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ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 191 (2007) 216–221
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

A novel way to prepare luminescent hybrid materials derived from 5-chloromehtyl-8-hydroxyquinoline and silylated monomer with coordination to aluminum ion

Qunbo Mei [a,b], Bihai Tong [c], Liyan Liang [a], Mangeng Lu [a,*]

[a] *Guangdong Key Laboratory of Polymer Materials for Electronics, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650 , PR China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China*
[c] *Sun Yat-sen University, School of Physics and Engineering, Guangzhou 510275 , PR China*

Received 6 December 2006; received in revised form 19 April 2007; accepted 30 April 2007
Available online 3 May 2007

Abstract

In this article, a new method to synthesize novel metaloquinolate-contained electroluminescent hybrid materials is reported. The small molecule metal complex monomer was obtained from the reaction of 3-piperazinepropylmethyldimethoxysilane and 5-chloromethyl-8-quinolinol hydrochloride. Then the silylated metaloquinolate-contained monomer was complexed with aluminum ion and further introduced into silica matrices by Si–O bonds and formed hybrid materials after hydrolysis and polycondensation processes. FT–IR, UV, NMR, SEM, TGA, luminescence spectra and luminescence quantum yields were used to characterize the obtained hybrid materials. It was found from the scanning electron micrographs (SEM) results that no phase separation occurred in 8-hydroxyquinoline aluminum complexes-silicone hybrid materials. The target materials were thermally stable until 380 °C and exhibited high quantum yield (43%). Such materials should combine the fluorescent properties of metalloquinolate and good mechanical properties, stability, and processability of organosilicone to improve device efficiencies and work lifetimes, and should be of interest for OLED applications.

Keywords: Siloxane; Tri(8-hydoxyquinolinato)aluminum (AlQ_3); Organic light-emitting diodes (OLED); Hybrid materials

1. Introduction

Tris(8-hydroxyquinolinato) aluminum (AlQ_3) is a milestone for the development of organic light-emitting diodes (OLEDs), which was used as the electron-transport and emitting material in the first efficient small molecule OLED in 1987 [1]. Since then, metaloquinolates have become a very important class of electroluminescent materials in OLED for their many excellent properties such as thermal stability, high fluorescence and excellent electron-transporting mobility [2,3]. However, metaloquinolates have some fatal deficiencies in practice such as crystallization, high-cost and poor processability [4,5]. Grafting of 8-hydroxyqinoline ligands on to the compounds that can be polymerized or cross-linked may solve the above problems. Two kinds of soluble polymers, containing 8-hydroxyquinoline aluminum complex of which metaloquinolate can be attached to the polymer backbone by covalent bond, have been reported by researchers recently [6,7]. Amy Meyers's synthetic method was based on a fully functionalized monomer, which was polymerized in a controlled fashion by ring-opening metathesis polymerization (ROMP), eliminating the cross-linking [8–10]. But the productive rate, solubility of the copolymer, and AlQ_3 contents in the copolymer are limited. Up to now, chemically bonded hybrids in which powerful covalent bonds link the organic and inorganic parts have been paid much more attention [11–13]. Organic–inorganic hybrid materials, in which organic parts are dispersed in inorganic matrix at a nanometer or molecular level, have attracted tremendous attention and been widely investigated because of unique properties of the materials resulted from nanocomposite such as high gas-barrier property, excellent solvent resistance, flame resistance, and high transparency.

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[*] Corresponding author. Tel.: +86 20 85231089; fax: +86 20 85231119.
E-mail address: mglu@gic.ac.cn (M. Lu).

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doi:10.1016/j.jphotochem.2007.04.026

More recently, we had designed and synthesized a series of novel metaloquinolate-contained homopolymers and copolymers [14–18]. This is the first report of the synthesis of metaloquinolate-contained polymers by free-radical copolymerization, which can be induced by UV light or heating polymerization. The cross-linking nature, selectivity of patterning, high thermal stability, and EL efficiency might render these polymers a promising material in fabricating large-scaled multilayered sub-pixellation organic light-emitting diodes.

