

Construction of luminescent molecular-based hybrid material with double chemical bond from functional bridge ligand through in-situ sol-gel process

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Modification of ortho tolylacetic acid (OTA) by means of the amidation reaction with a crosslinking molecule (3-aminopropyl)trimethoxysilane, abbreviated as APMS) was afford to a functional molecular bridge (OTA-APMS) with double activity. Then the modified functional molecular bridge further exhibits (behave) double function: one is to coordinate to terbium ion through amide' oxygen atom, the other is to form the covalent bond with the Si-O network matrix precursor (tetraethoxysilane, TEOS) by an in-situ sol-gel process. (resulting in) A novel molecular hybrid material (named as Tb-OTA-APMS) with double chemical bonds (Tb-O coordination bond and Si-O covalent bond) resulted. The photophysical properties of the molecular hybrid material were determined by ultraviolet absorption, phosphorescent, and fluorescence spectra. The strong luminescence of Tb³⁺ verifies optimum energy match and effective intramolecular energy transfer between the triplet state energy of modified ligand bridge and emission energy level of Tb³⁺.

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1. Introduction

Inorganic-organic hybrid materials have obtained extensive attention in the last few years as potential attractive hosts in diverse technological fields such as electronics, mechanics, dyestuff, optics, and biology [1, 2]. According to the interaction among the different components or phases in hybrid systems, these hybrid materials can be divided into two major classes [3]. 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 chemical bonded with powerful covalent bonds linking the organic and inorganic parts [4-8]. Naturally, the latter hybrids belong to the molecular-based composite materials, which can realize the possibility of tailoring the complementary properties of novel multifunctional advanced materials through the combination with a chemical bonding within the different components in a single material [9]. To presence, sol-gel technology is (the) one of the most versatile methods for the preparation of inorganic-organic hybrid materials for its low processing temperature which permits the incorporation of active species into host matrix through the hydrolysis and polycondensation [10]. Luminescent rare earth organic complexes, such as europium and terbium chelates with β -diketones, aromatic carboxylic acids and heterocyclic ligands exhibit intense narrow band emissions via an energy transfer from the ligands to the metal ions under near UV excitation [11]. Among rare earth complexes with (some) benzoic acid derivatives, some possess high thermal

or optical stability due to the fact that (for) they readily form the dimeric or polymeric structure [12, 13]. These complexes can be used as photoactive center to be introduced into matrix through hydrolysis and condensation process [14, 15]. Naturally, these hybrid sol-gel derived host materials belong to physical class which is hard to be dispersed homogeneously. So the key problem is how to develop luminescent rare earth-based hybrids with chemical bonding, namely rare earth molecular hybrids [16-22]. At the basis of this assumption, we have achieved novel molecular hybrids derived from modification of amino group of benzoic acids [23, 24].

In the context, we put forward another modification technology to modify the carboxyl group of ortho tolylacetic acid (abbreviated as OTA) which is different from above by the amidation between carbonyl groups of OTA and the amino group of a cross-linking ligand (3-aminopropyl)trimethoxysilane, APMS), and further afford a novel luminescent molecular-based terbium hybrid material. The photophysical properties were discussed in detail.

2. Experimental

OTA was first converted to acyl chloride by refluxing in excess SOCl₂ under argon at 70 °C in water bath(ing) for 4 hours. After isolation, the acyl chlorides were directly reacted with APMS in ethyl ether in presence of pyridine. A typical procedure for the preparation (of was according to reaction) is presented in the scheme given in Fig. 1. The date of FTIR spectra and the date of ¹H NMR and ¹³C NMR

of OTA-APMS reagent used in the procedure are as follows.

$C_{15}H_{25}NO_4Si$: - IR (KBr): $-\text{CONH}-$ (1644 cm^{-1} , 1553 cm^{-1}), C-Si (1210 cm^{-1}) ν_{NH} , 3412 cm^{-1} .

- ^1H NMR: - 0.42(2H,t), 1.48(2H,m), 2.25(3H,s), 3.01(2H,m), 3.20(3H,S), 3.29(2H,s), 3.39(2H,b), 3.46(2H,s), 4.09(2H,b), 7.08(2H,t), 7.12(2H,b), 7.90(1H,s).

