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Designing a family of luminescent hybrid materials by 3-(triethoxysilyl)-propyl isocyanate grafted 2-hydroxynicotinic acid bridge molecules

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Abstract

The study concentrates on the syntheses of modified 2-hydroxynicotinic acid by 3-(triethoxysilyl)-propyl isocyanate (TESPIC) and the preparation of their corresponding organic-inorganic molecular-based hybrid material with the two components equipped with covalent bonds. The bridging unit is a derivative of 2-hydroxynicotinic acid which is utilized to coordinate to Tb^{3+}, Eu^{3+} or Zn^{2+} and further occurred hydrolysis and polycondensation processes by functional triethoxysilyl groups. Ultraviolet absorption, phosphorescence spectra, and luminescence spectra were applied to characterize the photophysical properties of the obtained hybrid material and the above spectroscopic data present that the triplet energy of modified 2-hydroxynicotinic acid efficiently initiates the antenna effect and matches with the emissive energy level of metal ions. As a result, the intramolecular energy transfer process completed within these molecular-based hybrids and strong green or red emissions of Ln^{3+} have been obtained.
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Keywords: Molecular-based hybrids; Covalently bond; Rare earth ions; Photoluminesccence

1. Introduction

The incorporation of metal ions into silica gels and glasses is quite attractive for a variety of technological applications including optical components, for example, fiber amplifiers, solid-state lasers [1,2]. Lanthanide containing hybrid materials have been utilized as phosphors or luminescent materials on the grounds of their sharp, intense f–f electronic transitions. Moreover, a large amount of rare earth complexes exhibit a bright and narrow metal ions characteristic emission. These corresponding emissions are often aroused by a mechanism called as "antenna effect", defined as a light conversion mechanism through an energy absorption and transfer order which is that the diverse ligands choose distinct absorptions and

lead to lanthanide ions emissions. In recent studies, anchored lanthanide complexes by aromatic carboxylic acids, β-diketones or heterocyclic ligands in a sol–gel derived matrix has been researched in detail [1–6]. However, the two networks remain as individual moieties connected only via physical mixture and it seems difficult to solve the problem of clustering of emitting centers because only weak interactions (such as hydrogen bonding, van der waals force or weak static effect) present between organic and inorganic components. Besides, inhomogeneous dispersion of two phases and bleaching of the photoactive molecules frequently occur in this kind of hybrid system for which the concentration of complexes is also prohibited. Following the classification by Sanchez and Lebeau [7], class II is called the one that has the structure properties of chemical connections, through covalent bonding, between the organic and inorganic parts. Lately, a few researches in terms of the covalently bonded hybrids have appeared and the as-derived

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molecular-based materials exhibit monophasic appearance even at a high concentration of rare earth complexes [8–15]. Compared with diverse synthetic approaches, sol–gel technique which is established on hydrolysis/poly-condensation reactions of metal alkoxides has been used to prepare silicate hybrids with a wide range of unusual properties such as convenience, low temperature, versatility [3–6]. The describing tremendous excellence can be further realized by altering the sol–gel processing conditions that permit the control of the microstructure, the external shape or the degree of combination between the two phases.

