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Molecular design and photophysical properties of acylamido side functionalized polysiloxanes with lanthanide ions as luminescent centers

Haifeng Lu, Xiaochen Wang, Hua Wang, Shengyu Feng*

Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Shanda South Road 27, Ji'nan 250100, People's Republic of China

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ABSTRACT

Two series of acylamido side functionalized polysiloxanes were designed and synthesized from the modifications of amino silane with different acylating agents. They were complexed with lanthanide ions (Tb^{3+}, Eu^{3+}, Dy^{3+} and Sm^{3+}) to obtain functionalized polysiloxane–lanthanide ions composite materials and exhibit the molecular assembly behaviors. The structures of products were characterized by Fourier transform infrared (FT-IR), ^{1}H-NMR spectra and diffuse reflectance ultraviolet–visible spectra (DRUVS). Thermal stability was investigated by thermogravimetric analysis (TGA). Narrow-width red and green emissions of the functionalized polysiloxane–lanthanide ions complexes were recorded under the exposure to ultraviolet light. The results show that four kinds of lanthanide ions were all cooperated successfully with the functionalized polysiloxanes and an intra-molecular energy transfer process took place in these systems. Further investigations into the luminescence properties of the functionalized polysiloxane–lanthanide ions composite materials show that the triplet state energy of the benzoylamido side functionalized polysiloxane is more suitable for the emissive energy level of lanthanide ions than that of acetamido side functionalized polysiloxane. According to the rules between photophysical properties and diverse chromophoric conjugate groups, we could design and control the properties of the polysiloxane–lanthanide ion assembly complexes.

1. Introduction

Functionalized polysiloxanes, including hydroxyl, carboxyl and amino modification, have been widely applied as coatings, adhesives, impact resistance plastics in daily life [1–5] due to their intriguing physical and chemical properties, such as excellent thermal stability, weatherability, anti-ageing, electrical insulation, water-repellent and flame retardant properties [6,7]. Among all functionalized polysiloxanes, amino modified polysiloxanes were found wide commercial applications. It is well known that as a new generation of softener, amino modified polysiloxanes will supply cotton, silk, wool, nylon fabric with soft, smooth and elastic effects [8].

Recently, potential lanthanide complexes have attracted great interests in view of their long-lived excited state characteristics and efficient strong narrow-width emission bands in the visible region [9–12]. However, defects with poor thermal stability and mechanical properties restrict, to some extent, applications of lanthanide compounds as luminophors [13–15]. A normal way to solve this problem is the entrapping of lanthanide complexes into different inorganic and composite hosts [12,16–23]. This method actually improved the thermal stability of the lanthanide compounds; nevertheless the resulting products are generally stiff and hard to be processed. So polysiloxanes with excellent thermal stabilities and easy-machinable abilities are prior to be selected as hosts [24,25]. In our previous work, ester side polysiloxanes were coordinated with lanthanide ions and the obtained lanthanide ions composite materials exhibited narrow-width luminescence [26].

In this paper, we put forward the design and assembly of acylamido side functionalized polysiloxanes. Amino side functionalized polysiloxanes have outstanding chemical and physical performance but they could not show luminescence because they have no chromophoric groups. After amino group was modified by acylchloride to turn to acylamido group, carbonyl group could be introduced in, and coordinate with lanthanide ions and provide the bridge for intra-molecular energy transfer process which is usually called antenna effect [22]. What's more, from the view of molecular design, we select two kinds of acylchloride to prepare acylamido-functionalized polysiloxanes. After the assembly of the polysiloxanes with lanthanide ions, the relationship between the luminescent properties and the chromophoric groups could be found.

Acylamido side functionalized polysiloxane was first synthesized from N-β-aminoethyl-γ-aminopropylmethyl- dimethoxysi-

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* Corresponding author. Tel.: +86 531 88364866; fax: +86 531 88564464.
E-mail address: fsy@sdu.edu.cn (S. Feng).

