

# From chemistry to materials, design and photophysics of functional terbium molecular hybrids from assembling covalent chromophore to alkoxysilanes through hydrogen transfer addition

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Received 6 January 2006; received in revised form 16 March 2006; accepted 23 March 2006

Available online 30 March 2006

## Abstract

Two silica-based organic–inorganic hybrid materials composed of phenol (PHE) and ethyl-*p*-hydroxybenzoate derivatives (abbreviated as EPHBA) complexes were prepared via a sol–gel process. The active hydroxyl groups of PHE/EPHBA grafted by 3-(triethoxysilyl)-propyl isocyanate (TESPIC) through hydrogen transfer reaction were used as multi-functional bridged components, which can coordinate to  $Tb^{3+}$  with carbonyl groups, strongly absorb ultraviolet and effectively transfer energy to  $Tb^{3+}$  through their triplet excited state, as well as undergo polymerization or crosslinking reactions with tetraethoxysilane (TEOS), for anchoring terbium ions to the silica backbone. For comparison, two doped hybrid materials in which rare-earth complexes were just encapsulated in silica-based sol–gel matrices were also prepared. NMR, FT-IR, UV/vis absorption and luminescence spectroscopy were used to investigate the obtained hybrid materials. UV excitation in the organic component resulted in strong green emission from  $Tb^{3+}$  ions due to an efficient ligand-to-metal energy transfer mechanism.

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*Keywords:* Molecular hybrid materials; Covalent bond; Photoluminescence; Sol–gel

## 1. Introduction

Rare-earth ions (noted as RE) have been well known as important components in luminescent materials for they have sharp and intense emission bands based on *f–f* electronic transitions and a wide range of lifetimes suitable for various applications. Complexation of these ions by organic ligands, such as  $\beta$ -diketones, aromatic carboxylic acids, and heterocyclic derivatives, offers several advantages to design efficient light-conversion molecular device (LCMDs) [1–4]. In these systems, ligands absorbed light energy and transferred the absorbed energy to the emitting metal ion (the so-called antenna effect), thus markedly increasing the absorption coefficients [5]. Recently, lanthanide organic–inorganic hybrid materials, incorporation of RE complexes in inorganic matrices, have attracted considerable interest, not only because of the potential

important use as various functional materials with attractive luminescent properties, but also because of the application of the sol–gel process, a simple and convenient approach to synthesize this kind of organic–inorganic materials, which allows mixing of inorganic and organic components at the predicated scale and under mild temperature processing conditions. Many studies have been devoted to encapsulation of lanthanide luminescent molecules in silica-based sol–gel matrices with the purpose of combining the good photophysical properties of the organic component with the favorable thermal and mechanical characteristics of inorganic networks [6–15]. However, many problems, including clustering of the emitters, inhomogeneous dispersion of both components, leaching of dopants, and limited concentration of organic species, occur in these kinds of organic–inorganic materials for only weak interactions (hydrogen bonding, van der Waals force, or weak static effect) exist between lanthanide complexes and silica networks [16]. Thus, attention has been drawn to covalently grafting the ligands to the

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inorganic networks via Si–C bonds, which can overcome the above-mentioned problems [17–28].

Our recent work concerns the latter system. We have successfully realized two paths to construct RE hybrid materials with chemical bonds. One is to modify the amino groups of aminobenzoic acids using 3-(triethoxysilyl)propyl isocyanate (abbreviated as TESPIC) through the reaction between the amino group of acids and the internal ester group (isocyanate) of TESPIC, further assembling the above modified bridge ligands with RE ions and inorganic precursors (TEOS) to hybrid systems [26,27]. The other path is to modify the carboxylate group of aromatic carboxylic acids through the amidation reaction between the carbonyl groups of acids and the amino group of amino-silane crosslinking reagents, then composing hybrid materials with covalent bonds [29–31]. Moreover, according to the molecular fragment principle to assembly of ternary RE complexes, we also achieved the cooperative design of RE hybrid materials with crosslinking reagent as structural ligand and photoactive sensitizer as functional ligand [32]. Based on the above research, we can modify the two typical crosslinking reagents with different groups (TESPIC and 3-aminopropyl-methyl-diethoxysilane) together through the hydrogen transfer addition reaction to form di-urea linkages between isocyanate and the amino groups, and then design ternary hybrid materials with chemical bonding [33]. In view of these researches, it can be recognized that the key procedure to construct molecular-based materials is to design a functional bridge molecule (ligand) by the grafting reaction, which can behave as double functions of both coordinating RE ions and sol-gel processing to constitute a covalent Si–O network [26–33]. With the idea, in this paper, two novel kinds of precursor containing functional groups [denoted phenol (PHE)–Si and ethyl-*p*-hydroxybenzoate (EPHBA)–Si] were synthesized through the new technology path, hydrogen atom between hydroxyl group of organic ligands (PHE and EPHBA) and the internal ester group of TESPIC (see Fig. 1). The luminescent materials (denoted Hybrid I) were prepared using PHE–Si/EPHBA–Si as one of the precursors, which was reacted with tetraethoxysilane (TEOS) by hydrolysis and condensation in the presence of lanthanide ion  $Tb^{3+}$  (see Fig. 2). For comparison, two doped hybrid materials consisting of a simple mixture of PHE/EPHBA,  $Tb^{3+}$ , and the silica gel (denoted Hybrid II) was also prepared. A comparative study on the luminescence properties of Hybrid I and Hybrid II was performed.