- ^{13}C NMR: - 169.6(C=O), 136.5(C6), 135.1(C1), 129.8(C2), 129.7(C3), 126.3(C5), 125.6(C4), 49.4(CH_3 ,-O CH_3)), 41.7(C8), 23.2(C9), 19.3(Ph- CH_2 -), 11.3(- CH_3), 5.9(C10).

A sol-gel derived hybrid material was prepared as follows: OTA-APMS was dissolved in ethanol, 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 $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the final stirring mixture. The mole ratio of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /OTA-APMS/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 $60\text{ }^\circ\text{C}$ until the sample solidified (see Fig. 1).

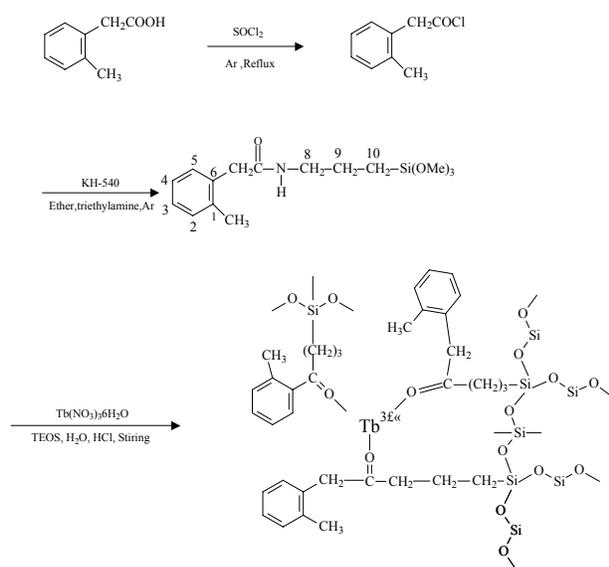


Fig. 1. Scheme of the synthesis process of OTA-APMS and predicted structure of hybrid materials.

3. Physical measurements

All measurements were completed under room temperature except for phosphorescence at 77 K . ^1H NMR

spectra was recorded in DMSO on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples ($5 \times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$ chloroform (CHCl_3) solution) were recorded with an Agilent 8453 spectrophotometer. Phosphorescence spectra ($5 \times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$ CHCl_3 solution) and fluorescence excitation and emission spectrums were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm , emission slit width = 5 nm . The microstructure was estimated by scanning electronic microscope (SEM, Philips XL-30).

IR method and the equipment used is not presented.

4. Results and discussion

The reaction model for the hybridization formula of TEOS and OTA-APMS may be illustrated in Fig. 2. The hybridization of TEOS and OTA-APMS, accordingly, proceeds through a polycondensation reaction between the terminal silanol groups of PAB-Si and the OH groups of hydrolyzed TEOS. At the beginning of the reaction, as shown in Fig. 2 (Step I), the individual hydrolysis of OTA-APMS and TEOS are predominant. The Step II, however, is related to the polycondensation reactions between hydroxyl groups of both OTA-APMS 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 OTA-APMS and TEOS during the in-situ sol-gel process as cohydrolysis and copolycondensation (similar to copolymerization of organic monomer).

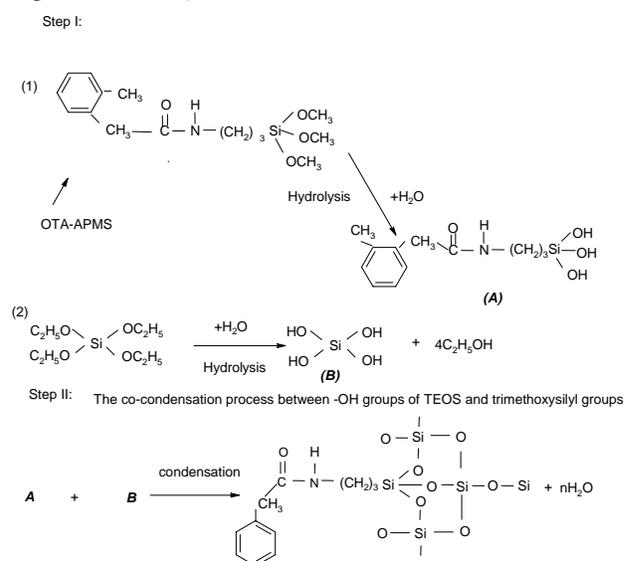


Fig. 2. Scheme of hydrolysis and polycondensation processes between OTA-APMS and TEOS.