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lane [$H_2N(CH_2)_2HN(CH_2)_3SiCH_3(OCH_3)_2$, AEP for short] as a starting material in this paper. It was modified via acylamidation with benzoyl chloride (PhCOCl) or acetyl chloride (CH_3COCl) to get two new silane intermediates. Innovation of selecting different chlorides modification builds upon the introduction of disparate conjugated systems. Then the intermediates were copolymerized with octamethylcycoltetrasiloxane and hexamethyldisiloxane to give two different acylamido side functionalized polysiloxanes, namely benzoylamido side functionalized polysiloxane and acetamido side functionalized polysiloxane. These functionalized polysiloxanes are chelated to lanthanide ions (Tb^{3+}, Eu^{3+}, Dy^{3+} and Sm^{3+}, separately) at room temperature to obtain the anticipant luminescent polysiloxane–lanthanide ion composite materials. The photophysical performances of the materials were discussed and the intra-molecular energy transfer processes were compared in detail.

2. Experimental

2.1. Chemicals and procedures

All the starting materials and solvents were purchased from China National Medicines Group and were distilled before utilization according to procedures in previous articles [26–28]. Rare earth nitrates ($Ln(NO_3)_3 \cdot 6H_2O$, Ln = Tb, Eu, Dy or Sm) were obtained from the corresponding oxides in dilute nitric acid [26,28].

The general procedures for the preparation of acylamido side functionalized polysiloxanes and luminescent materials are expounded in the Scheme 1. The acylation reaction was described as follows: N-β-aminoethyl-γ-aminopropylmethyldimethoxysilane (2.47 g, 12 mmol) was first dissolved in 20 mL pyridine by stirring and then benzoyl chloride (1.68 g, 12 mmol) (or 0.942 g, 12 mmol acetyl chloride) was added to the solution dropwise at room temperature. The mixture was refluxing at 70 °C for 4 h. After the filtration, the resulting solution was condensed to evaporate the solvent and then the residue was dried on a vacuum line (10 mm Hg). Yellow liquid was obtained with yield of about 91%.

Benzoylamido side functionalized silane (BA-AEP for short): $C_{15}H_{26}N_2O_3Si$: ^{1}H-NMR ($CDCl_3$): δ7.49 (d, 2H, –phenyl-H–), 7.41 (d, 1H, –phenyl-H–), 7.38 (d, 2H, –phenyl-H–), 7.86 (s, 1H, –phenyl-CONH–), 3.76 (s, 6H, $-OCH_3$), 3.28 (t, 2H, $-CH_2-$), 3.17 (t, 2H, $-CH_2-$), 2.94 (t, 2H, $-CH_2-$), 1.95 (s, IH, –N–H–), 1.63 (m, 2H, $-CH_2-$), 0.64 (t, 2H, $-CH_2-$), 0.15 (t, 3H, $-Si-CH_3$).

Acetamido side functionalized silane (AA-AEP for short): $C_{15}H_{26}N_2O_3Si$: ^{1}H-NMR ($CDCl_3$): δ6.75 (s, 1H, $-CH_3-CONH-$), 3.51 (s, 6H, $-OCH_3$), 3.02 (t, 2H, $-CH_2-$), 2.90 (t, 2H, $-CH_2-$), 2.77 (t, 2H, $-CH_2-$), 2.09 (s, 3H, $-CH_3$), 1.86 (s, 1H, –N–H–), 1.61 (m, 2H, $-CH_2-$), 0.63 (t, 2H, $-CH_2-$), 0.15 (t, 3H, $-Si-CH_3$).

The preparation of functionalized polysiloxane was as follows: benzoylamido side functionalized silane (1.59 g, 5 mmol) (or acetamido side functionalized silane (1.28 g, 5 mmol)), octamethylcycoltetrasiloxane (7.61 g, 25 mmol), hexamethyldisiloxane (0.32 g, 2 mmol) and a stoichiometric proportion tetramethylammonium silanolate (used as catalyzer) were added to a flask under N_2. The mixture was heated to 85–95 °C for 8 h under uniform mechanical stirring. After the catalyzer is decomposed at 130–140 °C and the low-boilings are removed in vacuum (10 mm Hg), yellow viscous liquid was obtained.

