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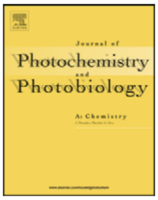

Coordination bonding assembly and photophysical properties of Europium organic/inorganic/polymeric hybrid materials

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Ternary organic/inorganic/polymeric hybrid material PVP-Eu-(DBM-Si)$_3$ (DBM = dibenzoylmethane; PVP = poly(4-vinylpyridine)) have been synthesized through the coordination bonds. The precursor DBM-Si is obtained by the modification of DBM molecule with a cross-linking reagent TEPIC (3-(triethoxysilyl)-propyl isocyanate), which is used to form the inorganic Si–O–Si networks with TEOS (tetraethoxysilane) after a hydrolysis and polycondensation process. PVP, which is obtained through the polymerization reaction using 4-vinylpyridine as the monomer in the presence of BPO (benzoyl peroxide), is used to form the organic polymeric C–C chains. For comparison, the binary organic/inorganic hybrid material Eu-(DBM-Si)$_3$ was also synthesized simultaneously. FT-IR (Fourier-transform infrared spectra), UV (ultraviolet absorption spectra), UV-DR (ultraviolet–visible diffuse reflection absorption spectra), SEM (scanning electron micrograph), PL (photoluminescence spectroscopy) and LDT (luminescence decay time) measurements are used to investigate the physical properties of the obtained hybrid materials. The results reveal that the ternary hybrids presents more regular morphology, higher red/orange ratio, stronger luminescent intensity, higher $^5D_0$ luminescence quantum efficiency and longer lifetime than the binary one, suggesting the property of the overall hybrid system is improved with the introduction of the organic polymer PVP.

1. Introduction

Nowadays, luminescent materials or devices based on rare-earth ions especially lanthanide organic/inorganic hybrid materials have received extensive attention for their potential applications in many aspects such as photonic crystal [1,2], optical glasses [3], and fluorescent or laser systems [4] because of their excellent optical properties, and specific functions. It is well known that lanthanide compounds have characteristic luminescence properties such as sharp and intense emission bands which are ascribed to the f–f electronic transitions of lanthanide ions, long radiative lifetimes and potential high internal quantum efficiency. However, their absorption coefficients are very low because the f–f electronic transitions are forbidden. Due to the poor absorption abilities of the lanthanide ions, it is common practice to construct lanthanide complexes with organic ligands which can strongly absorb light energy and transfer the energy to the emitting metal center effectively (antenna effect) [5–7].

Recently, most studies focused on the Eu^{3+} complexes especially β-diketones which are made on pure complexes in the solid state or on solutions of these complexes in organic solvents owing to their inherent sharp emission peaks and high quantum efficiency [8]. Nevertheless, it is better to incorporate the luminescent lanthanide complexes in matrix especially inorganic matrices for practical application (light-converting devices) [9–12]. These matrices can be sol–gel glasses [13–15], inorganic–organic hybrid materials [16,4], polymers [17–20] or liquid crystals [21,22]. This method can overcome the shortcomings of the lanthanide complexes such as poor heat stability, low mechanical strength, etc. There are two main routes to embed lanthanide complexes into a polymer matrix. One is so-called physically mixed with weak interactions, that is, dissolution or dispersion of discrete molecule complexes in the polymer matrix. But the non-homogeneous distribution of the compounds [23–26], and bleaching of the photoactive molecules frequently occur which lead to clustering of lanthanide ions and hence a decrease of the luminescence intensity [27] and the concentration of the complex is also largely restricted. Another possesses strong chemical or covalent bonds between the lanthanide complex and the polymer matrix named covalent attachment. Concentration quenching can be avoided and high concentration and more homogeneous distribution of the lanthanide complexes can be achieved using this method since it realized molecular level combination [28–35]. Many researches show the better thermal stabilities and photophysical properties of the lanthanide complexes improved by the matrices.

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In this paper, we report on the lanthanide ion Eu^{3+} coordinated not only with the inorganic polymeric chains (Si–O–Si) through the modification of the dibenzoylmethane (DBM, β-diketone) with 3-(triethoxysilyl)-propyl isocyanate (TEPIC) but also with the organic polymeric chains (C–C) using the monomer 4-vinylpyridine (VP) as the original reagent simultaneously. For the luminescence properties and the microstructure, we compared the binary hybrid Eu-(DBM-Si)$_3$ with the ternary hybrid PVP-Eu-(DBM-Si)$_3$ in detail. The results indicate both the photophysical properties and the microstructure were improved markedly.

