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Fabrication and photoluminescence of molecular hybrid films based on the complexes of 8-hydroxyquinoline with different metal ions via sol–gel process

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Abstract

A kind of monomer (abbreviated as HQ-TESPI) was prepared by modifying 8-hydroxyquinoline (abbreviated as HQ) with 3-(triethoxysilyl)-propyl isocyanate (abbreviated as TESPI) through the hydrogen transfer nucleophilic addition in this study. Then the monomer was used to coordinate with the metal ions (Al^{3+}, Zn^{2+}, Eu^{3+}, Tb^{3+}) according to the complexation theory. On the other hand, the monomer was simultaneously used to occur hydrolysis and condensation together with tetraethoxysilane (abbreviated as TEOS) to form silica-based organic–inorganic hybrid thin films (abbreviated as Al-HQ-TESPI, Zn-HQ-TESPI, Eu-HQ-TESPI and Tb-HQ-TESPI, respectively) by the means of spin-coating technology. The resultant thin films showed characteristic photoluminescence originated from the modified 8-hydroxyquinolinates. The target materials exhibit strong green-colored fluorescence (Al-HQ-TESPI), cyan-colored fluorescence (Zn-HQ-TESPI) and olivine-colored fluorescence (Eu-HQ-TESPI, Tb-HQ-TESPI). These hybrid thin films can be prospected to be used in the field of photoluminescence.

Keywords: Molecular hybrid films; Photoluminescence; 8-Hydroxyquinoline

1. Introduction

Since the first report of organic light-emitting diodes (OLEDs) fabricated from tris(8-hydroxyquinolinolate)-aluminum(III) (AlQ_3) in 1987 [1], organic metal chelate have attracted much attention due to their high thermal stability, adequate electron transport, and luminescent properties [2]. AlQ_3 is a stable metal chelate complex that can be sublimed to yield amorphous thin films and stands as the most widely used electron-transport host or emitting material for OLEDs [3,4]. However, metaloquinolates have some fatal deficiencies in practice. OLEDs are heterojunction devices, and layers made of small-molecule organic-transport materials are usually amorphous and thin solid films prepared through vacuum deposition. However, at times isomerizations or oligomerizations occur upon high-temperature sublimation [5]. Furthermore, crystallization takes place at the function time and results in a decrease in the work time. A convenient low-cost manufacturing method is solution processing, such as spin-coating and possibly inkjet printing [6], with a mixture of 8-hydroxyquinoline metal chelates and polymers [7,8]. However, in many cases phase separation occurs in these systems and leads to poor optical properties [7].

Recently hybrid materials are attractive because they can easily combine the superior properties of the organic and inorganic compounds. The hybrid matrix may be organic polymer matrix [9] or inorganic network. Covalently bonding the functional 8-hydroxyquinoline metal chelates in inorganic matrix to form the hybrid material can improve the thermal stability and transparency of the chelates. Based on the interaction among the different components or phases in hybrid systems, these hybrid materials can be divided into two major classes [10]. The first 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 second is named chemical bonded with powerful covalent bonds linking the organic and inorganic parts [11–17]. The powerful covalent bonds can be helpful to the forming of the single phase [10]. And among the ways of preparing hybrid materials sol–gel method is widely used because of the facility to produce adher-

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ent and crack-free silica materials. We have successfully realized two paths to construct rare earth hybrid materials with chemical bonds. One is to modify the amino groups of aminobenzoic acids using 3-(triethoxysilyl)-propyl isocyanate (abbreviated as TESPI) through hydrogen transfer addition reaction between the amino group of acids and internal ester group (isocyanate) of TESPI, further assembling the above modified bridge ligands with rare earth ions and inorganic precursors (TEOS) to hybrid systems [18,19]. The other path is to modify the carboxylate group of aromatic carboxylic acids through the amidation reaction between the carbonyl groups of acids and the amino group of amino-silane cross-linking reagents, then composing hybrid materials with covalent bonds [20–22]. Moreover, according to the molecular fragment principle to assembly of ternary rare earth complexes, we also achieved the cooperative design of rare earth hybrid materials with cross-linking reagent as structural ligand and photoactive sensitizer as functional ligand [23]. On the basis of the above research, we can modify the two typical cross-linking regents with different groups (TESPI and 3-aminopropyl-methyl-diethoxylsiliane etc.) together through the hydrogen transfer addition reaction to form di-urea linkages between isocyanate and the amino groups, and then design ternary hybrid materials with chemical bonding [24]. In view of these researches, it can be recognized that the key procedure

