JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 10, No. 12, December 2008, p. 3357 - 3363

Molecular based hybrid materials by assembling inorganic network with Schiff base compounds via covalent bonds

JIN L. LIU, SHUAI XU, BING YAN*
Department of Chemistry, Tongji University, Siping Road 1239 Shanghai 200092, PR China

Two novel silica-based organic-inorganic hybrid materials containing a Schiff-base organic compound were prepared through a covalent self-assembly process via a sol-gel technology. The organic Schiff-base compound N,N'-bis(salicylidene)ethylenediamine (BSEA) was first prepared and then functionalized with trialkoxysilyl group. The as-obtained silylated precursor (BSEA-Si) was used as a functional bridging molecular to submitted to hybridization with tetraethoxysilane (TEOS) through a polycondensation or cross-linking reaction between the terminal silanol groups of the silylated precursors and the OH groups of hydrolyzed TEOS. The resulting amorphous materials (BSEA-Hybrids and BSEA-Eu-Hybrids) exhibit regular uniform microstructures and no phase separation happened for the organic and the inorganic compounds were covalent linked through Si-O bonds via a self-assemble process. BSEA-Hybrids has strong blue luminescence due to the Schiff-base functional group, BSEA-Eu-Hybrids can show the characteristic luminescence of Eu^{3+} ion for the energy transfer process take place successfully between the organic parts and the Eu^{3+} ion.

(Received December 21, 2007; accepted November 27, 2008)

Keywords: Schiff-base compound, Hybrid material, Covalently bonded, Sol-gel

1. Introduction

Nowadays, the development of hybrid materials is a subject of powerful interest in the chemistry and physics fields, because the hybrid materials combine some advantages of organic polymers (easy processing with conventional techniques, good elasticity, toughness, formability and organic functionalities) with properties of inorganic oxides (hardness, thermal and chemical stability, transparency) [1]. Sol–gel techniques, which allow combining in a synergic form, the physicochemical properties of the original components, have been widely used for the preparation of organic–inorganic hybrid materials. Additionally it is possible to monitor the morphological characteristics starting from the synthesis conditions [2–9]. The inorganic phase is mostly obtained from metal alkoxides via hydrolysis and condensation reactions in the sol–gel process. Tetraethoxysilane (TEOS) is commonly used as a precursor of silica in this process [10–15].

The narrow, intense emission bands of europium (III) make its compounds of interest for various optical source applications, and sol–gel derived silica glasses doped with rare earth (RE) ions complexes are an important class of sol–gel optics with applications including solid-state lasers and fiber amplifiers [16]. However, this conventional doping method seems unable to solve the problem of clustering of emitting centers because only weak interactions (such as hydrogen bonding, van der Waals forces, or week static effects) exist between organic and inorganic moieties. In addition, inhomogeneous dispersion of two phases and leaching of the photoactive molecules frequently occur in this sort of hybrid material for which the concentration of complexes is also prohibited. As a consequence, a few studies in terms of the covalently bonded hybrids (class□hybrid materials [17]) have appeared and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration of rare-earth complexes [18-30], besides, the reinforcement of thermal and mechanical resistances has been clearly established.

In this paper, we prepared two kinds of molar-based materials with a Schiff-base compound as the organic parts. The Schiff-base compound N,N'-bis(salicylidene) ethylenediamine (denoted as BSEA) was first synthesized by the reaction of salicylaldehyde with ethylenediamine, and then functionalized with trialkoxysilyl groups, the as-obtained silylated monomers (denoted as BSEA-Si) was used as the siloxane network precursors to introduce into silica matrixes by Si-O bonds after hydrolysis and polycondensation processes. Because the organic compounds are covalently bonded to the silicon network through Si–C bonds, the organic groups become an integral part of the materials and thus homogeneous complicated huge molecule systems with regular uniform microstructures were obtained.

2. Experimental Section

2.1 Physical measurements

FT-IR spectra (KBr) were measured within the 4000-400 cm^{-1} region on a Nicolet model 5SXC spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Melting points were measured on a XT4-100XA apparatus and were uncorrected. Scanning electronic microscope (SEM) images were obtained with a Philps XL-30. The X-ray diffraction (XRD) measurements were carried out on powdered samples via a BRUKER D8 diffractometer (40 mA /40 kV) using monochromated Cu $K_{\alpha1}$ radiation (λ=1.54 Å) over the 2θ range of 10° to 70°. Fluorescence excitation and emission spectra were obtained on a Perkin-Elmer LS-55 spectrophotometer with 5 nm excitation slit and 3 nm emission one.