This present work is focused on the hybrid system in which 8-hydroxyquinoline metal complexes is covalently linked to a silicone matrix through Si–O linkages. The monomer PQSi (as given in Fig. 1) was prepared by grafting 5-chloromethyl-8-quinolinol hydrochloride (CMQ) to 3-piperazinepropylmethyldimethoxysilane (PPS). Then it coordinated with triethylaluminum to form AlQ_3-containing monomer (APQSi). The hybridization of TEOS and APQSi, accordingly, was achieved by polycondensation reaction between the silanol terminated metal complexes and tetraethoxysilane (TEOS) [13]. Through the above treatments, the molecular-based hybrids can exhibit the strong luminescence of AlQ_3 moieties.

2. Experimental part

2.1. Chemicals and procedures

3-Piperazinepropylmethyldimethoxysilane was purchased from Yantai YuSheng Chemical Co., Ltd and purified by vacuum distillation. Triethylaluminum solution in hexane (1 M) was purchased from Tokyo Kasei Kogyo Co Ltd. Diethyl-zinc solution in hexane (1 M) was purchased from Fluka. Other solvents and chemicals were used as received, such as 8-hydroxyquinoline, formaldehyde and hydrochloric acid. Tetrahydrofuran (THF), dimethylformamide (DMF), triethylamine, and petroleum ether

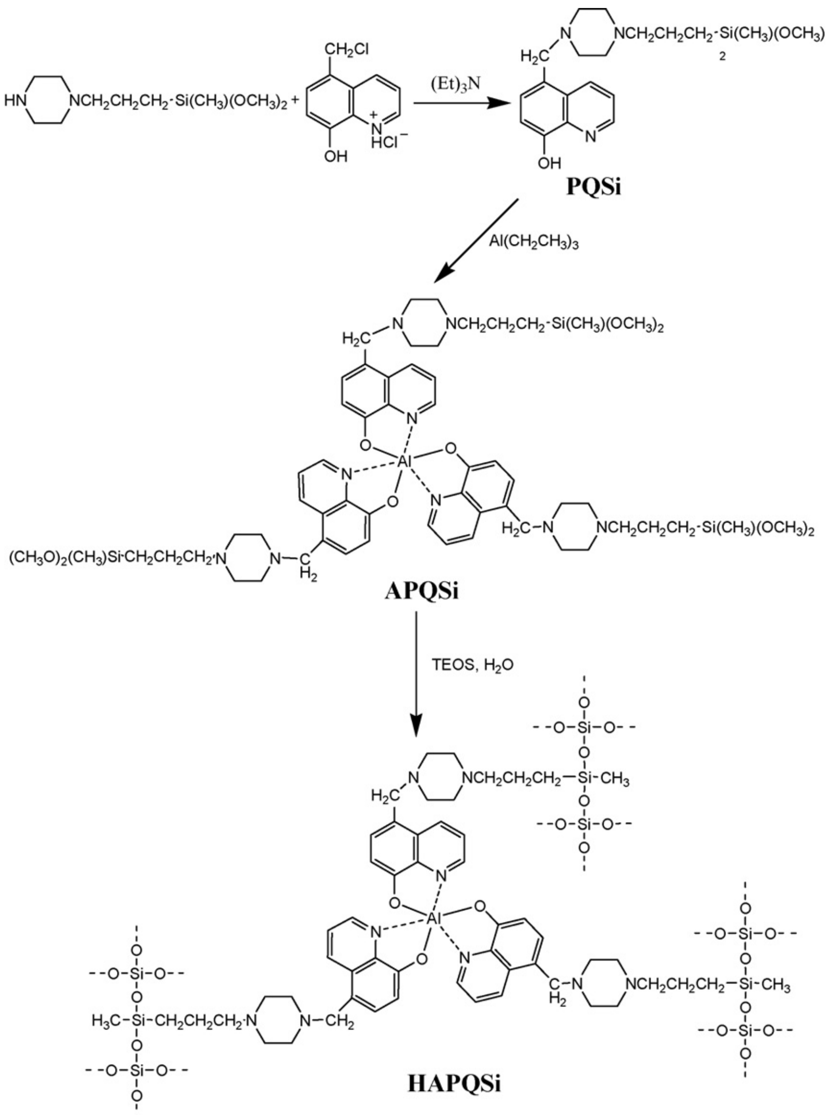

Fig. 1. Scheme of the synthesis process of PQSi, APQSi and predicted structure of hybrid materials.

were dried, and distilled with sodium before use. CMQ was synthesized according to reference [19].