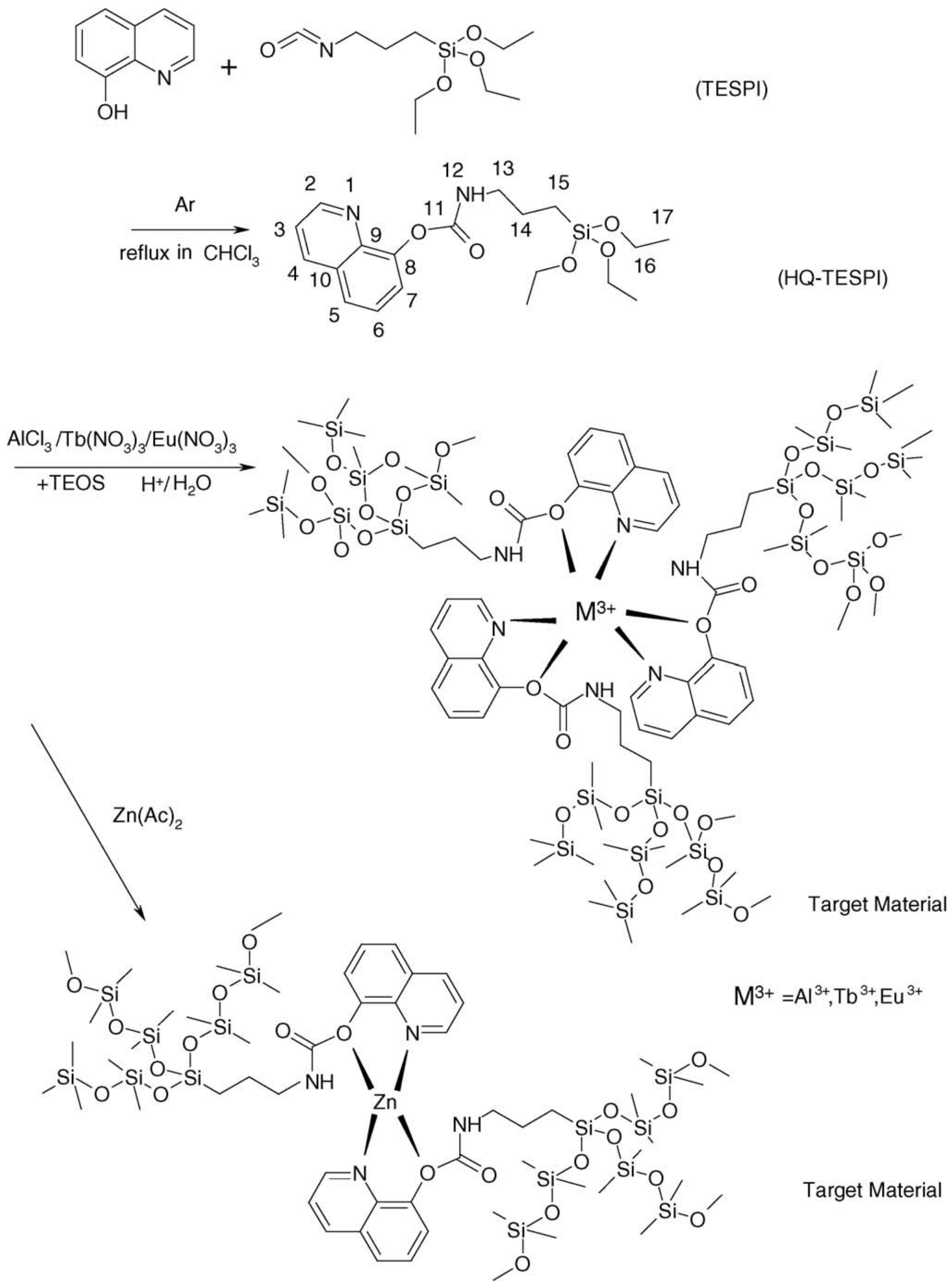

Fig. 1. Scheme of the synthesis process of HQ-TESPI and predicted structure of hybrid materials.

