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Design of a Novel Sort of Luminescent Terbium(III) Hybrid Materials with Potential Molecular Bridge

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Summary. A kind of precursor molecule (abbreviated as *EPDA–APMS*) was synthesized by means of the amidation reaction of 5-ethylpyridine-2,3-dicarboxylic acid (*EPDA*) with a crosslinking molecule (3-aminopropyl)trimethoxysilane (*APMS*). Then the hybrid materials were obtained by reaction of this kind of monomer (*EPDA–APMS*), tetraethoxysilane (*TEOS*) and $Tb(NO_3)_3 \cdot 6H_2O$ by an *in-situ* sol-gel process, resulting in a novel molecular hybrid material (named as Tb–*EPDA–APMS*) with double chemical bonds (Tb–O coordination bond and Si–O covalent bond). Ultraviolet absorption, phosphorescence, and fluorescence spectra were applied to characterize the photophysical properties of the obtained hybrid material. The strong luminescence of Tb^{3+} substantiates optimum energy match and effective intramolecular energy transfer between the triplet state energy of modified ligand bridge and emissive energy level of Tb^{3+}.

Keywords. Molecular hybrids; Double chemical bond; Bridge molecule; Terbium; Luminescence.

Introduction

The field of inorganic–organic hybrid materials has evolved in recent years as researchers have sought out advanced applications that require materials with characteristics beyond what can be attained with conventional materials [1–3]. Hybrid materials not only combine the beneficial properties of the inorganic and organic components in a single material, but also often exhibit exceptional properties that exceed what would be expected for a simple mixture of the components [4]. The materials discussed can be classified according to several criteria. A classification of hybrids has been previously proposed according to the nature of the organic–inorganic interface, that is, according to the type of chemical interaction between the components [5]: Class I materials would be composed of "embedded" phases, forming hybrids where the interaction between organic and inorganic components

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is limited to weak bonds (ionic, hydrogen bonds, or *van der Waals* interactions), and class II hybrids would be those materials where the organic and inorganic phases are linked together through strong chemical bonds (covalent, ion-covalent, or coordination bonds). The class II belongs to the molecular-based composite materials, which can realize the possibility of tailoring the complementary properties of novel multifunctional advanced materials through the combination of chemical bonding within the different components in a single material [6–8]. Lanthanide complexes within various hosts make attractive materials for optical applications owing to their excellent luminescence characteristics from the electronic transitions between the 4f energy levels. In recent years, some works have been reported on the incorporation of lanthanide into the alkoxysilane modified by organic group to form the inorganic–organic hybrid material, which can modify the mechanic properties of matrix and material effectively and bear excellent luminescence characteristic [9–18].

Here, we present the preparation of novel luminescent molecular-based terbium hybrid materials by using modified 5-ethylpyridine-2,3-dicarboxlic acid (*EPDA*) as organic ligand and utilizing the sol-gel reaction of tetraethoxysilane (*TEOS*) as previously published in our group [11–13]. FT-IR and NMR have been used in order to study the structural properties, the photophysical properties were discussed in detail.

Results and Discussion

From the IR spectra, the bands located at $\bar{\nu} = 1656\,\mathrm{cm}^{-1}$ due to the absorption of amide groups (–CO–NH–) suggested that (3-aminopropyl)triethoxysilane had been successfully grafted on to *EPDA*. Then the presence of the stretching vibration (ν_{NH}, $3395\,\mathrm{cm}^{-1}$) and bending vibration (δ_{NH}, $1569\,\mathrm{cm}^{-1}$) further proved the formation of amide groups. The stretching vibration ($\nu_{\mathrm{Si-C}}$) located at $\bar{\nu} = 1198\,\mathrm{cm}^{-1}$ still existed in the IR spectra of hybrid materials, which was in agreement with the fact that no (Si–C) bond split happened during the course of hydrolysis/polycondensation reactions. What is more, the broad absorption band at $\bar{\nu} = 1018\,\mathrm{cm}^{-1}$ ($\nu_{\mathrm{Si-O-Si}}$) originated from the formation of siloxane bonds. ^{1}H NMR and ^{13}C NMR data farther testified the structure of *EPDA–APMS*.