2. Experimental

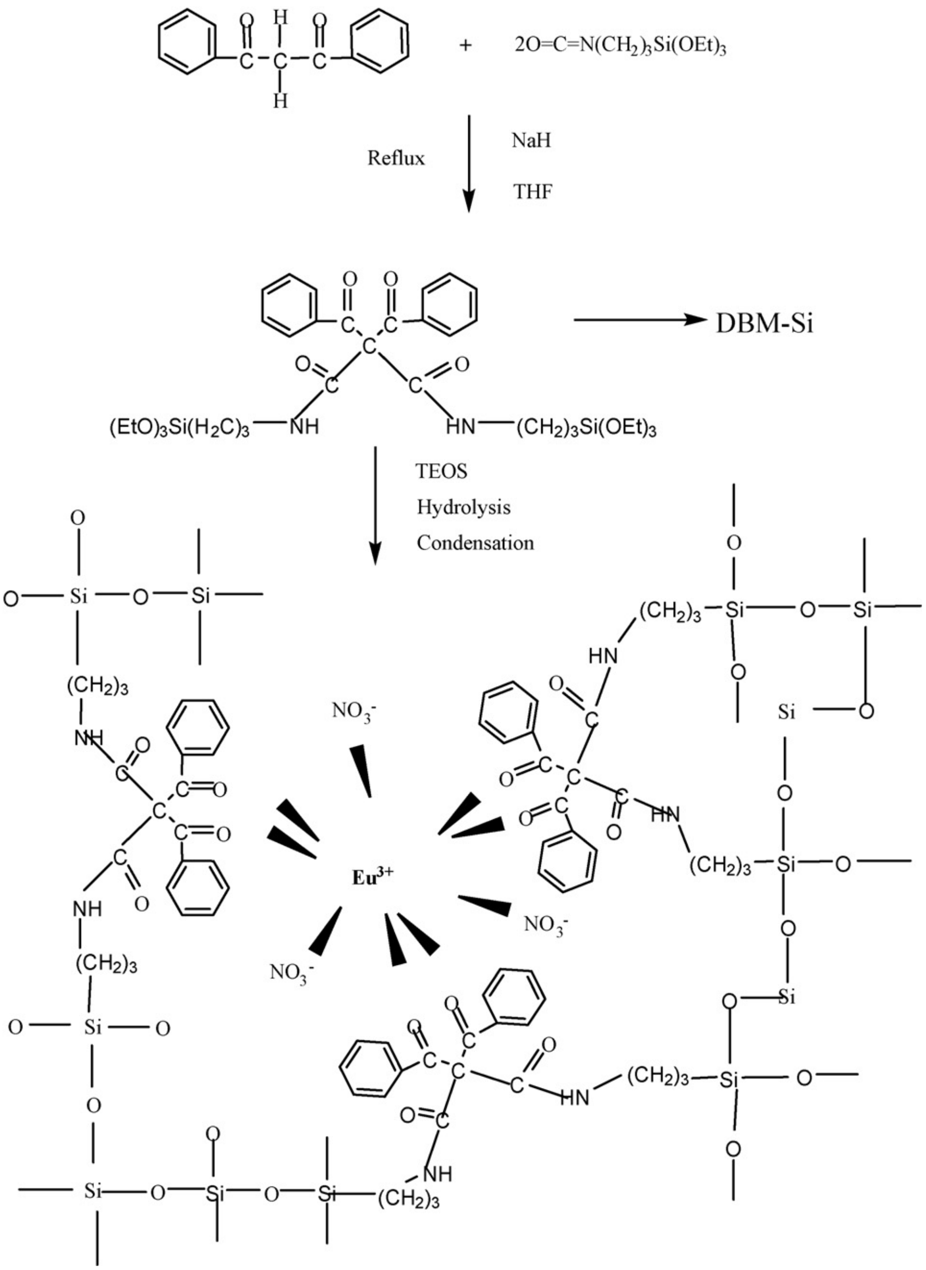
2.1. Starting materials

3-(Triethoxysilyl)-propyl isocyanate was provided by Lancaster Synthesis Ltd., and the tetraethoxysilane (TEOS) by Aldrich. The solvents used were purified by common methods. Other starting reagents were used as received.