The reaction model for the hybridization formula of tetraethoxysilane and APQSi was illustrated in Fig. 1. A typical procedure for the preparation of new monomer PQSi and its complex APQSi was as follows: 5-chloromethyl-8-quinolinol hydrochloride was obtained in a very high yield (94%) according to a well-known method [19] with slight modification. After isolation, the hydrochlorate was directly reacted with PPS (the molar ratio of CMQ/PPS was 1:1.2) in anhydrous THF in the presence of triethylamine [20]. 3-Piperazinepropylmethyldimethoxysilane (PPS) 2.7840 g (12 mmol) and triethylamine 2.9 mL (20 mmol) were dissolved in 30 mL of anhydrous THF with stirring. The solution was stirred at room temperature for 0.5 h, then 2.3 g (10 mmol) CMQ was added. The suspension resulting was kept stirred in a covered flask under room temperature for approximately 10 h. The precipitated triethylamine hydrochloride was filtered and a clear THF solution of PQSi was obtained. $C_{20}H_{31}N_3O_3Si$: MS (EI) m/e = 390.0 (M^+), IR (KBr, cm^{-1}): 3300 (–OH), 2956 ($-CH_3$) 1613, 1581 (C–C and pyridine ring), 1506, 1475 (aromatic), 1384, 1319 (C–N), 1200(C–Si), ^{1}H NMR ($CDCl_3$): 8.68–7.41 (5H, Ph–H), 4.26 (2H, s, $-CH_2-Ph$), 3.45 (4H, s, $-OCH_3$), 2.67–2.07 (10H, t, $-CH_2-N$), 1.68 ($C-CH_2-C$), 0.75 (2H, $-CH_2-$Si), 0.54 (3H, $Si-CH_3$).

Ttriethylaluminum in hexane solution (3.33 mL, 3.33 mmol) was added via syringe to the above filtrate under nitrogen. After stirring at room temperature for 24 h, the reaction mixture was filtered through centrifugal separation to remove any precipitate. Then the filtrate was added dropwise to petroleum ether (200 mL). The precipitate of APQSi was filtered off and washed by hot petroleum ether, then dried at 40 °C in vacuum.

Sol–gel derived hybrid material containing 8-hydroxyquinoline aluminum complex was prepared as follows: The small molecule metal complex monomer APQSi was dissolved in DMF, and TEOS, H_2O were added while stirring, and then one drop of diluted hydrochloric acid was added to promote hydrolysis. The mole ratio of APQSi/TEOS/H_2O was 2:3:30. After hydrolysis, 2 mL of DMF and an appropriate amount of hexamethylene–tetramine was added to adjust the pH value to 6–7, and then filtered through a 0.45 mm filter. The resulted mixture was agitated magnetically to achieve a single-phase system, which can be used to obtain the solidifed thin film sample by spin-coating.