## 2. Experimental

### 2.1. Chemicals and procedures

Terbium nitrate was obtained by dissolving  $Tb_4O_7$  in concentrated nitric acid. All the other reagents are analytically pure.

A typical procedure for the preparation of PHE–Si/EPHBA–Si was as follows: PHE (or EPHBA) (1 mmol)

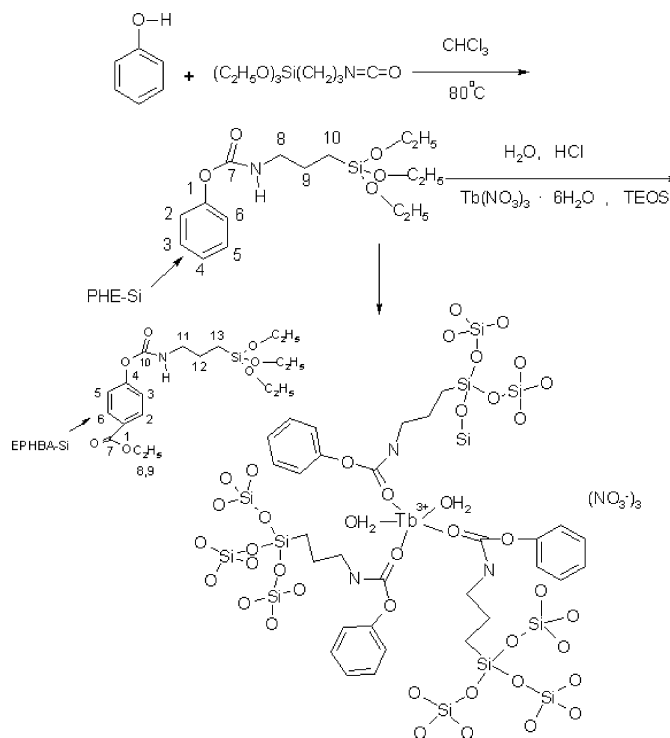


Fig. 1. Scheme of the synthesis process of PHE–Si and predicted structure of hybrid materials.

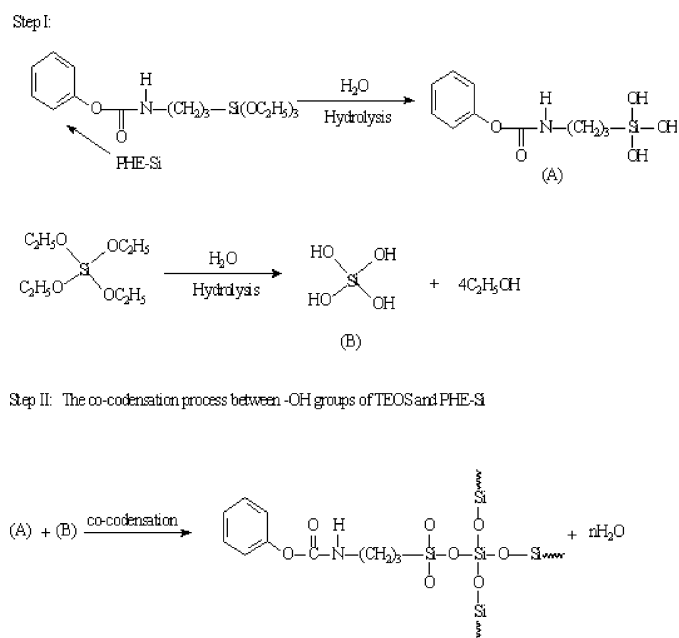


Fig. 2. Scheme of hydrolysis and polycondensation processes between PHE–Si and TEOS.

was dissolved in 15 mL of  $CHCl_3$ . 1.0 mmol (2.5 g) of TESPIC was added dropwise into the solution with stirring. The mixture was heated at  $80^\circ C$  in a covered flask for approximately 10 h. Then cold hexane was added to precipitate the white powder. The powder was obtained by filtration, purified in hexane and dried in a vacuum. PHE–Si ( $C_{16}H_{27}O_5NSi$ ): Element analysis data: *Anal.*

