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Journal of Photochemistry and Photobiology A: Chemistry 175 (2005) 159–164

Journal of Photochemistry and Photobiology A:Chemistry
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Construction of lanthanide luminescent molecular-based hybrid material using modified functional bridge chemical bonded with silica

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Received 12 January 2005; received in revised form 24 March 2005; accepted 27 April 2005
Available online 6 June 2005

Abstract

The study focuses on the syntheses of modified chloronictinic acid by (3-aminopropyl)triethoxysilane 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-chloronictinic acid (ClNIC-Si) which is utilized to coordinate to Tb^{3+} or Eu^{3+} (abbreviated as RE^{3+}) and further introduced into silica matrices by Si─O bonds after hydrolysis and polycondensation processes. Ultraviolet absorption, phosphorescence spectra, and fluorescence 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 chloronictinic acid efficiently initiates the antenna effect and matches with the emissive energy level of RE^{3+}. Accordingly, the intramolecular energy transfer process completed within these molecular-based hybrids and strong green or red emissions of RE^{3+} have been obtained.
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Keywords: Terbium ions; Molecular-based; Luminescence; Hybrids

1. Introduction

Lanthanide containing hybrid materials have been utilized as phosphors or luminescent materials in the light of their sharp, intense f–f electronic transitions. Especially, a large amount of rare earth complexes exhibit a bright and narrow metal ions characteristic emission. These corresponding emissions are often aroused by a process 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 (the detailed diagram presenting the energy transfer process and antenna effect is given in Fig. 1). In recent studies, anchored lanthanide complexes by aromatic carboxylic acids, β-diketones or heterocyclic ligands in a sol–gel derived matrix has been discussed in detail [1–11]. 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 leaching 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 Ribot [12] class II is called the one which has the structure properties of chemical connections, through covalent bonding, between the organic and inorganic parts. Lately, a few researches in regard to the covalently bonded hybrids have emerged and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration of rare earth complexes [13–24]. Compared with diverse synthetic approaches, sol–gel method which is founded on hydrolysis/polycondensation reactions of metal alkoxides exhibits its unique features 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 combina-

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doi:10.1016/j.jphotochem.2005.04.030

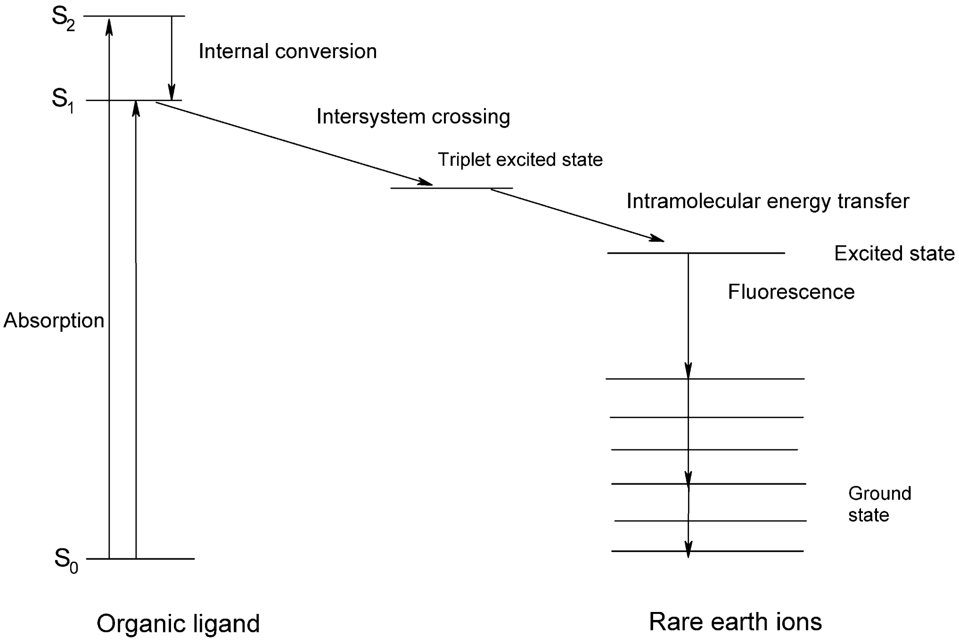


Fig. 1. The energy transfer process and antenna effect between organic ligand and rare earth ions.

