

Photofunctional terbium centered inorganic/organic hybrid material with the functionalized 5-dihydroxybenzoate linkage

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In this study, silica-based organic-inorganic hybrids were prepared using sol-gel methods. A new kind of monomer (DHBA-TESPI) was derived by modifying the double hydroxyl groups of 3, 5-dihydroxybenzoic acid (DHBA) with 3-(triethoxysilyl)-propyl isocyanate (TESPI) through the addition reaction. Then, the obtained compound and tetraethoxysilane (TEOS) were used as the inorganic and organic counterparts respectively. Coordination reaction between Tb³⁺ and the carboxylic groups of the monomer happen simultaneously. IR, NMR, UV/Vis absorption, low-temperature phosphorescence spectroscopy and fluorescence spectroscopy were used to characterize the hybrids. The final materials exhibited strong green-colored fluorescence (Tb³⁺), which can be explained by the intramolecular energy transfer caused by coordination of the organic counterpart. The spectroscopic data also revealed that the triplet state energy of the organic ligand matches the emissive energy level of Tb³⁺.

Keywords: chemical modification, photoluminescence, organic-inorganic hybrids, rare earth ions, sol-gel process

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1. Introduction

Hybrid silicate materials derived from the hydrolytic polycondensation of organo-bridged silsesquioxane precursors, Si(OR)₄ and RSi(OR')₃, where R and R' are organic groups, have received increasing attention over the past decade [1, 2]. Recently, efforts have targeted new diverse functional materials through use of sol-gel processes. During these processes the coupling agents are often used to form organic-inorganic hybrid systems that combine the desired properties of the two different components. In addition, it is easy to incorporate different functional species into the matrix and to form relatively transparent materials without phase separation between different phases.

Rare earth compounds are well known for their excellent luminescence properties [3, 4]. Their luminescence properties are widely

studied because they can be used as visible and near-IR radiation sources for lasers and optical communication devices. However, the luminescent rare earth compounds also have disadvantages in thermal stability and transparency. In order to develop these compounds into practical materials, matrices (organic or inorganic) are always used to form all kinds of hybrids and improve their thermal stabilities and transparency.

Rare earth complexes with β -diketones, aromatic carboxylic acids, and heterocyclic ligands are often incorporated into sol-gel-derived hosts to provide a stable environment [5-7]. These studies indicate that the thermal stabilities and transparency of sol-gel incorporated rare earth complexes are improved and the luminescence intensities are similar or superior to the complexes alone. In simply doped hybrids only weak physical interactions (hydrogen bonding, Van der Waals force or weak static effects) exist between the matrixes and the complexes. Hence, many problems such as clustering of the emitters,

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phase separation, and leaching of dopants can occur. Thus chemical bonding in rare earth-based hybrids is necessary to improve their physical properties. Based on the different interactions between organic-inorganic counterparts in hybrid materials, such hybrids can be divided into two major classes. The first is termed physically mixed hybrids with weak interactions between the organic and inorganic phases whereas the second is termed chemically bonded hybrids. The covalent bonds can be helpful in forming single phases [8]. In fact, chemically bonded hybrids belong to molecular-level materials [9–15], which combine the superior properties of the matrices and the luminescent complexes.

We have synthesized several types of compounds by modifying amino groups or carboxyl groups of aromatic carboxylic acids providing bridges to construct molecular hybrids with excellent luminescence properties [13–15]. Based on these studies, we recognized that a key method of constructing the molecular-based materials is to synthesize the bridge molecules (ligands) that can offer the double function of coordinating to rare earth ions and to form covalent Si-O networks during sol-gel processing. Carlos and co-workers have divided amino-functional hybrids lacking metal ions into two categories: di-ureasils(–NHC(=O)NH–) and di-urethanesils(–NHC(=O)O–) [16, 17]. The di-urethanesils encouraged us to investigate the reactions of hydroxyl groups with isocyanate groups to study the influence of di-urethane moieties on the luminescence of the resulting hybrids.

