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Photophysical Properties of Luminescent Quaternary Lanthanide Molecular Hybrid Systems with Chemical Bonds from the Cooperative Design and Assembly of Structure and Function

Bing Yan · Shuai Xu · Hai- Feng Lu

Abstract   Two long chain aliphatic acyl chlorides (do-decanoyl chloride ($C_{10}H_{19}OCl$, abbreviated as DC) and stearoyl chloride ($C_{18}H_{35}Ocl$, abbreviated as SC)) were modified by means of the amidation reaction with crosslinking molecules (N-aminopropyl-triethoxylsiliane, (APES, $H_2N(CH_2)_3Si(OC_2H_5)_3$)) and afford two kinds of structural molecular bridge DC (SC)–APES with double reactivity. Subsequently, according to the principle of coordination chemistry, ternary lanthanide (terbium and europium) molecular complex systems with two molecular bridges DC (SC)–APES and 1,10-phenanthroline (phen) of were successfully assembled. Then the modified molecular bridges behave as structural ligands to form the covalent bond Si–O network with matrix precursor (tetraethoxysilane, TEOS) through a sol-gel process (cohydrolysis and copolycondensation process), resulting in a novel quaternary molecular hybrid material (so called as phen-Tb(Eu)−DC(SC)–APES) with strong chemical bonds (N–Tb(Eu)–O coordination bonds and Si–O covalent bonds). And phen behaves as functional ligand to sensitize the luminescence of terbium or europium ions through the effective intramolecular energy transfer process, which gives rise to the characteristic emission of metal ion.

Keywords   Quaternary molecular hybrid materials ·
Photophysical property · Lanthanides · Long chain aliphatic acyl chloride derivatives · 1,10-phenanthroline · Chemical bonds

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Introduction

In order to combine various features together, a wide range of organic-inorganic hybrid materials have attracted great scientific interest in latest decades [1, 2]. Recently, hybrid system of lanthanide organic coordination compounds were introduced in silica matrix, which could display characteristic emission intensities compared with simple metal ions in inorganic hosts. In particular, anchored lanthanide complexes by aromatic carboxylic acids, β-diketones or heterocyclic ligands in a sol-gel derived matrix have been discussed in many latest studies [3–5]. However, the properties of these hybrid materials depend not only on those of the individual moieties but also on the degree of mixing between them. The concentration on the organic-inorganic hybrids is associated with the extraordinary implications for the tailoring of diverse multi-functional advanced materials induced by the mixture at the covalent bond level which was discussed by Sanchez et al [6]. Class I is named as mechanical mixture and it seems impossible 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) exist between organic and inorganic components. In addition, 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. In contrast to Class I, the other is called the type that contains the structure properties of true connections by way of covalent bonding between the organic and inorganic moieties in a single material. The synergy of the combination and the special role of the inner interfaces open up exciting novel areas in materials science. Lately, some researches about the covalently bonded hybrids have emerged and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration

Fig. 1 Scheme of hydrolysis and polycondensation processes between quaternary molecular hybrids
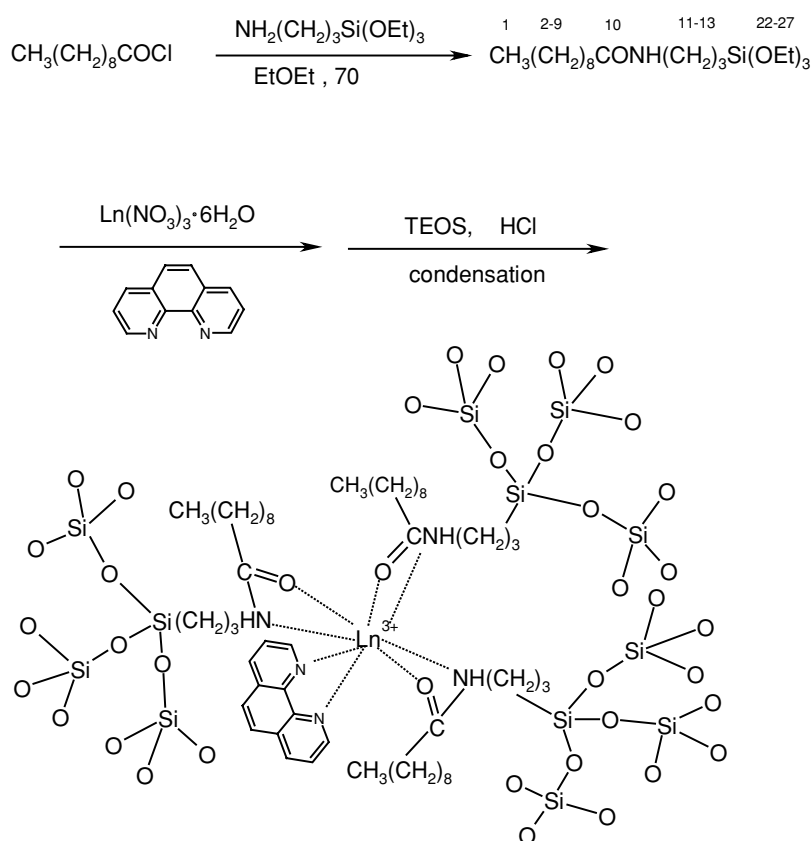
of rare earth complexes [7–18]. Hence, the critical step to prepare such materials is to synthesize a novel monomer as a covalent bridge which can not only develop chelating effects that can bind to lanthanide ions but also act as precursors of inorganic network. Our group presently concerns the preparation of –NHC(=O)NH- urea bridges connecting both siliceous backbone and aromatic carboxylic acids [12–18]. According to the previous work, we propose that the precursor containing non-hydrolyzable silicon-carbon bond, coordinative activity and hydrolyzable alkoxy-silicon parts will play an important role to form covalent linkage between the two phases.