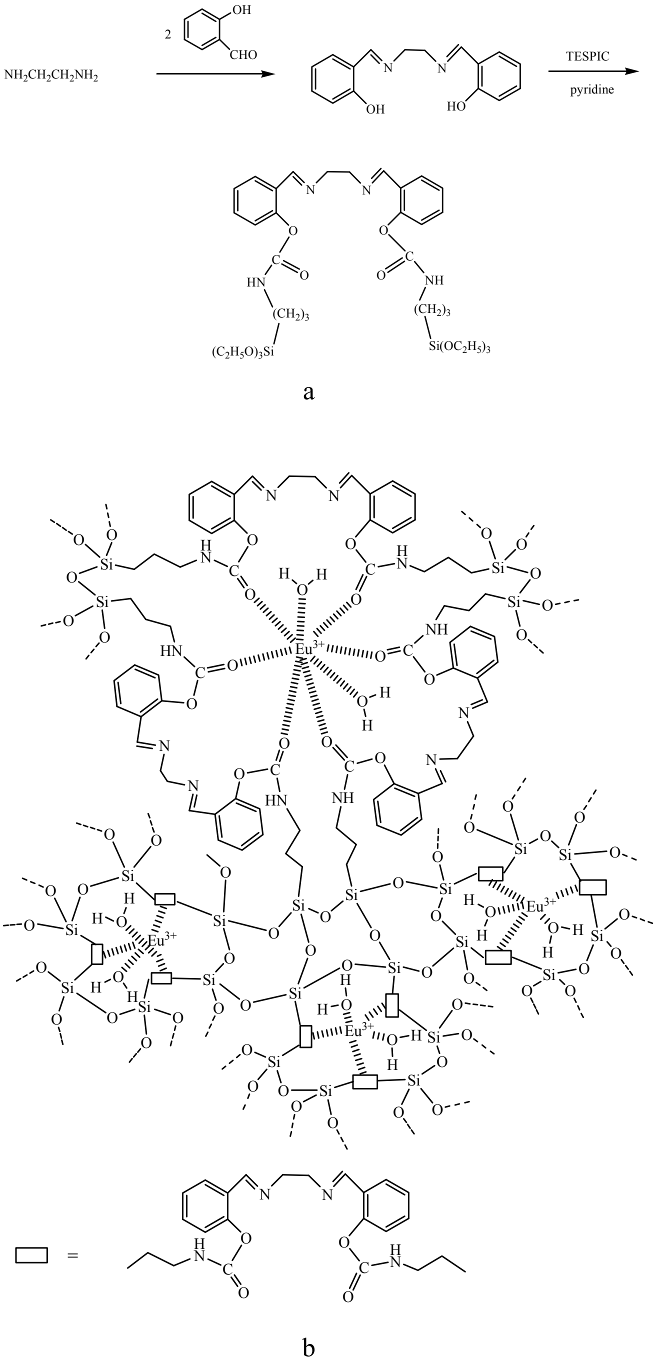
2.2 Materials

Starting materials were purchased from China National Medicines Group. Tetraethoxysilane (TEOS) was distilled and stored under a N_2 atmosphere. The solvents were purified according to the literature procedures [31]. Other starting reagents were used as received. Europium nitrate was obtained from its corresponding oxide in concentrated nitric acid.

2.3 Synthesis

The di-Schiffbase compounds N,N'-bis(salicylidene) ethylenediamine (BSEA) and the silylated precursors (BSEA-Si) were prepared according to the procedure depicted in Fig. 1a. The hybrid materials (BSEA-Hybrids, BSEA-Eu-Hybrids) were prepared by the hybridization of the precursors and TEOS through hydrolysis and polycondensation processes.