Some previous researches have concentrated on the modification of pyridine-dicarboxylic acid or their derivatives [12] and Zhang et al. focus on modification of hetero cyclic ligands like 1,10-phenanthroline and bi-pyridyl [8,9]. Our research team presently did extensive work in the preparation of –NHC(=O)NH– urea bridges connecting both siliceous backbone and aromatic carboxylic acids [10,16]. We have successfully realized two paths to construct rare earth hybrid materials with chemical bonds. One is to modify the amino groups of aminobenzoic acids using 3-(triethoxysilyl)-propyl isocyanate (TESPIC) through hydrogen transfer addition reaction between the amino group of acids and intern ester group (isocyanate) of TESPIC, furtherly assembling the above modified bridge ligands with rare earth ions and inorganic precursors (tetraethoxysilane, TEOS) to hybrid systems [10,16]. 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 [17–19]. Moreover, according as the molecular fragment principle to assembly of ternary rare earth complexes, we also achieved the cooperative design of rare earth hybrid materials with crosslinking reagent as structural ligand and photoactive sensitizer as functional ligand [20]. On the basis of the above research, we can modify the two typical crosslinking regents with different groups (TESPIC and 3-aminopropyl-methyl-diethoxylsiliane, etc.) 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 [21]. In view of these researches, it can be recognized that the key procedure to construct molecular-based materials is to design of functional bridge molecule (ligand) by the grafting reaction, which can behave double functions of coordinating to rare earth ions and sol–gel processing to constitute covalent Si–O network [10,16–21]. Besides, it is worthy pointing out that Carlos and co-workers divided amino-functional hybrids lacking metal ions into two major parts such as di-ureasils (–NHC(=O)NH–) and di-urethanesils (–NHC(=O)O–) [22,23]. The latter di-urethanesils stimulated us to investigate the hydroxyl groups activity in regard to isocyanate groups and put emphasis on the influence of di-urethane moieties on the luminescence of resulting hybrids, in this present work, we firstly use 2-hydroxynicotinic acid as organic ligand, then we designed a covalently bonded hybrid inorganic-organic system that founded on the hydrolysis and poly-condensation reactions by triethoxysilyl groups of modified 2-hydroxynicotinic acid (2-(3-(triethoxysilyl)propylcarbamoyloxy)nicotinic acid denoted as HNIC-Si). The reaction model for the hybridization formula of this molecular-scale hybrid may be described in Fig. 1.

2. Experimental

2.1. Chemicals and procedures

2-Hydroxynicotinic acid and 3-(triethoxysilyl)-propyl isocyanate were provided by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents were used as received. A typical procedure for the preparation of HNIC-Si was as follows: 2 mmol of 2-hydroxynicotinic acid was first dissolved in dehydrate tetrahydrofuran by stirring and 2 mmol of 3-(triethoxysilyl)-propyl isocyanate was then added to the solution by drops. The whole mixture was refluxing at 65 °C under argon for 12 h. After isolation, a pale yellow powder HNIC-Si was furnished. ^{1}H NMR (CDCl$_3$) C$_{16}$H$_{26}$O$_7$N$_2$Si: δ 14.77 (1H, s), 8.40 (1H, m), 7.97 (1H, m), 6.69 (1H, t), 4.26 (1H, t), 3.60 (2H, m), 3.66 (1H, d), 3.30 (2H, s), 1.77 (7H, m), 1.1 (5H, d), 1.05 (4H, s). ^{13}C NMR (CDCl$_3$): δ 164.9 (C$_6$), 164.5 (C$_4$), 146.1–141.4 (C$_1$–C$_5$), 116.6 (C$_7$), 108.6–106.9 (C$_2$–C$_3$), 66.5 (CH$_2$(OEt)), 40.3 (C$_8$), 33.1 (C$_9$), 23.3 (CH$_3$(OEt)), 14.6 (C$_{10}$). The sol–gel derived hybrid containing metal ions was prepared as follows: HNIC-Si was dissolved in dimethylformamide(DMF) with stirring, minimal NaOH was used to adjust the pH to 6–7. A stoichiometric amount of Ln(NO$_3$)$_3$ · 6H$_2$O (Eu(NO$_3$)$_3$ · 6H$_2$O, Tb(NO$_3$)$_3$ · 6H$_2$O) was added to the solution. Then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. The mole ratio of Ln(NO$_3$)$_3$ · 6H$_2$O/HNIC-Si/TEOS/H$_2$O was 1:3:6:9. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, then it was aged at 50 °C until the onset of gelation which occurred within 7 days. The gels were collected as monolithic bulks and ground as powder materials for the photophysical studies (see Fig. 2). The concentration of Ln(III) ions in covalent hybrids were measured under the traditional complexometric titration method [24]. Hybrids were through nitration and titrated with EDTA solution, using a buffer (pH 5.8) and xylenol-orange as indicator. The measured contents of Eu(III) and Tb(III) ions in hybrids were 10.73% and 11.04%, respectively, that were in agreement with the stoichiometry [Ln(a)$_3$] · 6SiO$_2$ (a = HNIC-Si after hydrolysis reactions, Anal. Calc.: 10.70 for Eu; 11.11 for Tb, %). For the comparison purpose and studying the coordination status between carboxyl groups and d^{10} metal ions (Zn^{2+}), we also introduced Zn(Ac)$_2$ · 2H$_2$O into this hybrid backbone using the same technique.
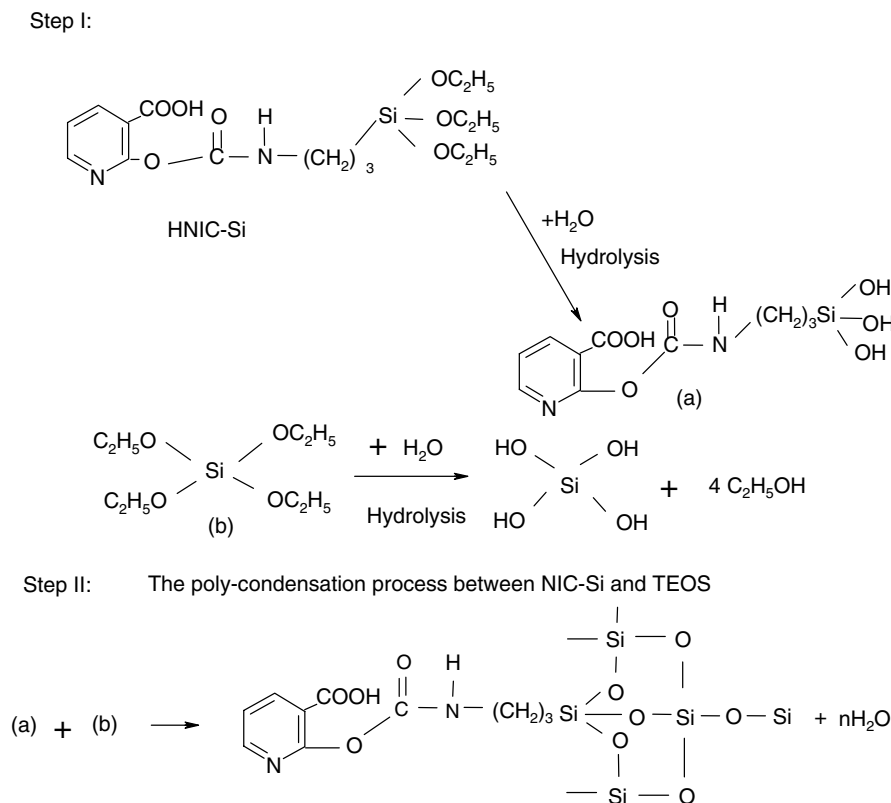
Step I:

Fig. 1. Scheme of hydrolysis and polycondensation processes between HNIC-Si and TEOS.

2.2. Measurements

All measurements were completed under room temperature. ^{1}H NMR spectra was recorded in $CDCl_3$ on a bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol L^{-1} acetone solution) were recorded with an Agilent 8453 spectrophotometer. Fluorescence excitation and emission spectra were obtained on a Perkin–Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm. Scanning electronic microscope (SEM) was measured with JSM-6360LV. Luminescent lifetimes for hybrid materials were obtained with an Ediburg FLS 920 phosphorimeter using a 450 W xenon lamp as excitation source (pulse width, 3 μs).

3. Results and discussion

The reaction model for the hybridization formula of TEOS and HNIC-Si may be illustrated in Fig. 1. The hybridization of TEOS and HNIC-Si, accordingly, proceeds through a polycondensation reaction between the terminal silanol groups of HNIC-Si and the OH groups of hydrolyzed TEOS. At the beginning of the reaction, as shown in Fig. 1 (Step I), the individual hydrolysis of HNIC-Si and TEOS are predominant. The Step II, however, is related

to the polycondensation reactions between hydroxyl groups of both HNIC-Si and TEOS. By these methods, the molecular-based hybrids bearing the Ln–O coordination bond and Si–O covalent bond exhibit the strong green luminescence of Ln^{3+}. Here, we named the cooperation of both HNIC-Si and TEOS during the in situ sol–gel process as cohydrolysis and copolycondensation (similar to copolymerization of organic monomer).