Figure 1 shows the ultraviolet absorption spectra of (A) *EPDA*, (B) *EPDA–APMS*, (C) Tb–*EPDA–APMS*. From the spectra, we can observe almost the same absorption band for the major $\pi - \pi^{*}$ electronic transitions in A and B (both show the maximum absorption peaks at about 260 nm), suggesting the electron distribution of the modified *EPDA–APMS* has hardly changed compared to the free *EPDA* ligand. Furthermore, an obvious blue shift of 12 nm is observed on Tb–*EPDA–APMS* (from 260 to 248 nm), proving the formation of a complex between Tb^{3+} and *EPDA–APMS*.

Figure 2 shows the low temperature phosphorescence spectra of *EPDA* (A) and *EPDA–APMS* (B) at 77 K. The phosphorescence spectrum explains the characteristic of the organic molecular ligands and different phosphorescence bands correspond to different ligand molecules, so a red shift of 8 nm appears between A (442 nm) and B (450 nm) because of modification of the amino group. According

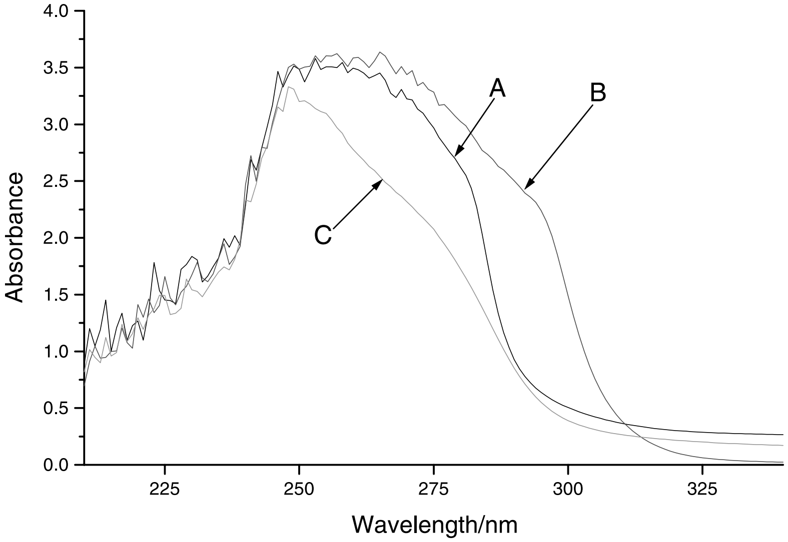


Fig. 1. Ultraviolet absorption spectra for (A) *EPDA*, (B) *EPDA–APMS*, (C) Tb–*EPDA–APMS* hybrids

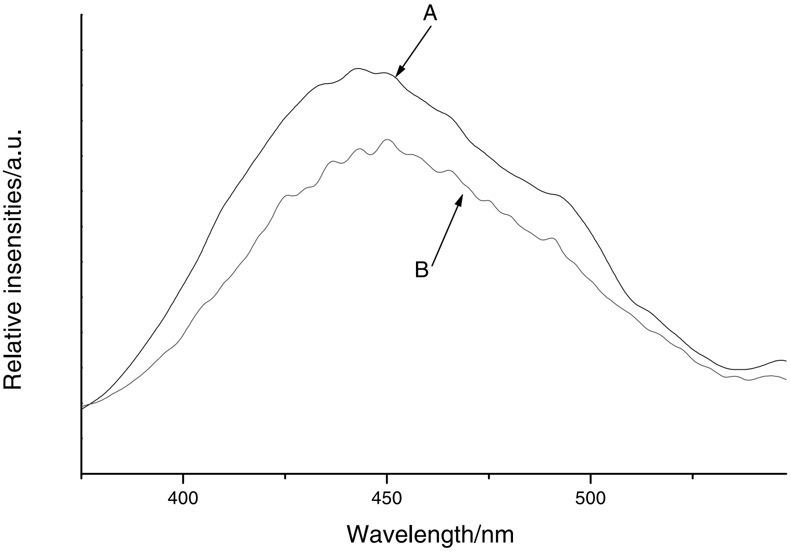


Fig. 2. Phosphorescence spectra of 5-ethylpyridine-2,3-dicarboxylic acid (A) and *PDA*–Si (B)

to intramolecular energy transfer mechanism [19, 20], the corresponding intramolecular transfer efficiency from the *EPDA–APMS* to Tb^{3+} mainly depends on the energy match between the triplet state energy of *EPDA–APMS* (corresponding to the phosphorescence band, $25000\,cm^{-1}$) and the resonant emissive energy level of the central Tb^{3+} ($20500\,cm^{-1}$). Therefore, it can be predicted that *EPDA–APMS* shows a good energy couple and can sensitize the luminescence of Tb^{3+} effectively.

