

A novel path to assemble luminescent terbium / inorganic polymer hybrid material chemical bearing functional molecular bridge of hydroxyl group modification

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Firstly, para hydroxybenzoic acid (PHA) was modified by the hydrogen transfer addition reaction with a crosslinking molecule 3-(triethoxysilyl)-propyl isocyanate (TEPIC), which afford to a functional molecular bridge (PHA-Tb) with double activity. Subsequently, the terbium precursor complex (PHA-TEPIC-Tb) with functional ligands was synthesized through the coordination bond, resulting in the hybrid material after the hydrolysis and polycondensation process. The composition of the hybrid material was characterized by FT-IR and the photophysical property of them was investigated by UV spectra, luminescent spectra. The emission spectrum of hybrid materials present the characteristic fluorescence of Tb^{3+} , suggesting para hydroxybenzoic could coordinate to Tb^{3+} ions effectively through carboxyl and the effective intramolecular energy transfer process within PHA-TEPIC-Tb accomplished in hybrids material.

(Received October 25, 2006; accepted August 24, 2007)

Keywords: Functional molecular bridge, Coordination bond, Hybrid material, Chemical bond, Photophysical property, Terbium

1. Introduction

In past decades since Lehn pointed out that the lanthanide complexes could be used as light conversion molecular devices [1], relevant research on such complexes has grown extensively, namely the term "antenna effect" to describe the absorption, energy transfer, emission processes, thus solving the problem of very low absorption coefficients of the lanthanide ions. The design of efficient rare earth complexes, especially rare-earth inorganic/organic hybrid materials with luminescent properties has attracted the attention of many research groups. According to the interaction among the different components or phases in hybrid systems, these hybrid materials can be divided into two major classes [2]. One is so-called physically mixed with weak interactions (hydrogen bonding, van der Waals force or weak static effects) between the organic and inorganic phases; the other is named chemically bonded with powerful covalent bonds linking the organic and inorganic parts [3-7]. Because the latter hybrids belong to the molecular-based composite materials, we can realize the possibility of tailoring the complementary properties of novel multifunctional advanced materials through the combination with chemical bonding within the different components in a single material [8]. Still further, luminescent rare-earth organic complex, such as rare-earth organic complex bonding β -diketones, aromatic carboxylic acids and heterocyclic ligands, cryptands, etc, possess an improved processing ability, chemical stability, and mechanical strength. Zolin et al. have systemically investigated the luminescence and co-ordination structure of ternary lanthanide complexes [9-15]. Nevertheless, it is very difficult to achieve homogeneous dispersion of fine particles of a rare-earth organic/inorganic complex through

a general blending method, and it is also difficult to obtain an excellent interfacial interaction within the rare-earth organic/inorganic complex because of the lack of advanced and effective blending method at present.

In recent years, more attention has been paid to the sol-gel method in the development of luminescent rare-earth hybrid materials [16, 17]. And sol-gel-derived siloxane hybrid materials have attracted much interest for photonic applications as they potentially combine the optical quality of silica, its thermal stability, and its mechanical strength, together with the optical characteristics of active organic molecules [18-20]. This approach seems to be suitable for the design of highly luminescent materials. Indeed, rare-earth organic complexes embedded in silica gels have been shown to exhibit improved emission properties with respect to simple metal ions in similar matrixes [21]. Organic chelates are known to be efficient sensitizers for the luminescence of lanthanide ions (Eu^{3+} and Tb^{3+} in particular), the so-called antenna effect [22]. They also reduce both the concentration and the OH quenching, which have shown to be very important in siloxane matrixes [23-25]. Entrapping of rare-earth complexes with β -diketones, aromatic carboxylic acids, and heterocyclic ligands in sol-gel-derived host structures has been described in some recent studies [21, 26-31]. Franville et al. have devoted to the modification of pyridine-dicarboxylic acid or their derivatives [32]. Zhang and co-workers dedicated to modification of heterocyclic ligands including 1, 10-phenanthroline and di-pyridine [33, 34] in order to construct molecular-based hybrids. However, several shortcomings still have made them prohibited from practical applications, because of them having many problems in processing. For example, hybrid materials frequently contain too many inner-coordinated

water molecules, which bring to low emission quantum efficiency due to the non-radiative dissipation of energy on the high energy -OH vibrations. In outstanding optical, electrical and magnetic properties rare-earth aromatic carboxylates complex are highly functional compounds, which have found widespread applications in various fields as luminophors. Then herein, our team bring forward another path to form the rare-earth hybrid materials. Firstly, para hydroxybenzoic acid (PHA) was modified by 3-(triethoxysilyl)-propyl isocyanate (TEPIC) and then a yellow liquid (PHA-TEPIC) was obtained. The yellow liquid was coordinated with terbium ion through complexation interaction. At last, a rare-earth organic/inorganic hybrid material was obtained (PHA-TEPIC-Tb). The luminescence properties of terbium organic/inorganic hybrid material were investigated and the energy transfer mechanism completed smoothly within this systems.

