f energy levels [1–3]. Weissman and co-workers reported the light-emission characteristics of a lanthanide complex of β -diketone [4] for the first time. Since then, much work has been carried out to obtain various rare earth compounds with special structures and luminescence behaviour [5–7]. However, the practical use of these complexes as luminescent devices or tunable solid-state lasers has not been realized because of their poor photo and thermal stability and mechanical properties. These weaknesses could be overcome by forming hybrid materials. Among all the synthetic methods, the sol-gel approach, which is based on hydrolysis/polycondensation reactions of metal alkoxides, exhibits its unique characteristics, namely, convenience, low temperature, and versatility [8–12]. Sanchez and Ribot divide hy-

brid materials into two major classes according to interaction between the different components or phases [13]. The class I hybrid materials are connected only by the weak functional interactions (such as hydrogen bonding, van der Waals force or static effect) between the organic and inorganic components, which seems impossible to solve the problems of uneven distribution of rare earth complexes, limitation of doped concentration, quenching effect of luminescent centers, separation of different phases [14–17]. On the other hand, the class II hybrid materials are connected by covalent grafting, which can achieve true interconnection between the organic and inorganic moieties and successfully solve the above-mentioned problems. In nature, the organic components play a role of network modifiers, which not only can realize the molecular-based material but also tailor the complementary properties of novel multifunctional advanced materials through covalent grafting between the different components [18]. Lately, a few studies concerning the covalently bonded hybrids have emerged and the as-derived molecular-based materials exhibit the monophasic appearance even

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at a high concentration of lanthanide complexes [19–25]. So, the key to prepare the class II hybrid materials is to synthesize an intermediate as a covalent bridge, which not only would be able to coordinate to RE ions but also act as a precursor of inorganic network.

In nature, these hybrids belong to the molecular-based systems which can realize the tailoring of the complementary properties of novel multifunctional advanced materials through the combination with chemical bonding within the different components in a single material [10, 11, 18, 26]. Some previous research was concentrated on the modification of pyridine-dicarboxylic acid or their derivatives, and Zhang focused on the modification of heterocyclic ligands such as 1, 10-phenanthroline and bipyridyl [22]. Our research team has carried out extensive work on the preparation of molecular hybrids with a functional bridge connecting both the siliceous backbone and aromatic carboxylic acids by modification of amino or carboxyl groups of aromatic acids [24–26]. Carlos *et al.* lately pointed out that amino-functional hybrids lacking metal ions could be divided into two major categories (di-ureasils and di-urethanesils) and that the Eu^{3+} coordination shell involves the carbonyl-type oxygen atoms of the urea bridges [27, 28].

In the present work, we put forward another path to modify the hydroxyl group of ethylparaben (EPB) and design a new covalently bonded hybrid inorganic–organic system based on hydrolysis and polycondensation reactions by triethoxysilyl groups of modified EP. We try, for the first time, to incorporate both Eu and Tb into one hybrid system. This is a new kind of hybrid material with the functionalization of ester compounds.

2. Experimental

2.1. Material

Ethylparaben (abbreviated as EPB) and 3-(triethoxysilyl)-propyl isocyanate (abbreviated as TESPIC) were supplied by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents were used as received.

2.2. Synthesis of monomers

A typical procedure for the preparation of organic-inorganic intermediate (EPB-TESPIC) was as follows: 2 mmol EPB (0.364 g) was first dissolved in 30 mL dry diethyl ether by stirring and 2 mmol TESPIC (0.495 g) was then added to the solution dropwise. The whole mixture was refluxed at 65 °C under argon atmosphere for 12 h. After isolation, a yellow oil of EPB-TESPIC was obtained. The typical procedure was consistent with the reaction scheme in Fig. 1. The ^1H NMR are as follows, EPB-TESPIC ($\text{C}_{19}\text{H}_{31}\text{O}_7\text{NSi}$): ^1H NMR (CDCl_3) δ (ppm) 7.91 (2H, d), 7.32 (2H, d), 6.28 (1H, t), 4.11 (2H, q), 3.81 (6H, q), 2.25 (2H, q), 1.89 (2H, q), 1.25 (3H, t), 1.04 (9H, t), 0.68 (2H, t).