tion between the two phases. At present, the crucial step to prepare such materials is to synthesize a new monomer as a covalent bridge which cannot only develop chelating effects that can bind to rare earth ions but also act as precursors of inorganic network [13–16]. Some previous researches have concentrated on the modification of pyridine-dicarboxylic acid or their derivatives [23] and some others focus on modification of aminobenzoic acid [16–18] or di-pyridine [14]. In this paper, we firstly use 2-chloronicotinic acid as organic ligand, then we designed a covalently bonded

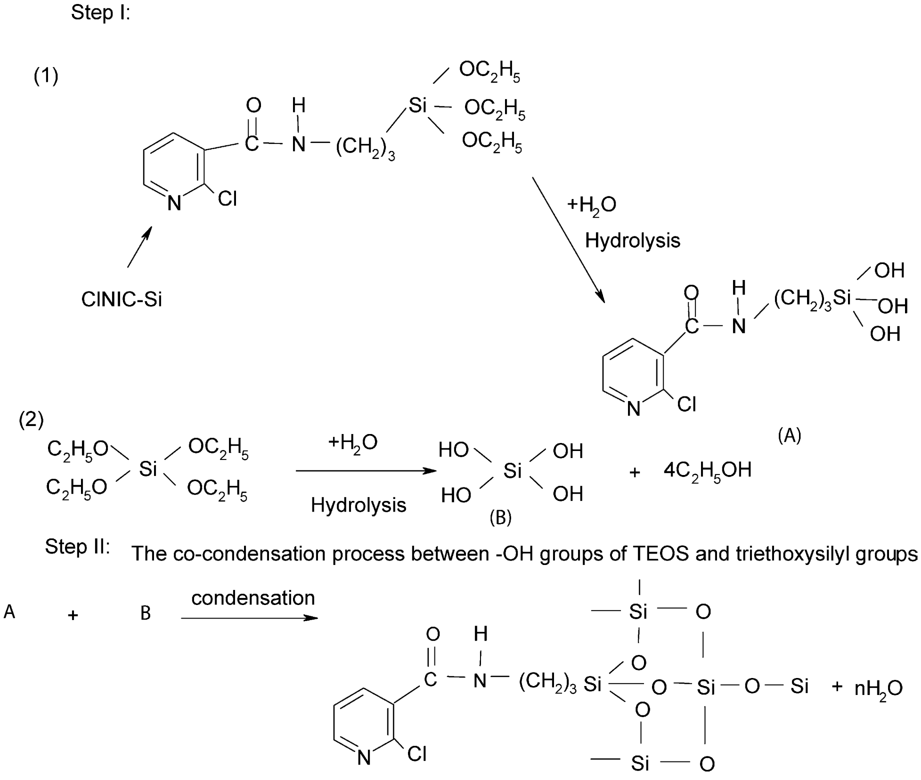


Fig. 2. Scheme of hydrolysis and polycondensation processes between ClNIC-Si and TEOS.

hybrid inorganic–organic system that incorporated modified 2-chloronicotinic acid (denoted as ClNIC-Si) and tetraethoxysilane (TEOS) with water. The reaction model for the hybridization formula of TEOS and ClNIC-Si may be described in Fig. 2. During the start of the reaction, as shown in Fig. 2 (Step I), the individual hydrolysis of ClNIC-Si and TEOS are predominant. The Step II, different from the former, is concerning to the polycondensation reactions between hydroxyl groups of both ClNIC-Si and TEOS. Through the above treatments, the molecular-based hybrids bearing the RE–O coordination bond and Si–O covalent bond can exhibit the strong green luminescence of RE^{3+}.

