

Molecular design and photo-physics of quaternary hybrid terbium centered systems with novel functional di-urea linkages of strong chemical bonds through hydrogen transfer addition

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Received 12 October 2006; received in revised form 7 February 2007; accepted 9 February 2007

Available online 24 February 2007

Abstract

Two kinds of crosslinking reagents, 3-aminopropyl-methyl-diethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$, abbreviated as APMES) and *N*-2-aminoethyl-3-aminopropyltriethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_2\text{HN}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, abbreviated as AEAPES) are modified by 3-(triethoxysilyl)-propyl isocyanate (TESPIC) to afford two novel crosslinking molecular derivatives as bridge ligands. Then the ternary organic–inorganic molecular-based hybrid system with these functional bridge ligands and 1,10-phenanthroline (phen) are constructed with the two components equipped with covalent bonds. The two components of APMES (or AEAPES) and TESPIC is linked through –NHC(=O)NH– groups which is applied to coordinate to Tb^{3+} and further formed Si–O backbones after co-hydrolysis and co-polycondensation processes, while phen behaves as the main energy donor for the sensitization of luminescence of Tb^{3+} . Luminescence spectra were utilized to characterize the photo-physical properties of the obtained hybrid system and the above spectroscopic data reveal that the phen in this favorable hybrid system behaves the main energy donor for the luminescence of Tb^{3+} . In this way, the intra-molecular energy transfer process took place within these molecular-based hybrids and strong green and blue emissions of Tb^{3+} have been achieved. © 2007 Elsevier B.V. All rights reserved.

Keywords: Molecular-based hybrid systems; Covalent bond; Photo-physics; Terbium ions

1. Introduction

Inorganic–organic hybrid systems have appeared over the past decade with the expansion of soft inorganic chemistry processes and they provide a wealth of opportunities of both organic and inorganic networks to exhibit their extraordinary properties such as luminescent systems in lighting and displays, optical amplifiers, and lasers [1,2]. Generally speaking, inorganic matrices doped with metal complex especially lanthanide organic complexes introduced in silica matrix have already been found to show superior emission intensities and organic components are considered to be efficient sensitizers for the luminescence of rare earth ions, in short, the antenna

effect. Our research group presently is concentrated on the lanthanide ions complexes with aromatic carboxylic acid, heterocyclic ligands or their derivatives [3–10]. In addition, anchored lanthanide complexes with various ligands in a sol–gel derived matrix have been investigated in many latest studies [11–14]. Indeed, the mild synthetic methods provided by sol–gel approach which is based on hydrolysis/polycondensation reactions of metal alkoxides allow the composites to exhibit high versatility offering a wide range of chances for preparation tailor-made systems in terms of their unique features. In particular, the microstructure, the external shape or the degree of combination between the two phases can be controlled by changing the sol–gel reaction conditions. In recent years, the good control of the coupling between the host and the guest molecule is quite useful for the design of hybrid systems especially for definite applications. For conven-

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tional doping method, because of the only weak functional interactions (such as hydrogen bonding, van der Waals force or static effect) between organic and inorganic components [15], the problems including the uneven distribution of rare earth complexes, the limitation of doped concentration, the quenching effect of luminescent centers and the separation of different phases are difficult to solve. But the synthetic methods based on hydrolysis/polycondensation reaction, which achieve covalent grafting between inorganic and organic components, can solve the above problems successfully. Up to now, a few studies in terms of the covalently bonded hybrids have appeared and the derived molecular-based systems exhibit single-phase appearance even at a high concentration of rare earth complexes [16–22]. We have successfully realized three paths to construct rare earth hybrid systems with chemical bonds. The first is to modify the amino groups of aniline using ester group of TESPIC [23]. The second path is to modify the carboxylic group of aromatic carboxylic acids using the amino group of amino-silane crosslinking [24]. The third is to modify the hydroxyl groups of hydroxyl compounds using ester group of TESPIC [25]. After the modification, we assemble the above modified bridge ligands with rare earth ions and inorganic precursors (TEOS) to construct hybrid systems. Moreover, according to the molecular fragment principle to assemble the ternary rare earth complexes, we also achieved the cooperative design of rare earth hybrid systems with crosslinking reagent as structural ligand and photoactive sensitizer as functional ligand [26]. In view of these researches, it can be recognized that the key procedure to construct molecular-based systems is to design functional bridge molecule (ligand) by the grafting reaction which can behave double functions of coordinating rare earth ions and sol-gel processing to constitute covalent Si–O network [23–26].