2.2. Characterization

^{1}H-NMR spectra were recorded on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer. The FT–IR spectra were carried out using an RFX-65A (Analects) Fourier Transform Infrared Spectrometer. Thermal analyses were performed on TA differential scanning calorimetry (DSC) 2910 and NETZSCH thermogravimetric analysis (TGA) TG 209 C Iris at a heating rate of 10 °C min^{-1} under nitrogen purge of 50 mL min^{-1}. Thin films of the hybrid materials were prepared by spin coating from a 5–10 wt% solution [silylated metal complex monomer in THF] onto quartz substrates, which were coated with Indium tin oxide (ITO), cleaned and treated with oxygen plasma (Plasma-Preen-862). All glassware was thoroughly cleaned by rinsing with acetone and then distilled water and isopropyl alcohol and was dried at 100 °C for 60 min. All sample processing was carried out in a dry-nitrogen-filled glove box to avoid oxygen and water contamination. Optical absorbance measurements were made with a Shimadz 2550 ultraviolet–visible (UV–vis) spectrophotometer. Photoluminescence (PL) measurements of the solutions were conducted with a Fluorolog-3 fluorescence spectrometer at 350 nm with a spectral range of 200–700 nm and a resolution of 2 nm. The PL spectra of the films were recorded with an Oriel Intaspeciv CCD spectrograph with a fiber probe. The PL quantum yields were tested similarly to Greenham's way in an integrating sphere (IS-80, LabSphere Co.) under an excitation of 325 nm. Scanning electron microscope (SEM) images were obtained with a JEOL JSM-6330F.

3. Results and discussion

From FT–IR measurements for PPS (A), PQSi (B), APQSi (C), and HAPQSi (D) as shown in Fig. 2, the occurrence of N-hydrocarbylation reaction was supported by the disappearance of the characteristic absorption of stretching vibration (–N–H) in 3-piperazinepropylmethyldimethoxysilane located at 3385 cm^{-1} and bending vibration at 1580 cm^{-1}. In addition, the appearance of the bands located at 1634 cm^{-1}, 1578 cm^{-1} of 8-hydroxyquinoline, suggested that CMQ has been successfully grafted onto PPS (Fig. 2, A, B). It can be found that the strong peak at 3322 cm^{-1} from O–H stretching vibration and 1234 cm^{-1} from O–H deformation vibration of 8-hydroxyquinoline were markedly weakened due to the coordination of oxygen atom in phenolic hydroxyl groups, with metal ion (Al^{3+}), and the stretching vibration peak located at 1632 cm^{-1} was red shifted to 1604 cm^{-1} nearby due to the reduction of electron cloud and force constant (Fig. 2, B, C). The hydrolysis/polycondensation reactions were homogeneras since no (Si–C) bond split occurred. Furthermore, from Fig. 2 C and D, the disappearance of the characteristic absorption of stretching vibration ($Si-OCH_3$) located at 2824 cm^{-1}(ν_{C-H}),

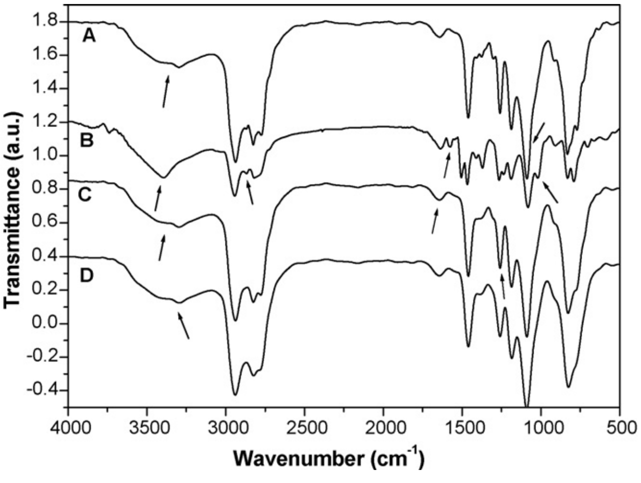

Fig. 2. FT–IR spectra for PPS (A), PQSi (B), APQSi (C), and HAPQSi (D).

Table 1
Properties of APQSi and HAPQSi

Sample	UV–vis λ_{max} (nm)		PL λ_{max} (nm)		TGA (°C)
	Solution	Film	Solution	Film	
APQSi	396	393	523	516	–
HAPQSi150	–	398	–	520	372
HAPQSi180	–	398	–	521	380

ASN150: the film of AlQ_3-containing hybrid materials was heated to 150 °C and kept 1.5 h; ASN180: the film of AlQ_3-containing hybrid materials was heated to 180 °C and kept for 3 h.