2.3. Sol–gel polymerization

The modified precursor EPB-TESPIC was dissolved in dimethylformamide (DMF), then tetraethoxysilane (TEOS) was added, which actually allowed better miscibility of rare earth (RE) nitrate solution with the reaction mixture and increased the degree of cross-linking and the total silica content. H_2O was added while stirring, and then one drop of diluted hydrochloric acid was added to promote hydrolysis. A different stoichiometric ratios of RE^{3+} (blend of terbium and europium nitrate) were added to the final mixture under stirring. The molar ratio of $\text{RE}^{3+}/\text{EPB-TESPIC}/\text{TEOS}/\text{H}_2\text{O}$ was 1: 3: 6: 24. After the hydrolysis treatment, an appropriate amount of hexamethylene-tetramine was added to adjust the pH value to about 6.5. The mixture was stirred to achieve a single phase and a thermal treatment was performed at 60 °C until the sample solidified. Using the same method, we also prepared hybrid Tb^{3+} , hybrid Eu^{3+} and hybrid 11 ($\text{Tb}^{3+}:\text{Eu}^{3+} = 1:1$).

2.4. Characterization

Infrared spectroscopy was carried out in KBr flake and recorded on a Nexus 912 AO446 FT-IR spectrophotometer in the range of 4000 – 400 cm^{-1} . ^1H NMR spectra were recorded in CDCl_3 on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of the chloroform (CHCl_3) solution of the sample (5×10^{-4} mol/L) were

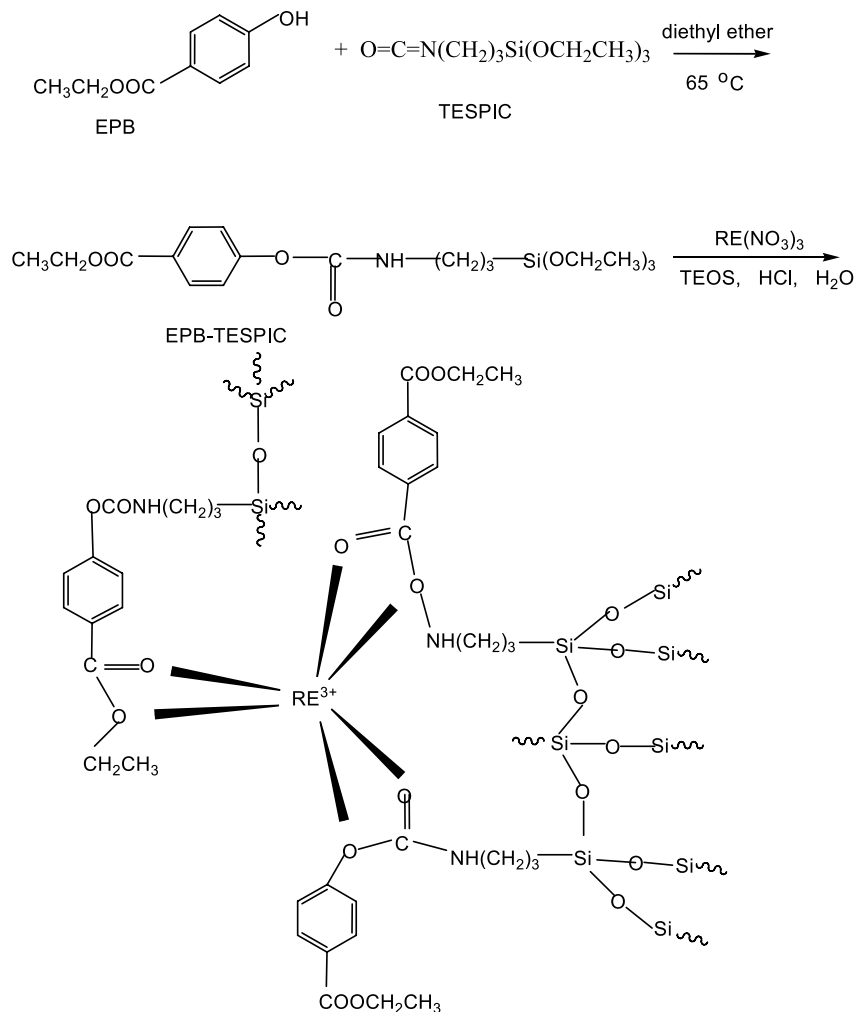


Fig. 1. Scheme of the synthesis process of EPB-TESPIC ligand and predicted structure of the resulting hybrid system.

recorded with an Agilent 8453 spectrophotometer. Luminescence excitation and emission spectra were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 1.5 nm, emission slit width = 3.0 nm. All measurements were carried out at room temperature.