2. Experimental

2.1. Chemicals and procedures

2-Chloronicotinic acid was provided by Lancaster Synthesis Ltd. (3-aminopropyl)triethoxysilane (APS) was purchased from Shanghai YaoHua chemical plant. Other starting reagents were used as received. A typical procedure for the preparation of ClNIC-Si was as follows: 2-chloronicotinic acid was first converted to acyl chloride by refluxing in excess $SOCl_2$ under argon for 5 h. After isolation, the acyl chlorides were directly reacted with APS in ethyl ether in presence of triethylamine. The resulting solution was stirred under argon for 5 h at room temperature. After the filtration of the precipitates, a clear oil ClNIC-Si was furnished and dried on a vacuum line. ClNIC-Si – $C_{15}H_{25}O_4N_2ClSi$: IR (KBr): –CONH– (1647, 1566 cm^{-1}), C–Si (1198 cm^{-1}). ^1H NMR ($CDCl_3$): ClNIC-Si δ 9.07 (1H, s), 8.59 (1H, t), 8.15 (1H, d), 8.03 (1H, s), 4.93 (1H, t), 4.52 (1H, s), 3.66 (1H, d), 3.34 (10H, m), 3.05 (1H, s), 2.70 (1H, t), 1.56 (4H, s), 0.59 (2H, s). ^{13}C NMR ($CDCl_3$): ClNIC-Si: δ 166.5 (C_6), 151.1–150.4 (C_2–C_4), 136.7–136.5 (C_1–C_5), 122.1 (C_3), 50.3 (CH_2(OEt)), 43.3 (C_7), 22.5 (C_8), 15.1 (CH_3(OEt)), 6.4 (C_9). The sol–gel derived hybrid containing terbium was prepared as follows: ClNIC-Si was dissolved in ethanol, and TEOS, H_2O were added while stirring, Then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. A stoichiometric amount of $RE(NO_3)_3{\cdot}6H_2O$ was added to the final stirring mixture. The mole ratio of $RE(NO_3)_3{\cdot}6H_2O$/ClNIC-Si/TEOS/H_2O was 1:3:6:24. After the treatment of hydrolysis, 2 ml DMF (dimethylformamide) and appropriate amount of hexamethylene-tetramine were added to adjust the pH value of 6–7. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, then it was aged at 60 °C until the onset of gelation which occurred within 3 days. The gels were collected as monolithic bulks and ground as powder materials for the photophysical studies (see Fig. 3).

2.2. Measurements

All measurements were completed under room temperature. ^1H NMR spectra was recorded in $CDCl_3$ on a bruker AVANCE-500 spectrometer with tetramethylsilane (TMS)