3-(Triethoxysilyl)-propyl isocyanate belongs to a special silane crosslinking reagent molecule for its inter-ester group of isocyanate, which can be 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 –NH_2 derivatives [10,16,21]. Hydroxyl group also belongs to be active group for its hydrogen atoms readily to lose, and so it can be predicted that there may exist the hydrogen transfer addition reaction from –OH to isocyanate of TESPIC. The bridge ligands HNIC-Si then play two roles: one is that they can coordinate to terbium (or europium) ions through the oxygen atoms of their carboxyl group; the other is that they can occur the cohydrolysis and copolycondensation process with TEOS with their ethoxy groups belonging to the TESPIC component through sol–gel reaction (similar to the copolymerization of organic monomer with unsaturated bonds). Finally, the molecular-based hybrid materials can be assembled with strong chemical bonds (the coordination bond between Ln^{3+} and the amide
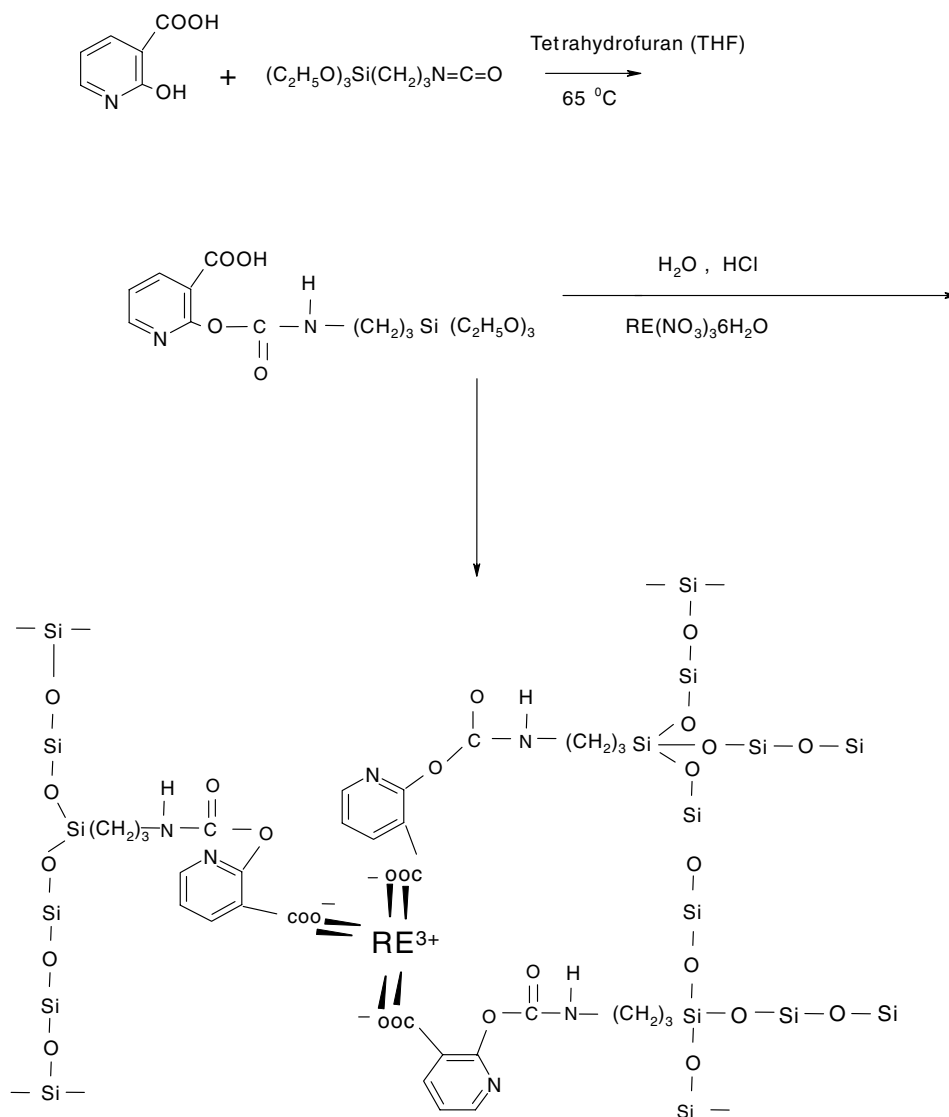
Fig. 2. Scheme of the synthesis process of HNIC-Si and predicted structure of hybrid materials.
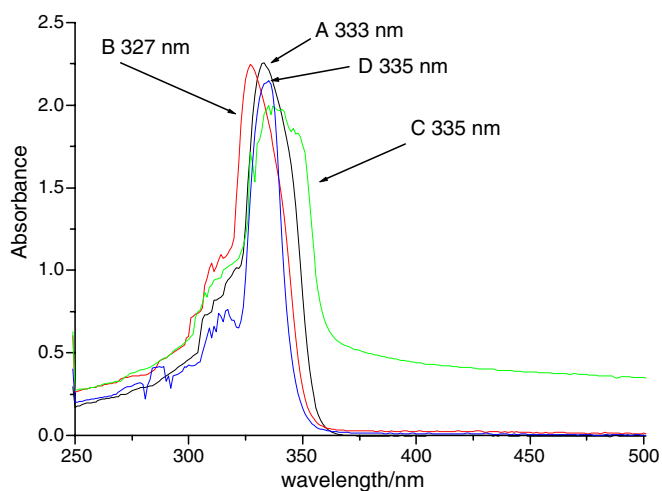

