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Molecular assembly of red and green nanophosphors from amine-functionalized covalent linking hybrids with emitting centers of Eu^{3+} and Tb^{3+} ions

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Abstract

We report a novel technology for fabricating sol–gel derived nano-scale molecular hybrid materials that contain −NHC(=O)NH− groups anchored to a silica network. The modified 2-amino pyridine is grafted by 3-(triethoxysilyl)-propyl isocyanate and applied to coordinate to RE^{3+} (Eu^{3+}, Tb^{3+}) through nitrogen atoms of the heterocycle of pyridine group and further formed Si−O backbones after hydrolysis and polycondensation processes. For analogy and luminescence efficiency purpose, we added 1,10-phenanthroline to the above hybrids in order to increase the conjugating effects and sensitize rare earth ions emissions. IR, ultraviolet absorption and luminescence spectra were utilized to characterize the structure and photophysical properties of the obtained hybrid material and the above spectroscopic data reveal that the triplet energy of 1,10-phenanthroline in this favorable hybrid system matches with the emissive energy level of RE^{3+}.

Keywords: Nanophosphors; Molecular-based hybrid materials; Luminescence; Rare earth ions

1. Introduction

Increasing interest in the field of photoactive nanometer structured materials has motivated the design of both organic and inorganic networks to exhibit their mutual advantageous properties such as luminescence in lighting and displays, optical amplifiers, and lasers [1,2]. It is known to us that inorganic matrices doped with metal complex especially lanthanide organic complexes introduced in silica gel have already been found to show extraordinary emission intensities and organic parts are regarded as efficient sensitizers for the luminescence of rare earth ions, in short, the antenna effect. Our research group at present is concentrated on the lanthanide ions (Eu, Tb, Sm, Dy) complexes with aromatic carboxylic acid, bipyridyl or their derivatives [3–11]. Additionally, anchored lanthanide complexes with diverse ligands in a sol–gel derived matrix have been studied in various latest researches [12–16]. In recent years, the delicate control of the coupling between the hosts and the guest molecule will be a promising channel to the design of hybrid materials especially for definite applications. For example, conventional doping method seems impossible to solve the problem of quenching effect of luminescent centers because the high-energy vibration by the surrounding hydroxyl groups and only weak interactions (such as hydrogen bonding, van der waals force or weak static effect) functionalize between organic and inorganic components [17]. Presently, a few studies in terms of the covalently bonded hybrids have appeared and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration of rare earth complexes [18–32]. Some previous researches have been done on complexes of rare earth–pyridine–dicarboxylic acid or their derivatives and the feasibility of dicarboxylic acid system has been firmly proved [24]. Zhang and co-workers initiated to modify 1,10-phenanthroline and di-pyridine in order to prepare the predicted molecular-level hybrid materials [19,20]. Our research team recently put more emphasis on rare earth coor-

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dination behavior and have now developed modified ortho, meta-aminobenzoic, acid [28,29], ortho, meta methyl acid [31] and nicotinic/picolinic acid [32] as "molecular bridges" which cannot only develop chelating effects that can bind to rare earth ions but also bonded to a silica host with an aminoalkoxysilane group. According to Carlos's latest research [33–35], amino-functional hybrids lacking metal ions could be classified into two major parts (di-ureasils and di-urethanesils) and the Eu^{3+} coordination shell involves the carbonyl-type oxygen atoms of the urea bridges. In order to restrict the phase separation between organic molecules and the rigid inorganic network, and to increase the concentration of dopant, in this report, for the sake of investigating the unique coordination feature of pyridine nitrogen and rare earth ions in the molecular-level hybrids, we firstly adopt modified 2-amino pyridine by 3-(triethoxysilyl)-propyl isocyanate carrying tri-alkoxysilyl group as a functionalized organic ligand (APY-Si), then we designed a covalently bonded hybrid inorganic–organic system that incorporated rare earth (Eu, Tb) nitrate to APY-Si and second ligand 1,10-phenanthroline was inserted into the hybrids. In contrast to the general nano composites arising from dopant distribution or special template synthesis method, we interestingly fabricate molecular level luminescent hybrids in the nanometer regime with the particle produced to be uniform in size and shape through in-situation preparation among molecule bridge monomer, rare earth ions and 1,10-phenanthroline. Furthermore, the first results on luminescence are promising and the coordination behavior between nitrogen atoms of 2-amino pyridine and rare earth ions were efficient to exhibit the green, red luminescence of RE^{3+}.