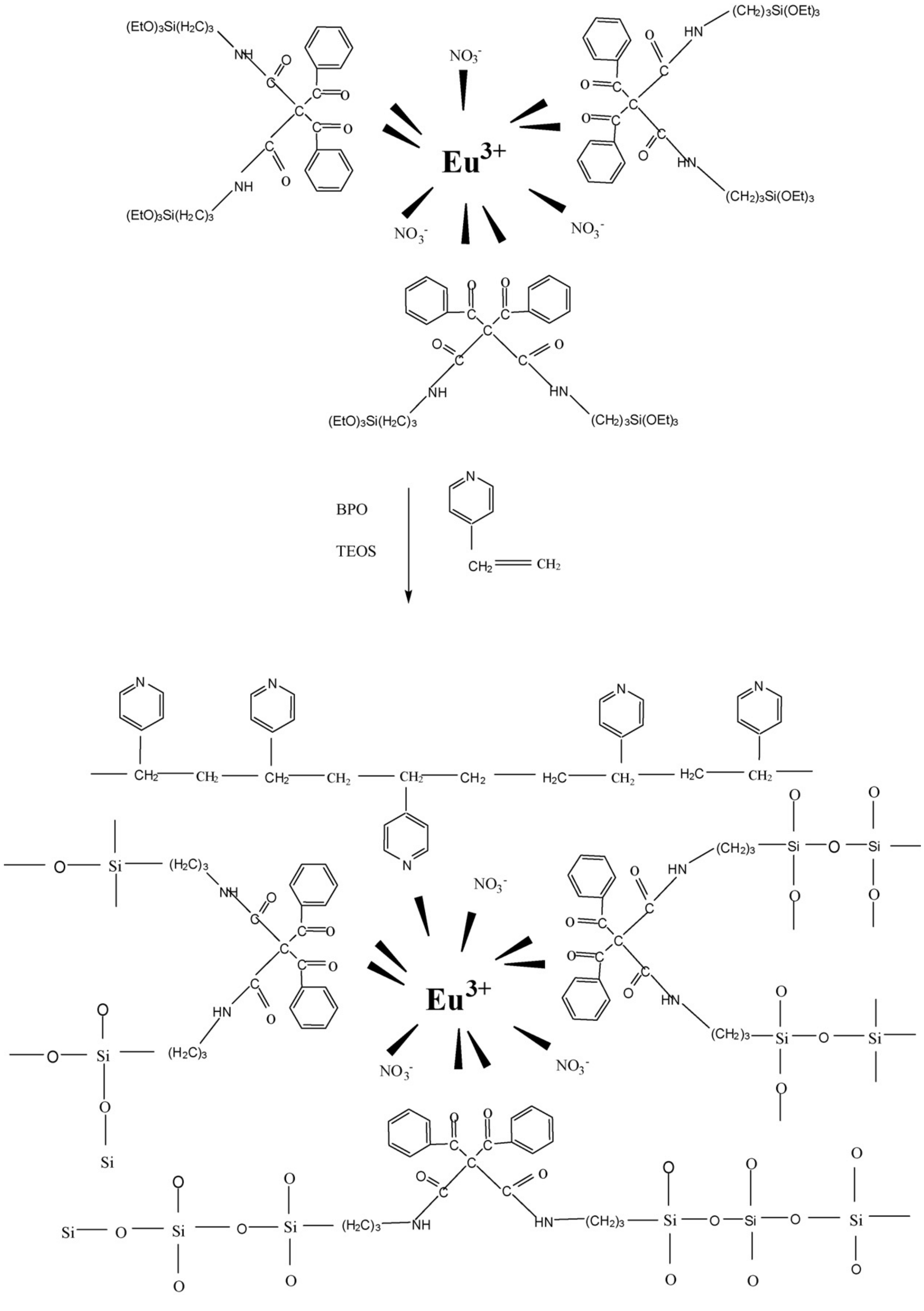
2.2. Synthetical procedures

2.2.1. The synthesis of the precursor DBM-Si

1 mmol of dibenzoylmethane (DBM) was first dissolved in refluxing anhydrous tetrahydrofuran (THF) by stirring, and then 2 mmol of NaH (0.08 g, 60%) was added to the solution. Two hours later, 2.5 mmol (0.56 g) of 3-(triethoxysilyl)-propyl isocyanate was put into the solution by drops. The whole mixture was refluxed at 65 °C under argon for 8 h. After isolation and purification of the sample using a rotary vacuum evaporator, a yellow oil DBM-Si was obtained. IR: –CONH– 1700 cm^{-1}, –(CH$_2$)$_3$– 2930 cm^{-1}, Si–O 1090 cm^{-1}. Anal. Calcd. for $C_{35}H_{54}O_{10}N_2Si_2$ (719.01): C 58.5, H 7.52, N 3.90; Found: C 58.4, H 7.41, N 3.88. ^{1}H NMR (CDCl$_3$) $C_{35}H_54O_{10}N_2Si_2$: δ 8.05(2H, t), 7.58(4H, m), 7.18(2H, s), 6.91(2H,



Scheme 1. The synthesis route and the predicted structure of the binary hybrid material.



Scheme 2. The synthesis process and the predicted structure of the ternary hybrid material.

s), 6.60(2H, brs), 3.82(12H, m $CH_2(OEt)$), 3.62(2H, brs), 3.16(2H, m), 1.86(6H, m), 1.61(2H, m), 1.22(14H, m, $CH^3(OEt)$), 0.63(4H, t) (Scheme 1).

2.2.2. *The synthesis of the binary coordination complex: Eu(DBM-Si)₃*

DBM-Si was dissolved in dry ethanol. Then a stoichiometric amount of $Tb(NO_3)_3{\cdot}6H_2O$ was added to the solution by stirring drop by drop. After 2 h, a stoichiometric amount of tetraethoxysilane (TEOS) and one drop of diluted hydrochloric acid were put into the solution to promote hydrolysis. The molar ratio of $Eu(NO_3)_3{\cdot}6H_2O$/DBM-Si/TEOS/H_2O was 1:3:6:24. Then we get the hybrid material I after evaporation of the solvent at 80 °C in a few days (Scheme 2).

2.2.3. *The synthesis of the ternary coordination complex: PVP-Eu(DBM)₃*

The similar method was used in this process. When we get the solution of binary coordination complex, 0.3 mmol 4-vinylpyridine was added by stirring. Then the benzoyl peroxide (BPO) was put into the refluxing mixture at 80 °C. Twelve hours later, a stoichiometric amount of tetraethoxysilane (TEOS) and one drop of diluted hydrochloric acid were put into the solution at room temperature to promote hydrolysis. The mole ratio of $Eu(NO_3)_3{\cdot}6H_2O$/DBM-Si/VP/TEOS/H_2O was 1:3:1:6:24. Then the hybrid material II was obtained after evaporation of the solvent at 80 °C in a few days.

2.3. *Physical characterization*

All measurements were performed at room temperature. Infrared spectra were recorded on a Nexus 912 AO446 FT-IR spectrophotometer. We mixed the compound with the dried potassium bromide (KBr) and then pressed into pellets. The spectra were collected over the range 4000–400 cm^{-1} by averaging 32 scans at a maximum resolution of 4 cm^{-1}. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as an internal reference. The Ultraviolet absorption spectra were carried out on an Agilent 8453 spectrophotometer and the ultraviolet–visible diffuse reflection spectra of the powder samples were recorded by a BWS003 spectrophotometer. X-ray powder diffraction patterns were recorded using a Rigaku D/max-rB diffractometer system equipped with a Cu anode in a 2θ range from 1° to 80°. The fluorescence excitation and emission spectra were obtained on a RF-5301 spectrofluorophotometer equipped with a stable spec-xenon lamp (450 W) as the light source. The fluorescence decay properties were recorded on an Edinburgh FLS920 phosphorimeter. The microstructures were checked by scanning electronic microscopy (SEM, Philip XL-30).

3. Results and discussion

3.1. *FT-IR spectra*

The Fourier-transform infrared (FT-IR) spectra of DBM (A) and DBM-Si (B) are shown in Fig. 1 from which we can observe that the vibration of $-CH_2-$ at 3050 cm^{-1} (A) was obviously replaced by a strong broad band located at 2930 cm^{-1} around which belonged to the three methylene of 3-(triethoxysilyl)-propyl isocyanate. Furthermore, the appearance of the broad band centered at 3350 cm^{-1} was attributed to the stretching vibration of grafted –NH groups and the peak at 1560 cm^{-1} ascribed to the bending vibration of N–H groups proved the formation of the amide group corresponding to the “amide II” mode [36,37]. Several new peaks at 1770 and 1700 cm^{-1} are due to C═O absorptions, indicating that 3-(triethoxysilyl)-propyl isocyanate was successfully grafted onto the $-CH_2-$ groups of the coupling agent. In addition, the evident vibration absorption located at 1160 and 1090 cm^{-1} are assigned to Si–C and Si–O absorption bands, respectively, characteristic of trialkoxylsilyl functions [38].

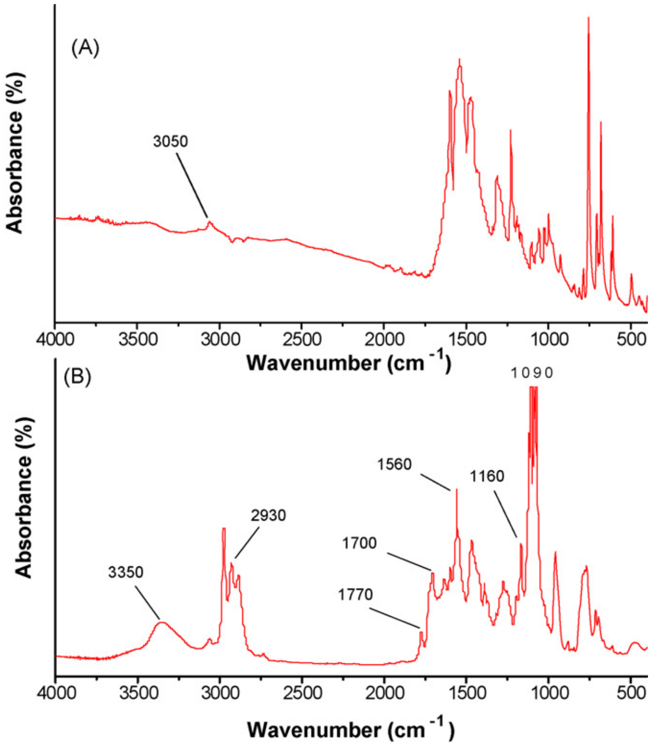


Fig. 1. The Fourier transform infrared spectra of the free ligand DBM (A) and the precursor DBM-Si (B).