Fig. 3. Ultraviolet absorption spectra of: (A) 2-hydroxynicotinic acid, (B) HNIC-Si, (C) HNIC-Si with excess Eu^{3+} ions, and (D) HNIC-Si with excess Tb^{3+} ions.

bond of bridge ligand and the covalent bond of Si–O network). These hybrid materials pertain to molecular degree, which can be consider as the complicated huge molecular network.

Fig. 3 exhibits ultraviolet absorption spectra of: (A) 2-hydroxynicotinic acid, (B) HNIC-Si, (C) HNIC-Si with excess Eu^{3+} ions, and (D) HNIC-Si with excess Tb^{3+} ions. From the spectra, it is observed that a blue shift (A → B) of the major π–π^* electronic transitions (from 333 to 327 nm) occur and it is estimated that during the grafting reaction of 2-hydroxynicotinic acid, the diverse ligand may limit the conjugating effect of double bonds and enlarge the energy difference levels among electron transitions. In terms of monomer and its lanthanide complexes, the coordination between rare earth ions and HNIC-Si decreases the energy levels of the corresponding transitions and exhibits an obvious red shift from 327 to 335 nm (B → C) and (B → D).
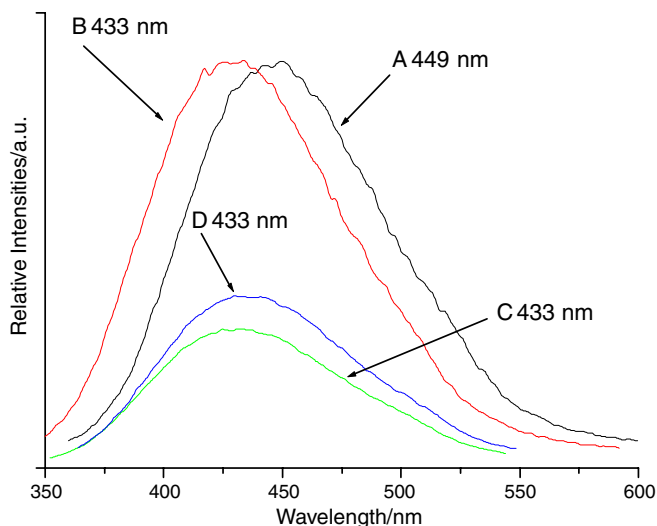
Fig. 4. The phosphorescence spectra of: (A) 2-hydroxynicotinic acid, (B) HNIC-Si, (C) HNIC-Si with excess Tb^{3+} ions, and (D) HNIC-Si with excess Eu^{3+} ions.