On the basis of the later research, we put forward cooperative design and assembly of lanthanide molecular hybrid materials in accordance with coordination chemistry principle of ternary complexes. Two long chain aliphatic acyl chloride (dodecanoyl choride ($C_{10}H_{19}OCl$, abbreviated as DC) and stearoyl chloride ($C_{18}H_{35}OCl$, abbreviated as SC)) were modified by means of the amidation reaction with crosslinking molecules (N-aminopropyl-triethoxylsiliane, (APES, $H_2N(CH_2)_3Si(OC_2H_5)_3$)). 1,10-phenanthroline was used as the terminal functional ligand to sensitize the luminescence of lanthanide ions for the triplet state energies of phen are suitable for the resonant emissive energy level of Ln^{3+}. The reaction model for the hybridiza-

tion formula of quaternary hybrid materials has been described in Fig. 1, which can be divided into two steps: Step I: the individual hydrolysis of phen-Tb(Eu)−DC(SC)−APES and TEOS are predominant; Step II, however, is developed to the polycondensation reactions between hydroxyl groups of both phen-Eu(Tb)−DC(SC)−APES. After these treatments, the molecular-based hybrids bearing the Ln-O coordination bond and Si−O covalent bond can exhibit the luminescence of metal ions.

Experimental section

Modification of long chain aliphatic acyl chlorides (DC and SC) to molecular bridge

4 mmol APES (0.884 g) was dissolved into diethyl ether, two long chain aliphatic acyl chlorides, 4 mmol DC (0.763 g) (SC, 1.212 g) in diethyl ether solution were directly reacted with APES by stirring under argon atmosphere. Heating and refluxing at 70°C for 4 hours, yellow oil liquid products were achieved. A typical procedure for the preparation of was according to the reaction scheme in Fig. 1. Elemental data: DC−APES ($C_{19}H_{41}NO_4Si$): *Anal*. Calcd.: C, 60.75; H, 11.00; N, 3.73. Found: C, 61.01; H, 10.62; N, 3.56. Yields

86%. SC–APES ($C_{27}H_{57}NO_4Si$): *Anal*. Calcd.: C, 66.48; H, 11.78; N, 2.87. Found: C, 66.21; H, 11.42; N, 2.69. Yields 82%.

Synthesis of ternary lanthanide (Eu, Tb) complex systems with molecular bridge and phen

The alcohol solution of europium and terbium nitrate was added with the molar ratio 3:1 of to $RE(NO_3)_3 \cdot 6H_2O$ (RE = Eu, Tb), the resulting solution was stirred for 2 hour and ethanol solution of 1,10-phenanthroline was added into the mixture gradually (phen: RE = 1:1). After stirring for 2 hrs, a stoichiometric amount of tetraethoxysilane (DC(SC)–APES): TEOS = 1: 1) and minimum water were added to the solution simultaneously. Element analysis data: *Anal*. Calcd. for $EuC_{69}H_{131}N_5Si_3O_{12}$: C, 56.80; H, 9.05; N, 4.80; Eu, 10.38%; Found: C, 56.62; H, 8.89; N, 4.60; Eu, 10.16%. *Anal*. Calcd. for $TbC_{69}H_{131}N_5Si_3O_{12}$: C, 56.53; H, 9.01; N, 4.78; Tb, 10.84%. Found: C, 56.29; H, 8.71; N, 4.59; Tb, 10.67%. $EuC_{93}H_{179}N_5Si_3O_{12}$: C, 62.21; H, 10.05; N, 3.90; Eu, 8.46%. Found: C, 62.37; H, 9.79; N, 3.71; Eu, 8.59%. *Anal*. Calcd. for $TbC_{93}H_{179}N_5Si_3O_{12}$: C, 61.97; H, 10.01; N, 3.89; Tb, 8.82%. Found: C, 62.21; H, 9.71; N, 3.73; Tb, 8.91%. It should be pointing out that the precursor complex is so easily to hydrolyze that the store of samples has to be done as carefully as possible. (Figure 1)