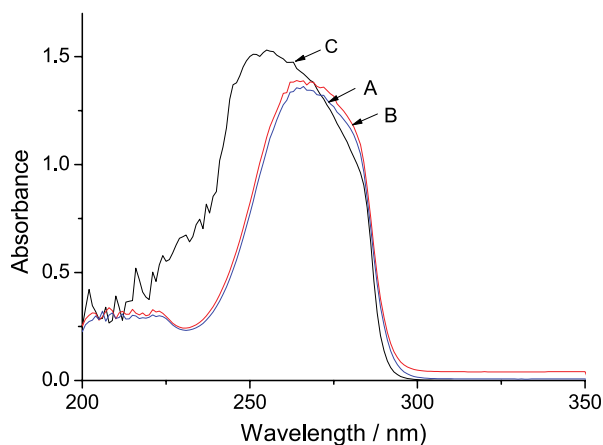
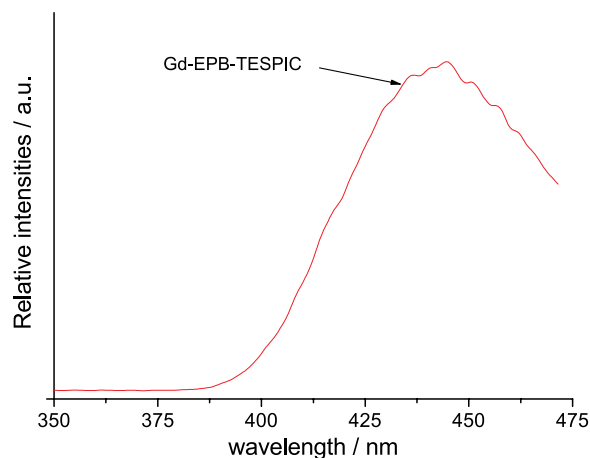
3. Results and discussion

The IR spectra of EPB, TESPIC and the modified bridge EPB-TESPIC were compared, and the main absorption peaks and their assignments are shown in Table 1. The formation of acylamino group and Si–O–Si network can be proved by these results. Comparing the IR spectra of EPB-TESPIC

with EPB and TESPIC, we can observe that ν (C=O) stretching vibrations are shifted to lower frequencies (from 1704 cm^{-1} to 1688 cm^{-1}) and ν (O–H) stretching vibrations, located at around 3217 cm^{-1} , disappear in the I.R. spectra of EPB-TESPIC, which suggests that 3-(triethoxysilyl)propyl isocyanate has been successfully grafted onto ethylparaben. In addition, the presence of the bending vibration (δ_{NH} , 1430 cm^{-1}) also suggests the occurrence of the covalent grafting reaction. The stretching vibration ($\nu_{\text{Si-O}}$) located at around 1070 cm^{-1} and the stretching vibration ($\nu_{\text{Si-C}}$) located at 1160 cm^{-1} occurred in the IR spectra of the bridging molecule (EPB-TESPIC) compared with the IR spectra of EPB, which is the

Table 1. The main bands and their assignments of IR spectra for the EPB, TESPIC and EPB-TESPIC.