3.2. *Ultraviolet absorption spectra*

The ultraviolet absorption spectra of DBM (A) and DBM-Si (B) are presented in Fig. 2. From the spectra, it can be observed that a blue-shift (A → B) of the major $\pi-\pi^*$ electronic transitions (from 343 to 333 nm) occurred and this indicates the electronic distribution has been changed (compared to the free ligand DBM) due to the introduction of the TEPIC, which can support the fact that the 3-(triethoxysilyl)-propyl isocyanate, influencing the

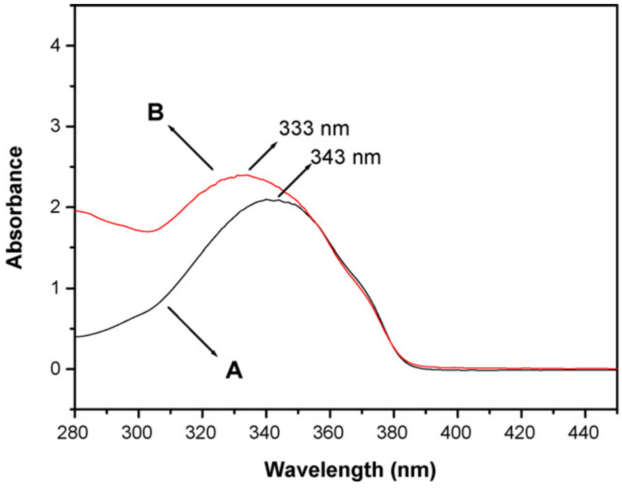


Fig. 2. The ultraviolet absorption spectra of the free ligand DBM (A) and the precursor DBM-Si (B).

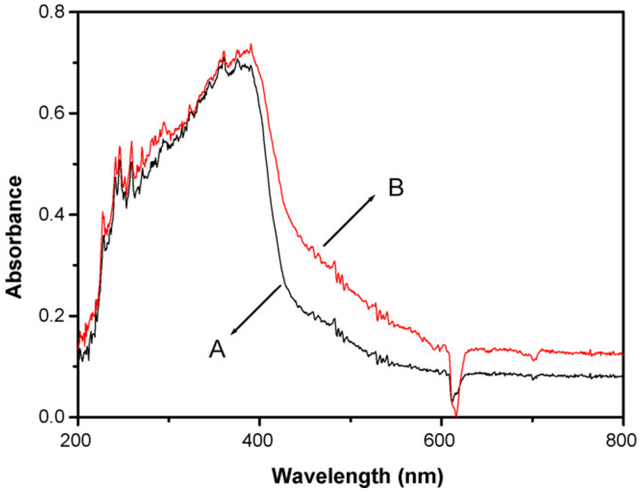


Fig. 3. The ultraviolet–visible diffuse reflection absorption spectra of the hybrid polymeric materials (Eu-DBM-Si for A and PVP-Eu-DBM-Si for B).

corresponding absorption, was successfully grafted onto the DBM. It can be inferred that the difference between the energy levels of the electron transitions of the new electronic conjugating system was enlarged after the modification of DBM.

3.3. Ultraviolet–visible diffuse reflection absorption spectra

Fig. 3 exhibits the ultraviolet–visible diffuse reflection absorption spectroscopy of the rare-earth/inorganic/organic polymeric hybrid materials: the binary complex Eu-DBM-Si for A and the ternary complex PVP-Eu-DBM-Si for B, respectively. As is visible in Fig. 3, there is a large broad band in each hybrid which could result in the strong emission luminance. It is worth noting that there are overlaps between the absorption band (220–420 nm, in Fig. 3) and the excitation band (350–410 nm, in Fig. 4A) which indicate that the organic ligand can absorb abundant energy in ultra-visible range and transfer the energy to lanthanide ion, and thus confirms that the lowest triplet energy level of the macromolecule ligand can match the excited state energy level of the lanthanide ion very well on the basis of Dexter's exchange energy transfer theory [39]. In addition, from the picture we can see an obvious inverse peak in curves both A and B at about 613 nm, the characteristic transition of europium. And the intensity of the ternary complex is higher than the binary complex in the whole range. In a word, we can come to a conclusion that with the presence of the polyvinylpyridine (PVP), the intramolecular energy transfer is more efficient and this is also sustained by the emission spectra (Fig. 4B).

3.4. Photoluminescence properties

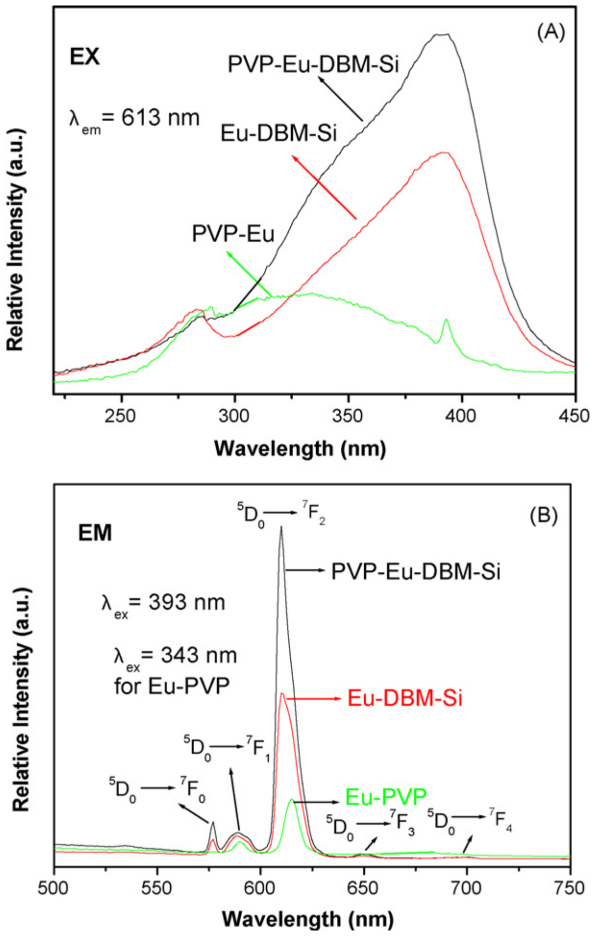


Fig. 4. The fluorescent excitation (A) and emission (B) spectra of the materials.