Assembly of quaternary molecular hybrid materials

A sol-gel derived quaternary hybrid material was prepared as follows: DC(SC)–APES was dissolved in pyridine, and TEOS (tetraethoxysilane), H_2O were added while stirring, then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. A stoichiometric amount of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Eu, Tb) was added to the final stirring mixture. The molar ratio of $Ln(NO_3)_3 \cdot 6H_2O$/ DC (SC)–APES / 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 about 6.5. The mixture was stirred to achieve a single phase and thermal treatment was performed at 60°C in a covered Teflon beaker until the sample solidified (Fig. 1).
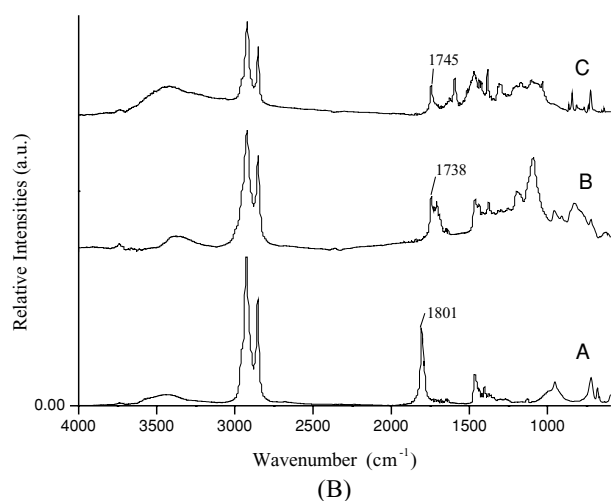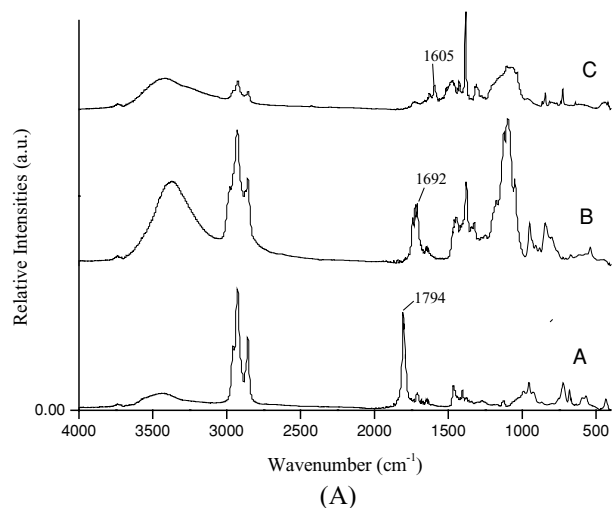
Physical measurements

All measurements were completed under room temperature. Elemental analyses (C, H, N) were carried out by the Elementar Cario EL elemental analyzer. FT-IR spectra were measured within the 4000–400 cm^{-1} region on an infrared spectrophotometer with the KBr pellet technique. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol·L^{-1}

chloroform ($CHCl_3$) solution) were recorded with an Agilent 8453 spectrophotometer (precision of bands at 1 nm). Phosphorescence spectra (5×10^{-4} mol·L^{-1} $CHCl_3$ solution) and fluorescence excitation and emission spectrums were obtained on a Perkin-Elmer LS-55 spectrophotometer.
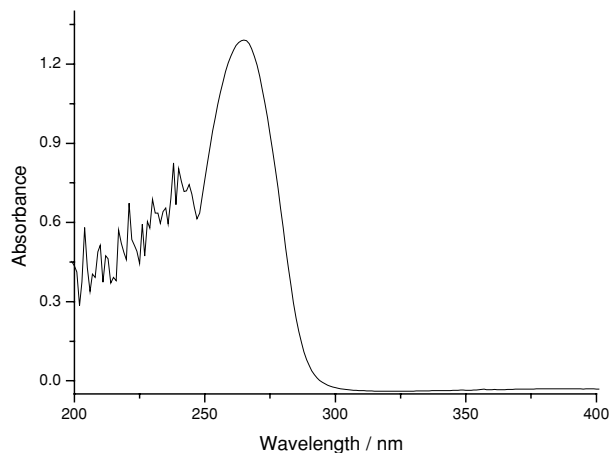
Results and discussion

The reaction model for the hybridization formula of TEOS and DC(SC)–APES may be described as follows: The hybridization of TEOS and DC(SC)–APES, accordingly, proceeds through a polycondensation reaction between the terminal silanol groups of DC(SC)–APES and the OH groups of hydrolyzed TEOS. At the beginning of the reaction, the individual hydrolysis of DC(SC)–APES and TEOS are predominant. 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 DC(SC)–APES and TEOS during the in-situ sol-gel process as cohydrolysis and copolycondensation (similar to copolymerization of organic monomer).