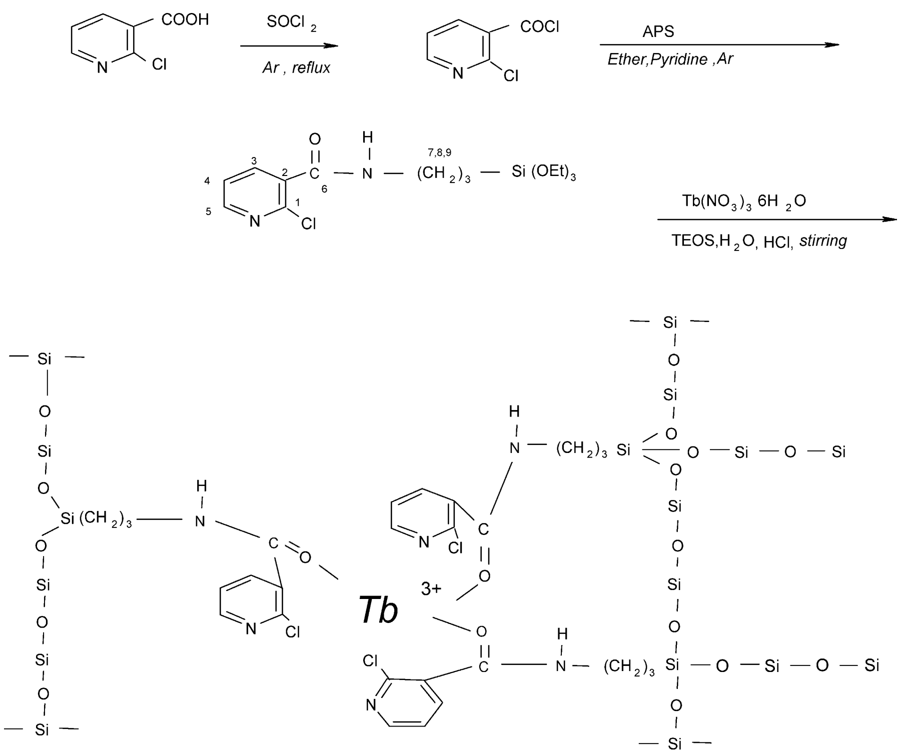


Fig. 3. Scheme of the synthesis process of ClNIC-Si and predicted structure of hybrid materials.

as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol l^{-1} chloroform ($CHCl_3$) solution) were recorded with an Agilent 8453 spectrophotometer. Phosphorescence spectra (5×10^{-4} mol l^{-1} $CHCl_3$ solution, under 77 K) and fluorescence excitation and emission spectra were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

3. Results and discussion

Fig. 4 exhibits ultraviolet absorption spectra of (A) 2-chloronicotinic acid, (B) ClNIC-Si, (C) ClNIC-Si with excess Tb^{3+} ions, (D) ClNIC-Si with excess Eu^{3+} ions. From the spectra, it is observed that a blue shift (A → B) of the major π–π^* electronic transitions (from 286 to 279 nm) occur and it is estimated that during the modification of 2-chloronicotinic acid, the different ligand may hinder the conjugating effect of double bonds (C=O) and enlarge the energy difference levels among electron transitions. In regard to C and D, the complexation between rare earth ions and ClNIC-Si further increases the energy levels of the corresponding transitions and exhibits a obvious blue shift from 279 to 270 nm (B → C and B → D).

As for the phosphorescence spectra of (A) 2-chloronicotinic acid, (B) ClNIC-Si, (C) ClNIC-Si with excess Tb^{3+} ions (Fig. 5). Phosphorescence spectrum represents the character of the organic molecular ligands and a 6 nm shift was found between A and B (from 389 to 395 nm). However, there is no change between B and C because they belong to the same organic groups with the exception that C can sensitize terbium ions and transfer part of energy to decrease the relative intensities. It can be indicated that the maximum phosphorescence band (B) is located at 395 nm and the triplet state energy of ClNIC-Si can be determined to be 25316 cm^{-1}. According to the energy transfer and intramolecular energy mechanism [25–30], it can be predicted that the bridging ClNIC-Si is quite suitable for the sensitization of fluorescence of terbium ions (20500 cm^{-1}) because the optimal energy match between ligands and the resonant emissive energy level of the central Tb^{3+} ions is around 4000 ± 500 cm^{-1}. While the energy match of ligand and Eu^{3+} appears to be not as proper as terbium ions for the emissive energy level of europium ions is approximately 17265 cm^{-1} and this was further proved by the following emission spectra of central lanthanide ions.