In order to restrict the phase separation between organic molecules and the rigid inorganic network, and to increase the concentration of dopant, in this context, we use inner-ester crosslinking reagents, 3-(triethoxysilyl)-propyl isocyanate (TESPIC) to modify two kinds of amino group crosslinking reagents, 3-aminopropyl-methyl-diethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$, abbreviated as APMES) and *N*-2-aminoethyl-3-aminopropyltriethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_2\text{HN}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, abbreviated as AEAPES), then we designed a covalently bonded hybrid inorganic-organic system that incorporated rare earth (Tb) nitrate to T–A and second ligand 1,10-phenanthroline was inserted into the hybrids.

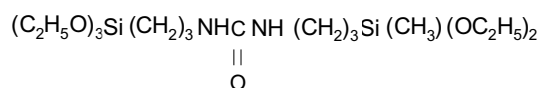
2. Experimental

2.1. Preparation of bridge molecules (T–A) with two kinds of crosslinking reagents

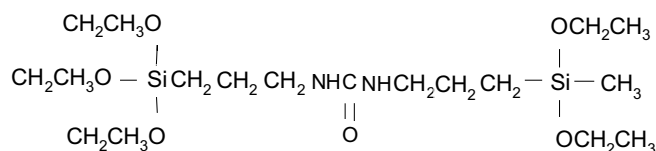
A typical procedure for the preparation of T–A was as follows: 2 mmol 3-(triethoxysilyl)-propyl isocyanate

(0.495 g) was first dissolved in acetone by stirring and 2 mmol APMES (0.382 g) or AEAPES (0.528 g) was then added to the solution by drops. The whole mixture was refluxed at 65 °C under argon atmosphere for 12 h. After isolation, a pale-yellow oil T–A was furnished (abbreviated as T–A1 and T–A2). the data of ^1H NMR are as follows. T–A1 ($\text{C}_{18}\text{H}_{42}\text{N}_2\text{O}_6\text{Si}_2$): ^1H NMR (CDCl_3) d (ppm): δ 4.75 (2H, d), 3.70 (10H, q), 3.02 (4H, q), 2.05 (4H, m), 1.48 (4H, t), 1.12 (15H, t), 0.50 (3H, s). T–A2 ($\text{C}_{21}\text{H}_{49}\text{N}_3\text{O}_7\text{Si}_2$): ^1H NMR (CDCl_3) d (ppm): δ 5.15 (2H, t), 3.85 (12H, q), 3.68 (1H, m), 3.48 (2H, q), 2.87 (2H, q), 2.63 (2H, q), 2.17 (2H, q), 2.02 (2H, m), 1.83 (2H, m), 1.23 (18H, t), 0.58 (4H, t).

The scheme for the molecular composition were shown in the below.



T-A1



T-A2

2.2. Construction of terbium molecular hybrids with molecular bridge T–A

The sol-gel derived hybrid containing rare earth ions was prepared as follows: T–A1/T–A2 was dissolved in absolute ethanol with stirring. A stoichiometric amount of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the final stirring mixture. After 1 h, 1,10-phenanthroline was added to the solution. Then, one drop of diluted hydrochloric acid was added to promote hydrolysis. The mole ratio of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /T–A/phen/ H_2O was 1:3:1:9. The mixture was agitated magnetically to achieve a single-phase, and thermal treatment was performed at 50 °C until the sample solidified (see Fig. 1). For the purpose of comparison, we also prepared hybrid material directly by $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and T–A ligands.