Figure 2 (A) shows the I.R. spectra of DC (A), DC–APES (B) and quternary phen-Tb–APES–Si hybrids (C), repsectively. Compared with the I.R. spectrum of DC, DC–APES presents a streching vibration peak of N-H at 3373 cm^{-1}, streching vibration peak1 of C=O at 1692 cm^{-1} and a bending vibration peak of N-H at 1608 cm^{-1}, which suggests that the acyl chloride group of DC has been modified succefully. Besides, the 1013 cm^{-1} of Si–O further verifies that the AMES molecular fragment has been grafed to DC. The I.R. spectra of quternary phen-Tb–APES–Si hybrids show the similar characteristic feature with the corresponding bridge ligand DC–APES except that the vibration frequency of 1652 cm^{-1} belonging to the phenyl ring of phen becomes weaker than that of free phen and the out-of plane bending vibrations of the hydrogen atom on the phenyl ring of phen shift from 865, 745 cm^{-1} of free ligand to lower frequency of 854, 737 cm^{-1}. This verified that phen participate the coordination with europium or terbium ions. Likewise, Eu^{3+} or Tb^{3+} exhibit a similar coordination behavior with DC–APES and phen. Furthermore, the stretching vibration (ν_{Si-C}) located at 1210 cm^{-1} still exists in the IR spectra of hybrid materials, which is in agreement with the fact that no (Si–C) bond split happens during the course of hydrolysis/polycondensation reactions. Figure 2 (B) presents the IR spectra for SC (A), SC–APES (B) and quternary phen-Tb-SC–APES–Si hybrids (C), which wears the similar feature with those of Fig. 2 (A). Different from the I.R. spectrum of SC, three apparent peaks appear in the I.R. spectra of SC–APES (3370 cm^{-1} (N-H streching vibration), 1680 cm^{-1} (C=O streching vibration) and 1633 cm^{-1} (N-H bending vibration), which indicate that the CO=NH

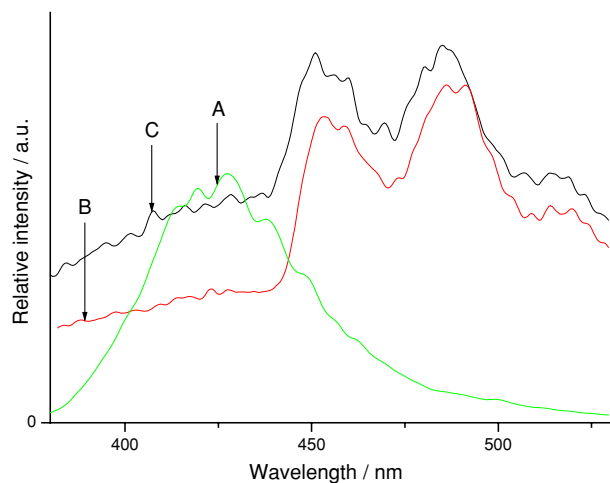Fig. 2 FT-IR spectra of (A) OLA, (B) OLA–AEAPMMS, (C) OLA–APMES

Fig 3 The ultraviolet absorption spectra of phen-Tb-SC–APES

Figure 3 exhibits ultraviolet absorption spectra of ternary phen-Tb–SC–APES molecular complex system. The obvious band at 266 nm shows characteristic absorption of 1, 10-phenanthroline, which can be ascribed as the absorption of phen for free phen presents one absorption peak at 265 nm. The red-shift of 1 nm is due to the more extensive conjugated system of electronic distribution form because the coordination between lanthanide ions and phen. Other ultraviolet absorption spectra of ternary molecular systems all show the similar features. Therefore, it can be predicted in quaternary hybrids phen-Ln–DC(SC)–APES–Si, 1, 10-phenanthroline behaves as the energy donor and will transfer energy to lanthanide ions.