Compounds	$\nu(\text{C}=\text{O})$ (cm^{-1})	$\nu(\text{N}=\text{C}=\text{O})$ (cm^{-1})	$\delta(\text{N}-\text{H})$ (cm^{-1})	$\nu(\text{O}-\text{H})$ (cm^{-1})	$\nu(\text{Si}-\text{O})$ (cm^{-1})	$\nu(\text{Si}-\text{C})$ (cm^{-1})
EPB	1704	—	—	3217	—	—
TESPIC	1630	2266	—	—	1069	1159
EPB-TESPIC	1688	—	1430	—	1070	1160

Fig. 2. Ultraviolet absorption spectra for (A) EPB, (B) EPB-TESPIC, (C) hybrid Tb^{3+} .Fig. 3. The phosphorescence spectrum of Gd^{3+} -EPB-TESPIC.

evidence of the emergence of E-TESPIC. In addition, the absorption peak at $2273 - 2378 \text{ cm}^{-1}$ for $\text{N}=\text{C}=\text{O}$ disappeared in the I.R. spectra of EPB-TESPIC, which indicates the occurrence of the covalent grafting reaction. We can observe that $\nu(\text{C}=\text{O})$ stretching vibrations are shifted to lower frequencies from 1688 cm^{-1} (EPB-TESPIC) to 1666 cm^{-1} (Eu-EPB-TESPIC) 1665 cm^{-1} (Tb-EPB-TESPIC) and 1663 cm^{-1} (Eu(Tb)-EPB-TESPIC) after complexation of Tb^{3+} or Eu^{3+} with the oxygen atom of the carbonyl group.

In addition, the ^1H NMR spectroscopy can also explain the structure of EPB-TESPIC. For the ^1H NMR spectrum of EPB-TESPIC, the peaks at chemical shifts of about 7.91, 7.32 ppm correspond to the H of the aromatic ring. The chemical shift of 6.28 ppm belongs to the H of NH, 4.11 ppm belongs to $-\text{O}-\text{CH}_2-$ and 0.68 ppm belongs to $-\text{CH}_2-\text{Si}-$.

Fig. 2 shows the ultraviolet absorption spectra of (A) EPB, (B) EPB-TESPIC and (C) hybrid Tb^{3+} . Almost the same absorption bands for the major $\pi-\pi^*$ electronic transitions $\text{A} \rightarrow \text{B}$ can be observed (both

absorption peaks have the maximum at 267 nm), suggesting that the electron distribution of the modified EPB-TESPIC has not been changed compared to free EPB ligand for the introduced TESPIC group. When the complex between Tb^{3+} and EPB-TESPIC is formed, a blue shift (13 nm) of the maximal absorbance wavelength is observed on the addition of Tb^{3+} to EPB-TESPIC (from 267 to 254 nm) because of the modification of the electron distribution of the conjugated system.

Fig. 3 shows the phosphorescence spectrum of Gd-EPB-TESPIC, showing that the complex with Gd^{3+} can enhance the phosphorescence intensity of the organic ligand. According to the intramolecular energy transfer mechanism, the corresponding intramolecular transfer efficiency from the EPB-TESPIC to Tb^{3+} mainly depends on the energy match between the triplet state energy of EPB-TESPIC (corresponding to the phosphorescence band) and the resonant emissive energy level of the central Tb^{3+} (approximately $4000 \pm 500 \text{ cm}^{-1}$). From the figure, it can be seen that the former energy