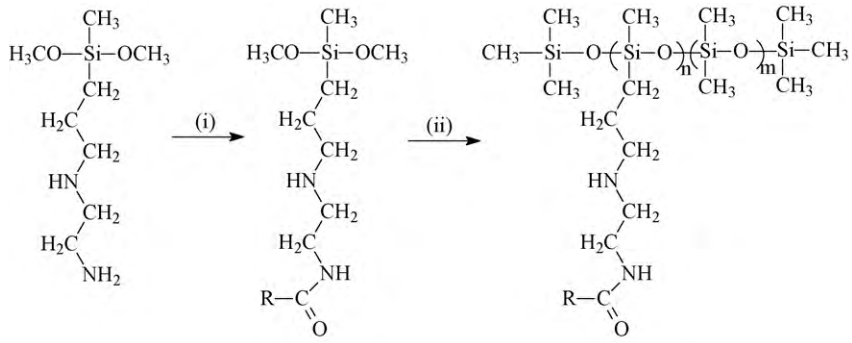
Benzoylamido side functionalized polysiloxane (BA-PS for short) (yield 83%): ^{1}H-NMR ($CDCl_3$): δ7.48 (d, 2H, –phenyl-H–), 7.39 (d, 1H, –phenyl-H–), 7.32 (d, 2H, –phenyl-H–), 8.04 (s, 1H, -phenyl–CONH–), 3.27 (t, 2H, $-CH_2-$), 3.01 (t, 2H, $-CH_2-$), 2.00 (s, IH, –N–H–), 1.61 (s, 2H, $-CH_2-$), 0.62 (m, 2H, $-CH_2-$), 0.34 (t, 2H, $-CH_2-$), 0.05(s, 108H, $-Si-CH_3$).

Acetamido side functionalized polysiloxane (AA-PS for short) (yield 85%): ^{1}H-NMR ($CDCl_3$): δ6.75 (s, 1H, $-CH_3-CONH-$), 3.01 (t, 2H, $-CH_2-$), 2.91 (t, 2H, $-CH_2-$), 2.78 (t, 2H, $-CH_2-$), 2.44 (s, 3H, $-CH_3$), 2.01 (s, 1H, –N–H–), 1.62 (m, 2H, $-CH_2-$), 0.52 (t, 2H, $-CH_2-$), 0.05(s, 114H, $-Si-CH_3$).

The luminescent polysiloxane–lanthanide ion composite material was achieved as follows: 0.945 g benzoylamido side functionalized polysiloxane (or 0.938 g acetamido side functionalized polysiloxane) was dissolved in 6 mL CH_3Cl with stirring, and 6 mmol $Ln(NO_3)_3 \cdot 6H_2O$ (0.2736 g $Tb(NO_3)_3 \cdot 6H_2O$, 0.2676 g $Eu(NO_3)_3 \cdot 6H_2O$, 0.2739 g $Dy(NO_3)_3 \cdot 6H_2O$ or 0.2666 g $Sm(NO_3)_3 \cdot 6H_2O$) was added to the solution at room temperature. The mixture was agitated magnetically for 4 h to achieve a single phase. Then 20 mL methanol was poured into the mixture. The viscous liquids were collected by filtration and washed with methanol, water and acetone. After dried under vacuum at room temperature [26], a yellow viscous liquid product (yield among 92–94%) was obtained. The luminescent polysiloxane–lanthanide ion composite materials were named BA-PS-Ln (Ln = Tb, Eu, Dy or Sm) and AA-PS-Ln (Ln = Tb, Eu, Dy or Sm).

2.2. Measurements

Bruker TENSOR27 infrared spectrophotometer was utilized to record the Fourier transform infrared (FT-IR) spectra with the KBr pellet technique within the 4000–400 cm^{-1} region. BRUKER AVANCE-400 spectrometer was used to determine the Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectra in $CDCl_3$ without internal reference. Diffuse reflectance ultraviolet–visible spectra (DRUVS) of samples were performed with a Shimadzu UV-2500. Thermal gravimetric analysis (TGA) was performed with a simultaneous TGA Q600 under N_2. Luminescence (excitation and emission)



Scheme 1. The procedures for the preparation of acylamido side functionalized polysiloxane. (i) RCOCl (R = $-CH_3$, $-C_6H_5$), pyridine, 70 °C. (ii) Hexamethyldisiloxane, octamethylcycoltetrasiloxane.