2.3. Physical properties

All measurements were completed under room temperature. Elemental analyses (C, H, N) were carried out by the Elementar Carlo EL elemental analyzer. Infrared spectroscopy with KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the 4000–400 cm^{-1} . ^1H NMR spectra was recorded in CDCl_3 on a bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Luminescent excitation and

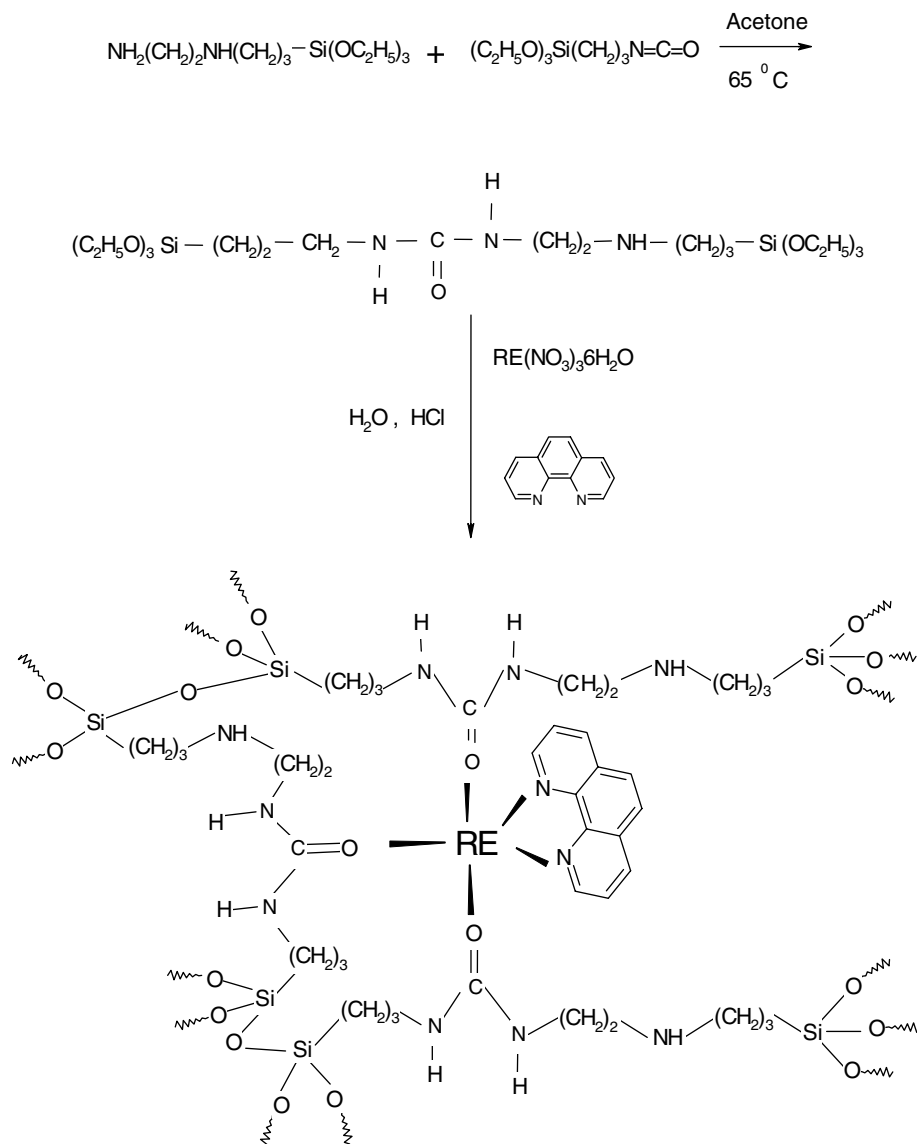


Fig. 1. Scheme of the synthesis process of T-A1 ligand and predicted structure of resulting hybrid systems, T-A1 shows the similar process.

emission spectrums were obtained on a Perkin–Elmer LS-55 spectrophotometer.