From the date of IR spectra, the occurrence of the amidation reaction was supported by the bands located at

1644 cm^{-1} assigned (due) to the characteristic absorption of amide groups ($-\text{CO}-\text{NH}-$), suggesting that APMS has been successfully grafted on to OTA. Then the presence of the stretching vibration (ν_{NH} , 3412 cm^{-1}) and bending vibration (δ_{NH} , 1553 cm^{-1}) further prove the formation of amide groups. The stretching vibration ($\nu_{\text{Si-C}}$) 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. What's more, the broad absorption band at 1085 cm^{-1} ($\nu_{\text{Si-O-Si}}$) originates from the formation of siloxane bonds. The dates of ^1H NMR and ^{13}C NMR also testify the formation of OTA-APMS.

Fig. 3 shows the ultraviolet absorption spectra of (A) OTA, (B) OTA-APMS, (C) Tb-OTA-APMS, it can be observed a red shift of 5 nm of the major $\pi-\pi^*$ electronic transitions A \rightarrow B (from 257 to 262 nm), suggesting that the electron distribution of the modified OTA-APMS has changed compared to free OTA ligand for the introduction of APMS group. Furthermore, an obvious blue shift of 16 nm is observed on addition of Tb^{3+} to OTA-APMS (from 262 to 246 nm) when conjugated system forms, proving the formation of a complex between Tb^{3+} and OTA-APMS.

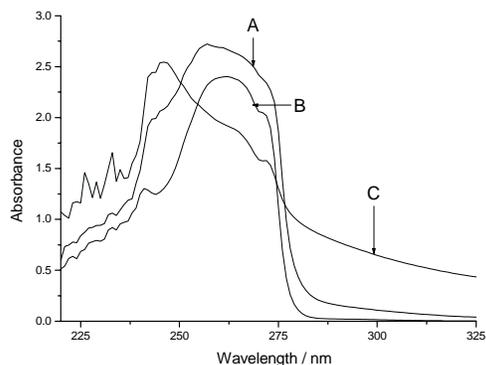


Fig. 3. Ultraviolet absorption spectra for (A) OTA, (B) OTA-APMS, (C) Tb-OTA-APMS hybrids.

Fig. 4 wears the low temperature phosphorescence spectra of OTA (A), OTA-APMS (B) at 77 K. Molecular phosphorescence belongs to the character of the organic molecular ligands and different phosphorescence bands correspond to different ligand molecules, so a red shift of 4 nm appears between A (435.5 nm) and B (439.5 nm) in terms of modification of amino group. According to intramolecular energy transfer mechanism [25, 26], the corresponding intramolecular transfer efficiency from the OTA-APMS to Tb^{3+} mainly depends on the energy match between the triplet state energy of OTA-APMS (corresponded to the phosphorescence band, 22750 cm^{-1}) and the resonant emissive energy level of the central Tb^{3+} (20500 cm^{-1}). Therefore, it can be predicted that OTA-APMS shows a good energy couple and can sensitize the luminescence of Tb^{3+} .

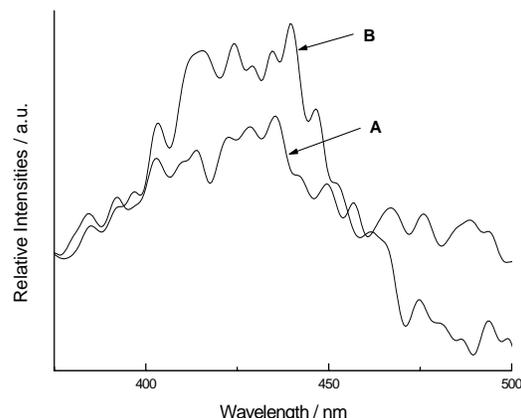


Fig. 4. Phosphorescence spectra of OTA (A), OTA-APMS (B) at 77 K.