The photoluminescence properties of the ternary europium complex obtained through not only inorganic hydrolysis and copolycondensation but also organic addition polymerization were studied and compared with the binary complex containing the inorganic Si–O networks only. At the same time, we also prepared Eu-PVP complex with only organic C–C chains for further study on the effect of luminescence influenced by coordination environment around Eu^{3+}. As shown in Fig. 4A, the excitation spectra of the two polymeric hybrid materials and Eu-PVP complex were all obtained by monitoring the strongest emission wavelength of the Eu^{3+} ion at 613 nm. For the two hybrid materials, a broad excitation band extend from 220 to 450 nm dominated by peak centered at 393 nm appears, as we discussed above, assigned to the conjugating $\pi \rightarrow \pi^*$ electron transition of the ligand [40]. For Eu-PVP complex, the intensity of excitation spectra with the peak at 343 nm was apparently lower than both of the two hybrids. As a result, the emission lines of the hybrid material were obtained from $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions at 577, 588, 610, 649 and 700 nm, respectively, for europium ions (Fig. 4B) under their optimal excitation wavelength (for the two hybrids at 393 nm, for Eu-PVP at 343 nm). Among these emission peaks, the most prominent red emission ($^5D_0 \rightarrow {}^7F_2$) is observed, which indicate that the symmetry around the Eu^{3+} ions in hybrid II system is the lowest due to the existence of the surrounding inorganic and organic polymeric networks but the effective energy transfer took place between the ligands and the rare-earth ions. As is well-known, the $^5D_0 \rightarrow {}^7F_2$ transition belongs to the electric dipole transition, so-called hypersensitive transitions, and very sensitive to the local symmetry of the coordination sphere of Eu^{3+} ions, while the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ is practically independent of the host material and therefore can be used as internal standard to explain the ligand differences. It should be noted that the intensity (arbitrary unit, a.u.) of the hybrid II (444.304 for PVP-Eu-DBM-Si at 610 nm) is higher than that of the hybrid I (221.581 for Eu-DBM-Si at 610 nm) and Eu-PVP complex (80.312 at 615 nm), and two reasons may contribute to the improving luminescence. One is the increasing of the asymmetry brought by the long organic chain of the polyvinylpyridine (PVP) and the other is the increasing of the coordination numbers of the lanthanide ions via interfusion of the monomer 4-vinylpyridine. In Eu-PVP system, the coordination numbers cannot be enough due to the space steric hindrance of the long organic C–C chains. While in hybrid II system, both the coordination numbers and the asymmetry character around Eu^{3+} can be enhanced due to the

Table 1
Photoluminescent data of the two hybrid materials.

	ν_{00} (cm^{-1})	ν_{01} (cm^{-1})	ν_{02} (cm^{-1})	ν_{03} (cm^{-1})	ν_{04} (cm^{-1})	I_{01}	I_{02}	I_{02}/I_{01}	τ (ms)	$1/\tau$ (ms^{-1})	A_r	A_{nr}	η (%)
H_I	17,331	17,007	16,393	15,408	14,286	31.22	221.58	7.10	0.204	4.902	474	4428	9.7
H_{II}	17,331	16,977	16,393	15,408	14,286	35.69	444.30	12.45	0.338	2.959	779	2180	26.3

synergistic action between the two kinds of ligands DBM-Si and PVP. Therefore, the above results indicate that the introduction of PVP into Eu-DBM-Si system remarkably increases the luminescent intensity of the hypersensitive transitions of the lanthanide ions.

3.5. Luminescence decay times (τ) and emission quantum efficiency (η)

According to the emission spectrum and the lifetime of the Eu^{3+} first excited level (τ, $^5D_0$), the emission quantum efficiency (η) of the $^5D_0$ Eu^{3+} excited state can be determined. Assuming that only non-radiative and radiative processes are essentially involved in the depopulation of the $^5D_0$ state, η can be defined as follows [41]:

$$\eta = \frac{A_r}{A_r + A_{nr}} \tag{1}$$

Here, A_r and A_{nr} are radiative and non-radiative transition rates, respectively. A_r can also be obtained by summing over the radiative rates A_{0J} for each $^5D_0 \to {}^7F_J$ (J = 0–4) transitions of Eu^{3+}.

$$A_r = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04} \tag{2}$$

The branching ratio for the $^5D_0 \to {}^7F_{5,6}$ transitions can be neglected as they are not detected experimentally, whose influence can be ignored in the depopulation of the $^5D_0$ excited state. Since $^5D_0 \to {}^7F_1$ belongs to the isolated magnetic dipole transition, it is practically independent of the chemical environments around the Eu^{3+} ion, and can be considered as an internal reference for the whole spectrum, the experimental coefficients of spontaneous emission, A_{0J} can be calculated according to the equation [42,43].

$$A_{0J} = A_{01}\left(\frac{I_{0J}}{I_{01}}\right)\left(\frac{\nu_{01}}{\nu_{0J}}\right) \tag{3}$$

Here, A_{0J} is the experimental coefficients of spontaneous emission. A_{01} is the Einstein's coefficient of spontaneous emission between the $^5D_0$ and $^7F_1$ energy levels. In vacuum, A_{01} as a value of 14.65 s^{-1}, when an average index of refraction n equal to 1.506 was considered, the value of A_{01} can be determined to be 50 s^{-1} approximately ($A_{01} = n^3 A_{01\,(\mathrm{vac})}$) [44]. I_{01} and I_{0J} are the integrated intensities of the $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_J$ transitions (J = 0–4) with ν_{01} and ν_{0J} ($\nu_{0J} = 1/\lambda_J$) energy centers, respectively. ν_{0J} refers to the energy barrier and can be determined with the emission bands of Eu^{3+}'s $^5D_0 \to {}^7F_J$ emission transitions. The emission intensity, I, taken as integrated intensity S of the $^5D_0 \to {}^7F_{0-4}$ emission curves, can be defined as below:

$$I_{i-j} = \hbar\omega_{i-j} A_{i-j} N_i \approx S_{i-} \tag{4}$$

Here, i and j are the initial ($^5D_0$) and final levels ($^7F_{0-4}$), respectively, ω_{i-j} is the transition energy, A_{i-j} is the Einstein's coefficient of spontaneous emission, and N_i is the population of the $^5D_0$ emitting level. On the basis of reference [45], the value of $A_{01} \approx 50$ s^{-1} and the lifetime (τ), radiative (A_r), and non-radiative (A_{nr}) transition rates are related through the following equation:

$$A_{tot} = \frac{1}{\tau} = A_r + A_{nr} \tag{5}$$

On the basis of the above discussion, the quantum efficiencies of the two kinds of europium hybrid materials can be determined, as shown in Table 1. Seen from the equation to calculate η, the value η mainly depends on the values of two quantum: one is lifetimes and