3. Results and discussion

The IR spectra of modified bridge ligands T-A1, T-A2 are compared to those of precursor crosslinking reagents (TESPIC and AMPES, AEAPES). The main data and their assignments are shown in Table 1. The occurrence of the grafting reaction is also proved by the bands about 1661 cm^{-1} (T-A1), 1665 cm^{-1} (T-A2) due to the stretching vibration $\nu(\text{C}=\text{O})$ compared with the spectra of AMPES and AEAPES, which suggest that 3-(triethoxysilyl)propyl isocyanate has been successfully grafted onto amidogen group of AMPES and AEAPES, respectively. After the modification, the peaks at 3321 cm^{-1} (T-A1) and 3325 cm^{-1} (T-A2) originate from the presence of the stretching vibration $\nu(\text{N}-\text{H})$ and the peaks at 1491 cm^{-1}

Table 1

The main bands and their assignments of IR spectra for the three crosslinking reagents and their modified bridge ligands

Compounds	$\nu(\text{C}=\text{O})$ (cm^{-1})	$\nu(\text{N}=\text{C}=\text{O})$ (cm^{-1})	$\nu(\text{N}-\text{H})$ (cm^{-1})	$\delta(\text{N}-\text{H})$ (cm^{-1})	$\nu(\text{C}-\text{N})$ (cm^{-1})	$\nu(\text{Si}-\text{C})$ (cm^{-1})
TESPIC	1630	2273–2378			1375	1170
AMPES			3348	1613	1175	1173
T-A1	1661		3321	1491	1341	1168
AEAPES			3335	1613	1131	1172
T-A2	1665		3325	1495	1366	1169

(T-A1), 1495 cm^{-1} (T-A2) derive from the presence of the bending vibration $\delta(\text{N}-\text{H})$. The stretching vibration ($\text{Si}-\text{C}$) located at 1168 cm^{-1} (T-A1) and 1169 cm^{-1} (T-A2) are still evident in the IR spectra of bridge molecules. Compared the IR spectra of TESPIC with T-A1 and T-A2, the absorption peak at $2273\text{--}2378\text{ cm}^{-1}$ for

Table 2
 $\nu(\text{C}=\text{O})$ Stretching vibration frequencies for free and coordinated ligands

	Free ligand	T-A-Tb ³⁺	T-A-phen-Tb ³⁺
T-A1	1661	1638	1641
T-A2	1665	1645	1643

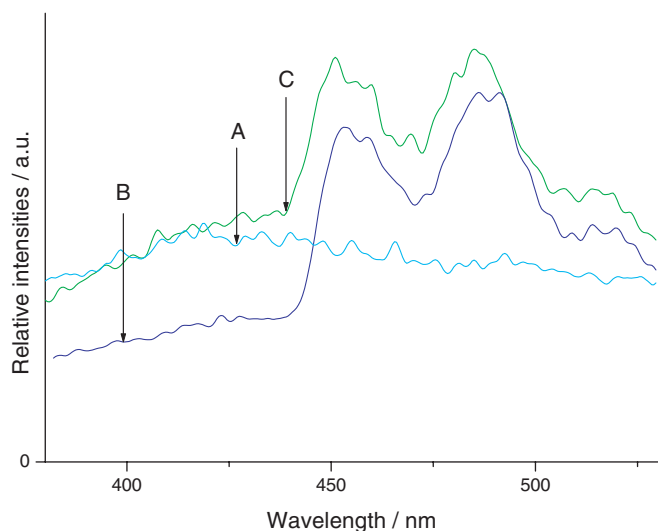


Fig. 2. The phosphorescent spectra of (A) Tb-T-A1 complex, (B) Tb-phen complex and (C) phen-Tb-T-A1 ternary complex.