Based on the studies of the coordination environment of carboxylic acid groups, we synthesized a novel molecular monomer DHBA-TESPI by reacting 3, 5-dihydroxybenzoic acid (DHBA) with 3-(triethoxysilyl)-propyl isocyanate (TESPI). Afterwards the monomer and TEOS were used to form a molecular-based hybrid system through sol-gel processing.

2. Experimental

2.1. Materials

DHBA was purchased from Lancaster. TESPI was acquired from Tokyo Chemical Industry (TCI). TEOS was received from Nanjing Shuguang chemical plant. The solvents were purified by common methods. The other starting reagents were used as received.

2.2. NMR analysis

All ^1H and ^{13}C -NMR were performed in CDCl_3 and recorded on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as an internal reference.

2.3. IR analysis

The IR spectra were measured on a Nexus 912 AO446 FT-IR spectrophotometer using KBr pellets. The spectra of DHBA, TESPI, DHBA-TESPI and the hybrid Tb-DHBA-TESPI were measured and recorded in one graph.

2.4. UV analysis

The UV absorption spectra of the samples (about $5 \times 10^{-4} \text{ mol L}^{-1}$ CHCl_3 solution) were recorded with an Agilent 8453 spectrophotometer using a 1 cm width quartz cell.

2.5. Phosphorescence and fluorescence analysis

The phosphorescence spectra (about $5 \times 10^{-4} \text{ mol L}^{-1}$ CHCl_3 solution) were measured on a Perkin-Elmer LS-55 spectrophotometer at 77 K. The luminescence excitation and emission spectra were measured with a SHIMADZU RF-5301 spectrophotometer.

2.6. Synthesis of DHBA-TESPI

The procedure to prepare the DHBA-TESPI bridge ligand is shown in Fig. 1. DHBA in the amount of 0.462 g (3.00 mmol) was directly reacted with 1.482 g (6.00 mmol) TESPI in 40 mL CHCl_3 under argon at 70 °C in an oil-bath for 8 h. The resulted product was used as a

bridging precursor to prepare the hybrids. UV, IR, ^1H NMR and ^{13}C NMR were used to characterize the product. The NMR data for DHBA-TESPI ($\text{C}_{27}\text{H}_{50}\text{O}_8\text{N}_2\text{Si}_2$) were as follows: ^1H NMR (CDCl_3): δ 12.1(1H), 6.85(2H), 6.47(1H), 5.95(2H), 3.75(12H), 3.50(4H), 2.02(4H), 1.86(4H), 1.21(18H). ^{13}C NMR (CDCl_3): δ 134.4(C_1), 106.4(C_2 , C_6), 108.5(C_3 , C_5), 106.1(C_4), 168.3(C_7), 165.6(C_8), 50.8(C_9), 50.4(C_{10}), 44.2(C_{11}), 43.5(C_{12}), 15.2(C_{13}).

2.7. Synthesis of the hybrid material (Tb-DHBA-TESPI)

The hybrid materials were prepared as follows: 3.00 mmol DHBA-TESPI was dissolved in 20 mL ethanol (95 %). Then 1.248 g (6.0 mmol) TEOS and several drops of H_2O were added while stirring. Additionally, one drop of diluted nitric acid was put into the above solution to promote the hydrolysis. After one hour, 0.452 g (1.00 mmol) $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the mixture while stirring for 1 h. The mole ratio of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /DHBA-TESPI/TEOS/ H_2O was 1: 3: 6: 24. After the hydrolysis, 2 mL DMF (dimethylformamide) and an appropriate amount of hexamethylene-tetramine were added to adjust the pH at about 6.5. The mixtures were stirred to achieve a single phase and heated at 60 °C until the samples solidified. The procedure is shown in Fig. 1.

3. Results and discussion

Fig. 1 shows the synthetic routes and the predicted structure of the hybrid material. In the structure the water molecules and nitrate ions coordinating to the Tb^{3+} are omitted. The existence of water molecules and nitrate ions has been proved by IR spectra (peaks at 3416 cm^{-1} and 1377 cm^{-1}).