Synthesis of N,N'-bis(salicylidene)ethylenediamine (BSEA) 0.493 g (4.4 mmol) salicylaldehyde was dissolved in 20 ml of absolute ethanol, and then 0.120g (2 mmol) ethylenediamine dissolved in 10 ml of absolute ethanol was added dropwise. The resulting mixture was heated under reflux for about 5 hours. After cooling, the precipitate was filtered off. The crude product was purified by recrystallization form absolute ethanol and finally obtained as yellow crystals, yield 0.468 g (87.2%). m.p.129 ~ 131 ℃. ^1H NMR ($CDC1_3$, 500 MHz): δ 3.92 (t, 4H, NCH_2); 6.87, 6.96, 7.23, 7.30 (8H, Ar); 8.33 (s, 2H, *Ar*CH); 13. 2 (s, 2H, OH). ^{13}C NMR ($CDC1_3$, 100 MHz): δ 59.6 (NCH_2); 56.8 (NCH_2CH_2); 160.9, 132.3, 131.4, 119.7, 118.6, 116.4 (Ar); 166.4 (*Ar*CH)



a

b

Fig. 1. Scheme of the synthesis process of the Schiff-base compound BSEA and the precursor BSEA-Si a) and the predicted structure of the hybrid BSEA-Eu-Hybrids b)

Synthesis of silylated precursors (BSEA-Si) To a warm solution of BSEA (1 mmol) in 10 ml of pyridine, 3-(triethoxysilyl)-propyl isocyanate (TESPIC) (2.2 mmol) dissolved in 10 ml of pyridine was added dropwise with stirring, the mixture was warmed at 80 ℃ overnight under argon in a covered flask. The solvent was removed in vacuo, and the residue was washed with 20 ml of hexane three times then clear yellow oil was obtained in a 96.9 % yield. ^{1}H NMR ($CDC1_3$, 500 MHz): δ 0.58 (t, 4H, CH_2Si); 1.22 (t, 18H, $CH_3\mathit{CH_2}$); 1.67(m, 4H, $\mathit{NHCH_2}CH_2\mathit{CH_2}Si$); 3.08(m, 4H, $\mathit{NH}CH_2$); 3.75(q, 12H, $SiOCH_2$); 3.95 (t, 4H, NCH_2); 6.85, 6.98, 7.30, 7.42 (8H, Ar); 8.01 (t, 2H,NH); 8.12 (s, 2H, *Ar*CH). ^{13}C NMR ($CDC1_3$, 100 MHz): δ 12.7 (CH_2Si); 18.4($CH_3\mathit{CH_2O}$); 25.5 ($NH\mathit{CH_2}CH_2\mathit{CH_2}Si$); 43.2 ($NHCH_2$); 58.4($\mathit{CH_3}CH_2\mathit{O}$); 68.8 ($NCH_2$); 151.1, 130.2, 130.0, 125.3, 123.6, 122.7, (Ar); 155.4 (C=O), 160.5(*Ar*CH).

Preparation of the sol-gel derived hybrid materials (BSEA-Hybrids and BSEA-Eu-Hybrids) To a solution of BSEA-Si (1 mmol) in 10 ml of DMF, $Eu(NO_3)·6H_2O$, H_2O and TEOS were added while stirring, the mole ratio of $Eu(NO_3)·6H_2O$/BSEA-Si/TEOS/H_2O was 1:3:12:48. And then one drop of diluted hydrochloric acid was added to promote hydrolysis. The resulting solution was vigorously stirred for 3 h. After the treatment of hydrolysis, an appropriate amount of hexamethylene-tetramine was added to adjust the pH value of 6~7. The mixture was agitated magnetically to achieve a single phase, the resulting sol was aged in covered Teflon beakers at room temperature until the onset of gelation, and thermal treatment was performed at 60 ℃ until the sample solidified. The powder materials BSEA-Eu-Hybrids were then obtained after being washed with ethanol and dried for 2 days.

BSEA-Hybrids was prepared by the same manner only without the addition of $Eu(NO_3)·6H_2O$.

3. Results and discussion

3.1 Di-Schiffbase compound N,N'-bis(salicylidene)ethylenediamine (BSEA) and the silylated precursor (BSEA-Si)

As detailed in the Experimental Section, ^{1}H as well as ^{13}C spectra relative to the Schiff-base compound BSEA and the corresponding silylated precursor BSEA-Si are in full agreement with the proposed structure. The accomplishment of the hydrogen transfer reaction between OH group of BSEA and the TESPIC can be proved by the ^{1}H NMR chemical shifts relative to OH bond, which is observed in BSTA at 13. 2 δ and disappeared in the corresponding silylated precursor BSTA-Si, meanwhile, the single peak observed for carbonyl group in ^{13}C NMR spectra attributed to –CONH– groups demonstrate the whole amount of Schiff-base compound has reacted. Furtherly, integration of the ^{1}H NMR and ^{13}C signals corresponding to ethoxy groups shows that no hydrolysis of the precursors occurred during the grafting reaction.