As shown in Figure 4 for the phosphorescence spectra of (A) Tb-SC–APES complex, (B) Tb-phen complex and (C) phen-Tb-SC–APES ternary complex, it can be observed 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 intramolecular energy

group forms and the amidation reaction takes place. Futhermore, the Si–O peaks at 1095.27 cm^{-1} for SC–APES as well prove that the SC has been grafted with the crosslingking molecule (APES). Compared to free SC−APES bridge molecule, quternary phen-Tb-SC–APES–Si hybrids shows the the vibration frequency of 1653 cm^{-1} belonging to the phenyl ring of phen becomes weaker than that of free phen and the out-of plane bending vibrations of the hydrogen atom on the phenyl ring of phen shift from 865, 744 cm^{-1} of free ligand to lower frequency of 849, 736 cm^{-1}, which verifies the coordination of terminal phen ligand. For the finally quaternary hybrids, the stretching vibration (ν_{Si-C}) located at 1198 cm^{-1} still exists in the IR spectra of hybrid materials, corresponded to the fact that no (Si–C) bond split happens during the course of hydrolysis/polycondensation reactions. Moreover, the broad absorption band at 1085 cm^{-1} ($\nu_{Si-O-Si}$) originates from the formation of siloxane bonds.

Fig. 4 The phosphorescent spectra of (A) Tb-SC–APES complex, (B) Tb-phen complex and (C) phen-Tb-SC–APES ternary complex

mechanism [19–22], intramolecular 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 Ln^{3+} ion by Dexter's resonant exchange interaction [23]; the second one is just an inverse energy transfer by a thermal deactivation mechanism [24]. 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 around 429 nm of A shows SC−APES's triplet state energy level is approximately 23300 cm^{-1} which is higher than phen (453 nm, 22075 cm^{-1}), therefore, we suppose that energy transfer process will occur from SC−APES to phen, substantiating that the heterocyclic ligand will become main energy donor and have the possibility to sensitize Tb^{3+} ions.

The excitation spectra for the four kinds of quaternary molecular hybrids by monitoring the emission of Tb^{3+} or Eu^{3+} ions at 614 or 545 nm are shown in Fig. 5. Some
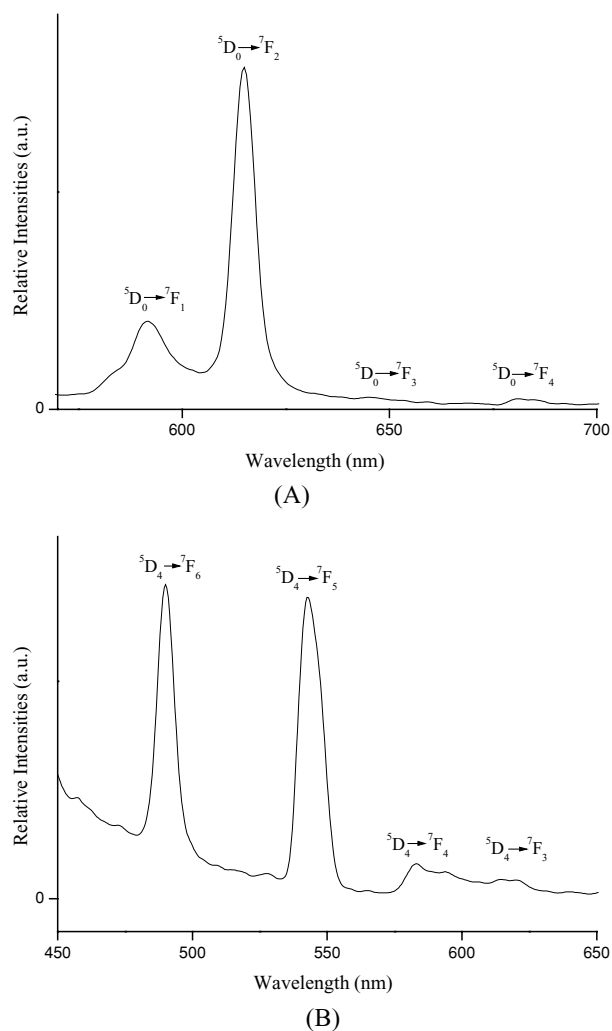

(A)