2. Experimental

2.1. Chemicals and procedures

3-(Triethoxysilyl)-propyl isocyanate was provided by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents are domestic chemical products and purified using common methods. A typical procedure for the preparation of APY-Si was as follows: 1 mmol 2-amino pyridine and 1 mmol 3-(triethoxysilyl)-propyl isocyanate were first dissolved in dehydrate tetrahydrofuran by stirring. The whole mixture was refluxing at 65 °C under argon for 12 h. After isolation, a pale-yellow oil APY-Si was furnished. Anal. Calcd. for $C_{15}H_{27}O_4N_3Si$: C, 52.8; H, 7.90; N, 12.30; Found: C 51.7; H, 7.85; N, 12.44. $C_{15}H_{27}O_4N_3Si$ (APY-Si): ^1H NMR ($CDCl_3$): δ 8.06(1H,d), 7.42(1H, m), 6.65(1H, t), 6.5(1H, d), 4.43(1H,s), 3.58(1H,s), 3.46(11H,m), 3.43(3H,d), 1.70(3H,m), 0.68(4H,m). The sol–gel derived hybrid containing rare earth ions was prepared as follows: APY-Si was dissolved in dimethylformamide (DMF) with stirring, A stoichiometric amount of $RE(NO_3)_3 \cdot 6H_2O$ was added to the final stirring mixture. One hour later, 1,10-phenanthroline was added to the solution. Then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. The mole ratio of $RE(NO_3)_3 \cdot 6H_2O$/APY-Si/phen/H_2O was 1:2:1:4. The mixture was agitated magnetically to achieve a single phase and thermal treatment was performed at 60 °C until the sample solidified (see Fig. 1, Hybrid I). For the purpose of comparison, we also prepared hybrid material directly by rare earth nitrate and APY-Si ligands (Hybrid II).