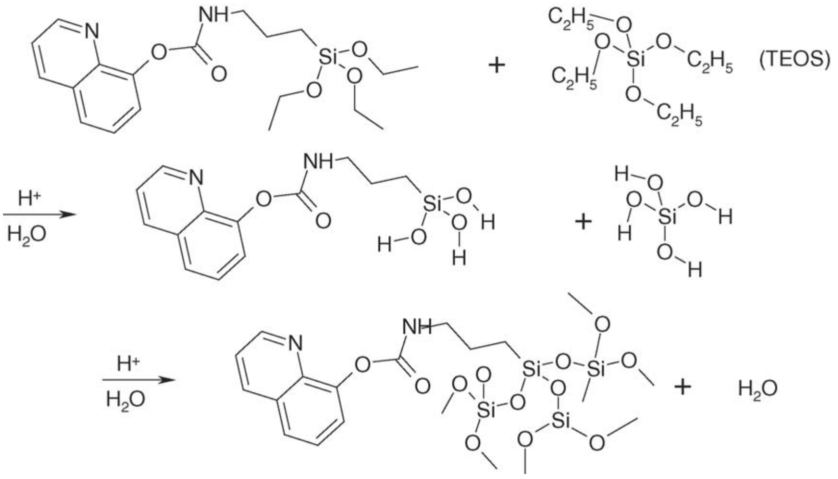

Fig. 2. Scheme of the hydrolysis-condensation reactions in the sol–gel process.

to construct molecular-based materials is to design functional bridge molecule (ligand) by the grafting reaction, which can behave double functions of coordinating to rare earth ions and sol–gel processing to constitute covalent Si–O network [18–31].

By modifying the 8-hydroxyquinoline to be double chemical bonded molecular, it can be used as precursor to prepare double chemical bonded hybrids. As beginning from solution process the hybrid is easy to prepare films by spin-coating. The final hybrid films have obviously improvement in thermal stability and transparency. In this work, we developed the 8-hydroxyquinoline metal chelates to hybrid materials in search of improvements in their physical properties and photoluminescence properties. In addition, some other ways to synthesize relative luminescent materials may be found.

2. Experimental

All the agents are used as received. 3-(Triethoxysilyl)-propyl isocyanate was got from Tokyo Chemical Industry (TCI). 8-Hydroxyquinoline was got from Lancaster and TEOS was got from Nanjing ShuGuang chemistry plant. The procedure for the preparation of HQ-TESPI bridge ligand was according to reaction scheme in Fig. 1. HQ was directly reacted with TESPI under argon at 70 °C in an oil-bathing for 8 h with $CHCl_3$ as solvent. The result production was used as a bridging precursor to prepare the hybrid films. UV, IR, ^{1}H NMR and ^{13}C NMR were used to inspect the reaction.

The hybrid films were prepared as follows: HQ-TESPI was dissolved in ethanol, and TEOS, H_2O were added while stirring, then one drop of diluted nitric acid was dropped into it to promote hydrolysis. A stoichiometric amount of $AlCl_3$, $Zn(Ac)_2$, $Tb(NO_3)_3 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ were added to the final stirring mixture respectively. The mole ratio of M^{3+}/HQ-TESPI/TEOS/H_2O and Zn^{2+}/HQ-TESPI/TEOS/H_2O were 1:3:6:24 and 1:2:4:16. After the treatment of hydrolysis, 2 ml dimethylformamide (DMF) and appropriate amount of hexamethylene–tetramine were added to adjust the pH value of about 6.5. The mixtures were stirred to achieve a single phase and thermal treatment was performed at 60 °C. Then the condensed sol was coated on the quartz substrate by a spin-coating process. The substrate is placed on a spin-coating machine (KW-4A) and spun at between 1000 and 3000 rpm. The chemical procedure and the sol–gel process are shown in Fig. 2. In addition, relative 8-hydroxyquinoline metal chelates (AlQ_3, ZnQ_2, TbQ_3 and EuQ_3) are also synthesized according to the references [25–29].