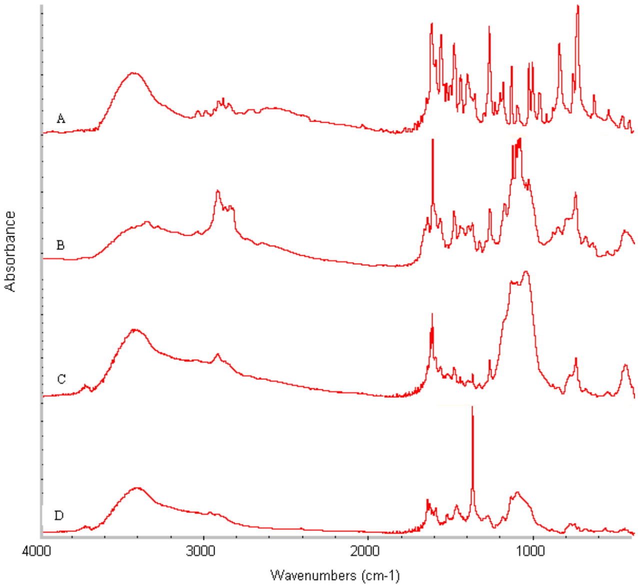


Fig. 2. Infrared spectra of BSEA (a), BSEA-Si (b), BSEA-Hybrids (c) and BSEA-Eu-Hybrids (d) in the 000-400 cm^{-1} range.

The synthesis of Schiff-base compound BSEA and the grafting reactions of BSEA with TESPIS can also be confirmed by the FT-IR. Fig. 2 shows the IR spectra of BSEA (A), BSEA-Si (B) in the 4000-400 cm^{-1} range. The emergence of the strong vibrations bonds of C=N at around 1615 cm^{-1}, together with the disappearance of the characteristic absorption peaks of NH_2 group located at 3272, 3203, proves the formation of the Schiff-base compound. The grafting reaction of BSEA with TESPIS was supported by the band located at 1629 cm^{-1}, which originated from the absorption of –CONH– group. In addition, the bending vibration (δ_{NH}, 1501 cm^{-1}) further proves the formation of amide group. Otherwise, the presence of a series of strong bands at around 2937, 2894, 2862 cm^{-1} due to the vibrations of methylene $–(CH_2)_3–$ and the disappearance of the stretch vibration of the absorption peaks at 2250-2275 cm^{-1} for N=C=O of TESPIC indicate that BSEA has been successfully grafted on to TESPIC. Besides, the stretching vibration of Si-C located at about 1200 cm^{-1}, and the stretching vibration of Si-O at 1103 cm^{-1} and 1079 cm^{-1}, together with the bending vibration at 460 cm^{-1} indicates the absorption of the siloxane bonds.

3.2 Hybrid materials (BSEA-Hybrids and BSEA-Eu-Hybrids)

3.2.1 FI-IR spectra

The obtained hybrid materials were also characterized by infrared spectroscopy. The IR spectra of BSEA-Hybrids (c), BSEA-Eu-Hybrids (d) and the assignments of main infrared absorption bands are also shown in Fig. 2 and Table 1, respectively. Both spectra are dominated by the broad absorptions of the ν(Si-C) vibration, which located in 1200-1192 cm^{-1} wavelength range, and the (ν(Si-O-Si)) vibration, which located in 1120-1050 cm^{-1} wavelength range. The presence of the ν(Si-C) absorption is consistent with the fact that no (Si-C) bond cleavage occurs [23], while the absorption of ν(Si-O-Si) indicates the formation of siloxane bonds during the hydrolysis/condensation reactions. However, The ν(O-H) vibration at around 3435 cm^{-1} can also be observed, which means the existence of residual silanol groups. And the ν(Si-OH) stretching vibration at 956 cm^{-1} is a further evidence of the incompleteness of condensation reactions.