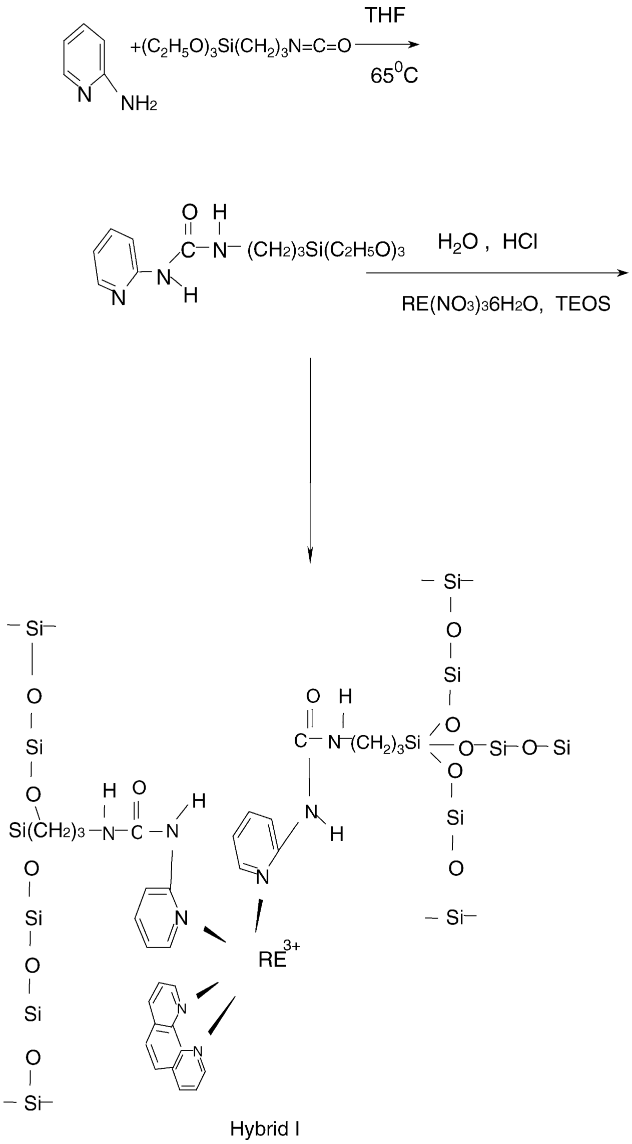

Fig. 1. Scheme of the synthesis process of APY-Si ligand and predicted structure of resulting hybrid materials.

2.2. Measurements

All measurements were completed under room temperature. FT-IR spectra were measured within the 4000–400 cm^{-1} region on an infrared spectrophotometer with the KBr pellet technique. ^1H 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} ethyl alcohol solution) were recorded with an Agilent 8453 spectrophotometer. Fluorescence excitation and emission spectrums directly using grinding powders were recorded on a Perkin-Elmer LS-55 spectrophotometer equipped with a xenon lamp as the excitation source. Excitation slit width = 10 nm, emission slit width = 5 nm. Luminescent lifetimes for hybrid materials were obtained with an Ediburg FIT120 phosphorimeter.

3. Results and discussion

Fig. 2 provides the FT-IR spectra of: (A) 2-amino pyridine; (B) APY-Si; (C) Hybrid II; (D) Hybrid I and (E) 1,10-phenanthroline. The three characteristic peaks at 1628, 1600 and 1560 cm^{-1} proves the stretching vibration of C=N in pyridine ring .We could observe that two new peaks located at 2921 and 1670 cm^{-1} emerged in B compared with A, the former refers to the vibration of $-CH_2-$ groups in grafted 3-(triethoxysilyl)-propyl isocyanate and the latter corresponds to the absorption of carbonyl groups in the –CO–NH– units. Additionally, the broad band at 1100 cm^{-1} is attributed to the vibration absorption of Si–O bonds and the similar bands situated at 1080 cm^{-1} still exist in Hybrid I and II (C and D). After coordination with europium ions, the dramatic differences are presented between B and C and the stretching vibration of C=N groups (1600 and 1560 cm^{-1}) downward to 1580 and 1540 cm^{-1}, respectively allowing us to conclude that the nitrogen atom in the pyridine ring actively participate to give its nonbonding electron pair to Lewis acid (RE^{3+} ions). Compared with D and E, the two peaks at 854 and 739 cm^{-1} ascribed to the twisting bending vibration of hydrogen atoms in heterocyclic ligands are sharply shifted to 843 and 726 cm^{-1} in Hybrid I, substantiating that 1,10-phenanthroline also contributes two coordination sites to rare earth ions.

Fig. 3 gives ultraviolet absorption spectra of: (A) 2-amino pyridine; (B) APY-Si. From the spectra, it is observed that an obvious red shift (A → B) of the major π–π^* electronic transitions (from 228 to 237 nm) occur and it is estimated that during the grafting reaction of 2-amino pyridine, the diverse ligand may enlarge the conjugating effect of double bonds and decrease the energy difference levels among electron transitions. A new peak locating at around 204 nm (B) substantiates that the chemical environment of the chromophore was greatly changed due to the reaction with 3-(triethoxysilyl)-propyl isocyanate.