N=C=O disappeared in the IR spectra of T-A1 and T-A2, which indicates the occurrence of the covalent grafting reaction. Table 2 summarizes the $\nu(\text{C}=\text{O})$ and $\nu(\text{N}-\text{H})$ frequencies for free and coordinated ligands. We can observe that $\nu(\text{C}=\text{O})$ stretching vibrations are shifted to lower frequencies after complexation of Tb³⁺ with the oxygen atom of the carbonyl group.

Fig. 2 shows the phosphorescence spectra of (A) Gd-T-A1 complex, (B) Gd-phen complex and (C) phen-Gd-T-A1 ternary complex. We can observe that B and C are rather similar in terms of the same organic ligand 1, 10-phenanthroline responsible for the emissions. According to the energy transfer and intra-molecular energy mechanism [27,28], intra-molecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one leads from the triplet level of ligands to the emissive energy level of the Tb³⁺ ion by Dexter's resonant exchange interaction [29]; the second one is just an inverse energy transfer by a thermal deactivation mechanism [30]. Established on this theory, the conclusion can be drawn that energy differences is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist. The peak at 419 nm of A shows T-A1's triplet state energy level is approximately 23865 cm⁻¹ which is higher than phen (453 nm, 22075 cm⁻¹), therefore, we suppose that energy transfer process will occur from T-A1 to phen, substantiating that the heterocyclic ligand will become main energy donor and have the possibility to sensitize Tb³⁺ ions [27,28].

The excitation spectra of binary molecular hybrids Tb-T-A and phen-Tb-T-A are shown in Figs. 3 and 4 by monitoring the emission of Tb³⁺ ion at 545 nm. For the excitation spectra of binary molecular hybrids, there exist weak narrow absorption in the short ultraviolet region (shorter than 230 nm), suggesting the bridge molecules cannot behave the dominant energy donor for the luminescence of terbium ions and no effective absorption has been take place. While for the excitation spectra of ternary molecular hybrids, both of phen-Tb-T-A1 (A) and phen-Tb-T-A2 (B) present a broad band at the range of 200–350 nm, centered at 221.5, 241, 255.5, 269, 294, 344 nm, respectively, which indicate that the introduction of phen creates the extensive localized system for the effective energy absorption to sensitize the luminescence of Tb³⁺.

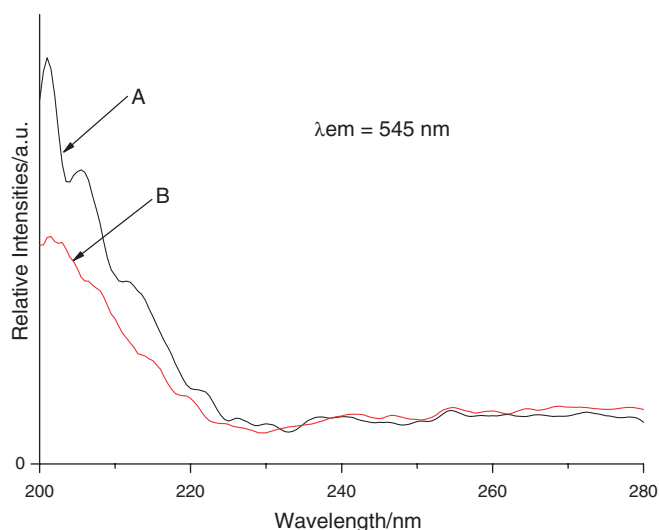


Fig. 3. Excitation spectra of binary molecular-based hybrids (A) Tb-T-A1 and (B) Tb-T-A2.