(B)
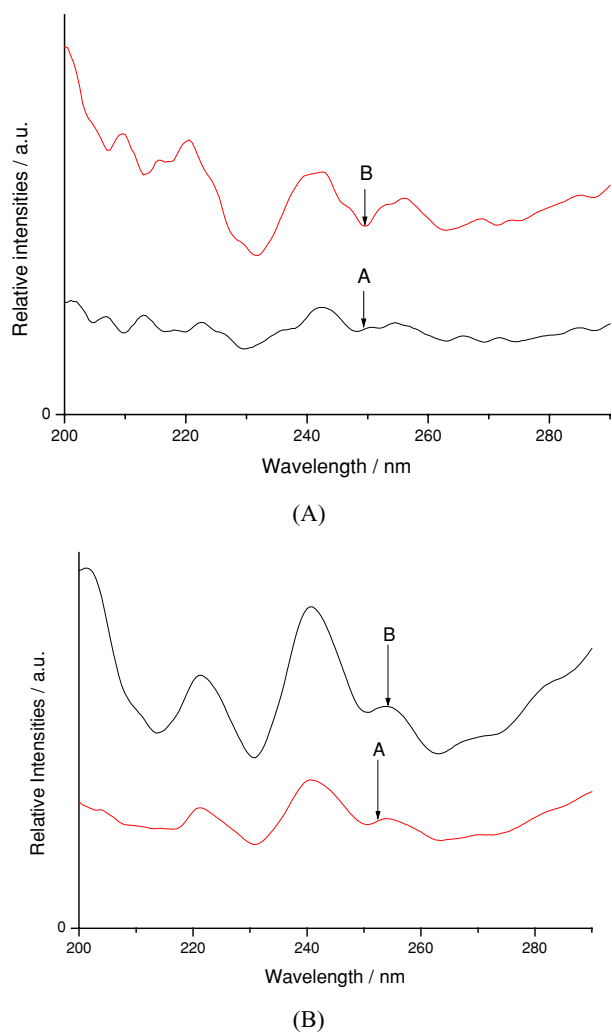
Fig. 5 Excitation spectra of quaternary molecular hybrids (A) phen-Ln−DC−APES, (B) phen-Ln−SC−APES

(A)

(B)
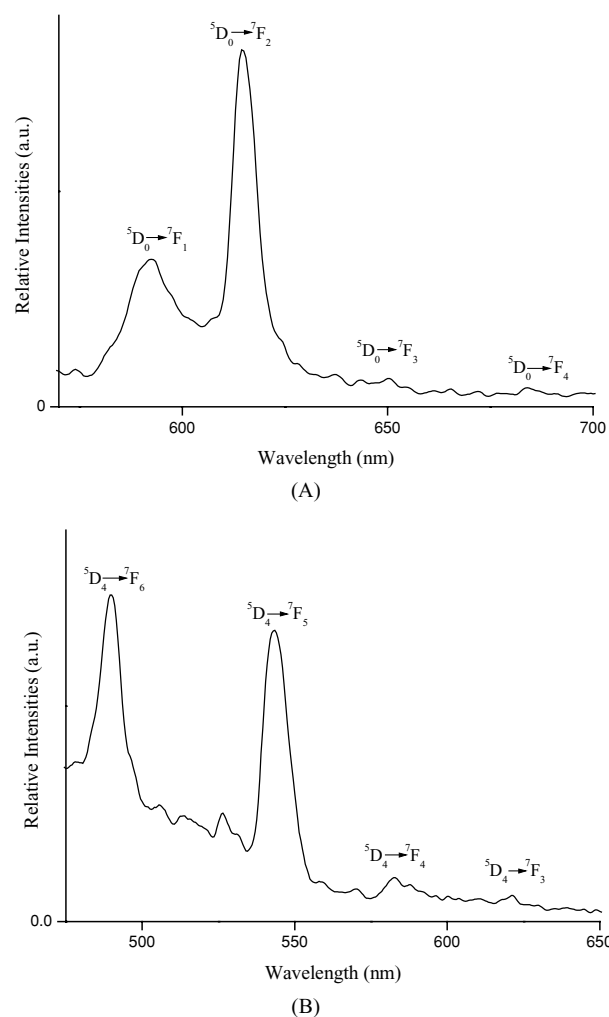
Fig. 6 Emission spectra of quaternary molecular hybrids (A) phen-Eu−DC−APES, (B) phen-Tb−SC−APES
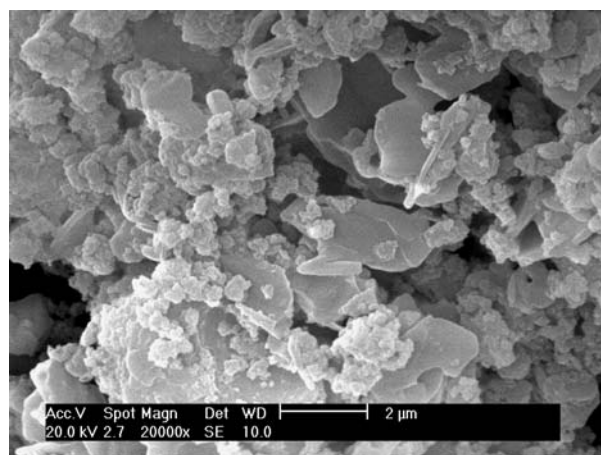
absorption bands were mainly situated at the short wavelength region of 200 to 300 nm, suggesting the absorption primary derives from the organic ligands (phen). Which take agreement with the prediction of ultraviolet absorption and phosphorescent spectra. The corresponding emission spectra of the resulting quaternary hybrid materials are shown in Figs. 6 and 7. For quaternary molecular hybrids phen-Eu(Tb)-DC−APES−Si (Fig. 6), the emission lines of the hybrid material were assigned to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions at 590 nm, 614 nm, 650 and 700 nm of Eu^{3+} and the transitions from the $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions at 490, 544, 587 and 622 nm for terbium, respectively. Among these emission peaks, the most striking green luminescence ($^5D_4 \rightarrow {}^7F_5$) 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 phen and the chelated Ln ions. The quaternary molecular hybrids phen-Eu(Tb)-SC−APES−Si presents the similar features (as shown in Fig. 7). Other factors still can
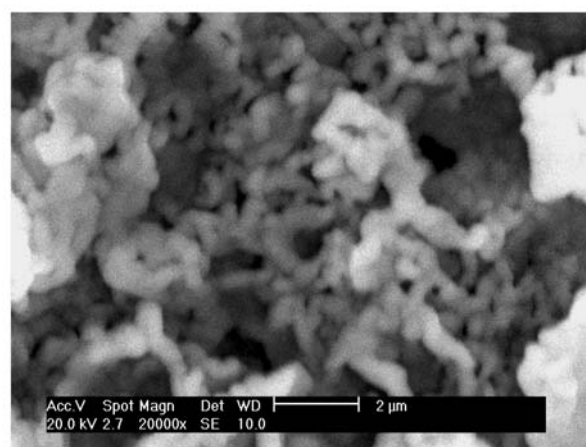
Fig. 7 Emission spectra of quaternary molecular hybrids (A) phen–Eu–SC–APES, (B) phen-Tb–SC–APES