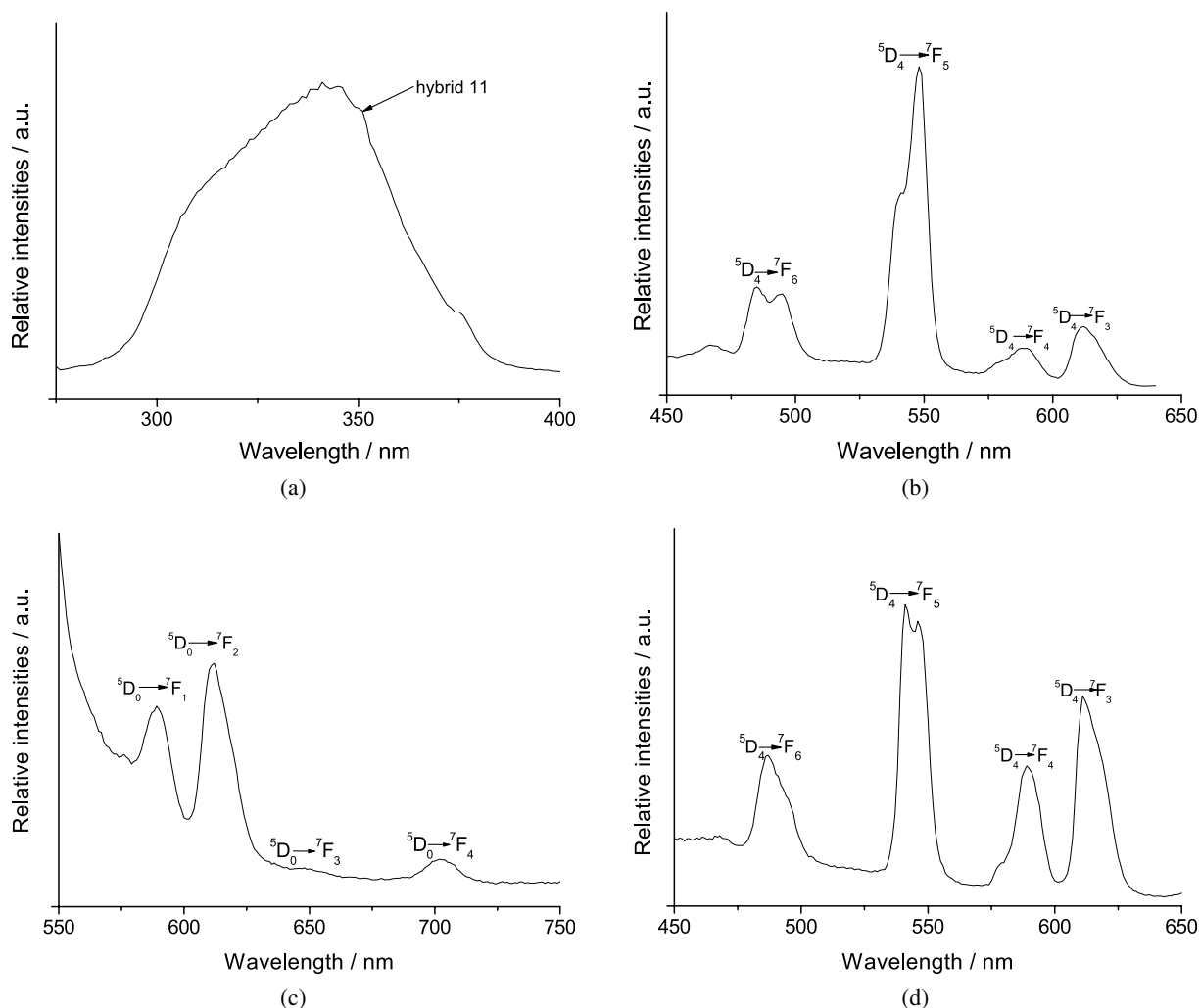


Fig. 4. Excitation spectrum of hybrid 11 (a) and emission spectra of hybrid Tb^{3+} (b), hybrid Eu^{3+} (c) and hybrid 11 (d).

level is equal to 22472 cm^{-1} (corresponding to the peak at 445 nm); likewise the latter energy level is 20400 cm^{-1} (490 nm, $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition). Therefore, it can be predicted that EPB-TESPIC shows a good energy match and sensitizes the luminescence of Tb^{3+} in terms of the inverse energy transfer theory.

The excitation spectrum for the hybrid 11 is shown in Fig. 4(a). The excitation spectrum was obtained by monitoring the emission of the Tb^{3+} at 5433 nm. It has been observed that all the systems have similar excitation spectra that are dominated by a broad band, ranging from 280 to 380 nm, with the maximum peak at about 341 nm, which can be

attributed to the f-f transition of Tb(III) ion. The emission spectra for the hybrid Tb^{3+} , hybrid Eu^{3+} , hybrid 11 are shown in Fig. 4(b–d), respectively. In Fig. 4(b), it can be seen that the emission lines of hybrid Tb^{3+} can be assigned to the characteristic $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) transitions of Tb^{3+} at 490, 548, 588 and 611 nm, respectively, and the fluorescence intensity at 548 nm is the strongest for the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission, which is the most prominent one. In Fig. 4(c), the emission lines of hybrid Eu^{3+} can be assigned to the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3, 4$) transitions of Tb^{3+} at 589, 612, 649 and 702 nm, respectively. The fluorescence intensity at 612 nm is the strongest for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission, which is