Calcd.: C, 56.28; H, 7.97; N, 4.10. Found: C, 55.91; H, 7.61; N, 3.95.  $^1\text{H}$  NMR (DMSO): 9.27(1H,s), 7.17(2H,m), 6.75(2H,m), 3.97(1H,m), 3.70(6H,m), 1.45(4H,t), 1.14(9H,m), 0.51(2H,t).  $^{13}\text{C}$  NMR (DMSO): 157.3–156.1 ( $\text{C}_3$ – $\text{C}_5$ ), 129.2–129.1( $\text{C}_4$ – $\text{C}_1$ ), 118.676( $\text{C}_7$ ), 44.9( $\text{C}_8$ ), 115.2–115.1( $\text{C}_2$ – $\text{C}_6$ ), 23.5( $\text{C}_9$ ), 57.6( $\text{CH}_2(\text{OEt})$ ), 18.2( $\text{CH}_3(\text{OEt})$ ), 7.2( $\text{C}_{10}$ ). EPHBASi ( $\text{C}_{19}\text{H}_{31}\text{O}_7\text{NSi}$ ): Element analysis data: Anal. Calcd.: C, 55.19; H, 7.56; N, 3.39. Found: C, 55.40; H, 7.29; N, 3.01.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.97(2H,d), 6.88(2H,d), 6.02(1H,s), 4.37(2H,m), 3.81(5H,m), 3.75(1H,m), 3.31(1H,s), 1.74(2H,m), 1.39(4H,m), 1.24(9H,m), 0.68(2H,d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 166.5( $\text{C}_7$ ), 159.1( $\text{C}_1$ ), 156.3–155.1( $\text{C}_2$ – $\text{C}_6$ ), 137.2–136.1( $\text{C}_3$ – $\text{C}_5$ ), 131.8( $\text{C}_4$ ), 115.1( $\text{C}_8$ ), 86.6( $\text{C}_9$ ), 58.5( $\text{CH}_2(\text{OEt})$ ), 7.8( $\text{C}_{10}$ ), 45.4( $\text{C}_{11}$ ), 25.1( $\text{C}_{12}$ ), 18.2( $\text{CH}_3(\text{OEt})$ ), 7.6( $\text{C}_{13}$ ).

A sol–gel-derived hybrid material was prepared as follows: PHE–Si/EPHBA–Si was dissolved in ethanol, and TEOS,  $\text{H}_2\text{O}$  were added while stirring; then one drop of diluted hydrochloric acid was added to promote hydrolysis. A stoichiometric amount of  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was added to the final stirring mixture. The molar ratio of  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ :PHE–Si (or EPHBA–Si):TEOS: $\text{H}_2\text{O}$  was 1:3:6:24. (TEOS 0.45 mL, 0.42 g;  $\text{H}_2\text{O}$  0.144 g) After hydrolysis, 2.0 mL of DMF (dimethylformamide) and an appropriate amount of hexamethylene-tetramine were added to adjust the pH to ca. 6–7. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, and then it was aged at  $80^\circ\text{C}$  until the onset of gelation which occurred in about 7 days. The gels were collected as monolithic bulks and were ground into powdered materials for photophysical studies (see Fig. 1).

## 2.2. Physical measurements

Elemental analyses (C, H, and N) were carried out by the Elementar Carlo EL elemental analyzer. FT-IR spectra were measured within the  $4000$ – $400\text{ cm}^{-1}$  region on an infrared spectrophotometer with the KBr pellet technique.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in DMSO on a BRUKER AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples [ $5 \times 10^{-4}\text{ mol L}^{-1}$  tetrahydrofuran (THF) solution] were recorded with an Agilent 8453 spectrophotometer. Phosphorescence spectra (under 77 K) ( $5 \times 10^{-4}\text{ mol L}^{-1}$  THF solution) and luminescence (excitation and emission) spectra of these solid complexes were determined with a Perkin-Elmer LS-55 spectrophotometer, whose excitation and emission slits were 5 and 5 nm, respectively. Scanning electronic microscope (SEM) images were obtained with a Philips XL-30 model instrument.

## 3. Results and discussion

TESPIC belongs to a special silane crosslinking reagent for its internal ester group of isocyanate, which is expected to realize hydrogen transfer reaction with some active

molecules with reactive hydrogen atoms. We have achieved the hydrogen transfer addition reaction between TESPIC and  $-\text{NH}_2$  derivatives [26,27,33]. The hydrogen atoms of the hydroxyl group are also easy to lose, and so it can be predicted that there may exist hydrogen transfer addition reaction from  $-\text{OH}$  to isocyanate of TESPIC. As shown in Fig. 1, hydroxyl group derivatives, PHE and EPHBA can be modified by TESPIC to form the amide (mono-urea,  $-\text{CO}-\text{NH}-$ ) linkage functional bridge molecules PHE–Si and EPHBA–Si. The bridge ligands (PHE–Si and EPHBA–Si) then play two roles: on the one hand, they can coordinate to terbium ions through the oxygen atoms of their amide group; on the other hand, they can facilitate the cohydrolysis and copolycondensation process with TEOS with their ethoxy groups belonging to the TESPIC component through the sol–gel reaction. Finally, the molecular-based hybrid materials can be assembled with strong chemical bonds. According to the reference, the coordination number of water molecules can be estimated to be 2 and the coordination number of  $\text{Tb}^{3+}$  can be predicted to be 8 in the hybrid materials from the experimental decay time by the empirical formula [34–36]. These hybrid materials pertain to molecular degree, which can be considered as the complicated huge molecular network.

The reaction model for the hybridization formula of TEOS and PHE–Si (or EPHBA–Si) is illustrated in Fig. 2. The hybridization of TEOS and PHE–Si (or EPHBA–Si), accordingly, proceeds through a polycondensation reaction between the terminal silanol groups of PHE–Si (or EPHBA–Si) and the OH groups of hydrolyzed TEOS. At the beginning of the reaction, as shown in Fig. 2 (Step I), the individual hydrolysis of PHE–Si (or EPHBA–Si) and TEOS are predominant. Step II, however, is related to the polycondensation reactions between hydroxyl groups of both PHE–Si (EPHBA–Si) and TEOS. By these methods, molecular-based hybrids bearing the Tb–O coordination bond and the Si–O covalent bond exhibit the strong green luminescence of  $\text{Tb}^{3+}$ . Here we name the cooperation of both PHE–Si (EPHBA–Si) and TEOS during the in situ sol–gel process as cohydrolysis and copolycondensation.