All measurements were completed under room temperature except for phosphorescence spectra which were measured on 77 K. IR spectra were measured on a Nexus 912 AO446 FT-IR spectrophotometer using KBr pellets. ^{1}H 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 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 excitation and emission spectra were obtained on a Perkin–Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm. The main NMR data of HQ-TESPI is shown as below. $C_{19}H_{28}O_5N_2Si$: ^{1}H NMR ($CDCl_3$): δ 8.81(1H, H_2), 8.45(1H, H_4), 7.44(1H, H_6), 7.35(1H, H_3), 7.35(1H, H_5), 7.15(1H, H_7), 5.82(1H, H_{12}), 3.75(6H, H_{16}), 3.50(2H, H_{13}), 2.02(2H, H_{14}), 1.86(2H, H_{15}), 1.22(9H, H_{17}) ^{13}C NMR ($CDCl_3$): δ 159.3(C_{11}), 152.4(C_8) 146.6(C_2), 139.3(C_9) 136.3(C_4), 128.9(C_{10}), 126.6(C_6), 122.3(C_3), 118.3(C_5), 109.3(C_7), 50.8(C_{13}), 50.4(C_{14}), 44.2(C_{15}), 43.5(C_{16}), 18.2(C_{17}).

3. Results and discussions

Fig. 1 shows the chemical procedure and the structure of the hybrid material. As lanthanide always has high coordination number (8 or 9), there are number of water molecules or nitrate ions coordinating to the Ln^{3+} which were omitted in the structure of Eu-HQ-TESPI and Tb-HQ-TESPI. The structure of the hybrid was predicted on the basis of the experimental results and the complex structure deriving from 8-hydroxyquinoline was also considered. 3-(Triethoxysilyl)-propyl isocyanate belongs to a special silane crosslinking reagent molecule for it's internal ester

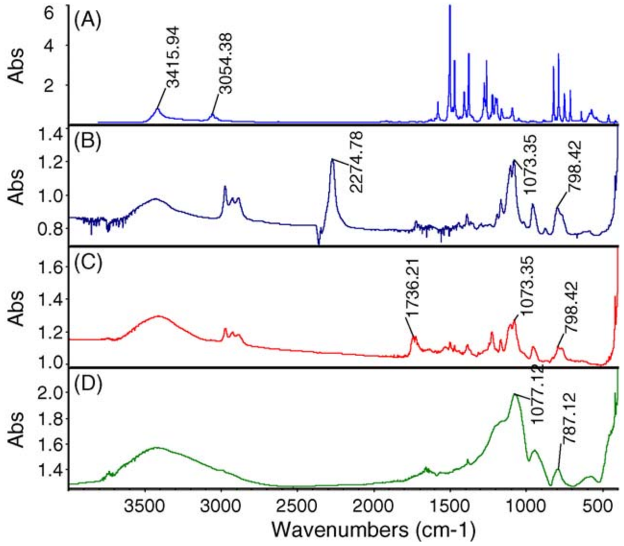

Fig. 3. FT-IR spectra for (A) HQ; (B) TESPI; (C) HQ-TESPI; (D) hybrid films (Al-HQ-TESPI).

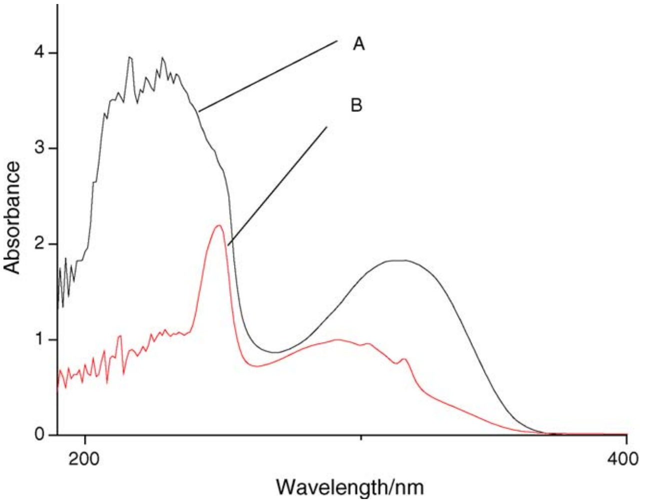

Fig. 4. Ultraviolet absorption spectra for (A) HQ; (B) HQ-TESPI.