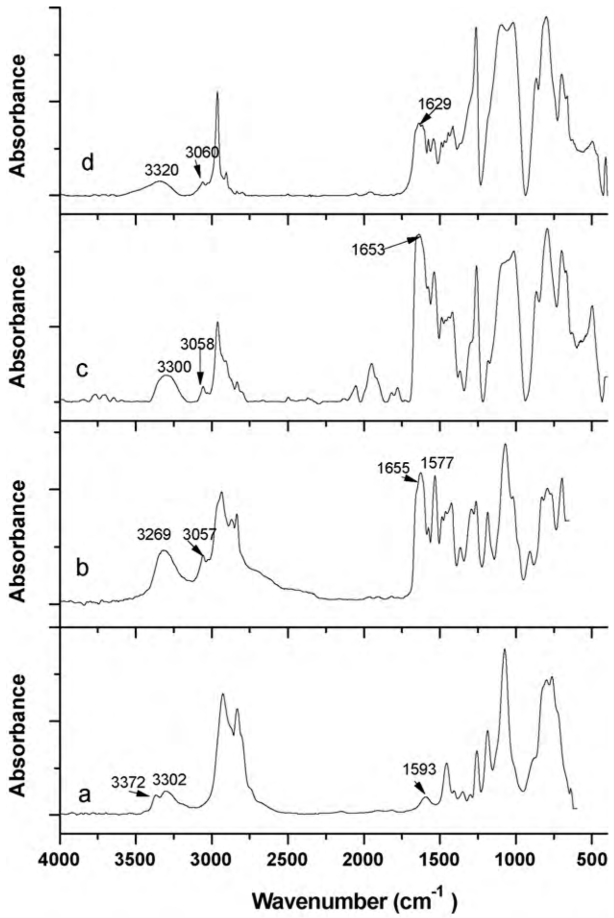


Fig. 1. Infrared spectra of AEP (a), BC-AEP (b), BA-PS (c) and BA-PS-Dy (d).

spectra were measured with a Perkin-Elmer LS-55 spectrophotometer and the excitation and emission slits were 2.5 and 5 nm.

3. Results

The FT-IR spectra for aminoethyl-γ-aminopropylmethyldimethoxysilane (AEP) (a), benzoylamido side functionalized silane (BC-AEP) (b), benzoylamido side functionalized polysiloxane (BA-PS) (c) and dysprosium-containing benzoylamido side functionalized polysiloxane (BA-PS-Dy) (d) are shown in Fig. 1. The stretching vibration peaks of N–H locate at 3372 and 3302 cm^{-1}, and a bending vibration peak of N–H appears at 1593 cm^{-1} [29] in curve (a). In curve (b), the double-hump absorption of N–H bond in $-NH_2$ group change to single peak (3269 cm^{-1} for N–H stretching vibration) and N–H bending vibration shifts to 1577 cm^{-1}. And the C=O stretching vibration (1655 cm^{-1} in curve (b)) was observed in BC-AEP. The absorption peaks of C–H stretching vibration in phenyl group are observed at 3057 cm^{-1} in curve (b). It indicates that the formation of benzoylamido group and grafting modification via acylamidation reaction are successful. Meanwhile, the similar vibration peaks were observed in BA-PS in curve (c), which shows that N–H vibration mode (3300 cm^{-1}) and C–H stretching vibration of phenyl group (3058 cm^{-1}). And the ν (Si–C) vibration mode appears at 1257 cm^{-1} in above three curves. Different from BC-AEP (b) and BA-PS (c), the ν (C=O) vibration mode was observed at 1629 cm^{-1} in BA-PS-Dy (d). The coordination of the oxygen atoms in C=O group with the metallic ion is confirmed by the shift of ν (C=O) (from 1649 to 1629 cm^{-1}, $\Delta = 20\ \text{cm}^{-1}$) [30–32]. The broad absorption bands at 1120–1000 cm^{-1} (ν Si–O–Si) originate from the formation of siloxane. The same results are observed in the system of acetamido side functionalized polysiloxane systems.