The IR spectra for PHE (A), PHE–Si (B), and the hybrid material containing  $\text{Tb}^{3+}$  (C) are shown in Fig. 3. The occurrence of the grafting reaction was evidenced by the bands at about  $1684.32\text{ cm}^{-1}$  due to the absorption of amide groups (CONH), suggesting that TESPIC has been successfully grafted onto the hydroxyl group of PHE. Additionally, a series of strong bands at around  $2981$  and  $2929\text{ cm}^{-1}$  are due to the vibrations of the methylene ( $-\text{CH}_2-$ ) groups in the TESPIC, proving the complete grafting reaction with the coupling agent. After modification of the amino groups of A, the peaks at  $3331$  (B) and  $3400\text{ cm}^{-1}$  (C) originate from the presence of the stretching ( $-\text{NH}-$ ) vibration. The stretching vibration ( $n\text{Si}-\text{C}$ ) located at  $1204\text{ cm}^{-1}$  is still evident in the IR spectra of PHE–Si and the hybrid materials. Furthermore, the strong absorption band at  $1068\text{ cm}^{-1}$  (Si–O–Si) substantiates the

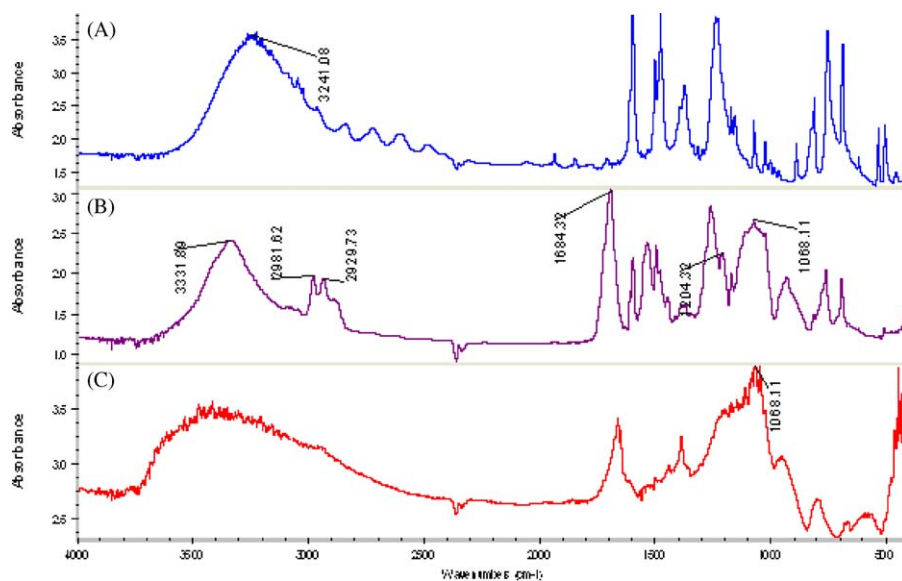


Fig. 3. IR spectra of (A) PHE, (B) PHE-Si, and (C)  $Tb^{3+}$ -PHE-Si-TEOS hybrids.

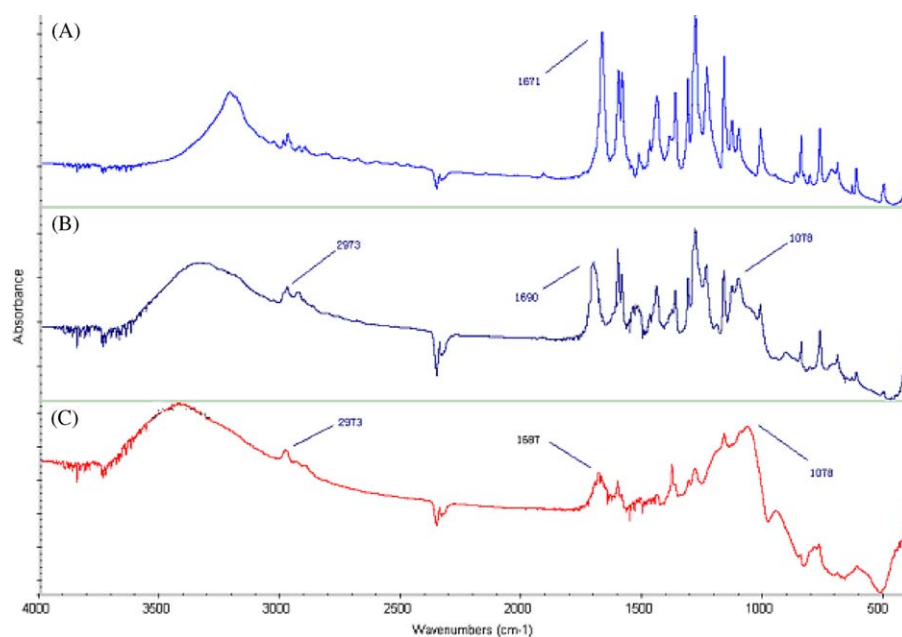


Fig. 4. IR spectra of (A) EPHBA, (B) EPHBA-Si, and (C)  $Tb^{3+}$ -EPHBA-Si-TEOS hybrids.