group of isocyanate, which can be expected to realize hydrogen transfer reaction with some active molecules with reactive hydrogen atoms. We have achieved the hydrogen transfer addition reaction between TESPI and $-NH_2$ derivatives [18,19,25]. Hydroxyl group also belongs to be active group for its hydrogen atoms readily to lose, and so it can be predicted that there may exist the hydrogen transfer addition reaction from –OH to isocyanate of TESPI. As shown in Fig. 1, HQ can be modified by TESPI to form the amide (mono-urea, –CO–NH–) linkage functional bridge molecules HQ-TESPI. The bridge ligands (HQ-TESPI) then play two roles: one is that they can coordinate to terbium ions through the oxygen atoms of their amide group; the other is that they can occur the cohydolysis and copolycondensation process with TEOS with their ethoxy groups belonging to the TESPI component through sol–gel reaction (similar to the copolymerization of organic monomer with unsaturated bonds). Fig. 2 shows the cohydrolysis and copolycondensation between the HQ-TESPI and TEOS. Finally the molecular-based hybrid materials can be assembled with strong chemical bonds (the coordination bond between metal ions and the amide bond of bridge ligand and the covalent bond of Si–O network). These hybrid materials pertain to molecular degree, which can be considered as the complicated huge molecular network.

Fig. 3 shows the IR spectra of HQ, TESPI, HQ-TESPI and the hybrid film Al-HQ-TESPI (the IR spectra of the hybrids are almost the same). The addition reaction is testified by the formation of the –COO– group which is located at 1736 cm^{-1} and the character stretching vibration of the –N=C=O group located 2274 cm^{-1} disappears after the reaction. The introduction of 3-(triethoxysilyl)-propyl isocyanate is testified by the broad bands located at 1073 cm^{-1} ($\nu_{Si–O–Si}$) and 798 cm^{-1} ($\delta_{Si–O–Si}$) in graph (C). The stretching vibration of the aromatic framework is invisible covered by the rigid Si–O–Si network in the final hybrids. The introduction of silica network is proved by bands located at 1077 cm^{-1} ($\nu_{Si–O–Si}$) and 787 cm^{-1} ($\delta_{Si–O–Si}$) in graph (D). Peaks located at 3416 cm^{-1} attributed to $\nu_{O–H}$ in the hybrid film.

Fig. 4 shows the UV absorption spectra of (A) HQ and (B) HQ-TESPI. From (A) to (B) there is an obvious change of the peak located at around 250 nm. The monomer showed strong absorption from 240 nm to 255 nm. The change attributes to the modifying the organic ligand. The strong absorption of the monomer may result in the fluorescence excitation at this area which is helpful for the photoluminescence of the complex system. Fig. 5 shows the phosphorescence spectra of HQ (A) and HQ-TESPI (B). Compared to the phosphorescent emission of (A) HQ, the modified HQ (B) shows a red-shift. So it can be predicted that the energy level of HQ-TESPI's triplet states is lower than that HQ. As we known, phosphorescence spectrum attributes to the excitation state characteristic of the organic molecular ligands and different phosphorescence bands correspond to different triplet states. So the change of phosphorescence emission also provides some proof for the modification of HQ.

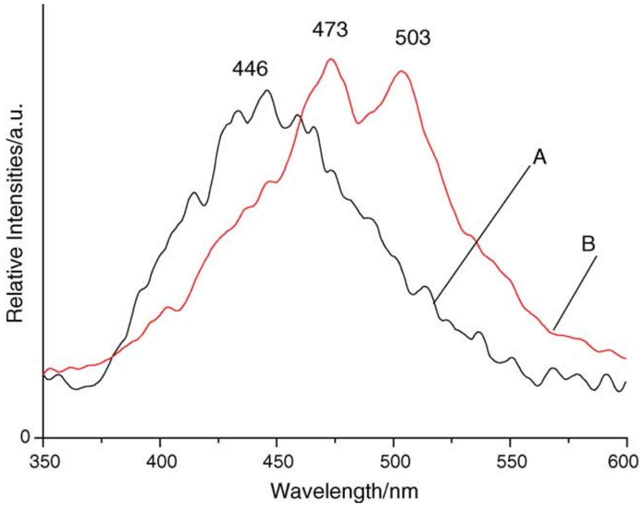

Fig. 5. Phosphorescence spectra of HQ (A); HQ-TESPI (B).