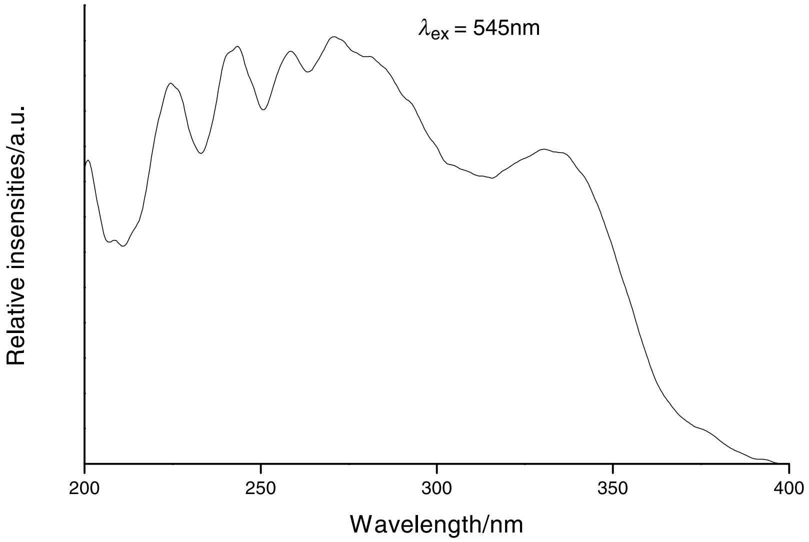


Fig. 3. Excitation spectrum of Tb–*EPDA–APMS* hybrid material ($\lambda_{ex} = 545$ nm)

The excitation spectrum of the molecular hybrids Tb–*EPDA–APMS* is shown in Fig. 3 by monitoring the emission of Tb^{3+} ions at 545 nm, which is dominated by two broad bands from 200 to 400 nm in narrow region and long one, respectively. The broad bands with maximum peaks located at 225, 243.5 nm and 258, 270 nm is the characteristic absorption of the lanthanide complexes arising from the efficient transition based on the conjugated double bonds of the heterocyclic ligand. Both these excitation spectra bands are the effective absorption for the luminescence of Tb^{3+}. As a result, the characteristic green luminescence was observed (hybrid I, see Fig. 4(A)), indicating that the effective energy transfer took place between the aromatic ligand *EPDA–APMS* and the chelated Tb^{3+} ions. The emission lines of hybrid material were assigned to the characteristic $^5D_4 \rightarrow {}^7F_J$

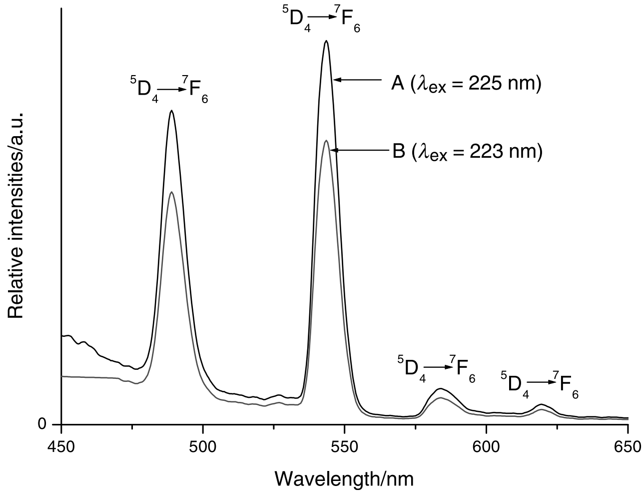


Fig. 4. Emission spectra of Tb–*TBBA–APMS* molecular hybrid materials (A) and doped hybrid materials (B)