The hydrolysis and condensation reactions in the sol-gel process can be depicted as follows. Here we term the interaction of both DHBA-TESPI and TEOS during the sol-gel processing as cohydrolysis and copolycondensation (similar to copolymerization of organic monomer). 3-(triethoxysilyl)-propyl isocyanate is a special

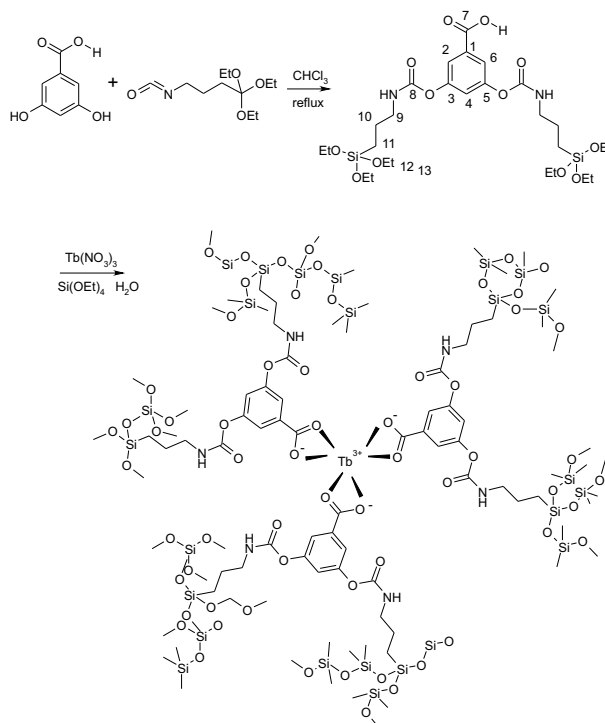


Fig. 1. Scheme of the synthesis of DHBA-TESPI and predicted structure of the resulting hybrid material.

silane coupling reagent that can be expected to offer hydrogen transfer reactions with some molecules containing reactive hydrogen atoms. We have observed the hydrogen transfer addition reaction between TESPI and $-\text{NH}_2$ derivatives. Hydroxyl group also belongs to active groups as its hydrogen atom can be readily lost. For this reason, it can be predicted that there may exist the hydrogen transfer addition reaction from $-\text{OH}$ to isocyanate of TESPI. As shown in Fig. 1, the two hydroxyl groups of DHBA can react with TESPI to form functional bridge molecules DHBA-TESPI. The bridge ligands DHBA-TESPI play then two roles: on the one hand side, they can coordinate Tb^{3+} through the oxygen atoms of the carboxylic group; on the other hand side, they can take part in the cohydrolysis and copolycondensation with TEOS through the sol-gel reactions (similar to the copolymerization of organic monomer with unsaturated bonds). Finally, the molecular-based hybrid materials can be assembled with chemically bonded counterparts. These hybrids belong to

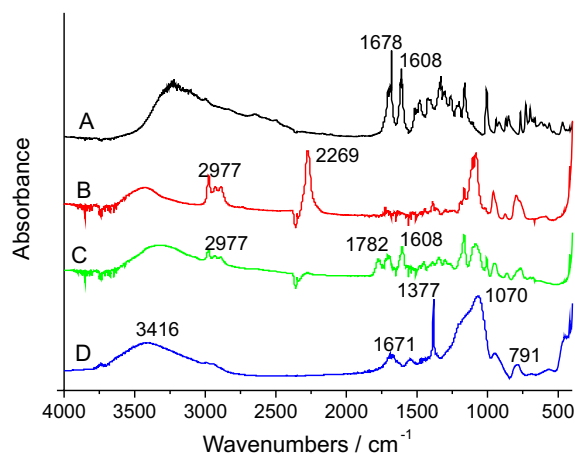


Fig. 2. FT-IR spectra for DHBA (A), TESPI (B), DHBA-TESPI (C) and the hybrid Tb-DHBA-TESPI (D).

molecular materials which can be considered as the complex molecular networks.