Fig. 4 presents the phosphorescence spectra of APY-Si and phosphorescence spectrum shows the character of the organic molecular ligands. It can be concluded that the maximum phosphorescence band locating at 449 nm determined triplet

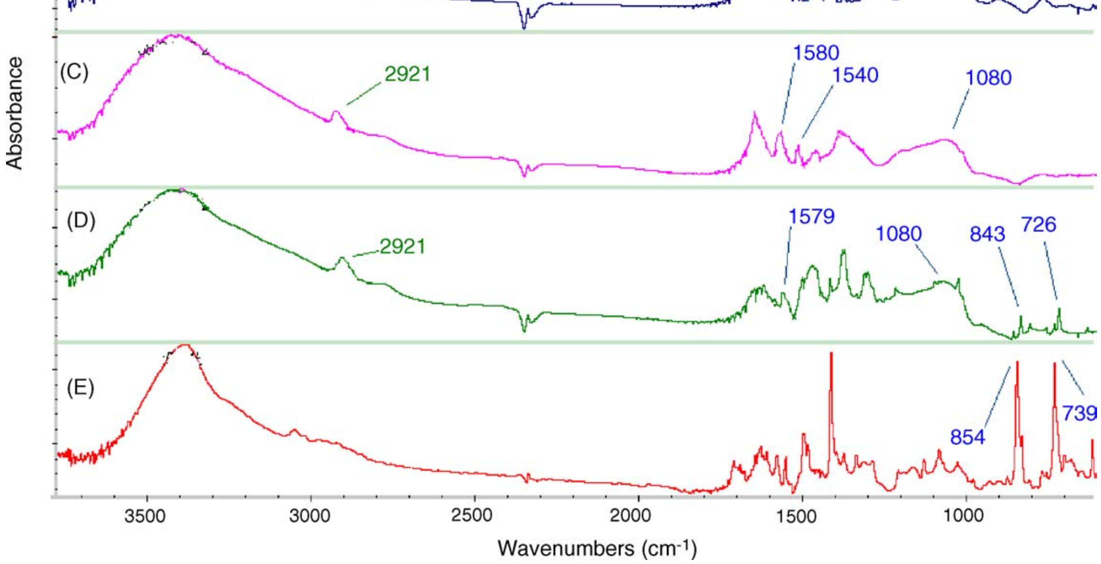

Fig. 2. The FT-IR spectra of: (A) 2-amino pyridine; (B) APY-Si; (C) Hybrid II; (D) Hybrid I and (E) 1,10-phenanthroline.

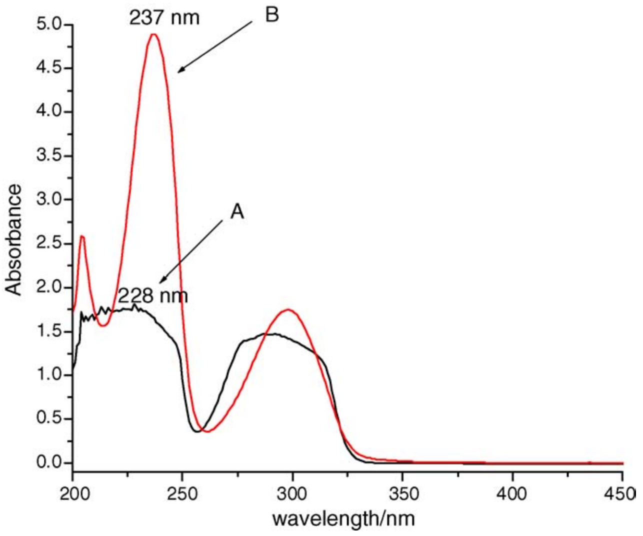

Fig. 3. Ultraviolet absorption spectra of (A) 2-amino pyridine and (B) APY-Si.

state energy of APY-Si to be 22,272 cm^{-1}. On the grounds of the energy transfer and intramolecular energy mechanism [36–41], there should exist an optimal energy difference between the triplet position of APY-Si and the emissive energy level Ln^{3+}, the larger and the smaller $\Delta E(Tr–Ln^{3+})$ will decrease the luminescence properties of rare earth complexes. In regard to lanthanide-phenyl complexes, the suitable value was proved to be around 4000–5000 cm^{-1}. It can be predicted that the bridging APY-Si is suitable for the luminescence of europium (17,265 cm^{-1}) ions and the energy transfer mechanism from energy donor to central ions functionalized efficiently.