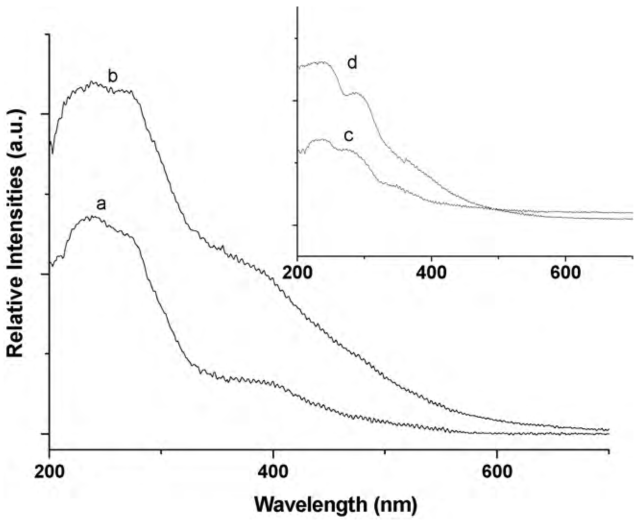


Fig. 2. Diffuse reflectance ultraviolet–visible spectra of BA-PS (a) and BA-PS-Tb (b).

Fig. 2 displays the diffuse reflectance ultraviolet–visible spectra (DRUVS) of benzoylamido side functionalized polysiloxane (BA-PS) (a) and terbium-containing benzoylamido side functionalized polysiloxane (BA-PS-Tb) (b). The absorption peak around 240–290 nm corresponds to the $\pi \rightarrow \pi^*$ electronic transition of aromatic group [29,33] in curve (a). There is no significant difference between the spectra of the BA-PS (a) and BA-PS-Tb (b), indicating that the addition of lanthanide ions did not affect conjugate system of benzoylamido in BA-PS. And this phenomenon was also found in acetamido side functionalized polysiloxane system between AA-PS (c) and AA-PS-Tb (d).

Thermal characterizations of polysiloxane–rare earth ion composite materials are examined by thermogravimetric analysis (TGA). Fig. 3 gives the TGA traces of BA-PS (a), AA-PS (b), BA-PS-Sm (c) and AA-PS-Sm (d). It is easy to see that all of the samples present the similar change trends in their weight loss. From curves (a) and (b), the thermal degradation of BA-PS and AA-PS are all clearly divided into two stages. The weight loss between 200 and 370 °C may be ascribed to the degradation of substitutional acylamido groups in side chains [34]. The second thermal region, ranging from 400 to 700 °C, is attributed to the degradation of the

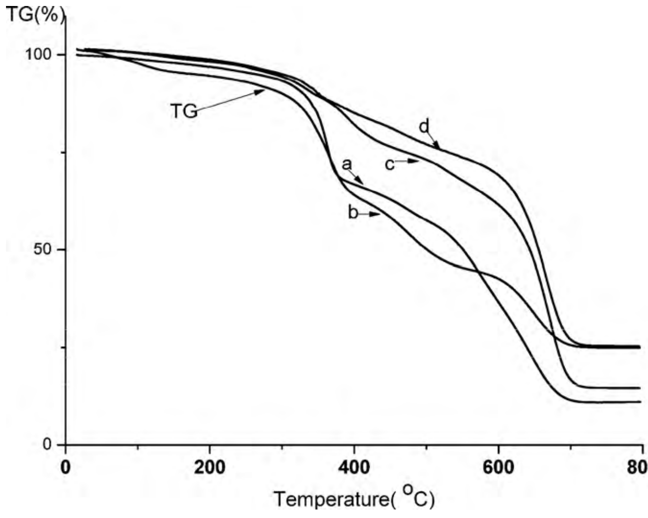


Fig. 3. Thermal gravimetric analysis of BA-PS (a), BA-PS-Eu (b), AA-PS (c) and AA-PS-Eu (d).