Fig. 2 shows the IR spectra of DHBA (A), TESPI (B) DHBA-TESPI (C) and the hybrid Tb-DHBA-TESPI (D). The addition reaction is proved by the formation of the -COO- group, which is evidenced by the presence of a peak at 1782 cm^{-1} , and the fact that the characteristic stretching vibration of the -N=C=O group at 2269 cm^{-1} disappeared after the reaction. After coordination, the 1678 cm^{-1} stretching vibration of the -C=O group in -COOH shifts to 1671 cm^{-1} which is slightly red-shifted because of the decreasing intensity of -C=O stretching after complexation. The formation of silica network is proved by the peaks at 1070 cm^{-1} ($\nu_{\text{Si-O-Si}}$) and 791 cm^{-1} ($\delta_{\text{Si-O-Si}}$) in the graph (D). The peaks at 3416 cm^{-1} attributed to $\nu_{\text{O-H}}$ in the hybrid and the peaks at 1377 cm^{-1} derived from the coordinating nitrate ions are a proof of the existence of coordinating nitrate ions.

Fig. 3 exhibits the UV absorption spectra of (A) DHBA and (B) DHBA-TESPI. From the spectra, it can be observed that a blue shift (A $\rightarrow$ B) of the major $\pi\text{-}\pi^*$ electronic transitions occurs and it is supposed that during the grafting reaction of DHBA, the diverse ligand may limit the conjugating effect of the double bonds and enlarge

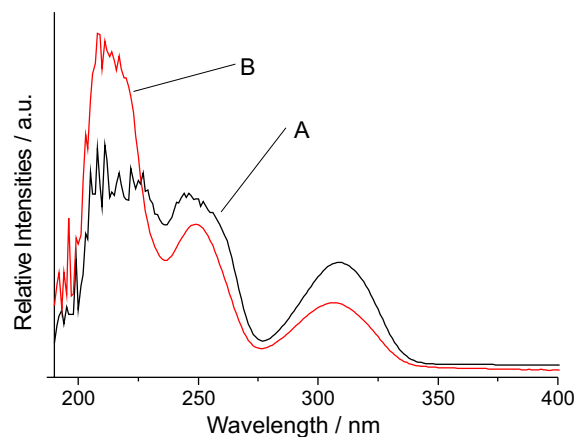


Fig. 3. Ultraviolet absorption spectra for (A) DHBA and (B) DHBA-TESPI.

the energy difference levels among the electron transitions.

Fig. 4 shows the phosphorescence spectra of DHBA (A) and DHBA-TESPI (B). There is a blue shift from 447 nm (B) to 431 nm (A) which is attributed to the modification of DHBA to DHBA-TESPI. The phosphorescence spectrum is characteristic of the organic molecular ligands and the different phosphorescence bands correspond to different ligand molecules. It can be found that the maximum phosphorescence band of B, located at 447 nm , determined the triplet state energy of $6\text{H}2\text{N}3\text{C-Si}$ to be 23095 cm^{-1} . According to the energy transfer and intramolecular energy mechanism, [18, 19] it can be predicted that the bridging of DHBA-TESPI is suitable for the luminescence of terbium (20500 cm^{-1}) ions.

The corresponding intramolecular transfer efficiency from the DHBA-TESPI to Tb^{3+} depends mainly on the energy match between the triplet state energy level of DHBA-TESPI (corresponding to the phosphorescence band) and the resonant emissive energy level of the central Tb^{3+} . Fig. 5 shows the excitation and emission spectra of the molecular hybrid (Tb-DHBA-TESPI). The emission spectrum excited at 280 nm shows characteristic emission peaks of $\text{Tb}^{3+} \text{ } ^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) transitions at 490 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$) and 544 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) which suggests that a very effective energy transfer from the ligand to Tb^{3+}