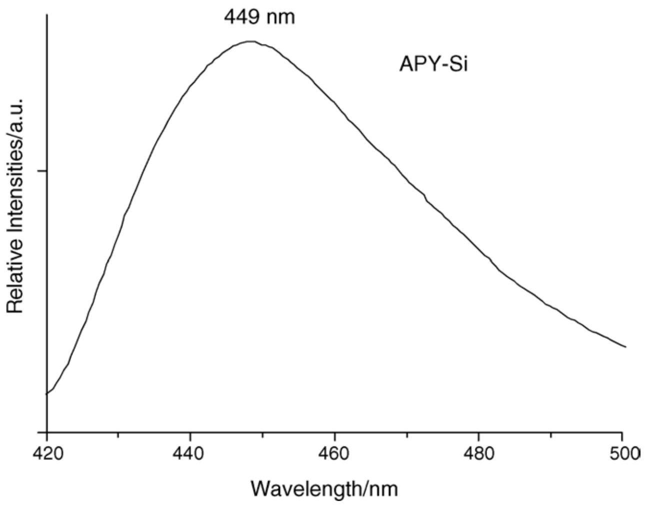

Fig. 4. The phosphorescence spectra of APY-Si.

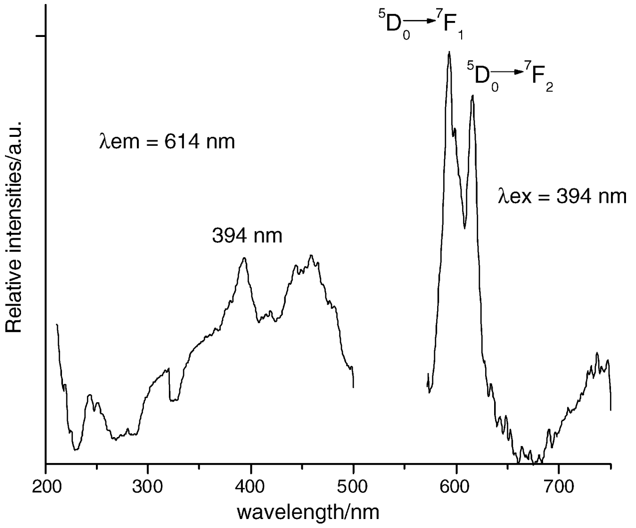

Fig. 5. Excitation and emission spectra of Eu-APY-Si covalently bonded hybrids (Hybrid II).

The excitation and emission spectra of the APY-Si bridged covalently bonded hybrid materials (Hybrid II) are shown in Fig. 5. The lifetimes for Hybrid I and II were measured within the $^5D_0 \rightarrow {}^7F_2$(614 nm) transitions and the values were 0.6652 and 0.1170 ms, respectively (Figures not given). Under room temperature, the excitation spectra monitored around 614 nm was composed of several large broad bands at 394 and 450 nm that had overlapped a series of sharp lines probably corresponding to intra-4f transitions of Eu ions between ^7F_j and $^5D_0$ levels. The existence of strong peaks near the visible spectral region (394 nm) will be ascribed to be two aspects. The former may be known as a ligand-to-metal charge transfer (LMCT) transition caused by interaction between the pyridine cycle and the lanthanide ions. Another contribution is approximately associated with the transitions of the lone pair of electrons in the NH-related groups (–NHC(=O)NH–). In accordance with the emission spectra recorded under excitation wavelength 394 nm, we could clearly find two sharp lines assigned to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}. In addition, the most important probe magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ transition displays the stronger intensity than electric dipolar $^5D_0 \rightarrow {}^7F_2$ levels, indicating that Eu^{3+} is located at higher symmetric coordination sites with two mono dentate identical APY-Si ligands. After the introduction of second ligand 1,10-phenanthroline (Hybrid I, Fig. 6), the emission spectrum is composed of $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3) emission lines of Eu^{3+} at 590 nm, 614 nm, 650 nm and 700 nm, with the hypersensitive red emission transition $^5D_0 \rightarrow {}^7F_2$ (peak at 614 nm) being the most prominent group. When the Eu^{3+} is bonded within low symmetry local sites (without inversion center) attributed by addition of heterocyclic ligand, the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ is often dominated in its emission spectrum which suggested that the effective energy transfer is much better from 1,10-phenanthroline and pyridine to chelated Eu ions whose ligands have more advantageous conjugating effects. Fig. 7 shows the excitation and emission spectra of terbium centered materials, providing that four characteristic emissions $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) were observed in the blue and