1084 cm^{-1}($\nu_{C\text{–}O}$) must be the results of hydrolysis and polycondensation reaction. The absorption band at 1105 cm^{-1} and 1087 cm^{-1} ($\nu_{Si\text{–}O\text{–}Si}$) and the bending vibration at 458 cm^{-1}, indicated the formation of Si–O–Si bonds.

Table 1 and Fig. 3 showed that the optical properties of new metaloquinolate-containing electroluminescent hybrid materials were not hindered by the polymer coils. We investigated UV–vis and PL of metaloquinolate-pendant monomers and hybrid materials and compared them with relevant metaloquinolates. For PPS (A), PQSi (B), APQSi (C), and HAPQSi (D), the absorption peak at 249 nm, π–π^* electron transition from quinoline, was red-shifted and the n–π^* transition at 324 nm was disappeared or weakened because the oxygen atom in phenolic hydroxyl group and *N* atom of 8-hroxyquinoline coordinated with aluminum ion. It was crucial evidence that the coordination bond was formed between 8-hydroxyquinoline ligands and Al ions. A new transition between aluminum metal ion with the ligand appeared in the UV spectra of coordination compounds. The new peak was found at 392 nm. The absorption spectra of hybrid materials showed the same peak positions as those in the literature [21,22], and this indicated the same ligand-centered electronic transitions.

Fig. 4 showed the PL spectra of APQSi (A), HAPQSi150 (B) and HAPQSi180 (C). The PL emission peak of AlQ_3-containing hybrid materials located at about 510 nm. The results were consistent with the data of metaloquinolate in literature [8], showing that the emission properties of the metaloquinolates were retained. Also, the PL emission spectra as given in Fig. 3 showed that APQSi and HAPQSi had the same band at about 510 nm, and is same as that in AlQ_3, which showed that the hydrolysis and polycondensation processes had not hindered the optical properties of functional moieties.

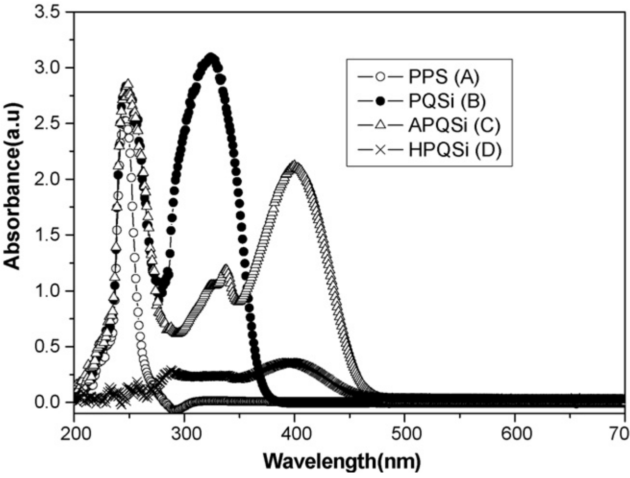

Fig. 3. Absorption spectra for PPS (A), PQSi (B), APQSi (C), and HAPQSi (D).

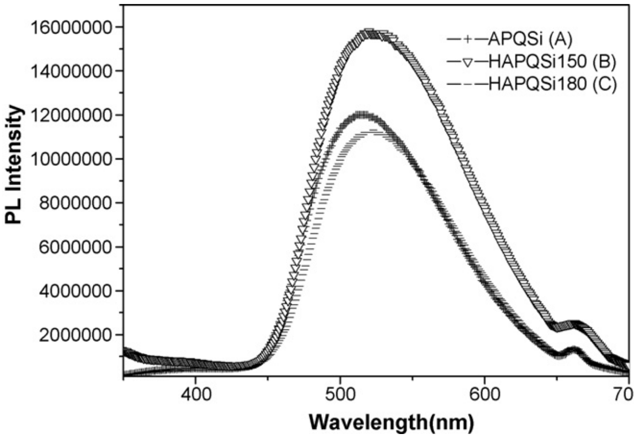

Fig. 4. PL spectra (λ_{ex} = 350 nm) for APQSi (A), HAPQSi150 (B) and HAPQSi180 (C).
Notes: HAPQSi150 is the film of AlQ_3-containing hybrid material that has been heated to 150 °C and kept for 1.5 h, HAPQSi180 is the film of AlQ_3-containing hybrid material that has been heated to 180 °C and kept for 3 h.