2. Experimental

2.1. General information

para hydroxybenzoic acid(PHA) was the domestic chemical products, and 3-(triethoxysilyl)-propyl isocyanate(TEPIC) was supplied by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents were used as received.

2.2. Synthetical processings

0.1 mol para hydroxybenzoic acid (PHA) was first dissolved in acetone by stirring and 0.1mol 3-(triethoxysilyl)-propyl isocyanate(TEPIC) was then added to the solution by drops. The whole mixture was refluxing at about 60 °C under argon for 14 hours. The coating liquid was concentrated to remove the solvent acetone using a rotary vacuum evaporator. After isolation, a yellow ropy liquid PHA-TEPIC was obtained. The ^1H NMR(CD_3SOCD_3) date of PHA-TEPIC($\text{C}_{17}\text{H}_{27}\text{O}_7\text{NSi}$) are as follows: δ 0.49(2H, t) , 1.09(9H, t), 1.45(2H, m), 2.93 (2H,t), 3.72(6H, m), 3.96(1H, t), 6.82(2H, d), 7.78(2H, d), 10.41(1H, s). And then a stoichiometric amount of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the solution of PHA-TEPIC in DMF, after acting for about 1 hour, a stoichiometric amount of TEOS and one drop of diluted hydrochloric acid were put into the solution to promote hydrolysis, furthermore a hybrid material containing metal ions was obtain. The molar ratio of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ / PHA/ TEOS / H_2O was 1: 3: 6: 9. And then minimal NaOH was added to adjust pH to 6-7, after hydrolysis cohydrolysis. At last, thermal treatment of mixture liquid was performed at about 80 °C until the sample solidified (Fig. 1). The gels were collected as monolithic bulks and ground to powder material for photophysical studies.

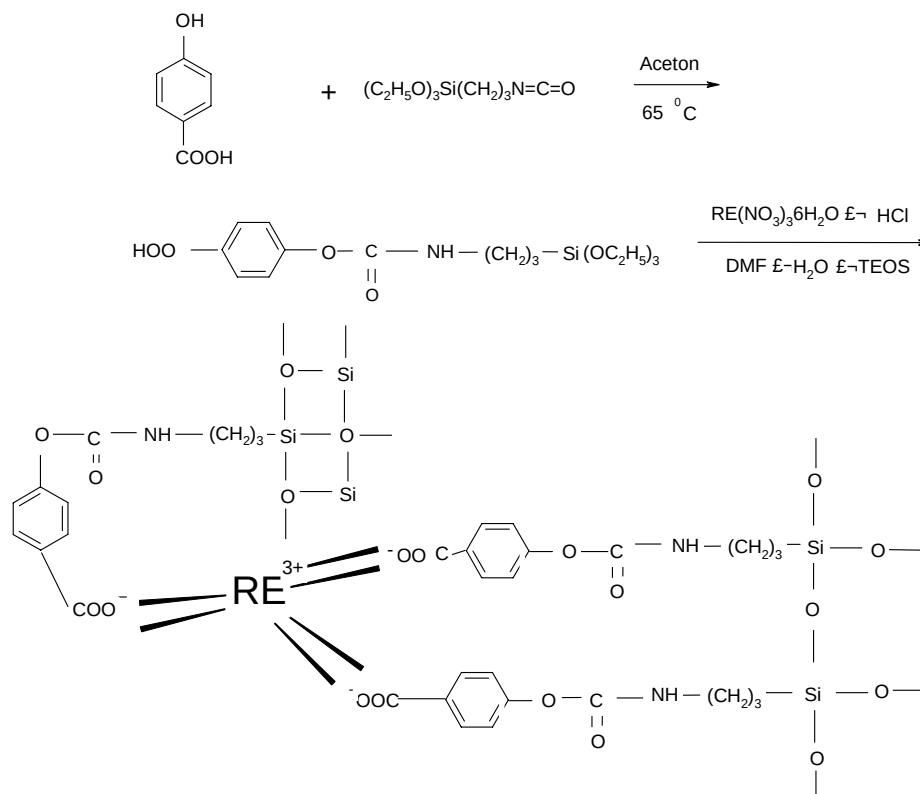


Fig. 1. Scheme of the synthesis process of PHA-TEPIC-Tb hybrid material.

2.3. Measurements

All measurements were carried out under room temperature. Infrared spectroscopies were obtained in KBr pellets and recorded on a Nexus 912 AO446 FT-IR spectrophotometer in the range of 4000-400 cm^{-1} . ^1H NMR spectra was recorded in CD_3SOCD_3 on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Fluorescence excitation and emission spectra were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 1.5 nm, emission slit width = 3.0 nm. The microstructure was estimated by scanning electronic microscope (SEM, Philips XL-30).