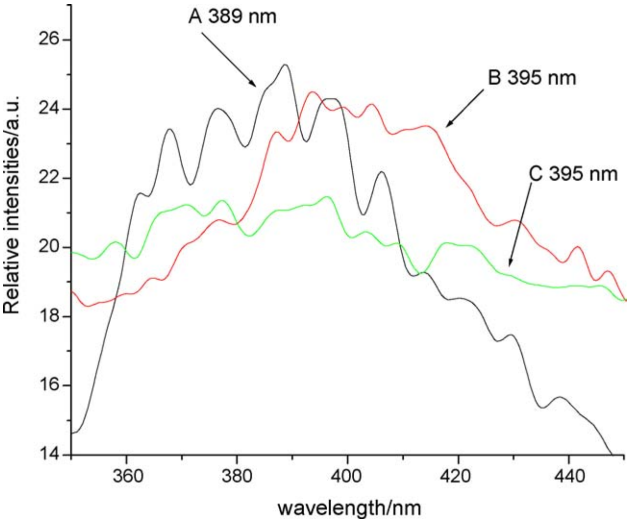


Fig. 5. The phosphorescence spectra of (A) 2-chloronicotinic acid, (B) ClNIC-Si, (C) ClNIC-Si with excess Tb^{3+} ions.

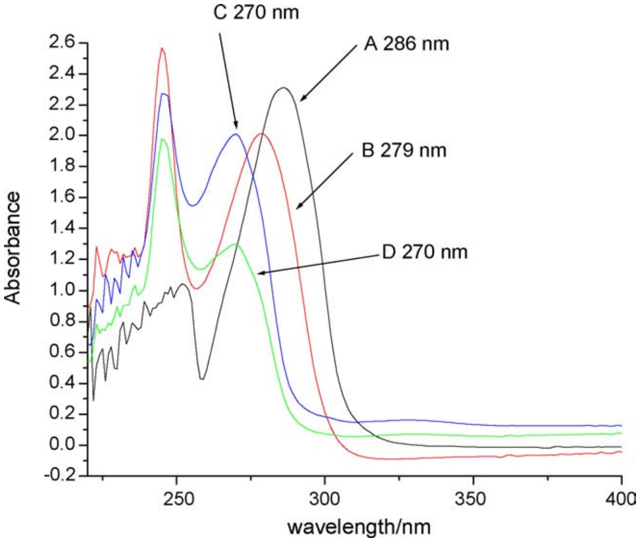


Fig. 4. Ultraviolet absorption spectra of (A) 2-chloronicotinic acid, (B) ClNIC-Si, (C) ClNIC-Si with excess Tb^{3+} ions, (D) ClNIC-Si with excess Eu^{3+} ions.

The fluorescent excitation and emission spectra of the resulting hybrid materials are shown in Figs. 6–8. The excitation spectra was obtained by monitoring the emission of Tb^{3+} (A) or Eu^{3+} (B) ions at 545 or 614 nm and dominated

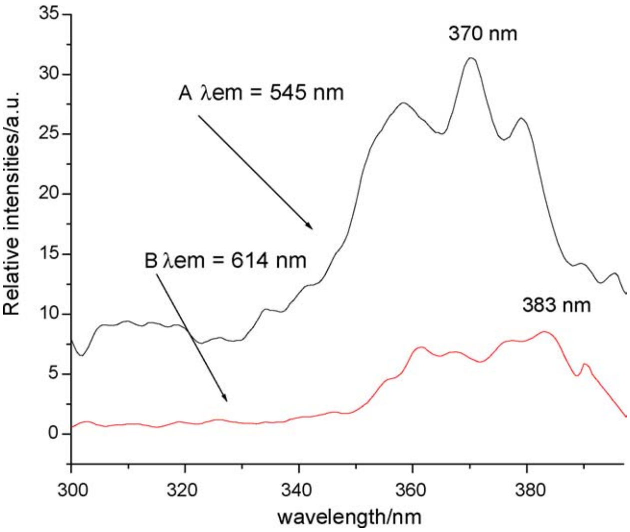


Fig. 6. The excitation spectra of (A) Tb^{3+} covalently bonded hybrid materials and (B) Eu^{3+} covalently bonded hybrid materials.