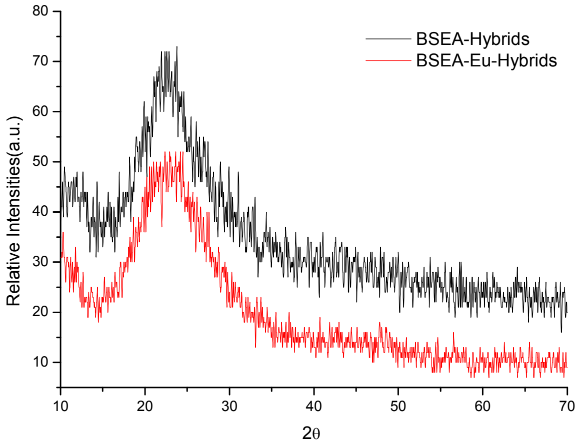


Fig. 3. The X-ray diffraction (XRD) graphs of BSEA-Hybrids (a) and BSEA-Eu-Hybrids (b).

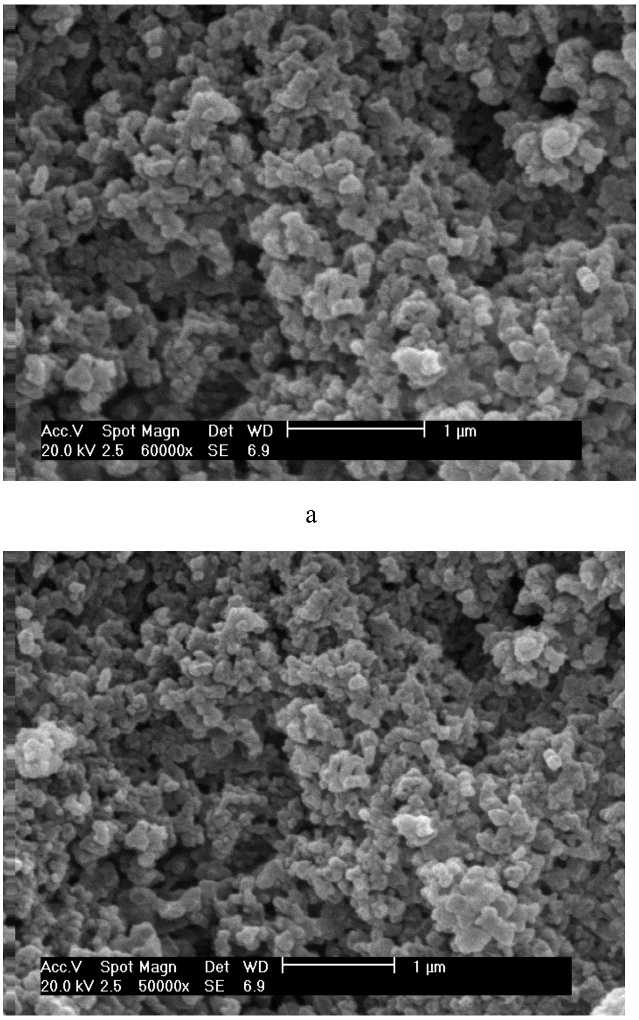
Furtherly, the complexation of Eu^{3+} in BSEA-Eu-Hybrids can be clearly shown by infrared spectroscopy. Compared with BSEA-Hybrids in which there is no Eu^{3+} ion, the ν(C=O) vibration is shifted to higher frequency (from 1632 cm^{-1} in BSEA-Hybrids to 1655 cm^{-1} in BSEA-Eu-Hybrids), This is ascribe to the complexation of the Eu^{3+} ion with the oxygen atom of the C=O group in BSEA-Eu-Hybrids [23].

3.2.2 Powder XRD

The X-ray diffraction patterns of the hybrid materials BSEA-Hybrids and BSEA-Eu-Hybrids reproduced in Figure 3 reveal that all the materials are totally amorphous. The broad peak is centered around 22.5° in the XRD and the structural unit distance, calculated using the Bragg law, is approximately 3.95 Å. This may be ascribed to the coherent diffraction of the siliceous backbone of the nanohybrids [32, 33]. The absence of any crystalline regions in these samples is due to the presence of organic chains in the host inorganic framework, By comparison with the two patterns, it seems that the introducing of Eu^{3+} ion has no influence on the disorder structure of the siliceous skeleton. In addition, neither of the hybrid materials contains measurable amounts of phases corresponding to the pure organic Schiff-base compound or free europium nitrate, which is an initial indication for the formation of the true covalent-bonded hybrid materials.

