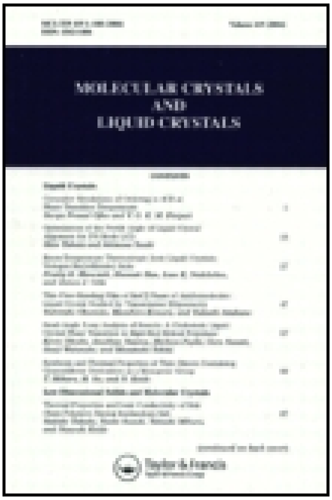

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Facile and Efficient Route to Prepare Luminescent Terbium Containing Covalently Anchored Hybrids Equipped with Molecular Bridge

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Facile and Efficient Route to Prepare Luminescent Terbium Containing Covalently Anchored Hybrids Equipped with Molecular Bridge

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A kind of monomer (abbreviated as BrBAA-APES) was prepared by modifying 2-bromophenylacetic acid (BrBAA) with a coupling agent (3-aminopropyl) triethoxysilane (APES). Then it was used to coordinate to Tb^{3+} and to react with tetraethoxysilane (TEOS) in the presence of water molecules simultaneously. During the reaction, cohydrolysis and cocondensation occurred at the same time as complexation happened to Tb^{3+}, which is called an in situ process. After 5 days, a kind of hybrid material was prepared. The hybrid exhibits the characteristic luminescence of Tb^{3+}, and the change of the hybrid's excitation wavelength also testifies to the energy couple and intramolecular energy transfer between the triplet state energy of BrBBA-APES and emissive level of Tb^{3+}.

Keywords: bridge molecule; double chemical bond; luminescence; molecular hybrids; terbium

INTRODUCTION

Rare-earth complexes are well known for their excellent luminescence properties. Their luminescence properties are widely studied because they can be used as visible, near-infrared radiation sources; lasers; and optical communication devices [1]. However, they also have disadvantages in their mechanical properties and thermal stability. To improve these properties, matrices are always used to form all kinds of hybrid materials. Rare-earth complexes with ß-diketones, aromatic carboxylic acids, and heterocyclic ligands are incorporated into the sol-gel-derived hosts, which can provide a stable environment for central

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particles [2–13]. These studies indicate that the physical properties of rare-earth complexes are improved, and the luminescence intensities of rare earth are similar or superior to the complexes. In this kind of hybrid, only weak physical interactions exist between the matrices and the complexes. Hence, many problems such as clustering of the emitters, inhomogeneous dispersion, and leaching of dopants occur. So, the chemical bonding of rare-earth-based hybrids is necessary. Based on the interaction among the different components or phases in hybrid systems, the hybrid materials can be divided into two major classes [14]. The first is called physically mixed with weak interactions (hydrogen bonding, van der Waals force or weak static effects) between the organic and inorganic phases; the second is named chemical bonded with powerful covalent bonds linking the organic and inorganic parts. The powerful covalent bonds can be helpful to the formation of the single phase [14]. In fact, the latter kind of hybrid belongs to molecular-level materials [15–29], to which is easy to tailor the complementary properties of novel luminescence materials. Sol-gel technology is known as one of the most versatile methods for the preparation of inorganic–organic hybrid materials because of its low processing temperature [30,31]. It allows the incorporation of luminescent species into all kinds of matrices through hydrolysis and polycondensation [32–34].

In our research, we have synthesized several sorts of compounds by modifying amino groups, which can be applied as molecular hybrids and which exhibit excellent luminescence properties [27–29]. Franville and coworkers modified pyridine-dicarboxylic acid and its derivatives [18]. On the ground of investigating the coordination environment of carbonyl groups, aromatic acid containing monocarboxyl group (which can also be utilized as the precursor for molecular hybrids) attracted our interest. Therefore, we attempt to use molecular monomer (BrBAA-APES) and TEOS to form a molecular-based hybrid by the sol-gel process. The monomer is prepared by the acylation between carbonyl groups of BrBAA (2-bromophenylacetic acid) and the amino group of a cross-linking ligand APES ((3-aminopropyl)triethoxysilane).