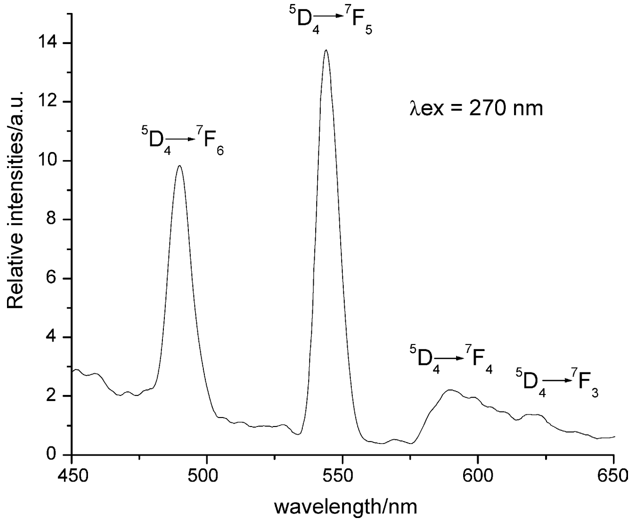


Fig. 7. Emission spectrum of Tb^{3+} covalently bonded hybrid materials.

by a broad band centered at 370 and 383 nm, respectively. 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 622 nm for terbium and $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions at 590, 614, 650 and 700 nm of Eu^{3+}, respectively. Among these emission peaks, the most striking green fluorescence ($^5D_4 \rightarrow {}^7F_5$) and red emissions ($^5D_0 \rightarrow {}^7F_2$) were observed in their emission spectra which indicated that the effective energy transfer took place between the ClNIC-Si and the chelated RE ions. Under the same concentration and other relative conditions, Eu^{3+} ions containing molecular hybrids give a weaker fluorescence than expectation because the rate constant of the intermolecular energy transfer (k_{ET}) is largely impeded with the increasing energy difference of both donor (ClNIC-Si) and acceptor (Eu^{3+}) even if the inverse energy transfer rate constant $k(T)$ is restricted. Other factors still cannot be excluded 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. Accordingly, we may expect that through this efficient way, leaching of the photoactive molecules can be avoided; higher concentration of metal ions is reached and clustering of the emitting centers may be prevented.

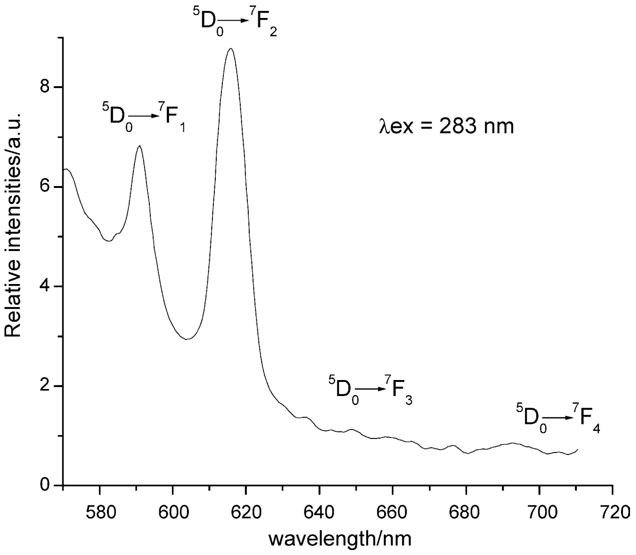
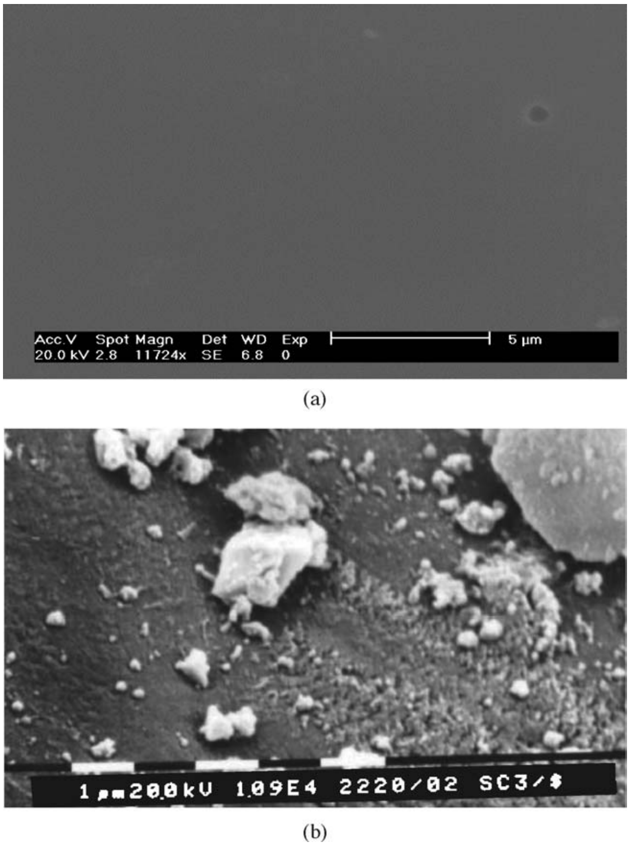