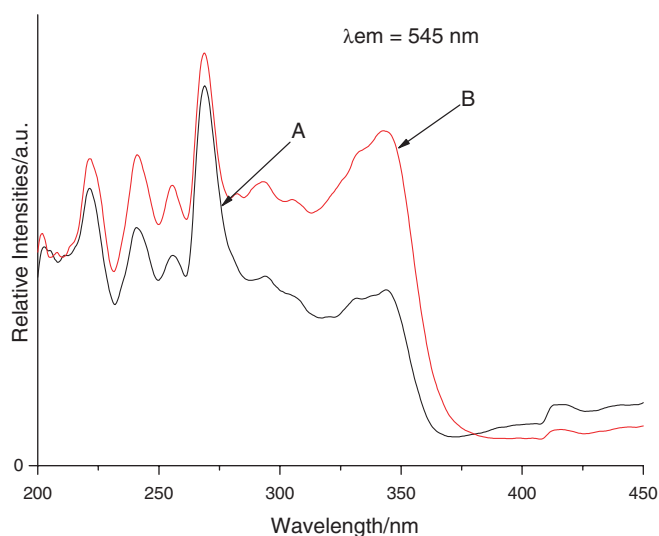


Fig. 4. Excitation spectra of ternary molecular-based hybrids (A) phen-Tb-T-A1 and (B) phen-Tb-T-A2.

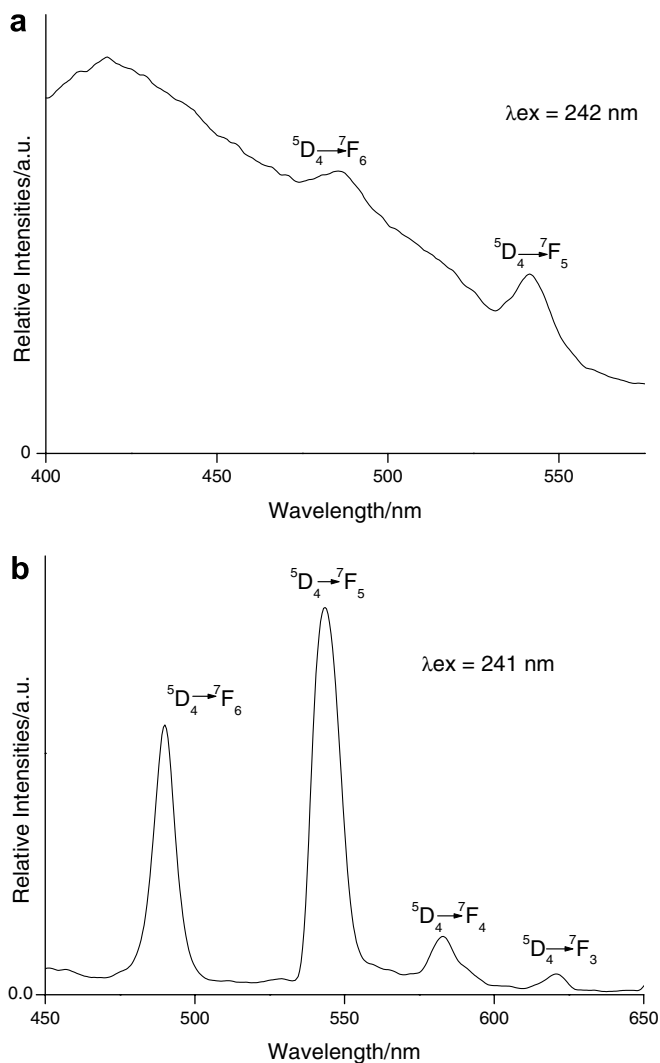


Fig. 5. Emission spectra of (a) Tb-T-A1 and (b) phen-Tb-T-A1 molecular-based hybrids.

The excitation spectra and emission spectra of the resulting hybrid systems are shown in Figs. 2–5. The corresponding emission spectra of these binary and ternary terbium molecular hybrids are shown in Figs. 5 and 6. As shown in Fig. 5, there exist very weak characteristic emission bands corresponded to the blue $^5D_4 \rightarrow ^7F_6$ and green $^5D_4 \rightarrow ^7F_5$ transitions of Tb^{3+} and the emission bands of $^5D_4 \rightarrow ^7F_4$ and green $^5D_4 \rightarrow ^7F_3$ transitions of Tb^{3+} are too weak to be observed, while a broad emission lines with quite high baselines were caused by the emissions of silica hosts. After the introduction of second ligand phen, the emission lines of the ternary terbium molecular-based hybrid systems which were assigned to the transitions from $^5D_4 \rightarrow ^7F_J$ ($J = 6, 5, 4, 3$) transitions at 489.5, 543, 582.5 and 620.5 nm for terbium ions were obtained. Among these emission peaks, the most striking green luminescence ($^5D_4 \rightarrow ^7F_5$) was found in their emission spectra which indicated that the effective energy transfer took place from phen to chelated Tb ions. Binary and ternary terbium molecular hybrids (Tb-T-A2 and phen-Tb-T-A2) show