As for the phosphorescence spectra of: (A) 2-hydroxynicotinic acid, (B) HNIC-Si, (C) HNIC-Si with excess Tb^{3+} ions, and (D) HNIC-Si with excess Eu^{3+} ions (Fig. 4). Phosphorescence spectrum indicates the character of the organic molecular ligands and a 16 nm blue shift was observed between A and B (from 449 to 433 nm). However, there is no difference between B, C and D because they belong to the same organic groups with the exception that C and D could transfer part of energy to terbium ions and transfer part of energy so as to reduce the relative intensities. It can be found that the maximum phosphorescence band (B) locating at 433 nm determined triplet state energy of HNIC-Si to be 23 095 cm^{-1}. According to the energy transfer and intramolecular energy mechanism [25–33], it can be predicted that the bridging HNIC-Si is suitable for the luminescence of terbium (20 500 cm^{-1}) and europium (17 265 cm^{-1}) ions.

Fig. 5 presents the Tb^{3+} 4f-5d absorption spectra of TEOS sol–gel materials doping directly with Tb^{3+} ions (A), TEOS hybrid materials doping with Tb-2-hydroxynicotinic acid complex (B) and terbium molecular-based hybrids (C). The different spectra correspond to various peak wavelengths (A 241 nm; B 274 nm; C 283 nm) which exhibit the difference in the covalency of terbium ions. According to Judd–Ofelt theory [34,35] and much previous work [36,37] concerning relationship among hosts, bonding forms of RE ions and the transition properties of these metal ions, it has been reported that along with the increase of the peak wavelength, a corresponding degree of covalency between rare earth ions and ligands will be increased. As for A, most non-covalent interactions and plentiful hydroxyl groups existed within Tb^{3+} ions and the surrounding environments. However, B and C that containing Tb–O covalent bonds reflect obvious red shift compared with A (241 → 274 nm; 241 → 283 nm) which are caused by nephelauxetic effects and sensitivity to hosts. In terms
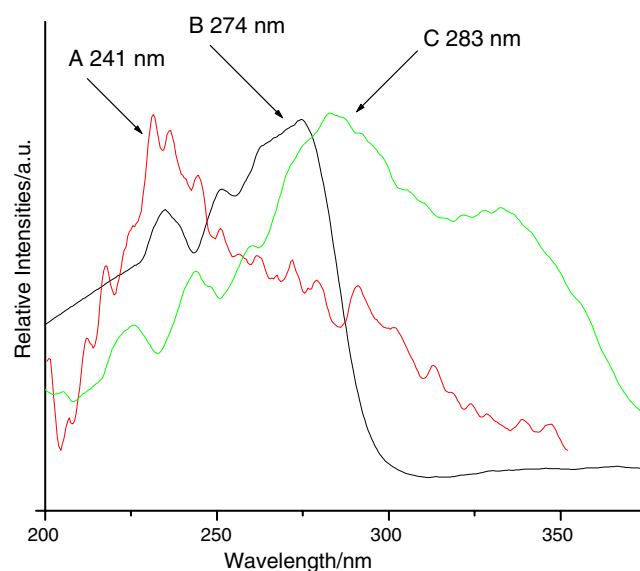

Fig. 5. The absorption spectra of TEOS sol–gel materials doping directly with Tb^{3+} ions (A), TEOS hybrid materials doping with Tb–2-hydroxynicotinic acid complex (B), and molecular-based hybrids (C).

of change between B and C, we may deduce that through the functionalization of strong covalent bonds like Si–O–Si and ureasils, the molecular-based materials decrease the energy difference between $4f^8 \rightarrow 4f^7 5d^1$ or increase the polarizability of oxygen ions and a higher degree of covalency (Tb–O) was successfully furnished [36,38].