Fig. 8. Emission spectrum of Eu^{3+} covalently bonded hybrid materials.



(a)

(b)

Fig. 9. SEM graphs of molecular-based materials (a) and hybrid materials by doping chloronicotinic acid–Tb complex directly into hosts (b).

Figs. 9 and 10 present the microstructures of the molecular-based hybrid materials and it can be clearly seen

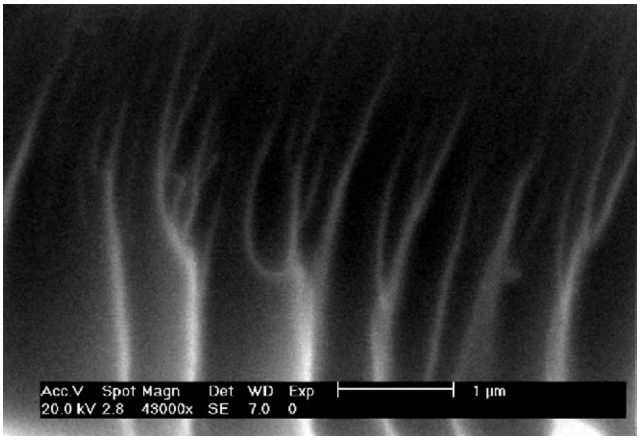


Fig. 10. SEM graphs of rupture section within the molecular-based materials.

that on the ground of bridging functionalization by the coupling agent APS, the hybrids with strong covalent bonds (Fig. 9a) are obviously more uniform and homogeneous than the common doping materials (Fig. 9b). Unexpectedly, locating at the rupture surface of hybrids, we found a variety of chains like structures distributed throughout the materials with the diameter size about 100 nm. To the best of our knowledge, no research concerning such nanoscale morphology in preparing the molecular-based hybrids has been previously reported. According to reference [31], the crystal structure of complex $[Tb(o\text{-}ClC_6H_4CO_2)_3 \cdot H_2O]_n$ shows that it forms a novel type of chain like formulation with four dentate carboxyl groups bridging the two neighboring terbium ions. Hence, we predict that the complex ClNIC-Si–Tb (Eu) may inherit the inclination of forming infinite chains from the crystallography growing view and it remains the coordinated behavior in corresponding macroscopic materials.

4. Conclusions

To sum up, this research work has brought about a discovery that the organic monomers attached to the hosts must carry a functional organic group like triethoxysilyl capable of forming covalent bonds with tetraethoxysilane, therefore, we have modified 2-chloronicotinic acid with functional (3-aminopropyl)triethoxysilane (APS) as a crosslinking intermediate. Since the hydrolysis and polycondensation reactions between triethoxysilyl of ClNIC-Si and tetraethoxysilane lead to the formation of Si–O–Si network structures for the same ethoxy group of them, a novel luminescent molecular-based hybrid material was firstly achieved using ClNIC-Si derivative coordinated to RE^{3+}. Accordingly, novel and specific development and improvement of opto-electronic researches will be performed towards such molecular-level hybrid material with homogeneous and especially the unique nanoscale chains like structure.

Acknowledgement

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

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