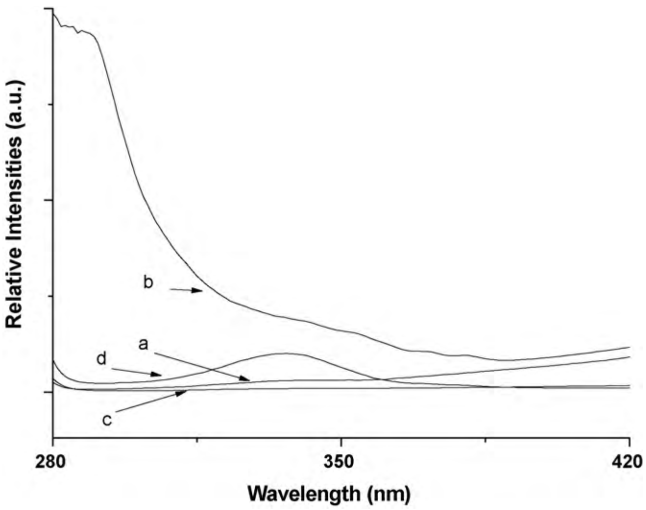


Fig. 4. The excitation spectra of BA-PS (a), BA-PS-Tb (b), AA-PS (c) and AA-PS-Tb (d) (λ_{em} = 545 nm).

main framework (Si–O and Si–C bonds) in polysiloxanes [26,35,36]. When added the lanthanide ion (Sm^{3+}), the slight differences of thermal stability appear in curves (c) and (d). The clear mass loss processes of BA-PS-Sm and AA-PS-Sm start at temperature of about 250 °C. Compared with acylamido side functionalized polysiloxanes (BA-PS and AA-PS), the composite materials BA-PS-Sm and AA-PS-Sm present the relatively higher degradation temperature and excellent thermal stability [26].

4. Discussion

Carbonyl groups have been already proved to be excellent chelating ligands to sensitize luminescence of lanthanide ions. The mechanism to sensitize emission in lanthanide complexes is usually described as follows [37]: After the acylamido side ligands absorb energy from ultraviolet light, the energy is transferred to lanthanide ions and the emission will be observed.

The excitation spectra for four functional polysiloxane compounds, namely BA-PS (a), BA-PS-Tb (b), AA-PS (c) and AA-PS-Tb (d), via monitoring the emission of Tb^{3+} ions at 545 nm under room temperature are displayed in Fig. 4. The spectrum of BA-PS-Tb (b) exhibits a sharp excitation band centered at around 280 nm, while the others show poor excitation characters. The band around 280 nm monitored in the DRUVS spectra (Fig. 2) corresponds to the singlet-to-singlet transitions of the benzoylamido group in materials [37]. The corresponding overlap between these two spectra exhibits the effective sensitization of lanthanide ions by the benzoylamido group. This arises from the efficient transition based on the conjugated double bonds of the benzoylamido group. As a result, strong luminescence could be observed in their emission spectra owing to the effective energy transfer took place between benzoylamido group and lanthanide ions. However, the poor excitation character in the spectrum of AA-PS-Tb (d) suggests that there would be lower efficient transition and poor luminescence for this composite material.

The luminescence behaviors of lanthanide-containing polysiloxane composite materials have been studied at 298 K by direct excitation of the ligands (acylamido). Figs. 5–8 give four different representative emission spectra of polysiloxane–lanthanide ion materials. There are narrow-width red emissions of BA(AA)-PS-Eu and BA(AA)-PS-Sm. Narrow-width green emissions are observed in BA(AA)-PS-Tb and BA(AA)-PS-Dy.

Curves (a) and (b) in Fig. 5 illustrate typical photoluminescence spectra of BA-PS-Tb and AA-PS-Tb (λ_{ex} = 300 nm), respectively.

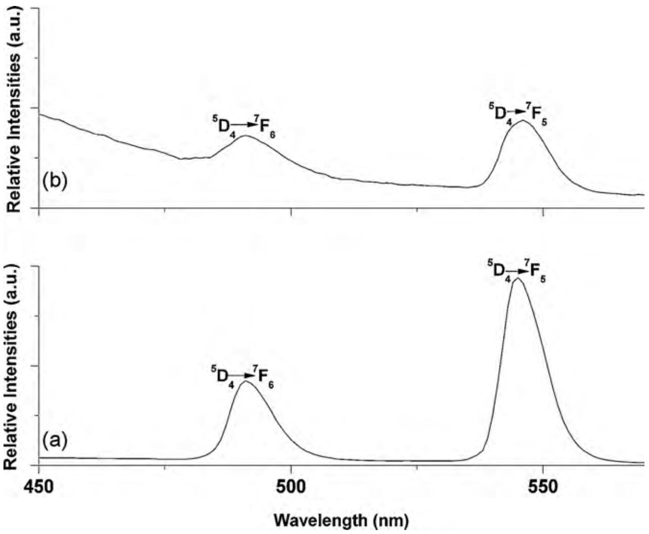


Fig. 5. Emission spectra of BA-PS-Tb (a) and AA-PS-Tb (b) (λ_{em} = 300 nm).