3.2.3 Scanning electron micrograph (SEM)

The scanning electron micrograph for the hybrid materials demonstrates that a homogeneous system was obtained. Fig. 4 shows the selected micrographs for BSEA-Hybrids (A) and BSEA-Eu-Hybrids (B). The regular ordered microstructures for both materials suggest that a self-assembly process might occur during polymerization reaction of the silylated precursors and TEOS. According to some previous work[29,34,35], the hybridization of the silylated precursors with TEOS proceeds through a polycondensation reaction between the terminal silanol groups of the silylated precursors and the OH groups of hydrolyzed TEOS. At the beginning of the reaction, the individual hydrolysis of the silylated precursors and TEOS are predominant, and then, the polycondensation reactions between hydroxyl groups of both the silylated precursors and TEOS will take place and then the inorganic and the organic parts were bridged by the strong covalent bonds through a functional bridge lignad. Fig. 1b shows the predict structure of BSEA-Eu-Hybrids as an example. Because BSEA-Si has two terminal silanol groups, they would be used as a bridge to introduce into the Si-O matrix network after the hydrolysis/polycondensation processes [36]. By this way, the organic Schiff-base compounds BSEA was grafted into the inorganic silica network as an integral part and thus a huge molecular hybrids was formed, they were composed quite uniformly during the hydrolysis/polycondensation process so that the two phases can exhibit their distinct properties together and no phase separation happened [25, 34, 37, 38].



a

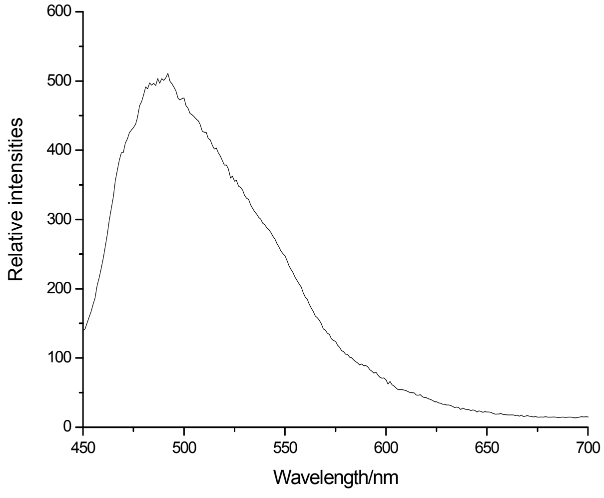
b

Fig. 4 The scanning electron micrograph (SEM) of BSEA-Hybrids (a) and BSEA-Eu-Hybrids (b).

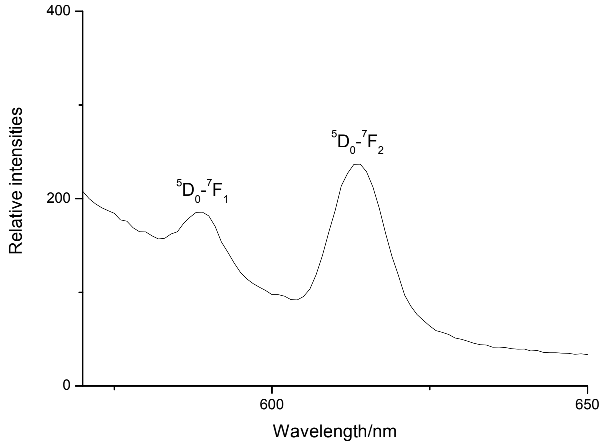
As can be seen from the scanning electron micrographs, both hybrid materials are composed of a homogenous coralloid microstructures. A large number of regular three-dimensional globes with sizes of 50-100 nm are dispersed homogenously on the coralline. The above phenomenon might be explained by the tendency of the construction for the three-dimensional polymeric network structure of Si-O-Si in the hydrolysis and copolycondensation reactions of silica. The pinholes in the coralline might be due to the lager difference in thermal expansion coefficients between the cross-linked Schiff-base organic ligand and the silica or to the evaporation of the solvent DMF and the adsorptive H_2O and ethanol originating from the hydrolysis/polycondensation reactions. Ulteriorly, compared with the two SEM pictures, There exists nearly no difference between them. This verifies that Eu^{3+} ion does not play an important role in the molecular assembly of the polymeric hybrids. Because the size of Eu^{3+} ion is too small compared with the huge molecular hybrids, the Eu^{3+} ion has no influence on the formation of the Si-O-Si network.