The excitation spectrum of the resulting hybrid materials was obtained by monitoring the emission of Tb^{3+} ions at 545 nm (Fig. 5). The excitation spectrum is dominated by a dominant broad band from 300 to 400 nm with maximum peak at 352.5 nm and 375.5 nm, which is the characteristic absorption of the lanthanide complexes arising from the efficient transition based on the conjugated double bonds of the aromatic cycle of OTA-APMS ligand. Besides this, there exist two weak peaks at 241, 259.5 nm. As a result, the strong green luminescence was observed (see Fig. 6), indicating that the effective energy transfer took place between the aromatic ligand OTA-APMS and the chelated Tb^{3+} ions. The emission lines of hybrid material were assigned to the characteristic $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) transitions of Tb^{3+} at 488.5, 543.5, 583 and 621.5 nm, respectively. Because OTA-APMS forms powerful chemical bonds of $-\text{Si}-\text{O}-\text{Si}-$ backbone with silica and the complexation of Tb^{3+} ($\text{Tb}-\text{O}$ bond), the hybrids finally exhibit relatively strong emission under such unique stable chemical environment of rigid molecular network structure.

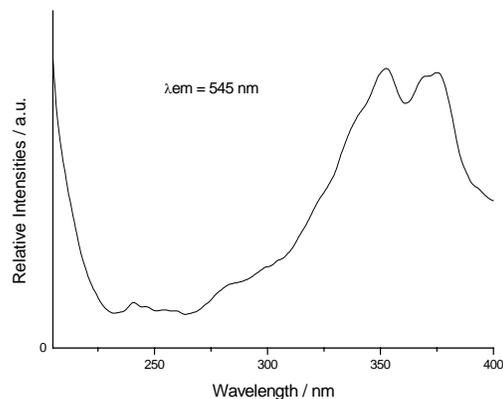


Fig. 5. Excitation spectrum of Tb-OTA-APMS hybrid material a.

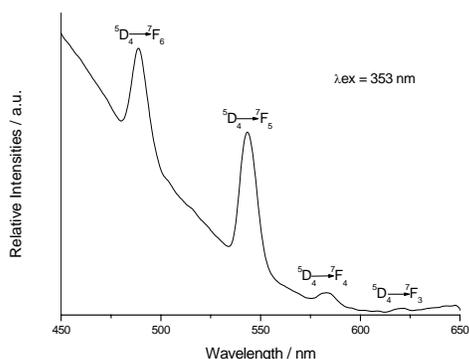


Fig. 6. Emission spectrum of Tb-OTA-APMS hybrid materials.

The SEM micrograph shows that the micromorphology of the Tb-OTA-APMS is very homogeneous(ly) (Fig. 7). We think that the hybrids was constructed by a functional bridge ligand to form an homogeneity (integrity) at the molecular scale with double chemical bonds. By the strong interaction of the coordination bond between Tb³⁺ and OTA-APMS bridge and of the covalent bond in the SiO₂ network from the alkoxy groups of OTA-APMS bridge and TEOS is easy to achieve the homogeneous structure and morphology.

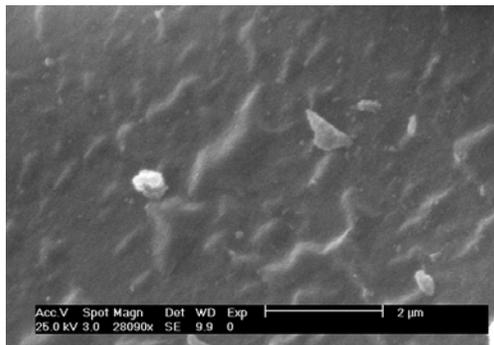


Fig. 7. SEM of Tb-OTA-APMS hybrid materials.

5. Conclusions

In summary, because the organic monomers attached to the hosts must carry a functional organic group like trimethoxysilyl capable of forming covalent bonds with tetraethoxysilane, we have modified ortho totylacetic acid to achieve a functional bridge molecule with a crosslinking molecule (3-aminopropyl)trimethoxysilane. Since the hydrolysis and polycondensation reactions between triethoxysilyl of OTA-APMS and TEOS lead to the formation of Si-O-Si network structures for the same alkoxy group (of them), a novel luminescent molecular-based hybrid material with double chemical bond was firstly constructed using OTA-APMS coordinated to Tb³⁺. This technology could be used to the assembly of other luminescent molecular-based hybrid material.

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