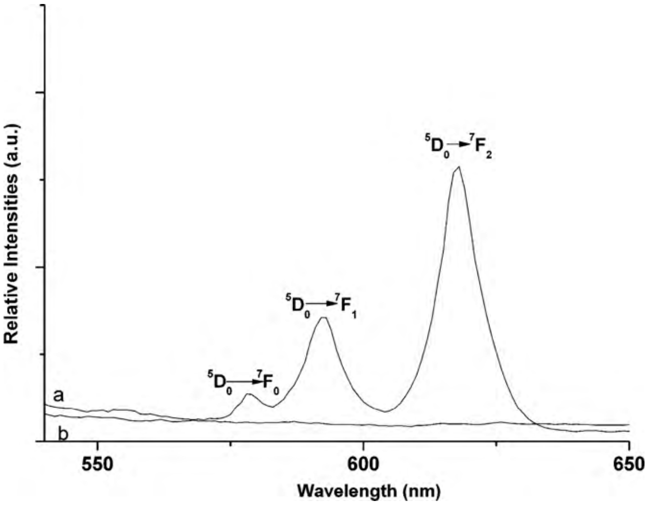


Fig. 6. Emission spectra of BA-PS-Eu (a) and AA-PS-Eu (b) (λ_{em} = 270 nm).

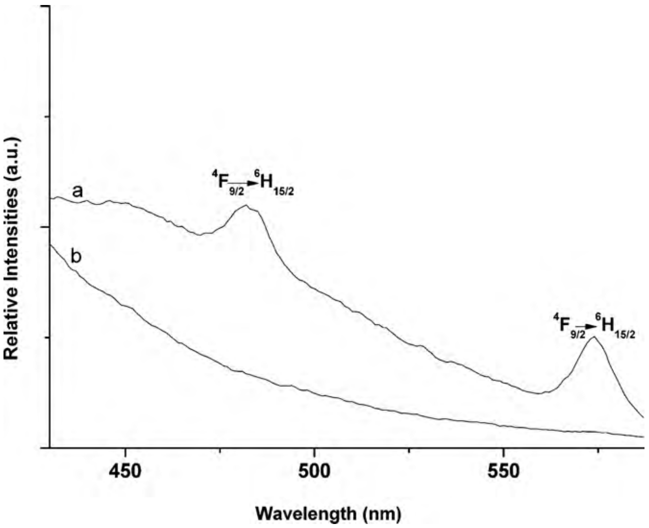


Fig. 7. Emission spectra of BA-PS-Dy (a) and AA-PS-Dy (b) (λ_{em} = 300 nm).

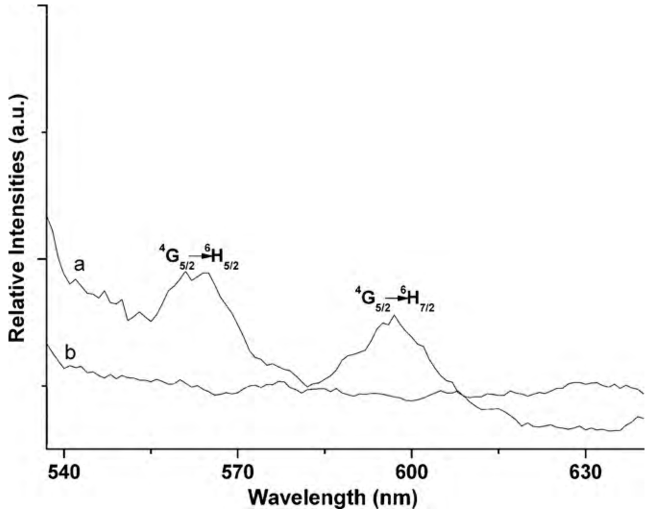


Fig. 8. Emission spectra of BA-PS-Sm (a) and AA-PS-Sm (b) (λ_{em} = 270 nm).