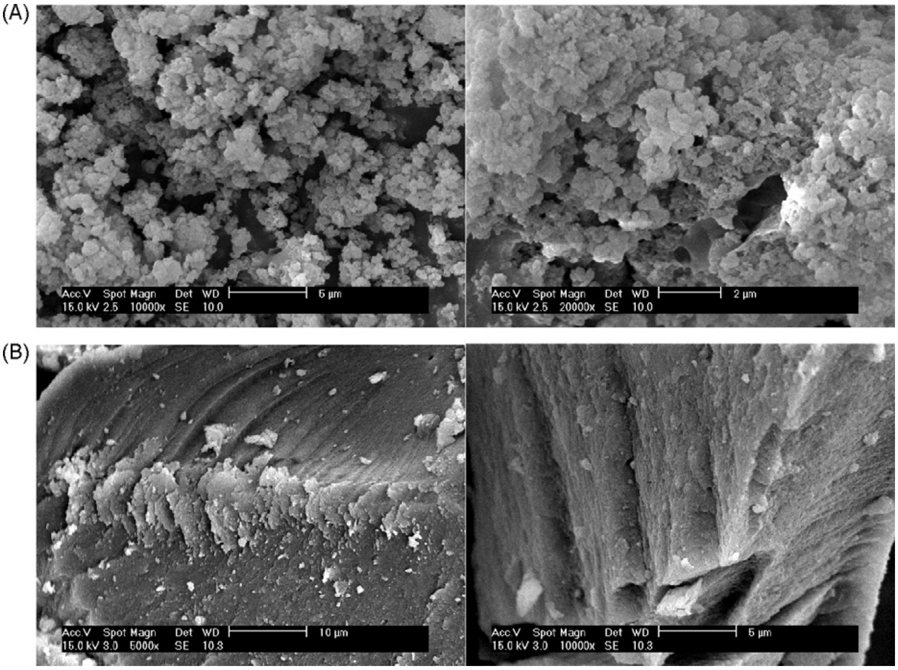


Fig. 5. SEM images of the hybrid materials (Eu-DBM-Si for A and PVP-Eu-DBM-Si for B).

the other is I_{02}/I_{01}. As can be clearly seen from Table 1, the result of quantum efficiencies of the two kinds of the hybrid materials confirm the conclusion that the polymer and the organic networks have successfully been grafted to the europium ions with the chemical bonds and the effective intramolecular transfer system has completely accomplished in the final products. Ulteriorly, the quantum efficiency of PVP-Eu-DBM-Si ($\eta = 26.33\%$) is higher than that of Eu-DBM-Si, which can be ascribe to the huge copolymeric structure in such a short unit of the carbon chains with tremendous steric hindrance effect, which could restrict the efficiency of the intramolecular transfer mechanism, or to the decrease in the level of non-radiative multiphonon relaxation by coupling to –OH vibrations and non-radiative transition rate. The results present that the fluorescence lifetime of hybrid polymer PVP-Eu-DBM-Si is longer than that of Eu-DBM-Si owning to the possible quenching by –OH– or silanol groups in the latter, while the quantum efficiencies of the latter are better, since the ratio of I_{02}/I_{01} of the former is bigger than that of the latter (the detailed date presented in Table 1) indicating that the hybrid polymer PVP-Eu-DBM-Si has the more effective red emission and the higher color purity.

3.6. Scanning electron micrographs

The scanning electron images for hybrid I (panel A) and hybrid II (panel B) are given in Fig. 5. It can be seen that homogeneous, molecular-based system corresponding to chemical bond between the inorganic and organic phase with the functional bridge molecule. Furthermore, in the whole experimental process we did not see the separation phenomenon which always appears in the conventional doping method. Comparing with the two hybrid materials, there exists evident distinctness. The hybrid II with more regular and uniform microstructure exhibits many long distance ordered stripes on the surface. This suggests that the organic polymeric chain plays an important role and act as a template to induce the formation of the complicated huge molecular system.

The formation process and the morphology for the two kinds of hybrid materials can be in the following way. For binary hybrids (hybrid I), the hybrid materials could be received through a polycondensation reaction between the terminal silanol groups of DBM-Si and the OH groups of hydrolyzed TEOS. At the beginning of the reaction, the individual hydrolysis of DBM-Si and TEOS are predominant. Then the step is related to the polycondensation reactions between hydroxyl groups of both DBM-Si and TEOS. Subsequently, the molecular-based hybrids bearing the Eu–O coordination bond and Si–O covalent bonds can also been obtained after the introduction of Eu^{3+}. Here we named the cooperative process of both DBM-Si and TEOS within the in situ sol–gel process as cohydrolysis and copolycondensation (similar to copolymerization of organic monomer). It needs to be referred that the coordination reaction between Eu^{3+} and DBM-Si has great influence on the sol–gel process and the microstructure or physical properties of the hybrids. While the DBM-Si is a chelated ligand with the two oxygen atoms of carbonyl groups and the $Eu(DBM\text{-}Si)_3$ hybrid is easy to form the chelate without polymeric structure. For PVP-Eu-DBM-Si hybrids, when PVP is introduced, the coordination effect between Eu^{3+} and PVP (as a terminal ligand) naturally influences on the hydrolysis and polycondensation process of DBM-Si directly, furtherly influence on the growth tendency or rate of the final hybrids, which can control the microstructure and luminescent properties of them. As we know, RE^{3+} possesses the high coordination number, so the chelated ability is strong and can play a role in the control of hybrids. Although PVP behaves as a terminal ligand through the simple chelation of nitrogen atom, the long organic chain possesses the template effect to change the morphology of the ternary hybrids, resulting in the stripe microstructure. Subsequently, the coordination effects play an important role in the molecular assembly of the hybrid materials.