The excitation and emission spectra of the resulting hybrid materials are shown in Figs. 6 and 7. The excitation spectra was obtained by monitoring the emission of Tb^{3+} (Fig. 6) at 545 nm and dominated by a distinguished band centered at 283 nm. As a result, the emission lines of the hybrid material were assigned to the transitions from the $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions at 490, 544, 587 and 620 nm for terbium and the most striking green luminescence was attained. Fig. 7 shows that maximum absorption
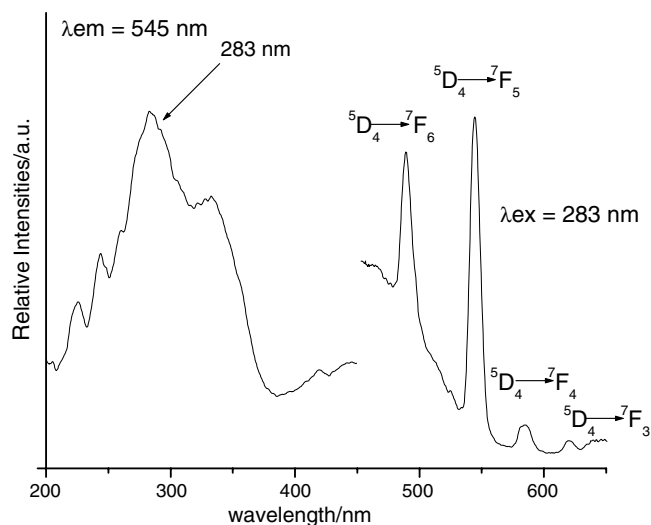

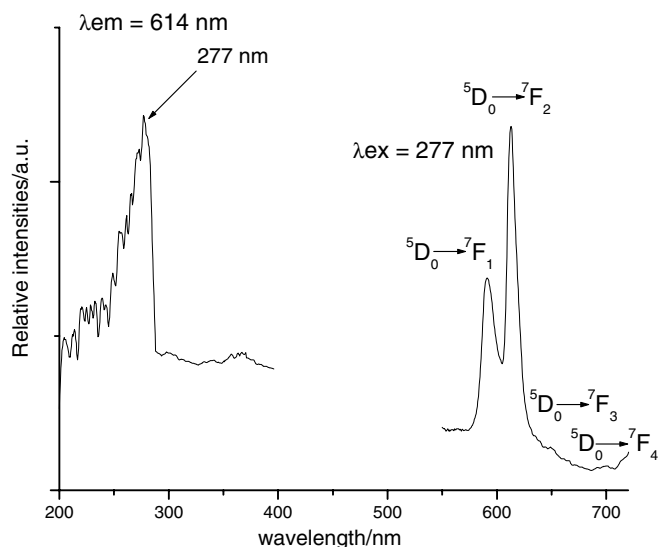Fig. 6. The excitation and emission spectra of Tb^{3+} covalently bonded hybrid materials.

Fig. 7. The excitation and emission spectra of Eu^{3+} covalently bonded hybrid materials.

Fig. 8. Emission spectrum of Zn^{2+} covalently bonded hybrid materials.

is at 277 nm which leads to $(^5D_0 \rightarrow {}^7F_J)$ $(J = 1, 2, 3, 4)$ $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions at 590, 614, 650 and 700 nm of Eu^{3+}, respectively. Among these emission peaks, red emissions $(^5D_0 \rightarrow {}^7F_2)$ were observed in their emission spectra which indicated that the effective energy transfer took place between the HNIC-Si and the chelated RE ions. In addition, we have measured decay curves of the hybrid materials (Tb, Eu, figures not presented, lifetimes were given in Table 1) and it can be described to be single exponential, showing that all the RE^{3+} ions lie in the identical coordination environment. Fig. 8 exhibits a blue emission that gives a structureless broad band (bandwidth at half height about 100 nm) when excited at 326 nm and the lifetime measured was 6.45 μs. The free HNIC-Si organic ligand display rather weak luminescence at room temperature and the characteristic blue emission supposes to be the result of fluorescence from the intraligand transition of the excited state. The quite enhanced luminescence efficiency of the Zn–HNIC-Si complex centers is therefore due to the coordination between the HNIC-Si ligands and Zn ions that firmly promotes the rigidity of the ligands and decreases the non-radiative energy loss of the ligand emission excited state. Other factors still should be considered such as relatively rigid structure of silica gel which limits the vibration of ligand of Tb^{3+} or Eu^{3+} and prohibits non-radiative transitions. Consequently, we may expect that through this efficient way, bleaching of the photoactive molecules can be avoided;