Fig. 8 Scanning electronic microscopy diagraphs of quaternary molecular hybrids: (A) phen-Tb–DC–APES–Si, (B) phen-Tb–SC–APES–Si

not 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 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.

Figure 8 wears the selected scanning electron micrographs for these quaternary molecular hybrids, (A) phen-Tb-DC–APES–Si and (B) phen-Tb-SC–APES–Si, which verifies that a homogeneous, molecular-based material 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 uniformly so that the two phases can exhibit their distinct properties together, which overcome the disadvantages of that the hybrid materials with doped rare earth complexes generally experience phase separation phenom-

ena [19, 20]. Ulteriorly, compared with the three SEM pictures, there exist a little distinction that the hybrid materials of phen-Tb-SC–APAES–Si possess the regular microstructure and micro morphology, which may be due to the difference of the precursor molecules. Phen-Tb-SC–APES is a derivative from SC (C_{18}), whose chain length is longer than that of phen-Tb–DC–APES from DC (C_{10}). So the template effect of phen-Tb–SC–APES are stronger than that of phen-Tb–DC–APES, resulting the stronger orientation and induction ability, which gives rise to the different microstructure in different quaternary molecular hybrids.

Conclusions

In summary, by means of the molecular modification of long chain aliphatic acyl chlorides (dodecanoyl choride and stearoyl chloride) with crosslinking molecule (N-aminopropyl-triethoxylsiliane) through the amidation

reaction, two kinds of structural molecular bridges DC(SC)–APES were designed to endue double reactivity. Furthermore, ternary molecular complex systems with four molecular bridges and 1,10-phenanthroline of lanthanides (terbium and europium) ions were successfully assembled. The modified molecular bridges behave as structural ligand to form the covalent bond Si–O network with matrix precursor (tetraethoxysilane, TEOS) through a sol-gel process (cohydrolysis and copolycondensation process) and phen acts as the energy donor to sensitize the luminescence of metal ions. A series of quaternary molecular hybrid materials (phen–Ln − OLA (STA)–APES) with strong chemical bonds were constructed, which show the characteristic luminescence and uniform microstructure.