Table 1. Luminescent properties of different Tb^{3+} containing hybrid materials

Tb^{3+}-containing hybrids	Emission peaks/nm				Relative intensities/a.u.
Tb^{3+}–*EPDA–APMS* hybrids	489	543.5	584	619.5	645.7
Tb^{3+}–*BIMA–APMS* hybrids	488	543	585	622	325.8
Tb^{3+}–*OTA–APMS* hybrids	488.5	543.5	583.5	621.5	114.9
Tb^{3+}–*TBBA–APMS* hybrids	489	543	585	621	234.5

EPDA = benzimidazole-5-carboxylic acid; *OTA* = *ortho*-tolylacetic acid; *TTBA* = 4-*tert*-butylbenzoic acid

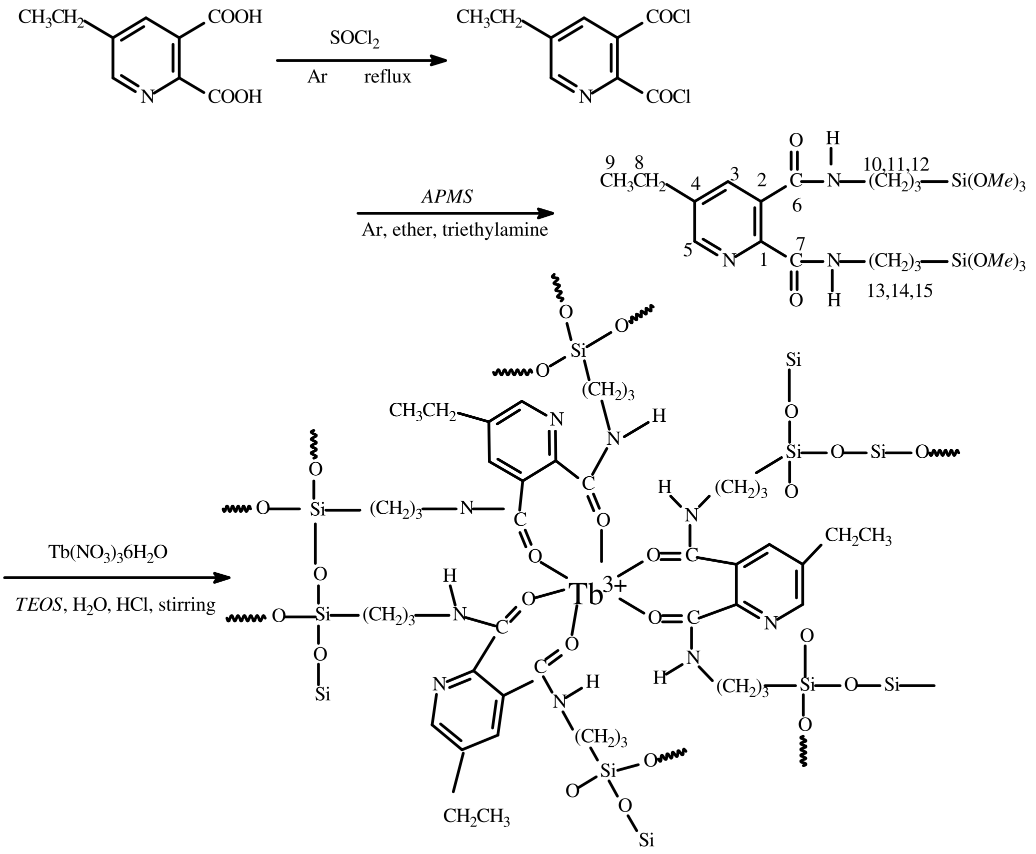
($J = 6, 5, 4, 3$) transitions of Tb^{3+} at 488.5, 543, 583, and 619 nm, respectively. We also measured the luminescent spectrum of doped hybrids (hybrid II: Tb–*EPDA* doped in *APMS*/*TEOS* matrix, as shown in Fig. 4(B)). It was also found that their comparative luminescent intensities belong to nearly the same order and stronger emissions of hybrid I compared to hybrid II which was prepared by the simple doping method were thought to be due to chemical covalent bond between the complexes and the silica. Other factors still can not be excluded such as relatively rigid structure of silica gel which limits the vibration of ligand of Tb^{3+} and prohibits non-radiative transitions. Therefore, we may expect that through this efficient way, leaching of the photoactive molecules can be avoided, higher concentration of metal ions is reached, and clustering of the emitting centers may be prevented. Furthermore, we compared the luminescent properties of Tb–*EPDA–APMS* hybrids with the other molecular hybrids with different aromatic carboxylic acid derivative bridge ligand (as shown in Table 1). The luminescent intensity for Tb–*EPDA–APMS* hybrids is the strongest, which suggests that optimum energy transfer between the *EPDA–APMS* bridge ligands and Tb^{3+} exists (the study on other three molecular hybrids are underway and will be reported in detail in aftertime).