Table 1
The luminescent lifetimes for two different hybrids

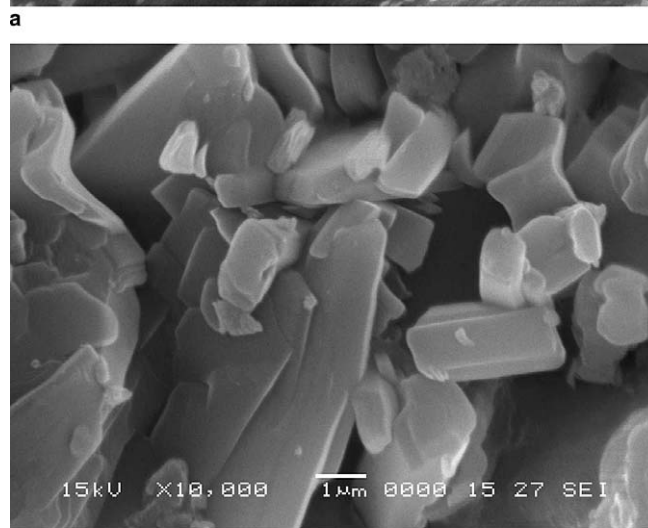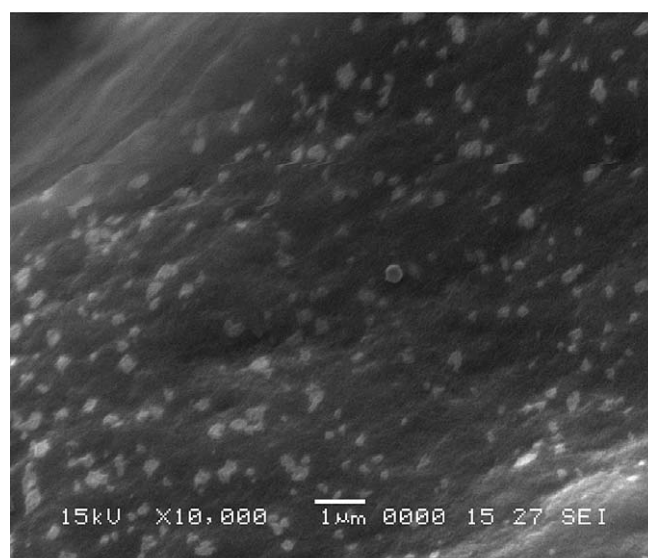| Lanthanide ions	Transition	Wavelength (nm)	τ (μs)
Tb	$^5D_4 \rightarrow {}^7F_5$	545	182.7
Eu	$^5D_0 \rightarrow {}^7F_2$	614	178.8

Fig. 9. SEM graphs of Zn based molecular-based hybrid materials.

higher concentration of metal ions is reached and clustering of the emitting centers may be restricted.

Fig. 9 presents the microstructures of the Zn based molecular-based hybrid materials and Eu, Tb hybrids also give the similar feature. It can be clearly seen that on the ground of bridging functionalization by the coupling agent TESPIC, the hybrids with strong covalent bonds (Fig. 9a) are obviously more uniform and homogeneous than the common doping materials which exhibit apparent phase separation phenomenon. Size distribution of particles is within 1–3 μm and the surface morphology consists of randomly oriented polygonal crystallites according to the cross-sections views of Fig. 9b.

4. Conclusions

In summary, this research work has attempt to synthesize an attracting organic monomers that bear a functional organic group like triethoxysilyl capable of forming covalent bonds with tetraethoxysilane, therefore, we have modified 2-hydroxynicotinic acid with functional 3-(triethoxysilyl)-propyl isocyanate as a crosslinking intermediate. Since the hydrolysis and polycondensation reactions between triethoxysilyl of HNIC-Si and tetraethoxysilane lead to the formation of Si–O–Si backbone structures for the same ethoxy group of them, three novel luminescent molecular-based hybrid materials were firstly achieved using HNIC-Si derivative coordinated to Ln^{3+}. In consequence, further detailed investigation of the above strong emission molecular-based hybrids will definitely contribute to the recognition of the paths needed for the fabrication of extending siloxane-based materials with interesting photo, electric luminescence features and high light emission efficiency.

Acknowledgement

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