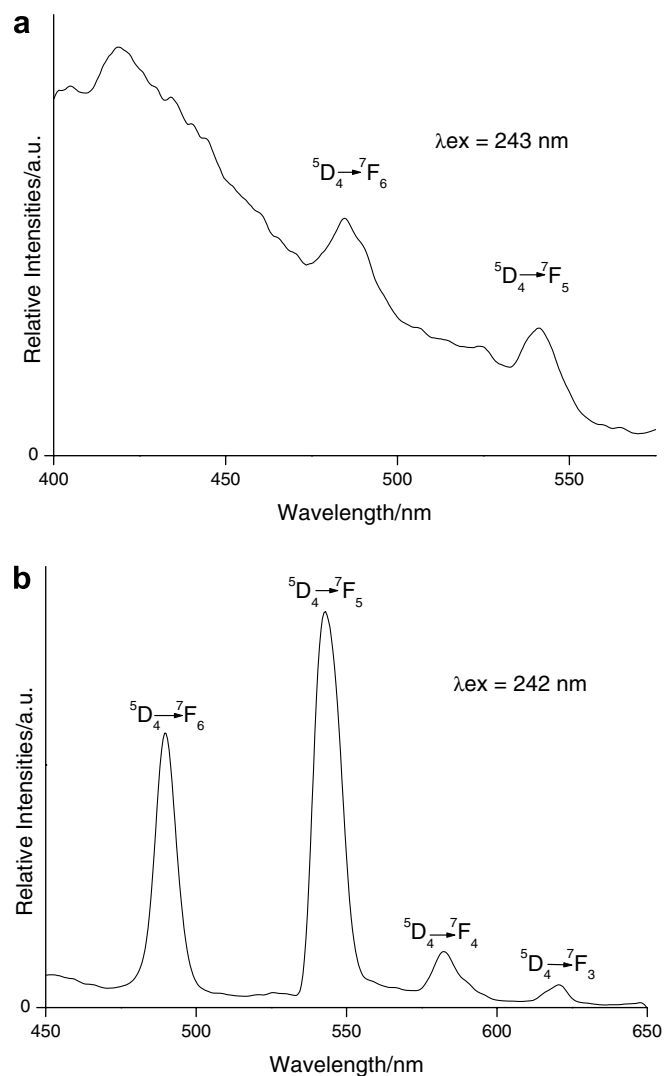


Fig. 6. Emission spectra of (a) Tb-T-A2 and (b) phen-Tb-T-A2 molecular-based hybrids.

the similar feature (Fig. 6). Therefore, we may expect that through this efficient way, leaching of the photoactive molecules can be avoided and higher concentration of metal ions is reached and clustering of the emitting centers may be prevented for the hybrids belong to molecular level. The luminescent lifetimes are longer than general lanthanide complexes whose lifetimes are mostly shorter than 1000 μs , suggesting the molecular hybrids with strong chemical bonds enhance the luminescent stability. Accordingly, we may expect that through this efficient method, leaching of the photoactive centers can be avoided; higher concentration of metal ions is reached and clustering of the emitting centers may be prevented.