In summary, we have modified 5-ethylpyridine-2,3-dicarboxylic acid to achieve a functional bridge molecule with a crosslinking molecule (3-aminopropyl)trimethoxysilane. Since the hydrolysis and polycondensation reactions between the triethoxysilyl-port of *EPDA–APMS* and TEOS lead to the formation of Si–O–Si network structures for the same alkoxy groups of them, a novel luminescent molecular-based hybrid material with double chemical bond was firstly constructed using *EPDA–APMS* coordinated to Tb^{3+}. This technology can be expected to be used for the assembly of other luminescent molecular-based hybrid materials.

Experimental

5-Ethylpyridine-2,3-dicarboxylic acid was supplied by Lancaster Synthesis Ltd., (3-aminopropyl)trimethoxysilane (abbreviated as *APMS*) was purchased from Shanghai YaoHua chemical plant. Other starting reagents were used as received.

EPDA was first converted to acyl chloride by refluxing in excess $SOCl_2$ under argon at 70°C for 4 hours. After isolation, the acyl chlorides were directly reacted with *APMS* in diethyl ether in presence of triethylamine. Detailed process conditions were according to the literature procedure. A typical procedure for the preparation of Tb–*EPDA–APMS* was as outlined in Scheme 1.



Scheme 1

EPDA–APMS: $C_{21}H_{39}O_8N_3Si_2$: IR (KBr): $\bar{\nu} = 1656, 1569$ (CONH), 1198 (C–Si), 3395 (ν_{NH}) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 8.96$ (s, 1H), 8.48 (s, 2H), 8.21 (d, 2H), 7.46 (s, 1H), 4.78 (s, 5H), 4.22 (m, 5H), 3.43 (s, 4H), 3.18 (s, 2H), 2.78 (m, 4H), 2.03 (s, 2H), 1.26 (s, 9H), 0.89 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 166.4$ (C_7), 149.1 (C_6), 144.0 (C_1), 142.1 (C_5), 139.1 (C_2) 131.4 (C_4), 123.1 (C_3), 77.3–77.2 (C_{10}–C_{13}), 45.6 (C_8), 42.33–40.0 (C_{11}–C_{14}), 29.6 ($CH_3(OMe)$), 22.6 (C_9),14.6–14.1(C_{12}–C_{15}).

A sol-gel derived hybrid material was prepared as follows: *EPDA–APMS* was dissolved in ethanol, and *TEOS* (tetraethoxysilane) and H_2O were added while stirring, then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. A stoichiometric amount of $Tb(NO_3)_3 \cdot 6H_2O$ was added to the final stirring mixture. The mol ratio of $Tb(NO_3)_3 \cdot 6H_2O$/*EPDA–APMS*/*TEOS*/H_2O was 1:3:6:24. After hydrolysis, 2 cm^3 *DMF* (dimethylformamide) and on appropriate amount of hexamethylenetetramine 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°C until the sample solidified (see Scheme 1). The other terbium containing hybrid material with different bridge molecules (Tb^{3+}–*BIMA–APMS*, Tb^{3+}–*OTA–APMS*, Tb^{3+}–*TBBA–APMS*) (*EPDA* = benzimidazole-5-carboxylic acid; *OTA* = *ortho* tolylacetic acid; *TTBA* = 4-*tert*-butylbenzoic acid) were obtained by a similar reaction process. Major results will be reported elsewhere.

All measurements were completed under room temperature except for phosphorescence spectra that were measured at 77 K. Infrared spectra 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 were recorded in $CDCl_3$ on a Bruker AVANCE-500 spectrometer with tetramethylsilane (*TMS*) as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} $mol \cdot dm^{-3}$ dimethylsulfoxide

(*DMSO*) solution) were recorded with an Agilent 8453 spectrophotometer. Phosphorescence spectra (5×10^{-4} mol · dm^{-3} $CHCl_3$ solution) and fluorescence excitation and emission spectra were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

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