3.2.4 Photoluminescence Properties

Fig. 5 shows emission spectra of BSEA-Hybrids (A) and BSEA-Eu-Hybrids (B). As for BSEA-Hybrids, the excitation wavelength is 396 nm selected from the excitation spectrum, as a result, the emission spectra shows a large broad band from 450 to 550 nm with the maximum emission wavelengths located at 487 nm, For this kind of materials, in which there is no metal ions contained, the strong dominant blue luminescence was dominating own to the organic Schiff-base ligand. It is presumed that different structures in the hybrid materials, especially the organic part, will induce to the different energy absorption and the different fluorescence emission. This kind of materials can be used as potential blue optical materials. As for BSEA-Hybrids, the emission lines of the hybrid materials were assigned to the transitions from the $^5D_0 \rightarrow {}^7F_j$ (j=1,2,3,4) transitions of Eu^{3+} ion at 590, 614, 650 and 700 nm. Among these emission peaks of the europium polymeric complexes, red emission intensities to electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ at about 614 nm are all stronger than the orange emission intensities of magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ at about 589 nm, which indicates europium ions locate in an environment without inversion symmetry. Emission of RE complexes usually results from the so called “antenna effect’’, which is defined as a light conversion process via an absorption energy transfer emission sequence involving distinct absorbing by a ligand (light collector) and emitting by a metal ion. The mechanism usually described for sensitized emission in rare-earth chelates proceeds through the following steps: (a) energy absorption via a ground singlet-excited singlet transition. (b) radiationless intersystem crossing from the excited singlet to the triplet states. (c) energy transfer from the ligands to lanthanide ions, and (d) lanthanide ions emission from the excited states [39-41]. 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.



a



b

Fig. 5. The emission spectra of BSEA-Hybrids (a) and BSEA-Eu-Hybrids (b).

4. Conclusions

In summary, a Schiff-base compound N,N'-bis(salicylidene)ethylenediamine (BSEA) has been modified with functional 3-(triethoxysilyl)-propyl isocyanate as a crosslinking intermediate, and the corresponding molecular based hybrid materials were obtained by the hydrolysis and polycondensation reactions among triethoxysilyl of silylated precursors with TEOS through the sol-gel process. For the inorganic and the organic parts were bridged by the strong covalent bonds and complicated huge molecular systems formed. These materials display the connection of their distinct properties together and no phase separation happened. From the further investigation into the luminescence properties, we can prove that the BSEA-Hybrids exhibits a strong fluorescence emission in blue range, this may due to the introduce of the Schiff-base organic functional groups in to the silica matrix network. The BSEA-Eu-Hybrids can show the characteristic luminescence of Eu^{3+} ion for the energy transfer process take place successfully between the organic parts and the Eu^{3+} ion. As the synthesis process can be easily applied to other organic ligands and to different alkoxysilanes, we may expect to obtain stable and efficient hybrid materials in optical or catalysis areas for the desired properties can be tailored by an appropriate choice of the precursors. However, the accurate structure and fluorescence emission quantum efficiency in such materials need further fundamental investigations.

Acknowledgement

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

References

[1] C. Sanchez, B. Julian, P. Belleville, M. Popall, J. Mater. Chem. **15**, 3559 (2005).
[2] L. R. Matthews, E. T. Knobbe, Chem. Mater. **5**, 1697 (1993).
[3] M. Casalboni, R. Senesi, P. Prospositio, Appl. Phys. Lett. **30**, 2969 (1997).
[4] B. Lebeau, C. E. Fowler, S. R. Hall, J. Mater. Chem. **9**, 2279 (1999).
[5] P. Innocenzi, H. Kozuka, T. J. Yoko, J. Phys. Chem. B. **101**, 2285 (1997).
[6] K. Mstsui, F. Momose, Chem. Mater. **9**, 2588 (1997).
[7] M. M. Collinson, Crit. Rev. Anal. Chem. **29**, 289 (1999).
[8] U. Schubert, N. Husing, A. Lorenz, Chem. Mater. **7**, 2010 (1995).
[9] D. S. F. Gay, Y. Gushikem, C. C. Moro, T. M. H. Costa, E. V. Benvenutti, J. Sol–Gel Sci. Technol. **34**, 189 (2005).
[10] M. Messori, M. Toselli, F. Pilati, E. Fabbri, P. Fabbri, S. Busoli, L. Pasquali, S. Nannarone, Polymer **44**, 4463 (2003).
[11] J. Jang, J. Bae, D. Kang, J. Appl. Polym. Sci. **82**, 2310 (2001).
[12] C. L. Chiang, C. C. M. Ma, Polym. Degrad. Stab. **83**, 207 (2004).
[13] Y. Wei, Q. Feng, J. Xu, H. Dong, K. Y. Qiu, S. A. Jansen, R. Yin, K. K. Ong, Adv. Mater.