4. Conclusion

In summary, we have synthesized novel ternary lanthanide hybrid materials containing inorganic networks and organic polymeric chains coordination bonding connected with the europium ions simultaneously through covalent bonds via cohydrolysis, copolycondensation for Si–O–Si network and addition polymerization for PVP chain. The physical properties, especially the microstructure and the photoluminescence, are investigated in detail and compared with the binary complex. The results demonstrate that with the introduction of the PVP, more ordered microstructure, higher red/orange ratio and stronger luminescent intensity were obtained. The data of the quantum efficiency illustrate that the ternary organic/inorganic/polymeric hybrid material present the more effective intramolecular energy transfer mechanism due to the tremendous steric hindrance effect within so narrow space in the coordination reactions. Thus, we can say that the method of covalent bonding polymeric chain in lanthanide organic/inorganic hybrid materials is effective and this kind of homogeneous rare-earth/organic/inorganic polymeric hybrid material may have potential and significant application in optical and electronic devices.

Acknowledgements

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References

[1] K.P. Velikov, A. van Blaaderen, Synthesis and characterization of monodisperse core–shell colloidal spheres of zinc sulfide and silica, Langmuir 17 (2001) 4779–4786.

[2] A. Moroz, Metallo-dielectric diamond and zinc-blende photonic crystals, Phys. Rev. B 66 (2002) 115109–115123.

[3] B. Klimesz, G. Dominiak-Dzik, M. Zelechower, W. Ryba-Romanowski, Optical study of GeO_2–PbO–PbF_2 oxyfluoride glass single doped with lanthanide ions, Opt. Mater. 30 (2008) 1587–1594.

[4] V. Bekiari, G. Pistolis, P. Lianos, Intensely luminescent materials obtained by combining lanthanide ions 2,2′-bipyridine, and poly(ethylene glycol) in various fluid or solid environments, Chem. Mater. 11 (1999) 3189–3196.

[5] S. Sato, W. Mada, Relations between intramolecular energy transfer efficiencies and triplet state energies in rare earth β-diketone chelates, Bull. Chem. Soc. 43 (1970) 1955–1966.

[6] Q.M. Wang, B. Yan, X.H. Zhang, Photophysical properties of novel lanthanide complexes with long chain mono-eicosyl *cis*-butene dicarboxylate, J. Photochem. Photobiol. A Chem. 174 (2005) 119–124.

[7] H.H. Li, S. Inoue, K. Machida, G. Adachi, Preparation and luminescence properties of organically modified silicate composite phosphors doped with an europium(III) beta-diketonate complex, Chem. Mater. 11 (1999) 3171–3176.

[8] L.D. Carlos, C. De Mello Donega, R.Q. Albuquerque, J.R.S. Alves, J.F.S. Menezes, O.L. Malta, Highly luminescent europium(III) complexes with naphtoiltrifluoroacetone and dimethyl sulphoxide, Mol. Phys. 101 (2003) 1037–1045.

[9] J. Kido, Y. Okamoto, Organo lanthanide metal complexes for electroluminescent materials, Chem. Rev. 102 (2002) 2357–2368.

[10] M. Borzechowska, V. Trush, I. Turowska-Tyrk, W. Amirkhanov, J. Legendziewicz, Spectroscopic and magnetic studies of mixed lanthanide complexes: LnL_3 alpha,alpha' dipy in solution and in solid, J. Alloys Compd. 341 (2002) 98–106.

[11] A. Kozanecki, B.J. Sealy, K. Homewood, Excitation of Er3+ emission in Er Yb codoped thin silica films, J. Alloys Compd. 300 (2000) 61–64.

[12] B. Viana, N. Koslova, P. Aschehoug, C. Sanchez, Optical-properties of neodymium and dysprosium doped hybrid siloxane-oxide coatings, J. Mater. Chem. 5 (1999) 719–722.

[13] L.R. Matthews, E.T. Kobbe, Luminescence behavior of europium complexes in sol–gel derived host materials, Chem. Mater. 5 (1993) 1697–1700.

[14] B. Yan, J.Y. You, In-situ sol–gel composition of luminescent hybrid material incorporated with terbium coordination polymers, J. Mater. Proc. Technol. 170 (2005) 363–366.

[15] A.M. Klonkowski, S. Lis, M. Pietraszkiewicz, Z. Hnatejko, K. Czarnobaj, M. Elbanowski, Luminescence properties of materials with Eu(III) complexes: role of ligand, coligand, anion, and matrix, Chem. Mater. 15 (2003) 656–663.

[16] P.A. Tanner, B. Yan, H.J. Zhang, Preparation and luminescence properties of sol–gel hybrid material incorporated with europium complex, J. Mater. Sci. 35 (2000) 4325–4329.

[17] C.Y. Yang, V. Srdanov, M.R. Robinson, G.C. Bazan, A.J. Heeger, Orienting Eu(dnm)(3)phen by tensile drawing in polyethylene: polarized Eu^{3+} emission, Adv. Mater. 14 (2002) 980–983.

[18] K. Kuriki, Y. Koike, Y. Okamoto, Plastic optical fiber lasers and amplifiers containing lanthanide complexes, Chem. Rev. 102 (2002) 2347–2356.

[19] Q.M. Wang, B. Yan, Assembly of hybrids from co-polymers bearing functional 4-vinyl pyridine and europium aromatic carboxylates, J. Photochem. Photobiol. A: Chem. 177 (2006) 1–5.

[20] B. Yan, Q.M. Wang, Covalently bonded assembly and photoluminescent properties of rare earth/silica/poly(methyl methacrylate-co-maleic anhydride) hybrid materials, J. Photochem. Photobiol. A Chem. 197 (2008) 213–219.

[21] L.H. Wang, W. Wang, W.G. Zhang, E.T. Kang, W. Huang, Synthesis and luminescence properties of novel Eu-containing copolymers consisting of Eu(III)-acrylate-beta-diketonate complex monomers and methyl methacrylate, Chem. Mater. 12 (2002) 2212–2219.

[22] B. Yan, L.M. Zhao, J.L. Liu, Molecular assembly and photophysical properties covalently bonded rare earth polymeric hybrid materials phen-RE-MSMA (MS), J. Photochem. Photobiol. A Chem. 199 (2008) 50–56.