formation of siloxane bonds. Fig. 4 shows the IR spectra of (A) EPHBA, (B) EPHBA-Si, and (C) EPHBA-Si with  $Tb^{3+}$  ions, giving similar results to guarantee the grafting reactions. The IR spectrum of EPHBA-Si compared with that of EPHBA presents a new band at  $1690\text{ cm}^{-1}$  ascribed to the absorption of amide groups ( $-\text{CO}-\text{NH}-$ ), which indicates that TESPIC has been successfully grafted onto the hydroxyl group of EPHBA. Besides, a series of strong bands at about  $2973\text{ cm}^{-1}$  are due to the vibrations of the methylene ( $-\text{CH}_2-$ ) groups in the TESPIC, further verifying the complete grafting reaction with the crosslinking reagent. After modification of the amino groups of

EPHBA, the peaks at  $3320\text{ (B)}$  and  $3406\text{ cm}^{-1}\text{ (C)}$  originate from the presence of the stretching ( $-\text{NH}-$ ) vibration. The stretching vibration ( $n\text{Si}-\text{C}$ ) located at  $1198\text{ cm}^{-1}$  is still evident in the IR spectra of PHE-Si and the hybrid materials. Moreover, the strong absorption band at  $1078\text{ cm}^{-1}$  ( $\text{Si}-\text{O}-\text{Si}$ ) substantiates the formation of siloxane bonds.

Fig. 5 shows the UV absorption spectra of (A) PHE, (B) PHE-Si and (C) PHE-Si with  $Tb^{3+}$  ions. Comparing the absorption spectra of PHE (A) with that of PHE-Si (B), we can find a blue shift (from  $256$  to  $254\text{ nm}$ ) caused by the grafted coupling agent interfering with the conjugating



major  $\pi$ - $\pi^*$  electronic transition. Furthermore, a red shift (from 254 to 273 nm) is observed upon addition of excess of  $Tb^{3+}$  ions to PHE-Si, which illuminates the formation of a complex between  $Tb^{3+}$  and PHE-Si. Moreover, the newly emerged band at about 210–220 nm proves the existence of C=O groups by isocyanate and its coordination to  $Tb^{3+}$ , further indicating that it is the ureasils (O-CONH-) bridges that play the critical role in coordination site with rare earth. The specific phenomenon was also supported by the EPHBA system (Fig. 6).

Molecular phosphorescence belongs to the excited state characteristic of organic molecules and different phosphorescent emission bands correspond to the different organic ligands. From the phosphorescence spectra of PHE (A) and PHE-Si (B) (Fig. 7), and EPHBA acid (A) and EPHBA-Si (B) (Fig. 8), the obvious blue shifts of 24 nm (9 nm) that occur between PHE and PHE-Si (EPHBA and

EPHBA-Si) in terms of modification of the hydroxyl group can be observed. It can be found that the maximum phosphorescence bands of PHE-Si and EPHBA are located at 409 and 401 nm, respectively, and the triplet state energies of them can be determined to be 24,450 and 24,940  $cm^{-1}$  or so, separately. Then the energy differences between the triplet state energies of PHE-Si and EPHB-Si and the resonant emissive energy level of  $Tb^{3+}$  (20,500  $cm^{-1}$ ) are calculated to be 3950 and 4440  $cm^{-1}$ , respectively. According to the intramolecular energy mechanism [37–46], the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one comes from the triplet level of ligands to the emissive energy level of the  $RE^{3+}$  ion by Dexter's resonant exchange interaction; the second one is just an inverse energy transfer by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy

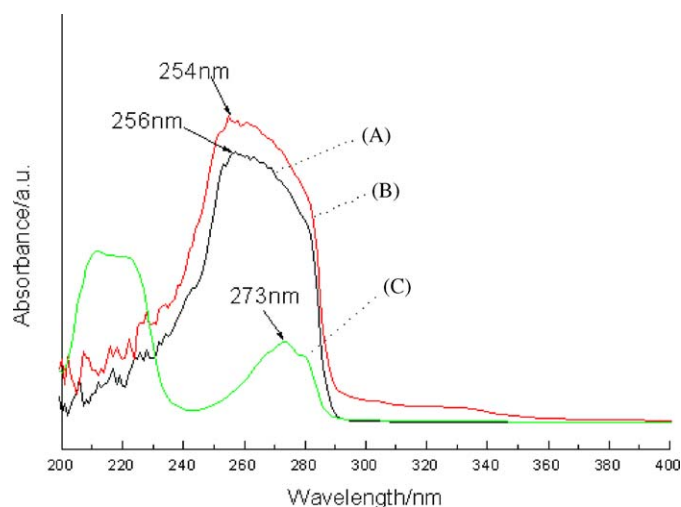


Fig. 5. Ultraviolet absorption spectra of (A) PHE, (B) PHE-Si, and (C)  $Tb^{3+}$ -PHE-Si-TEOS hybrids.