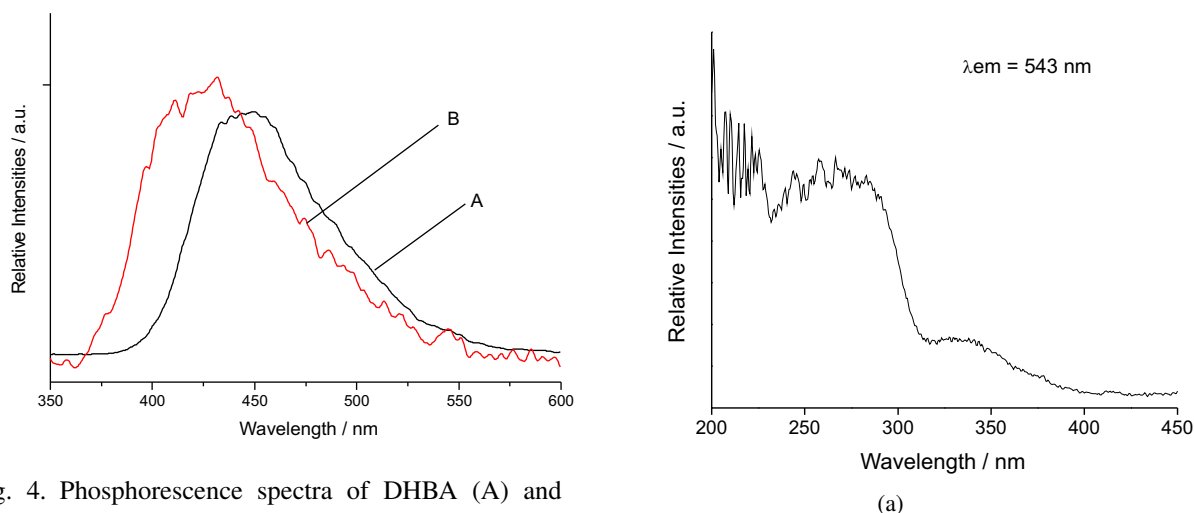


Fig. 4. Phosphorescence spectra of DHBA (A) and DHBA-TESPI (B).

in the molecular hybrids occurs. The broadness of the excitation spectra also strongly enhances the fluorescence. The hybrids finally exhibit characteristic emission under the environment of rigid molecular network formed by -Si-O-Si- backbone.

4. Conclusions

In summary, 3, 5-dihydroxybenzoic acid was successfully modified with coupling agents to form bridge molecule (DHBA-TESPI), which can be used as both fine organic ligands to Tb^{3+} and precursors to form the hybrid material based on silica network. The final hybrid materials show characteristic emission of Tb^{3+} by the intramolecular energy transfer from the triplet state energy of DHBA-TESPI to the resonant emissive energy level of the central Tb^{3+} .

Acknowledgement

This work is supported by the National Natural Science Foundation of China (20671072, 21101107).

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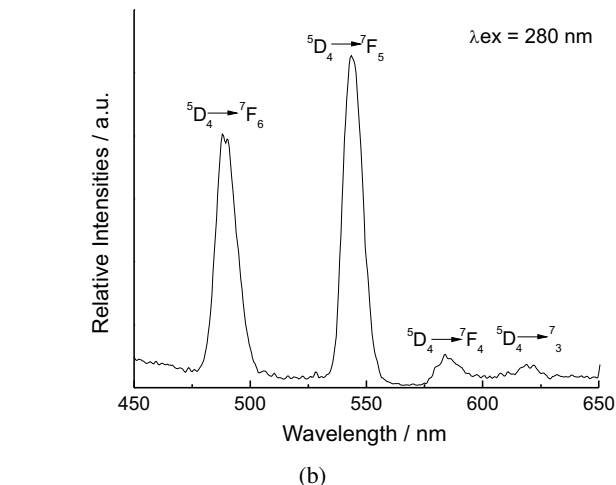


Fig. 5. Excitation (a) and emission (b) spectra of molecular hybrid material (Tb-DHBA-TESPI).

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Received 2011-03-28

Accepted 2012-05-03