EXPERIMENTAL

All the agents were used as received. Acids were obtained from Lancester, and APES was obtained from the Nanjing ShuGuang chemistry plant. The procedure for the preparation of BrBAA-APES bridge ligand is shown in Fig. 1. First, 3 mmol of BrBAA was converted to acyl chloride by refluxing in excess $SOCl_2$ under argon at 70°C in an oil

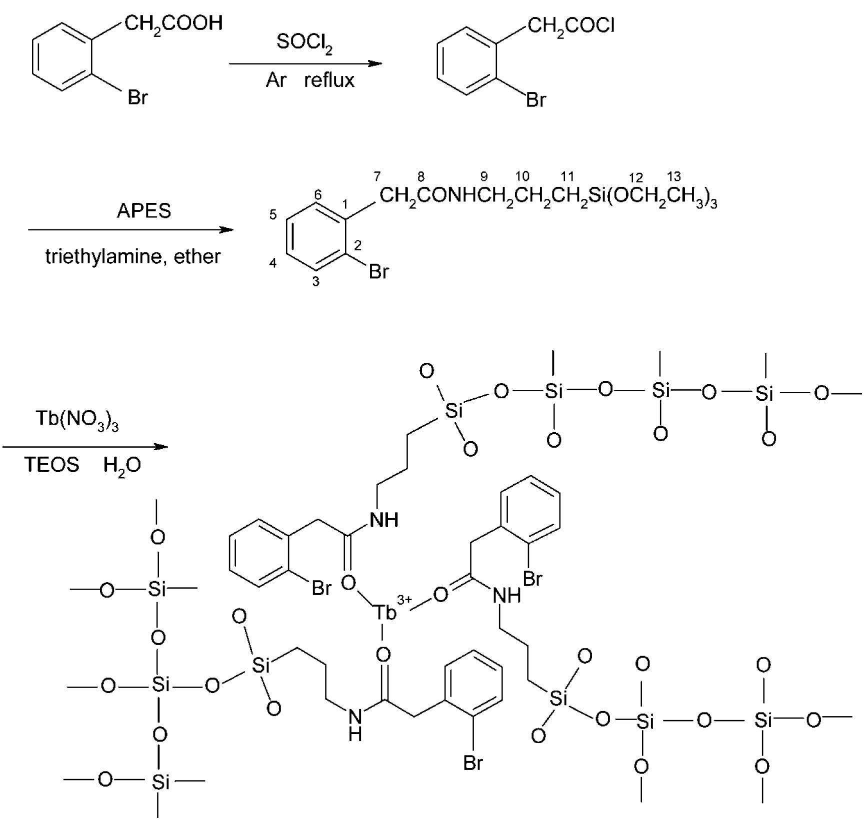

FIGURE 1 Scheme of the synthesis process of BrBAA-APES and predicted structure of hybrid materials.

bath for 4 h. After isolation, the acyl chlorides were directly reacted with APES in ethyl ether in the presence of triethylamine. The main IR peaks and NMR data of BrBAA-APES is shown. $C_{17}H_{28}NO_4SiBr$: IR (KBr): N–H (3267 cm^{-1}) –CONH– (1638 cm^{-1}, 1554 cm^{-1}), C-Si (1194 cm^{-1}). ^1H NMR ($CDCl_3$): δ 7.17(1H,s), 7.29(1H,s), 7.37(1H,s), 7.58(1H,s), 5.62(1H,s), 1.20(9H,t), 3.75(6H,q), 3.50(2H,t), 1.82(2H,q), 2.02(2H,t), 3.72(2H, s). ^{13}C NMR ($CDCl_3$): δ 125.4(C_1), 126.3(C_2), 135.4(C_3), 133.6(C_4), 129.6(C_5), 127.0(C_6), 72.5(C_7), 169.4(C_8), 45.8(C_9), 44.2(C_{10}), 41.9(C_{11}), 46.8(C_{12}), 18.3(C_{13}).