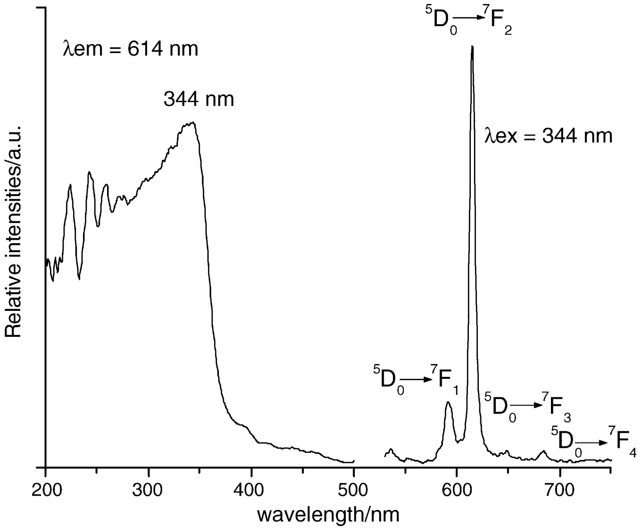

Fig. 6. Excitation and emission spectra of Eu-APY-Si-phen covalently bonded hybrids (Hybrid I).

green region among which $^5D_4 \rightarrow {}^7F_5$ transition (545 nm) is the highest. The broad band absorption locating at about 294–350 nm in the excitation spectrum proves the results of a combination between intrinsic absorption of functional ureasils and 4f–5d transitions of terbium ions. Hence, 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 scanning electron micrographs (Fig. 8) for the above hybrid materials also represent diverse morphology in regard to binary and ternary molecular-based materials. Fig. 8a (Hybrid II) reveals that nano level particles were unexpectedly produced without any specific template under room temperature using sol–gel technique and the mean values of the dimensions were around 100 nm. To our knowledge, it is rather rare to obtain the above nano scale rare earth luminescent hybrids at such common conditions. Unlike Fig. 8a, Hybrid I (b) gives a homogeneous surface which indicates strong covalent bonds exist between inorganic and organic phases and they composed rather uniformly so two phases can exhibit their distinct properties together. These different phenomena suggest that the formation of spherical shape particles (Hybrid II) were heavily affected along with the introduction of second ligand 1,10-phenanthroline which coordinated to rare earth ions so as to increase the ring conjugating effects. In other words, the addition of 1,10-phenanthroline situated in the vacant side drastically changes the symmetric building blocks of RE(APY-Si)$_2$ and connects the adjacent molecular structures to form unique appearance within macroscopic materials (Hybrid I).