[23] H.R. Li, L.S. Fu, J. Lin, H.J. Zhang, Luminescence properties of transparent hybrid thin film covalently linked with lanthanide complexes, Thin Solid Films 416 (2002) 197–200.

[24] C.X. Du, L. Ma, Y. Xu, W.L. Li, Synthesis and fluorescent properties of europium-polymer complexes containing naphthoate and 1 10-phenanthroline ligands, J. Appl. Polym. Sci. 66 (1997) 1405–1410.

[25] N.I. Koslova, B. Viana, C. Sanchez, Rare-earth-doped hybrid siloxane–oxide coatings with luminescent properties, J. Mater. Chem. 3 (1993) 111–112.

[26] P.P. Lima, R.A. Sá Ferreira, R.O. Freire, F.A. Almeida Paz, L.S. Fu, S. Alves Jr., L.D. Carlos, O.L. Malta, Spectroscopic Study of a UV-Photostable Organic-Inorganic Hybrids Incorporating an Eu^{3+} β-Diketonate Complex, Chem. Phys. Chem. 7 (2006) 735–746.

[27] Q.M. Wang, B. Yan, Novel luminescent terbium molecular-based hybrids with modified meta aminobenzoic acid covalently bonded with silica, J. Mater. Chem. 14 (2004) 2450–2455.

[28] H.R. Li, J. Lin, H.J. Zhang, L.S. Fu, Q.G. Meng, S.B. Wang, Preparation and luminescence properties of hybrid materials containing europium (III) complexes covalently bonded to a silica matrix, Chem. Mater. 14 (2002) 3651–3655.

[29] Q.M. Wang, B. Yan, A novel way to luminescent terbium molecular-scale hybrid materials: modified heterocyclic ligands covalently bonded with silica, Cryst. Growth Des. 5 (2006) 497–503.

[30] L.D. Carlos, R.A. Sá Ferreira, R.N. Pereira, M. Assuncao, V.D. Bermudez, White-light emission of amine-functionalized organic/inorganic hybrids: emitting centers and recombination mechanisms, J. Phys. Chem. B 108 (2004) 14924–14932.

[31] B. Yan, X.F. Qiao, Rare earth/inorganic/organic polymeric hybrid materials: molecular assembly, regular microstructure and photoluminescence, J. Phys. Chem. B 111 (2007) 12362–12374.

[32] B. Yan, Q.M. Wang, First two luminescent molecular hybrids composed of bridged Eu(III)-β-diketone chelates covalently trapped in silica and titanate gels, Cryst. Growth Des. 6 (2008) 1484–1489.

[33] B. Yan, H.F. Lu, Lanthanide centered covalently bonded hybrids through sulfide linkage: molecular assembly, physical characterization and photoluminescence, Inorg. Chem. 47 (2008) 5601–5611.

[34] J.L. Liu, B. Yan, Lanthanide (Eu^{3+}, Tb^{3+}) centered hybrid materials using modified Functional bridge chemical bonded with silica: molecular design, physical characterization and photophysical properties, J. Phys. Chem. B 112 (2008) 10898–10907.

[35] J.L. Liu, B. Yan, Molecular construction and photophysical properties of luminescent covalently bonded lanthanide hybrid materials: organic ligands containing 1,2 4-triazole grafted with silica by mercapto modification, J. Phys. Chem. C 112 (2008) 14168–14178.

[36] M.C. Goncalves, V.D. Bermudez, R.A. Sá Ferreira, L.D. Carlos, D. Ostroviskii, J. Rocha, Optically functional Di-urethanesil nanohybrids containing Eu^{3+} ions, Chem. Mater. 16 (2004) 2530–2543.

[37] P. Lenaerts, A. Storms, J. Mullens, J. Dhaen, C. Gorller-Walrand, K. Binnemans, K. Driesen, Thin films of highly luminescent lanthanide complexes covalently linked to an organic–inorganic hybrid material via 2-substituted imidazo[4,5-*f*]-1 10-phenanthroline groups, Chem. Mater. 17 (2005) 5194–5201.

[38] M.M. Coleman, K.H. Lee, D.J. Skrovanek, P.C. Painter, Hydrogen bonding in polymers 4. Infrared temperature studies of a simple polyurethane, Macromolecules 19 (1986) 2149–2157.

[39] L.S. Fu, R.A. Sá Ferreira, N.J.O. Silva, L.D. Carlos, Photoluminescence and quantum yields of urea and urethane cross-linked nanohybrids derived from carboxylic acid solvolysis, Chem. Mater. 16 (2004) 1507–1516.

[40] Y. Li, B. Yan, Construction, characterization and photoluminescence of mesoporous hybrids containing europium (III) complexes covalently bonded to SBA-15 directly functionalized by modified β-diketone, J. Phys. Chem. C 112 (2008) 3959–3968.

[41] P.C.R. Soares-Santos, H.I.S. Nogueira, V. Félix, M.G.B. Drew, R.A.S. Ferreira, L.D. Carlos, T. Trindade, Novel lanthanide luminescent materials based on complexes of 3-hydroxypicolinic acid and silica nanoparticles, Chem. Mater. 15 (2003) 100–108.

[42] R.A.S. Ferreira, L.D. Carlos, R.R. Gonçalves, S.J.L. Ribeiro, V.D. Bermudez, Energy-transfer mechanisms and emission quantum yields in Eu^{3+}-based siloxane-poly(oxyethylene) nanohybrids, Chem. Mater. 13 (2001) 2991–2998.

[43] M.H.V. Werts, R.T.F. Jukes, J.W. Verhoeven, The emission spectrum and the radiative lifetime of Eu^{3+} in luminescent lanthanide complexes, Phys. Chem. Chem. Phys. 4 (2002) 1542–1548.

[44] J.C. Boyer, F. Vetrone, J.A. Capobianco, A. Speghini, M. Bettinelli, Variation of fluorescence lifetimes and Judd–Ofelt parameters between Eu^{3+} doped bulk and nanocrystalline cubic Lu_2O_3, J. Phys. Chem. B 108 (2004) 20137–20144.

[45] O.L. Malta, H.J. Batista, L.D. Carlos, Overlap polarizability of a chemical bond: a scale of covalency and application to lanthanide compounds, Chem. Phys. 282 (2002) 21–30.