The hybrid material was prepared as follows: BA-APES was dissolved in ethanol, and TEOS (tetraethoxysilane) and H_2O were added while stirring; then one drop of diluted nitric acid was dropped into it to promote hydrolysis. After that, 1 mmol of $Tb(NO_3)_3{\cdot}6H_2O$ was added to the final stirring mixture. The molar ratio of $Tb(NO_3)_3 \cdot 6H_2O$/BrBAA-APES/TEOS/H_2O was 1:3:6:24. After the treatment of hydrolysis, 2 mL of DMF (dimethylformamide) and 1 mmL of hexamethylene-tetramine were added to adjust the pH value to about 6.5. The mixture was stirred to achieve a single phase, and thermal treatment was performed at 60°C until the sample solidified. Figure 1 shows the chemical procedure and the predicted structure of the hybrid material, and Fig. 2 presents the hydrolysis and condensation in the sol-gel process.

All measurements were completed at room temperature except for phosphorescence spectra, which were measured at 77 K. Infrared (IR) spectroscopy was measured on a Nexus 912 AO446 FT-IR spectrophotometer using KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance-500 spectrometer with tetramethylsilane (TMS) as internal reference. UV absorption spectra of these powder samples (about 5×10^{-4} mol·L^{-1} $CHCl_3$ solution) were recorded with an Agilent 8453 spectrophotometer. Phosphorescence spectra (about 5×10^{-4} mol·L^{-1} $CHCl_3$ solution) and fluorescence zexcitation 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).

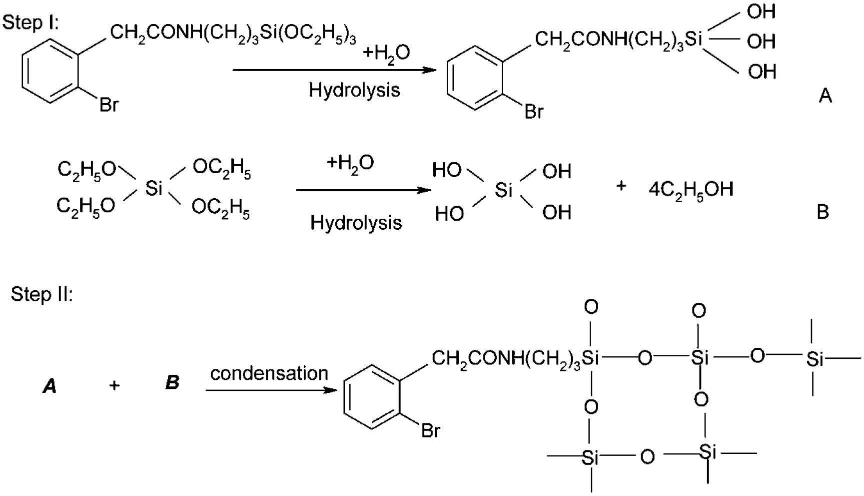

FIGURE 2 Scheme of hydrolysis and polycondensation processes between BrBAA-APES and TEOS.

RESULTS AND DISCUSSION

Figure 3 shows the IR spectra of BrBAA (a) and the final material (b). The occurrence of the amidation reaction was supported by the band located at 1650 cm^{-1}, due to the characteristic absorption of amide groups (–CO–NH–), suggesting that APES has been successfully grafted onto 2-bromophenylacetic acid. Then the presence of the stretching vibration (ν_{NH}, 3387 cm^{-1}) and bending vibration (δ_{NH}, 1548 cm^{-1}) further proved the formation of amide groups. The broad absorption bands locate in 1074 cm^{-1} ($\nu_{\text{Si-O-Si}}$) and 800 cm^{-1} ($\delta_{\text{Si-O-Si}}$) originate from the formation of the siloxane network.

Figure 4 shows the UV absorption spectra of (a) BrBAA, (b) BrBAA-APES, and (c) BrBAA-APES-Tb^{3+}. Comparing the absorption spectrum of BrBAA-APES (b) with that of BrBAA (a), we can see a major absorption peak located in 265 nm disappears after modification, and the peak (241 nm) derived from the major π–π^* electronic transitions of phenyl scarcely change (from 241 nm to 243 nm). So as far as both (b) and (c) are concerned, we still can observe a broad absorption band by a sharp peak due to the introduction of terbium ions, indicating that the coordination behavior functionalizes the carbonyl groups and central metal ions.