References

1. Suratwala T, Gardlund Z, Davidson K, Uhlmann DR (1998) Silylated coumarin dyes in sol-gel hosts. 1. Structure and environmental factors on fluorescent properties; Silylated coumarin dyes in sol-gel hosts. 2. Photostability and sol-gel processing. Chem Mater 10:190

2. Molina C, Dahmouche K, Santilli CV (2001) Structure and luminescence of Eu^{3+}-doped class I siloxane-poly(ethylene glycol) hybrids. Chem Mater 13:2818

3. Tanner PA, Yan B, Zhang HJ (2000) Preparation and luminescence properties of sol-gel hybrid material incorporated with europium complex. J Mater Sci 35:4325

4. Yan B, Zhang HJ, Wang SB, Ni JZ (1998) Luminescence properties of rare earth (Eu^{3+} and Tb^{3+}) complexes with conjugated carboxylic acids and 1,10-phenanthroline incorporated in silica matrix by sol-gel methods. J Photochem Photobiol A Chem 112:231

5. Yan B, Zhang HJ, Wang SB, Ni JZ (1998) Luminescence properties of rare earth (Eu^{3+} and Tb^{3+}) complexes with 1,10-phenanthroline incorporated in silica matrix by a sol-gel method." Mater Sci Eng B 52:123

6. Sanchez C, Ribot F (1994) Design of hybrid organic-inorganic materials synthesized via sol-gel chemistry. New J Chem 18:1007

7. Li HR, Lin J, Zhang HJ, Fu LS, Meng QG, Wang SB (2002) Preparation and luminescence properties of hybrid materials containing europium(III) complexes covalently bonded to a silica matrix. Chem Mater 14:3651

8. Dong DW, Jiang SC, Men YF, Ji XL, Jiang BZ (2000) Nanostructured hybrid organic-inorganic lanthanide complex films produced in situ via a sol-gel approach. Adv Mater 12:646

9. Franville AC, Zambon D, Mahiou R, Troin Y (2000) Luminescence behavior of sol-gel-derived hybrid materials resulting from covalent grafting of a chromophore unit to different organically modified alkoxysilanes. Chem Mater 12:428

10. Li HR, Lin J, Fu LS, Guo JF, Meng QG, Liu FY, Zhang HJ (2002) Microporous Mesoporous Mater 55:103

11. Binnemans K, Lenaerts P, Driesen K, Gorller-Walrand C (2004) A luminescent tris(2-thenoyltrifluoroacetonato) europium(III) complex covalently linked to a 1,10-phenanthroline-functionalised sol-gel glass. J Mater Chem 14:291

12. Wang QM, Yan B (2004) Novel luminescent terbium molecular-based hybrids with modified meta aminobenzoic acid covalently bonded with silica. J Mater Chem 14:2450

13. Wang QM, Yan B (2004) From molecules to materials: a new way to construct luminescent chemical bonded hybrid systems based with ternary lanthanide complexes of 1,10-phenanthroline. Inorg Chem Commun 7:1124

14. Wang QM, Yan B (2005) A novel way to luminescent terbium molecular-scale hybrid materials: modified heterocyclic ligands covalently bonded with silica. Cryst Growth Design 5:497

15. Wang QM, Yan B (2005) An unusual way to luminescent terbium molecular-level hybrid materials: modified methyl benzoic acid covalently bonded with silica as a bridge. J Mater Res 20:592

16. Wang QM, Yan B (2005) Construction of lanthanide luminescent molecular-based hybrid material using modified functional bridge chemically bonded with silica. J Photochem Photobiol A Chem 175:159

17. Yan B, Ma DJ (2006) From chemistry to materials, design and photophysics of functional terbium molecular hybrids from assembling covalent chromophore to alkoxysilanes through hydrogen transfer addition. J Solid State Chem 179:2059

18. Wang QM, Yan B (2006) Designing a family of luminescent hybrid materials by 3-(triethoxysilyl)-propyl isocyanate grafted 2-hydroxynicotinic acid bridge molecules. J Organomet Chem 691:3567

19. Zhang HJ, Yan B, Wang SB, Ni JZ (1997) The photophysical properties of binary and ternary complexes of lanthanide with conjugated carboxylic acids and 1,10-phenanthroline. J Photochem Photobiol A Chem 109:223

20. Yan B, Zhang HJ, Wang SB, Ni JZ (1998) Spectroscopic study of fluorescence and intramolecular energy transfer of binary and ternary lanthanide complexes with aromatic carboxylic acids and 1,10-phenanthroline. Spectro Lett 31:603

21. Yan B, Zhang HJ, Wang SB, Ni JZ (1998) Intramolecular energy transfer mechanism between ligands in ternary complexes with aromatic acids and 1,10-phenanthroline. J Photochem Photobiol A Chem 116:209

22. Wang QM, Yan B, Zhang XH (2005) Photophysical properties of novel lanthanide complexes with long chain mono-eicosyl cis-butene dicarboxylate. J Photochem Photobiol A Chem 174:119

23. Dexter DL (1953) A theory of sensitized fluorescence in solids. J Chem Phys 21:836

24. Brown TD, Shepherd M (1975) Evaluation of the intramolecular energy transfer rate constants in crystalline Eu(hfaa)4ButNH3. J Chem Soc Dalton Trans 336