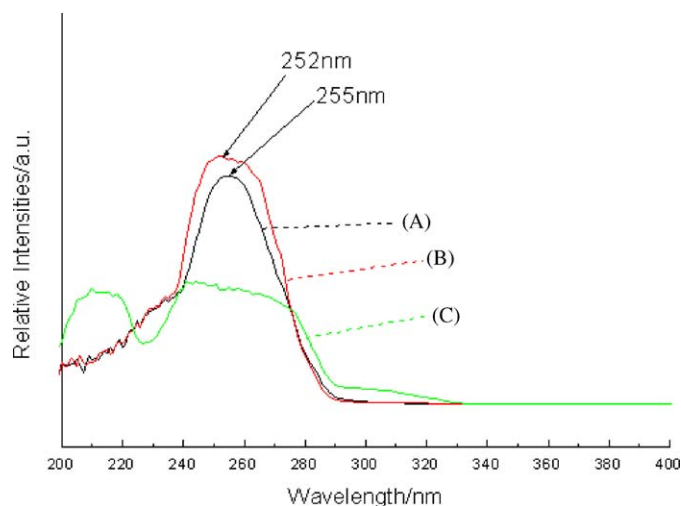


Fig. 6. Ultraviolet absorption spectra of (A) EPHBA, (B) EPHBA-Si, and (C)  $Tb^{3+}$ -EPHBA-Si-TEOS hybrids.

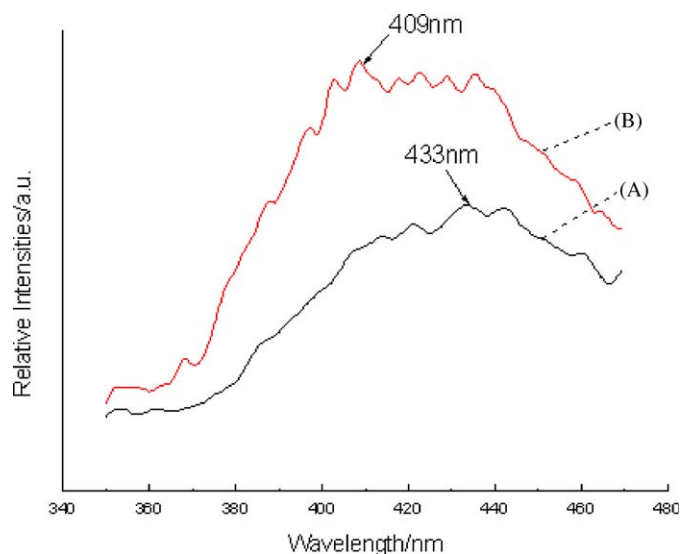


Fig. 7. Phosphorescence spectra of (A) PHE and (B) PHE-Si.

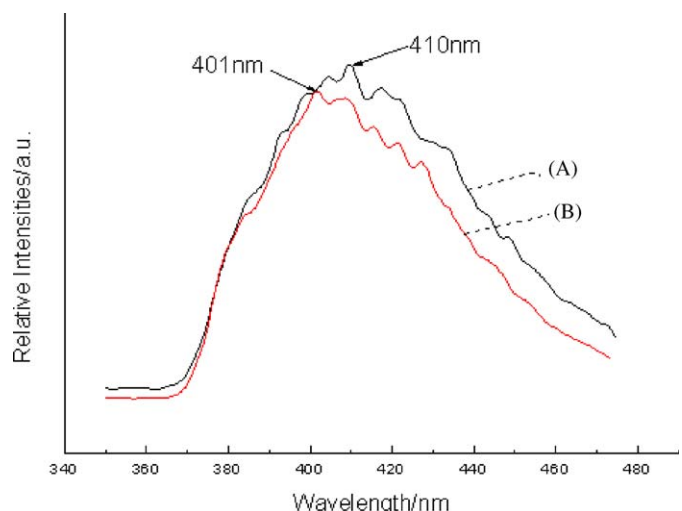


Fig. 8. Phosphorescence spectra of (A) EPHBA and (B) EPHBA-Si.

differences between the triplet level of the ligands and the resonant emissive energy of  $\text{RE}^{3+}$ . Intramolecular energy transfer efficiency in RE complexes follows Dexter's exchange energy transfer theory [47]: with the decrease of energy difference between the triplet state energy of ligands and the resonance emission energy of  $\text{Tb}^{3+}$ , the overlap between the luminescence spectrum of energy donor (ligand) and the absorption spectrum of energy acceptor ( $\text{Tb}^{3+}$ ) increases. Subsequently, the intramolecular energy transfer efficiency increases since it is directly proportional to the overlap integral of them. Thus, ligands with a large energy difference cannot sensitize RE ions effectively because the overlap integral is too small to produce effective intramolecular energy transfer. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity by temperature [48]. The activation energy is approximately equal to the energy difference in the inverse energy transfer process and then a decreasing energy difference increases the energy transfer ratio to decrease the luminescence intensity. Based on this evidence, the conclusion can be drawn that the energy difference is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist. Based on this discussion, it can be primarily predicted that the energy transfer between PHE–Si and EPHBA and  $\text{Tb}^{3+}$  is appropriate and the corresponding hybrid materials can be expected to have strong luminescence.