The PL quantum efficiency is defined as the number of photons emitted in PL per absorbed photon. In this paper, the PL quantum efficiency of AlQ_3-containing hybrid materials was measured using an integrating sphere. The measurement technique was similar to those reported on previously by Greeham [23]. The PL quantum efficiency, neglecting the spectral variation of the system response, is given by

$$x = \frac{X_{\text{sample}} - (R + T)X_{\text{sphere}}}{(1 - R - T)X_{\text{light}}} \tag{1}$$

Where T is the transmittance, R is the reflectance, and X_{light} is the signal measured with the laser incident on the sphere with no sample or filter. X_{sample} and X_{sphere} are the signals measured with the sample and filter in place, with the laser incident on the sample and the sphere wall, respectively. The results of measurement are summarized in Table 2.

As a reference to aluminum, the reflection of aluminum is regarded as 100%, $R_{Al}(w)$ is the signals measured with the aluminum flake, and $R_{\text{sample}}(mw)$ is the signals measured with the sample. So the reflectance is obtained by

$$R = \frac{R_{\text{sample}}}{1000 * R_{Al}} \tag{2}$$

The correction factor for the spectral response is given by

$$y = \int \frac{S_{\text{sphere}}(\lambda)L(\lambda)G(\lambda)F(\lambda)}{S_{\text{lamp}}(\lambda)} d\lambda \times \left(\frac{S_{\text{sphere}}(\lambda_{\text{ex}})G(\lambda_{\text{ex}})}{S_{\text{lamp}}(\lambda_{\text{ex}})} \int L(\lambda) d\lambda \right)^{-1} \tag{3}$$

Where $S_{\text{lamp}}(\lambda)$ is the spectrum of the tungsten lamp, $S_{\text{sphere}}(\lambda)$ is the spectral response of the sphere, $L(\lambda)$ is the emission spectrum

Table 2
The photoluminescence efficiency (PL) of AlQ_3-containing hybrid materials

Materials	$\lambda_{\mathrm{ex\ (nm)}}$	$X_{\mathrm{light(uw)}}$	$\lambda_{\mathrm{Sample\ (nm)}}$	$X_{\mathrm{sample(uw)}}$	$X_{\mathrm{sphere(uw)}}$	$R_{\mathrm{Al(w)}}$	$R_{\mathrm{sample(mw)}}$	T	K	x	y	PL (%)
ASN	325	142.5	523	62.3	18.3	0.14	20.5	0.587	15.7	1.29	9.75	13.22
ASN(150C/1.5 h)	325	142.5	523	143.5	18.3	0.14	18.7	0.34	15.7	1.80	9.75	18.47
ASN(180C/3 h)	325	142.5	524	117.4	18.3	0.14	19.6	0.69	15.7	4.21	9.74	43.19

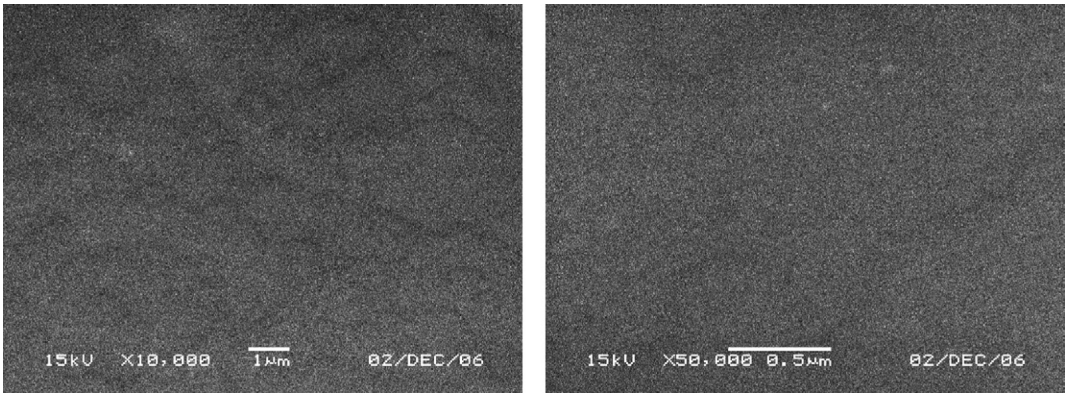

Fig. 5. SEM graphs of covalently bonded hybrid materials.