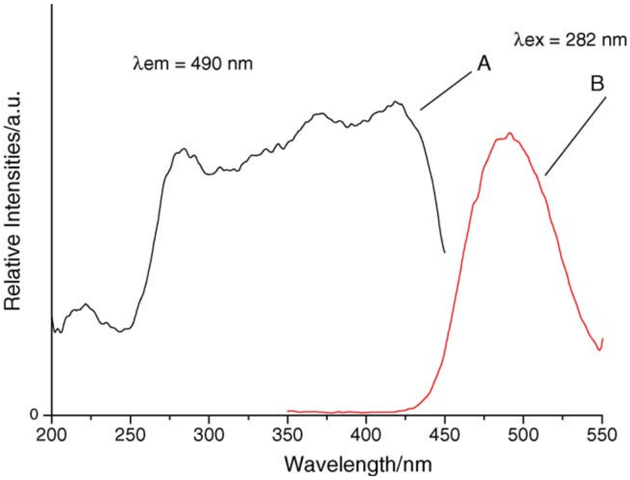

Fig. 6. Excitation and emission spectra of the hybrid film (Al-HQ-TESPI).

Fig. 6 shows the excitation and emission spectra of the hybrid film (Al-HQ-TESPI). The emission spectra excited at 282 nm shows characteristic emission of AlQ_3 located at 490 nm which is slightly different from the reported 520 nm. The excitation spectra derived from the π–π* absorption of the aromatic conjugated system. The wavenumber of the emission spectrum stands for the energy difference of 8-hydroxyquinolinate's HOMO-LUMO. For complexes, planeness is important for electron distribution and different structures also influence the luminescence of the organic phosphors. Graph C and graph D in Fig. 7 are the excitation and emission spectra of hybrids (Zn-HQ-TESPI). Graph A and graph B are excitation and emission spectra of the complex (ZnQ_2). Compared with the complex the hybrids also exhibit emission peaks at 495 nm excited at 280 nm. The excitation spectra are slightly different which are derived from different bands of 8-hydroxyquinolate's π–π* absorption.

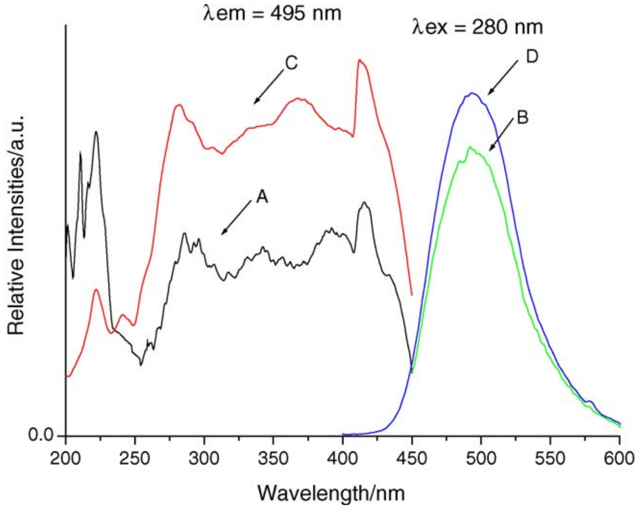

Fig. 7. Excitation and emission spectra of hybrid film (Zn-HQ-TESPI) and the complex (ZnQ_3).