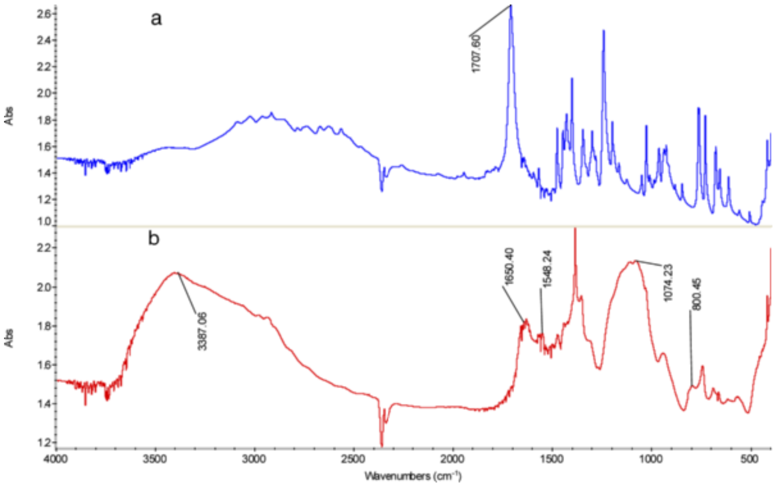

FIGURE 3 IR spectra for BrBAA (a) and hybrids (Tb-BrBAA-APES) (b).

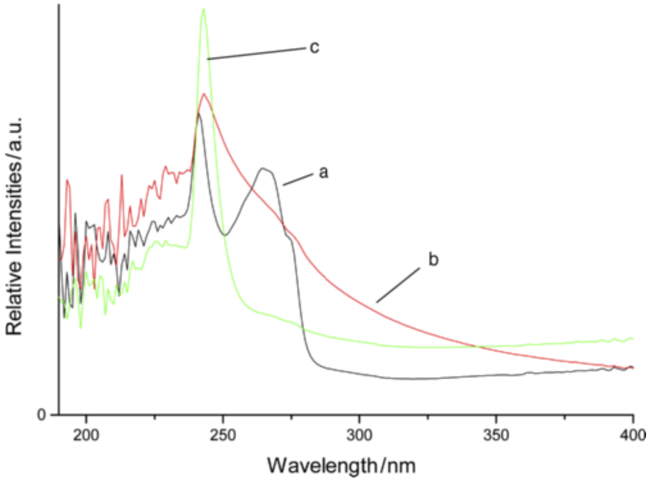

FIGURE 4 Ultraviolet absorption spectra for (a) BrBAA, (b) BrBAA-APES, (c) Tb-BrBAA-APES.

Figure 5 shows the phosphorescence spectra of BrBAA (a) and BrBAA-APES (b). There is an obvious blue shift from 408 nm to 444 nm, which we attribute to the modification of BrBAA.

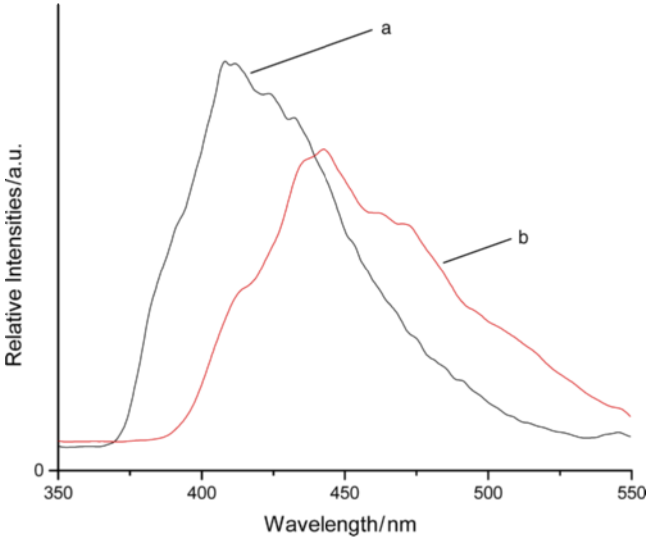

FIGURE 5 Phosphorescence spectra of BrBAA (a) and BrBAA-APES (b).