Fig. 7 wears the selected scanning electron micrographs for these ternary terbium molecular hybrids, (A) phen-Tb-T-A1 and (B) phen-Tb-T-A2, which verifies that a homogeneous, molecular-based system 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

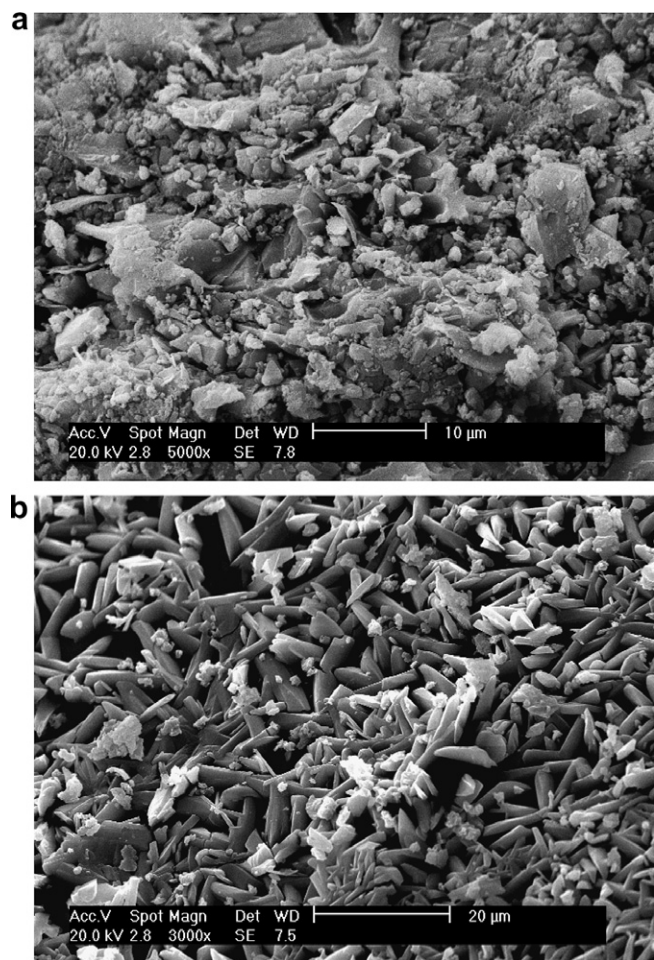


Fig. 7. SEM diagraphs of (a) phen-Tb-T-A1 and (b) phen-Tb-T-A2 molecular-based hybrids.

uniformly so that the two phases can exhibit their distinct properties together, which overcome the phase separation phenomena of the hybrid systems with doped rare earth complexes [28,29]. Ulteriorly, compared with the two SEM pictures, there exists a little distinction that the hybrid systems of phen-Tb-T-A2 possess the regular microstructure and micro morphology, which may be due to the difference of the precursor molecules. Different from phen-Tb-T-A1, phen-Tb-T-A2 is a derivative from (AEAPES) and its molecular fragment possesses two amino groups and longer chain, which readily provide orientation and induction ability, resulting in the template to control the microstructure of hybrids.

4. Conclusions

To investigate the coordination behavior between ureasils and rare earth ions, we designed ternary and quaternary molecular-based hybrid systems with crosslinking reagent derivatives and 1,10-phenanthroline. Among 3-aminopropyl-methyl-diethoxysiliane (APMES) and N-2-aminoethyl-3-aminopropyltriethoxysiliane (AEAPES) have been modified with by 3-(triethoxysilyl)-propyl

isocyanate (TESPIC) as a crosslinking intermediate which plays double roles. On the one hand, it can coordinate to lanthanide ions through carbonyl groups; on the other side of the coin, the hydrolysis and polycondensation reactions among triethoxysilyl of T-A are ascribed to the formation of Si-O-Si network structures for the same ethoxy group of them. Meantime, the strong red or green luminescent systems were achieved. In addition, the resulting hybrids could be shaped as monoliths or as transparent films with desired luminescence efficiency. Variations of the organic ligand structure doomed to diverse coordinating properties and to various absorption capabilities. As a consequence, the energy absorption and transfer from ligands to central ions, or the emission efficiency, could be increased by this potential method.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (20671072).

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