3. Results and discussion

The reaction model for the hybridization formula of TEOS and PHA-TEPIC may be illustrated as following: The hybridization of TEOS and PHA-TEPIC, accordingly, proceeds through a polycondensation reaction between the terminal silanol groups of PHP-TEPIC and the OH groups of hydrolyzed TEOS (called first Step). At the beginning of the reaction, the individual hydrolysis of PHA-TEPIC and TEOS are predominant. The second Step, however, is related to the polycondensation reactions between hydroxyl groups of both PHA-TEPIC and TEOS. By these methods, the molecular-based hybrids bearing the Tb-O coordination bond and Si-O covalent bond exhibit the strong green luminescence of Tb^{3+} . Here we named the cooperation of both PHA-TEPIC and TEOS during the in-situ sol-gel process as cohydrolysis and copolycondensation (similar to copolymerization of organic monomer).

The Fourier-transform infrared (FTIR) spectra of TEPIC and PHA-TEPIC are shown in the Fig. 2. In the spectra of PHA-TEPIC contrasting with the spectra of the TEPIC, a strong and broad band at about 2265-2369 cm^{-1} belonging to the stretching vibration of $\text{O}=\text{C}=\text{N}$ ($\nu_{\text{O}=\text{C}=\text{N}}$) of TEPIC disappeared and the bands located at 1723 cm^{-1} of the spectra of the TEPIC shifted to 1691 cm^{-1} of the spectra of PHA-TEPIC. Moreover the three peaks at 1691 cm^{-1} , 1671 cm^{-1} , 1604 cm^{-1} are assigned to the stretching vibration of carbonyl groups ($\nu_{\text{C}=\text{O}}$) and the absorption of carboxyl, respectively in the spectra of PHA-TEPIC. Furthermore the emergence of broadband located at 3370 cm^{-1} is owed to the stretching vibration of NH (ν_{NH}) and the peaks at 1243, 1278 cm^{-1} and at 1317 cm^{-1} in the spectra of PHA-TEPIC suggested the symmetrical stretching vibration of C=N and C-O, respectively. All of these above mean that TEPIC has been successfully grafted on to PHA. The chemical data of ^1H NMR also testify the structure of PHA-TEPIC.

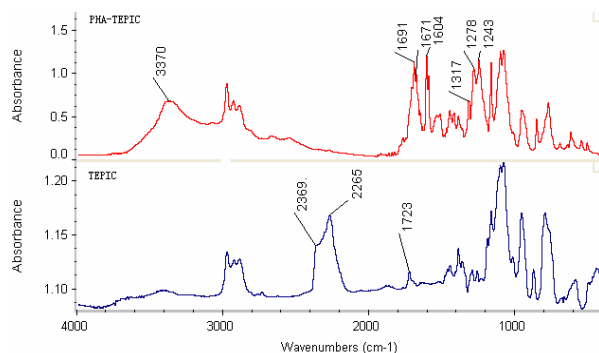


Fig. 2. FT-IR spectra of 3-(triethoxysilyl)-propyl isocyanate(TEPIC) and PHA-TEPIC hybrid material.

Fig. 3 exhibits ultraviolet absorption spectra of (A) PHA, (B) PHA-TEPIC, (C) PHA-TEPIC-Tb. From the spectra, it is observed that the obvious peak at 275 nm was due to the major $\pi-\pi^*$ electronic transitions occurred in (A) PHA conjugating units. It can be observed a blue shift of 5 nm the major $\pi-\pi^*$ electronic transitions A $\rightarrow$ B (from 270 to 275 nm), suggesting the electron distribution of the modified PHA-TEPIC has changed compared to free PHA ligand for the introduction of TEPIC group, and TEPIC has been successfully grafted on to PHA. After coordinating to terbium ions, the absorptions were totally different from A (PHA) and B (PHA-TEPIC), and the sharp peak was substituted by a large band at about 320 nm, suggesting the electron distribution of the modified PHA-TEPIC-Tb has changed compared to B (PHA-TEPIC) ligand for completion of coordination interaction with terbium ion. All of these changes means that the complexation between COO^- group of A(PHA) and terbium ions accomplished obviously. As a result, all of above verifies that our basic idea of PHA as sensitizing ligand was partly realized for the obtained hybrid material exhibits strong characteristic emissions of terbium.