12, 1448 (2000).
[14] C. J. T. Landry, B. K. Coltrain, B. K. Brady, Polymer **33**, 1486 (1992).
[15] K. F. Silveira, I.V.P. Yoshida, S.P. Nunes, Polymer **36**, 1425 (1995).
[16] I. M. Thomas, S.A. Payne, J.D.Wilke, J. Non-Crys. Solids **151**, 183 (1992).
[17] H. R. Li, J. Lin, H. J. Zhang, L. S. Fu, Chem. Mater. **14**, 3651 (2002).
[18] D. W. Dong, S.C. Jiang, Y.F. Men, X.L. Ji, B.Z. Jiang, Adv. Mater. **12**, 646 (2000).
[19] H. R. Li, L.S. Fu, H.J. Zhang, Thin Solid Films **416**, 197 (2002).
[20] H. R. Li, J. Lin, L.S. Fu, J. F. Guo, Q. G. Meng, F. Y. Liu, H. J. Zhang, Micropor. Mesopor. Mater. **55**, 103 (2002).
[21] F. Y. Liu, L.S. Fu, J. Wang, Z. Liu, H. R. Li, H. J. Zhang, Thin Solid Films **419**, 178 (2002).
[22] K. Binnemans, P. Lenaerts, K. Driesen, C. Gorller-Walrand, J. Mater. Chem. **14**, 291 (2004).
[23] A. C. Franville, D. Zambon, R. Mahiou, Chem. Mater. **12**, 428 (2000).
[24] Q. M. Wang, B. Yan, Inorg. Chem. Commun. **7**, 1124 (2004).
[25] Q. M. Wang, B. Yan, Appl. Organomet. Chem. **19**, 952 (2005).
[26] Q. M. Wang, B. Yan, J. Mater. Chem. **14**, 2450 (2004).
[27] Q. M. Wang, B. Yan, Inorg. Chem. Commum. **7**, 747 (2004).
[28] Q. M. Wang, B. Yan, J. Mater. Res. **20**, 592 (2005).
[29] Q. M. Wang, B. Yan, Cryst. Growth Des. **5**, 497 (2005).
[30] Q. M. Wang, B. Yan, J. Organomet. Chem. **691**, 540 (2006).
[31] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press: Oxford. 1980.
[32] L. D. Carlors, V. de Zea. Bermudez, R. A. Sa Ferreira, L. Marques, M. Assuncao, Chem. Mater. **11**, 581 (1999).
[33] M.C. Goncalves, V.de Zea. Bermudez, R.A. Sa Ferreira, L.D. Carlos, D. J. Ostrovskii, Rocha, Chem. Mater. **16**, 2530 (2004).
[34] Q. M. Wang, B. Yan, J. Photochem. Photobiol. A.**175,** 159 (2005).
[35] B. Yan, D. J. Ma, J. Solid State Chem. **179**, 2059 (2006).
[36] L. D. Carlors, R. A. Sa Ferreira, R. N. Pereira, M. Assuncao, V. de Zea. Bermudez, J. Phys. Chem. B. **108**, 14924 (2004).
[37] Q. M. Wang, B. Yan, J. Photochem. Photobiol. A. **178**, 70 (2006).
[38] B. Yan, F. F. Wang, J. Organomet. Chem. **692**, 2395 (2007).
[39] G. A. Crosby, R. E. Whan, R. E. Alire, J. Chem. Phys. **34**, 743 (1961).
[40] O. L. Malta, J. Lumin. **71**, 229 (1997).
[41] O. L. Malta, Spectrochim. Acta, Part A. **54**, 1593 (1998).

---

*Corresponding author : byan@tongji.edu.cn.