The excitation and emission spectra of (A) Hybrid I and (B) Hybrid II are shown in Fig. 9. The excitation spectra of the materials were obtained by monitoring the emission of the  $\text{Tb}^{3+}$  ions at 545 nm. As far as Hybrid I is concerned, the excitation spectrum is dominated by two bands located at 245 and 308 nm respectively, which are the characteristic absorptions of lanthanide complexes arising from the efficient transition based on the conjugated double bonds of the aromatic ligands. As a result, the strong green luminescence was observed in their emission spectra, which indicated that the effective energy transfer took place between the aromatic ligand-TESPIC derivative and the chelated  $\text{Tb}^{3+}$  ions. The emission line of the hybrid materials was assigned to the  ${}^5D_4 \rightarrow {}^7F_J$  ( $J = 6, 5$ ) transitions at 490 and 544 nm, respectively. The hybrids show relatively strong emission due to the chemically covalently bonded molecular Si–O network structure between the complexes and the silica. In the spectrum of Hybrid II, the excitation spectrum, mainly dominated by a broad band located at 369 nm, resulted in a broad emission band ranging from 450 to 600 nm with some sharp peaks, but the intensity of the corresponding excitation and emission spectrum is much weaker than in Hybrid I. These results indicate that the energy transfer from the ligands to  $\text{Tb}^{3+}$  is far from efficient in Hybrid II. Fig. 10 demonstrates the excitation and emission spectra of Tb–EPHBA–Si covalent bonded hybrid (A) and doped material (B), representing rather similar emission lines compared with PHE hybrids. Further, we compared the luminescent lifetimes for molecular hybrids and doped hybrids. The luminescent

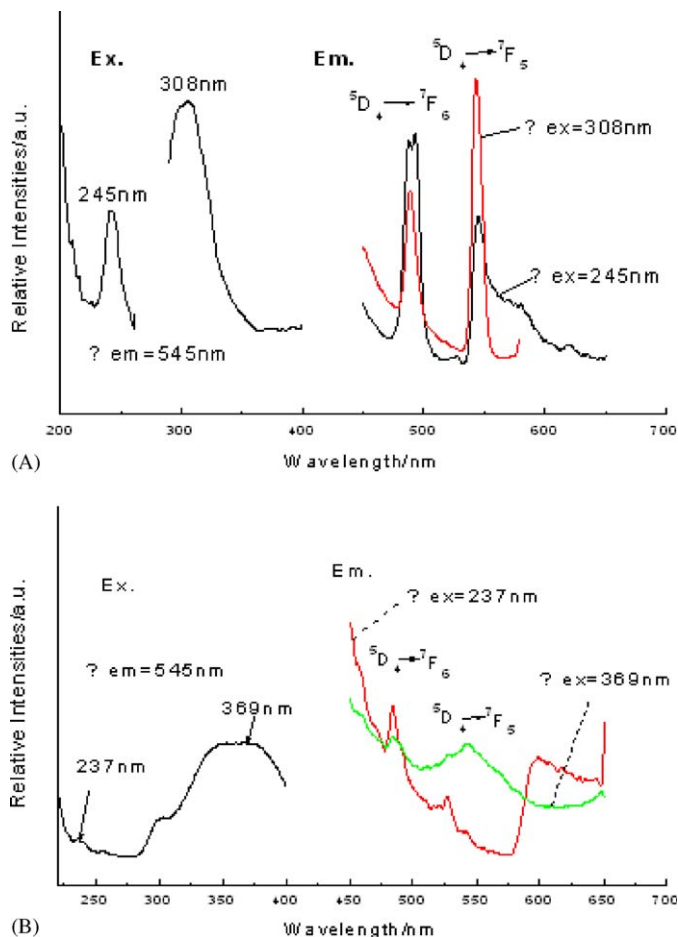
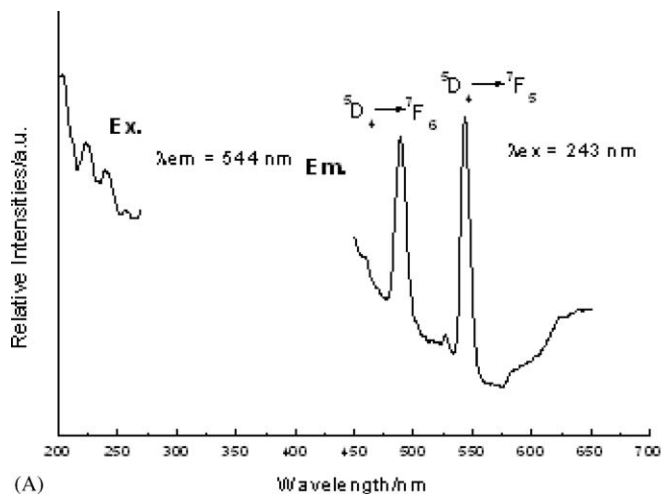