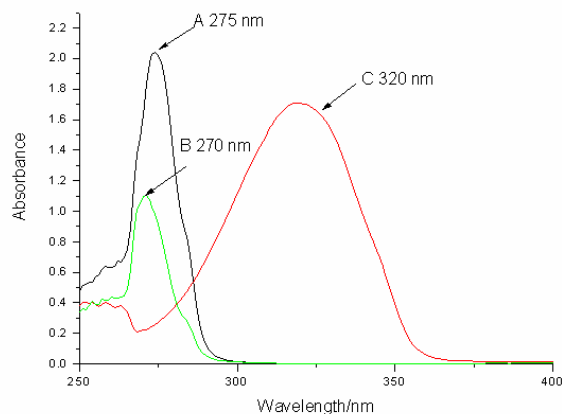


Fig. 3. Ultraviolet absorption spectra of A (para hydroxybenzoic acid, PHA), B (PHA-TEPIC), C (PHA-TEPIC-Tb) hybrid material.

The excitation and emission spectra of the resulting hybrid materials are shown in Figs. 5 and 6. The excitation spectra (Fig. 4) was obtained by monitoring the emission of Tb^{3+} at 543 nm and dominated by a series of peaks centered at about 369 nm, which is the characteristic absorption of the lanthanide complexes arising from the efficient transition based on the conjugated C=O double bonds of benzoic acids. As a result, the emission lines of the hybrid material were obtained for terbium ions (Fig. 5) under the excitation wavelength at 369 nm, which indicated that the effective energy transfer took place between the PHA and terbium ions. Among these emission peaks, green emission intensities (arbitrary unit, a.u.) to electric dipole transition of $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (264.618 for PHA-TEPIC-Tb at 543 nm) is stronger than the yellow emission intensities of magnetic dipole transition of $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (114.243 for PHA-TEPIC-Tb at 488 nm), indicating Tb^{3+} site in an environment without inversion symmetry [35].

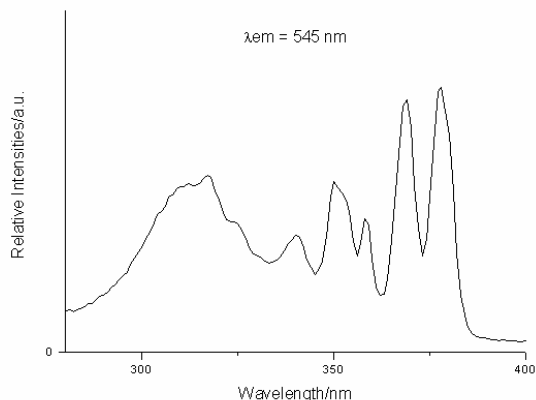


Fig. 4. Excitation spectrum of PHA-TEPIC-Tb hybrid material.

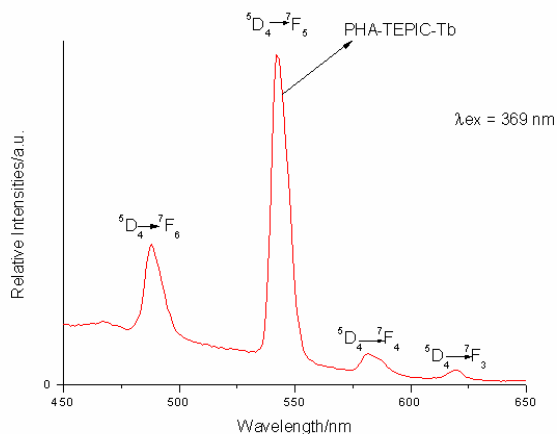


Fig. 5. Emission spectrum of PHA-TEPIC-Tb hybrid material.

The scanning electron microscope (SEM) images in Fig. 6 show the morphology of PHA-TEPIC-Tb hybrid materials. It has been seen that the PHA-TEPIC-Tb hybrid material has a relatively regular shape and homogeneous

states. As shown in Fig. 6, the particle sizes are in the micrometer range, which may be due to the introduction of polymer in the hybrid system. The above data suggest that the organic/inorganic hybrid material, conceived before the experiment was really obtained.

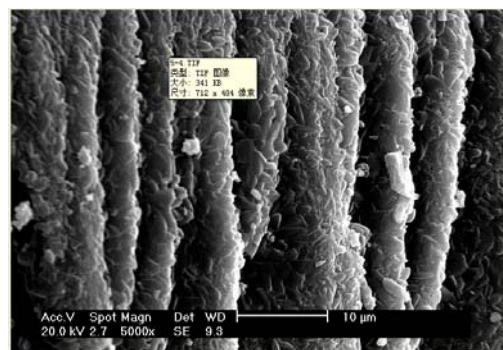


Fig. 6. SEM of PHA-TEPIC-Tb hybrid material.

4. Conclusions

In summary, para hydroxyl benzoic acid was grafted to achieve a functional bridge molecule with a crosslinking molecule 3-(triethoxysilyl)-propyl isocyanate. Since the hydrolysis and polycondensation reactions between triethoxysilyl of functional bridge molecule lead to the formation of Si-O-Si network structures for the same alkoxy group of them, a novel luminescent terbium molecular-based hybrid material with chemical bond was constructed.

Acknowledgements

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

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