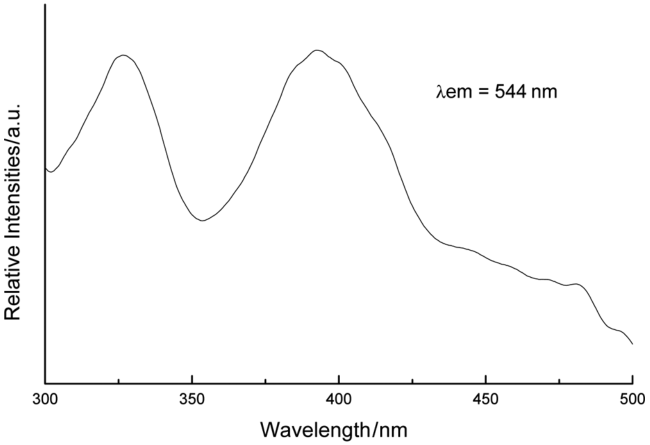

FIGURE 6 Excitation spectrum of hybrids Tb-BrBAA-APES.

Phosphorescence spectrum attributes to the excitation state characteristic of the organic molecular ligands and different phosphorescence bands correspond to different ligand molecules. According to the intramolecular energy transfer mechanism [35,36], the corresponding intramolecular transfer efficiency from the BrBAA-APES to Tb^{3+} mainly depends on the energy match between the triplet state energy of BrBAA-APES (corresponding to the phosphorescence band) and the resonant emissive energy level of the central Tb^{3+}. Therefore, it can be

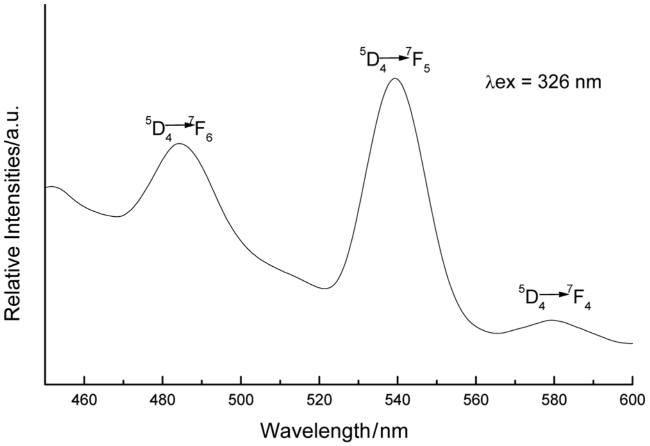

FIGURE 7 Emission spectra of hybrids Tb-BrBAA-APES.

predicted that BrBAA-APES shows an energy match and sensitizes the luminescence of Tb^{3+}.

Figures 6 and 7 show the excitation and emission spectra of the resulting hybrid material. The excitation spectrum monitored at 544 nm is dominated by two broad bands centered at 326 nm and 392 nm. The characteristic excitation spectrum located at about 250 nm arising from the efficient transition based on the aromatic ligand does not appear because there is no conjugation effect between phenyl and acyl. Upon excitation at 326 nm, only the characteristic emission peaks of $Tb^{3+}\,{}^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4, 3$) transitions at 490, 544, and 587 nm (${}^5D_4 \rightarrow {}^7F_3$ is covered by the double frequency of exciting wavelength) are observed, and no emission from the ligand is detected, suggesting energy transfer from the ligand to Tb^{3+}. Upon excitation at 392 nm, no emission is observed. As is shown in Fig. 6, the hybrid finally exhibits characteristic emission under a unique stable chemical environment of rigid molecular network formed by the $-Si-O-Si-$ backbone.

CONCLUSIONS

In conclusion, the modification of 2-bromophenylacetic acid with APES results in the formation of a new hybrid compound, which can act as both the ligand of Tb^{3+} and the sol-gel precursor. The final hybrid shows the characteristic emission of Tb^{3+} by the intramolecular energy transfer from the triplet state energy of BrBAA-APES to the resonant emissive energy level of the central Tb^{3+}. To our knowledge, it is the first example of luminescent molecular-based hybrid material on the basis of the modification of 2-bromophenylacetic acid.

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