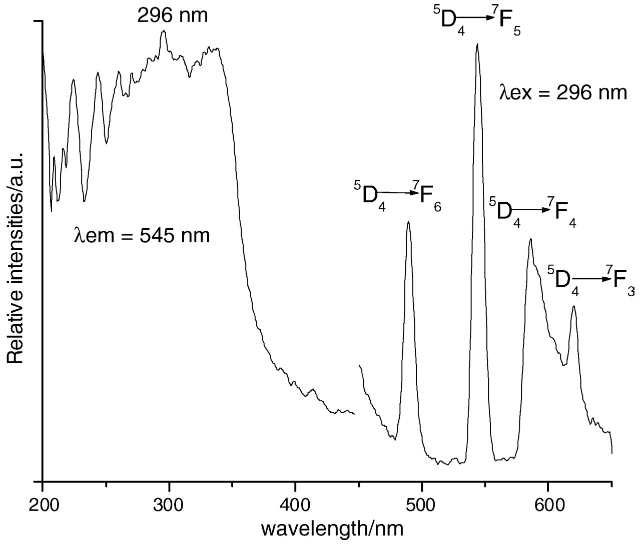

Fig. 7. Excitation and emission spectra of Tb-APY-Si-phen covalently bonded hybrids.

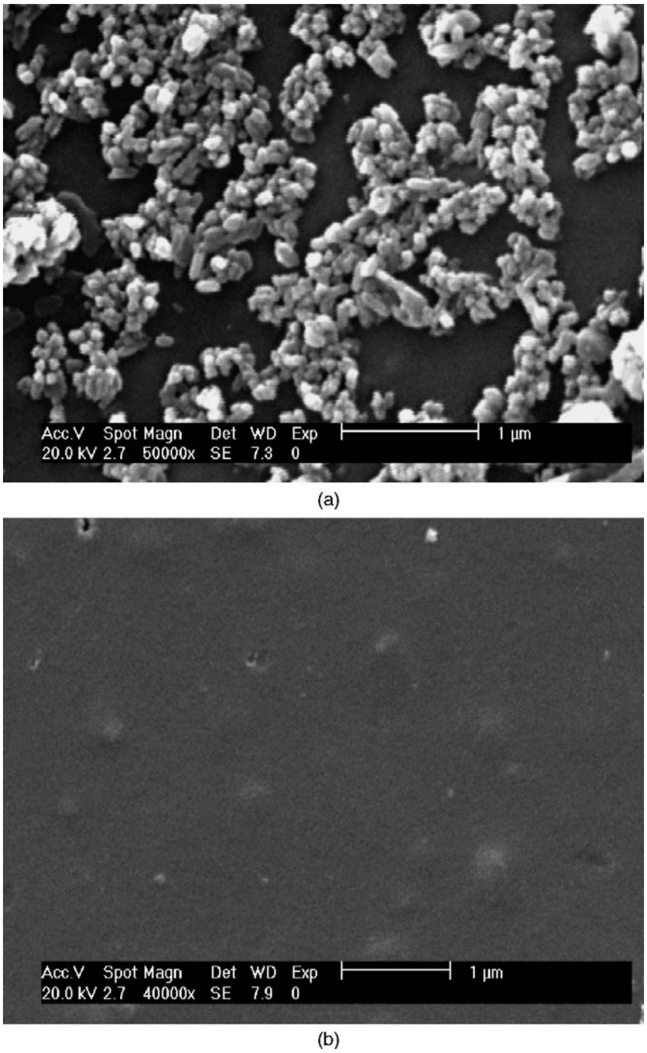

Fig. 8. SEM graph of molecular-based hybrids: (a) Hybrid II and (b) Hybrid I.

4. Conclusions

In order to study the coordination behavior between ureasils and lanthanide ions, we assembled three novel molecular-based hybrid materials. 2-Amino pyridine has been modified with functional 3-(triethoxysilyl)-propyl isocyanate as a crosslinking intermediate, which occupies double roles. On the one hand, it can coordinate to rare earth ions through nitrogen atoms; on the other side of the coin, the hydrolysis and polycondensation reactions among triethoxysilyl of APY-Si and TEOS are determined to be the formation of Si–O–Si network structures for the same ethoxy group of them. Additionally, the strong red or green nano meter luminescent systems were achieved. Consequently, the resulting hybrids could be shaped as monoliths or as transparent films with desired luminescence efficiency. Variations of the organic ligand structure correspond to diverse coordinating properties and to various absorption capabilities. In this way, the energy absorption and transfer from ligands to central ions, or the emission efficiency, could be increased by this potential method.

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