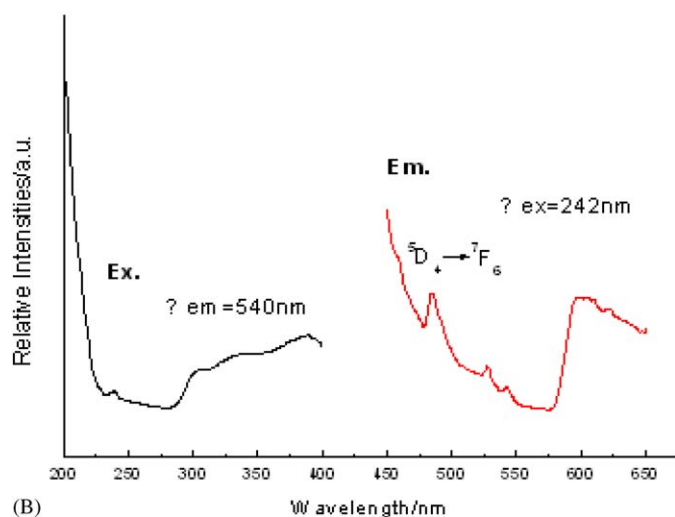
Fig. 9. Excitation and emission spectra of (A) Hybrid I-PHE-Si covalent hybrids and (B) Hybrid II-PHE doped silica hybrids.

lifetimes of Tb–PHE–Si and Tb–EPHBA–Si are 1344 s and 1875  $\mu\text{s}$ , respectively, longer than those of doped hybrids with  $\text{Tb}^{3+}$ .

The scanning electron micrographs for the hybrid materials demonstrate that a homogeneous, molecular-based material was obtained because of strong covalent bonds bridging between the inorganic and organic phase which belongs to a complicated huge molecule in nature, and that they are composed quite uniformly so that the two phases can exhibit their distinct properties together (see Figs. 11(A) and (B)). The hybrid materials with doped RE complexes generally experience phase separation phenomena [29,30]. Ultimately, compared with the two SEM pictures, there exists a little distinction that the hybrid materials of the Tb–EPHBA–Si system wear the complicated microstructure and micro-morphology, which may be due to the difference of the precursor molecules. Different from PHE–Si, EPHBA–Si is a derivative from EPHBA (aromatic carboxylic acids) and its corresponding complex may readily form polymeric structure [49]. Subsequently, the RE complex precursor Tb–EPHBA–Si from modified EPHBA (EPHBA–Si) may be prone to form a polymeric network and then have a great influence on the



(A)



(B)

Fig. 10. Excitation and emission spectra of (A) Hybrid I-EPHBA-Si covalent hybrids and (B) Hybrid II-EPHBA doped silica hybrids.

sol-gel process with TEOS, resulting in the intricate micro-morphology in SEM.

#### 4. Conclusions

In summary, through a novel modification path of an aromatic cycle of hydroxyl groups by hydrogen atom transfer addition reaction with functional TESPIC as crosslinking reagents, two novel luminescent hybrid molecular-based materials were firstly assembled using PHE-Si/EPHBA-Si derivatives coordinated to  $Tb^{3+}$  via a special sol-gel process. Further investigation into the luminescence properties of this material illuminates that the triplet state energy of PHE-Si or EPHBA-Si ligand is quite suitable for the emissive energy level of  $Tb^{3+}$ . Hence, this homogeneous hybrid material with a strong covalent bond has potential application in optical and electronic devices.

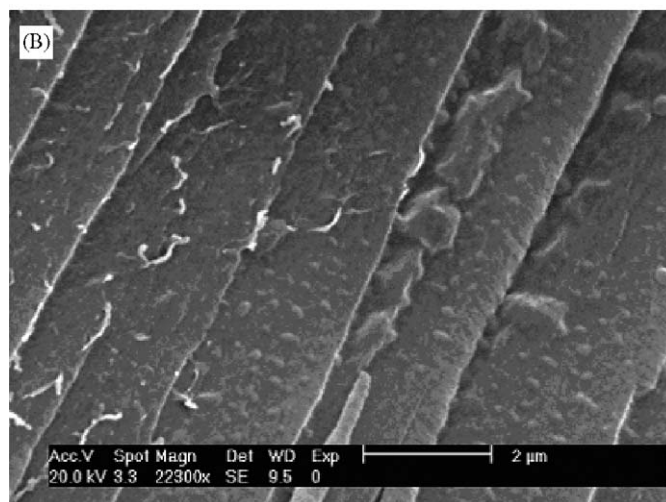
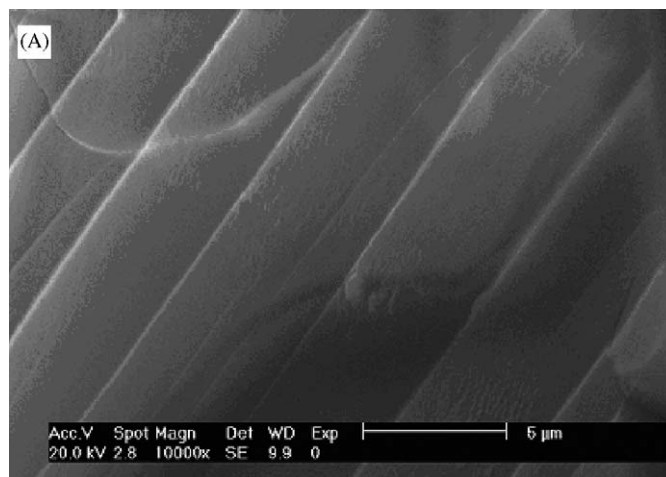


Fig. 11. SEM images for PHE-Si (A) and EPHBA-Si (B) covalent hybrid materials.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (20301013).

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