Narrow-width green emission bands with maximum wavelengths at 487 and 543 nm are recorded. These bands correspond to the transitions between the different levels of Tb^{3+} and are attributed to the ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+} ions [38]. The lower baseline in the spectra suggests that the energy transfer efficiency between the acylamido groups and Tb^{3+} ions is higher. Besides, the luminescent intensity of BA-PS-Tb (a) is slightly higher than that of AA-PS-Tb (b).

A weak emission before 480 nm (curve (b) in Fig. 5) could be noticed which was associated to the fluorescence of excited single state energy of the ligands. An interesting result is that this emission band is not observed in BA-PS-Tb (curve (a) in Fig. 5), indicating that energy transfer from benzoylamido group in BA-PS to lanthanide ions is very efficient. It is not surprise because the different efficient transitions in these two kinds of polysiloxanes have been described in analysis aspect of excitation spectra in this paper.

The similar situations are also observed in three other lanthanide ions contained polysiloxanes (Figs. 6–8). Fig. 6 shows the luminescence spectra of BA (AA)-PS-Eu (λ_{ex} = 270 nm). In curve (a), the maxima of these bands are observed at 580, 590 and 613 nm associated with ${}^5D_0 \rightarrow {}^7F_{0,}$ ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} in BA-PS-Eu [38]. But there is no luminescence in AA-PS-Eu (b). Green emission bands of BA-PS-Dy (Fig. 7) are related to the transition between the different levels of Dy^{3+} and are assigned to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (484 nm) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (578 nm) transitions in curve (a) (λ_{ex} = 300 nm) [38], while no emission signal of AA-PS-Dy appears in curve (b). In Fig. 8(a), red emission bonds (λ_{ex} = 270 nm) at 560 nm (${}^4G_{5/2} \rightarrow {}^6H_{5/2}$) and 590 nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$) associated to the fluorescence of Sm^{3+} which energy transfer took place from the benzoylamido group in BA-PS-Sm to Sm^{3+} [38]. And no emission peak could be monitored in AA-PS-Sm (b).

When the spectra of benzoylamido side functionalized polysiloxane system (BA-PS-Ln) and acetamido side functionalized polysiloxane systems (AA-PS-Ln) are compared, it is evident that the benzoylamido group in benzoylamido side functionalized polysiloxane (BA-PS) is more appropriate to sensitize the luminescence of lanthanide ions than the acetamido group in acetamido side functionalized polysiloxane (AA-PS). The differences of luminescence came from the different size of conjugated group of the acylamido groups between two matrixes. Because the f–f transitions of lanthanide ions are very weak, it is usually to take advantage of the strong absorbing capacity of organic ligands with π-electrons and the possibility of transferring the excitation energy from the triplet states of the ligands to the higher energy levels of the $4f^n$ configuration of the lanthanide ion to obtain a good luminescent material [39]. BA-PS-Ln has a superior performance in comparison with AA-PS-Ln. A major improvement is the much higher chromaticity of the conjugated π systems in benzoylamido side functionalized polysiloxane system (BA-PS-Ln). This means that the modification of benzoyl chloride is better than that of acetyl chloride. And this indicates that the luminescence of polysiloxane–lanthanide ion composite material is quite operative. Namely, diverse luminescence could be obtained by molecular design.

5. Conclusions

Two new types of acylamido side functionalized polysiloxanes were obtained via acylamidation reactions. Then two series of luminescent polysiloxanes were achieved by assembly with various lanthanide ions (Tb^{3+}, Eu^{3+}, Dy^{3+} and Sm^{3+}). Green and red narrow-width luminescences have been observed. It is anticipated that these functionalized polysiloxane–lanthanide ion composite materials would attract interests for their utilizations in optical or electronic applications. Investigations into the luminescence properties of these composite materials show that the benzoylamido group in functionalized polysiloxane is quite suitable for the sensitization of luminescence of lanthanide ions. And this strategy of preparing luminescent polysiloxane from molecular design is quite operative. After the desired group was tailored to the host, these functionalized polysiloxane–lanthanide systems via molecular assembly can be expected to possess desired properties.

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