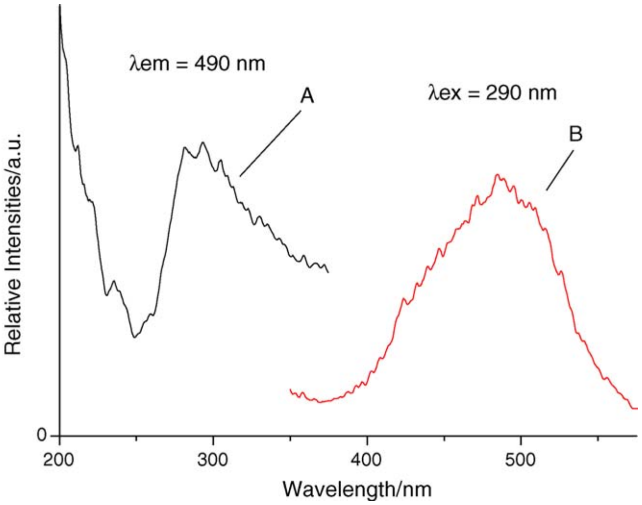

Fig. 8. Excitation and emission spectra of hybrid film (Eu-HQ-TESPI).

As we all known, the triplet state energy of HQ is too low to realize effective intramolecular energy transfer between HQ and rare earth ions [30,31]. Here the modified bridge molecule HQ-TESPI also presents the similar feature. Fig. 8 shows the excitation and emission spectra of hybrid film (Eu-HQ-TESPI). In the spectra character fluorescence of Eu^{3+} is not found. The emission spectra located at about 490 nm is also the photoluminescence of the 8-hydroxyquinolinate slightly interfered by central Eu^{3+} which means that there's no intramolecular energy transfer from ligands to lanthanides in the complex system and the photoluminescence of the 8-hydroxyquinolinate is just slightly disturbed by the central metal ions. Graph C and graph D in Fig. 9 are the excitation and emission spectra of hybrids (Tb-HQ-TESPI). The main emission spectrum located at 460 nm excited at 300 nm. From C to D the excitation spectrum of hybrid film is obviously strengthened (excitation peak located at 300 nm). Graph A and graph B are excitation and emission spectra of the complex (TbQ_3). The main emission spectrum located at 420 nm excited at 240 nm. And excited at different wavelength bring in different emission. The energy between the HOMO-LUMO is influenced by several factors (exchange of electrons between ligands and metal ions, planeness of the complex, polarity of the environment) and the multiplicity of energy level leads to the slight change of emission wavelength excited

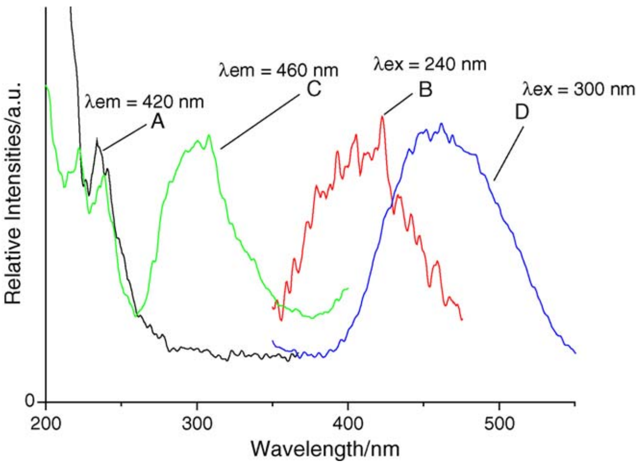

Fig. 9. Excitation and emission spectra of hybrid film (Tb-HQ-TESPI) and the complex (TbQ_3).

at different wavenumbers. There is no character fluorescence of Tb^{3+} which means that energy level doesn't match between the triplet state energy of HQ-TESPI (corresponded to the phosphorescence band) and the resonant emissive energy level of the central Tb^{3+}. Since the excitation spectrum of the hybrid film is obviously strengthened, improvement of the luminescence property is expected. The environment of rigid molecular network formed by −Si–O–Si– backbone is also helpful for the strengthen emission of the spectra.

4. Conclusions

In conclusion, we synthesized a kind of monomer by modifying 8-hydroxyquinoline that can act both as the ligands to the metal ions and precursor to form silica network by sol–gel process. Then spin-coating process was used to form hybrid films with excellent photoluminescence properties. Based on the metal chelates of 8-hydroxyquinoline, many electroluminescent and photoluminescent materials can be prepared for the use of lighting and displays.

Acknowledgement

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