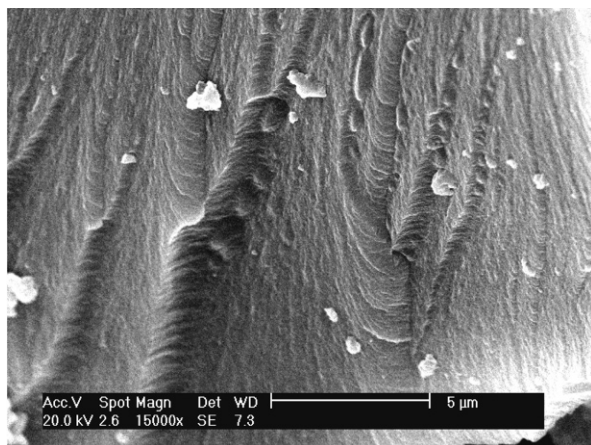


Fig. 5. Selected SEM image of hybrid Tb^{3+} molecular-based hybrids.

the most prominent one. Comparing the rare earth hybrids with the linkage derived by hydroxyl benzoic acid, it is found that the change of ester group and carboxylate group does not have an apparent influence on the luminescence because the coordination environment around rare earth ions is similar in the two kinds of the hybrid systems.

But for Eu^{3+} – Tb^{3+} co-doped hybrids, the fluorescence intensities at 589 and 611 nm, which are assigned to the characteristic transitions $^5\text{D}_4$ – $^7\text{F}_4$ and $^5\text{D}_4$ – $^7\text{F}_3$ of Tb^{3+} or $^5\text{D}_4$ – $^7\text{F}_1$ and $^5\text{D}_4$ – $^7\text{F}_2$ of Eu^{3+} , are as strong as the fluorescence intensity of the characteristic transitions $^5\text{D}_4$ – $^7\text{F}_5$ (at 542 nm). Composing the blue emission from $^5\text{D}_4$ – $^7\text{F}_6$, red emission from $^5\text{D}_4$ – $^7\text{F}_5$, yellow emission from $^5\text{D}_4$ – $^7\text{F}_4$ and red emission from $^5\text{D}_4$ – $^7\text{F}_3$, it can be expected to gain a kind of white luminescent hybrid system by co-doping Eu^{3+} and Tb^{3+} .

From Fig. 5, we can see that the scanning electron micrograph looks like the trunk of a pine tree, which demonstrates that rare earth complexes have been dispersed within silica homogeneously due to covalent bonds bridged between different phases. So we can conclude that the hybrid Tb^{3+} is apt to grow into infinite chainlike structure and retain the coordinated positions in corresponding bulk materials. In the process of co-hydrolysis and polycondensation, the structure of hybrids can be formed in accordance with different kinds of competitive mechanisms. The first one is the tendency to form

a one-dimensional chainlike structure which is due to ethylparaben ligand, and the second one is the tendency to form a polymeric network structure of Si–O, but the first one plays a major role. In this way, the trunk structure is achieved for the dominant growth along the direction of terbium coordination polymer chain in the former tendency.

4. Conclusion

In summary, we have designed the molecular-based hybrid systems with crosslinking reagent derivatives (TESPIC) and Ethylparaben (EPB), and successfully gained a functional bridge molecule which plays a double role. On the one hand, it can coordinate to lanthanide ions through carbonyl groups; on the other hand, the hydrolysis and polycondensation reactions between triethoxysilyl of EPB-TEAPIC and TEOS are responsible for the formation of Si–O–Si network structures for they have the same alkoxy groups. A series of luminescent molecular-based hybrid materials using EPB-TESPIC coordinated to a different ratio of Tb^{3+} and Eu^{3+} was constructed for the first time. Composing the blue emission from $^5\text{D}_4$ – $^7\text{F}_6$, red emission from $^5\text{D}_4$ – $^7\text{F}_5$, yellow emission from $^5\text{D}_4$ – $^7\text{F}_4$ and red emission from $^5\text{D}_4$ – $^7\text{F}_3$, it can be expected to obtain the white luminescence by co-doping Eu^{3+} and Tb^{3+} in these hybrid systems.

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