of sample, $G(\lambda)$ is the quantum efficiency of the detector, $F(\lambda)$ is the transmission of the filter, λ_{ex} is the excitation wavelength.

After integration, the correction factor for the spectral response is simplified,

$$y = \frac{K\lambda_{\mathrm{ex}}}{\lambda_{\mathrm{sample}}} \tag{4}$$

where K is the apparatus correction factor, the PL efficiency is then simply given by

$$PL\% = \frac{x}{y} \times 100\% \tag{5}$$

Table 2 showed that the photoluminescence efficiency of new AlQ_3-containing hybrid materials. It was found that the PL efficiency of 43.19% of the AlQ_3-containing hybrid materials (at 180 °C for 3 h) is higher than the cross-linked polymers containing tris(8-hydroxyquinoline) aluminium (about 20.42%) [18]. If the film was heated to 150 °C and kept for 1.5 h only, its PL efficiency was low. It may be attributed to its special structure. As known, siloxane can be hydrolyzed to form Si–OH group. But just small amount of Si–OH groups in silanol terminated metal complexes and hydrolyzed TEOS were condensed at a relatively low temperature and a short time (e.g.: 150 °C for 1.5 h). Heated to 180 °C and kept for 3 h, almost all Si–OH groups polycondensed to form a network structure. It has also been reported that the photoluminescence efficiency of porous silicon was improved greatly [24,25]. Silicon luminescence was not easy, but when it was reduced to nanosize, silicon was luminescent. This porous silicon was silicon quantum wire network structure, and it can restrict the generation of electron. That is to say, it appears “quantum confinement” effect. The quantum confinement effect enhanced the possibility of no-phonon quasi-direct optical transitions. Moreover, the three-dimensional network was composed of the low silicon dioxide and organic oligomer unit. It can protect them from the impaction of outside moist air. As a consequence, the nonradiative transition was excluded due to the high-energy vibrations of hydroxyl group.

The thermal stability of the metaloquinolate-containing electroluminescent hybrid material was examined with the thermogravimetric analysis measurements and estimated with the degradation temperature (Td, temperature at 5% weight loss). The developed metaloquinolate-containing electroluminescent hybrid material exhibited excellent thermal stability. The initial degradation temperatures was 380 °C, which was higher than the linear or cross-linked AlQ_3-containing polymers because of the existence of the Si–O–Si network structure in the hybrid material [14,18].

The scanning electron micrographs for the AlQ_3-containing hybrid materials demonstrated that a homogeneous, hybrid material was obtained. From the Fig. 5, phase separation was not observed since there existed strong covalent bonds between the inorganic and organic phases. Hence, it was anticipated that this homogeneous and porous hybrid material, with strong covalent bonds, would attract interest for its utilization in optical or electronic applications.

4. Conclusions

To sum up, this work has brought about a discovery that the electroluminescent monomers attached to the silane compound are capable of forming networks by polycondensation with TEOS. A novel thermally stable metaloquinolate AlQ_3-containing hybrid material was synthesized successfully by complexation with aluminum ion. The SEM demonstrated that it was homogeneous. TGA curve indicated that it was thermally stable until 380 °C. The method is suitable for the most of 8-hydroxyquinoline metal chelates. Furthermore, the current synthesis method can be easily applied to other ligands and to different modified alkoxysilanes. This technology can be expected to other luminescent hybrid materials. A further investigation into applications for the metaloquinolate-contained hybrid materials is currently under way.

Acknowledgements

This project was supported by the CAS "Century Program".

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