

# Preparation and Characterization of Lithium-8-Hydroxyquinolate-Containing Quaternary Ammonium Copolymers and Their Electrostatic Layer-by-Layer Self-Assembly

Dengbin Yu, Chuanzhi Zhang, Xu Wang, Chunxia Jiang, Ting Xiong, Wenqing Meng, Chen Liu, Deben Chen, Anyong Zhong

Faculty of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

Received 21 September 2007; accepted 30 April 2008

DOI 10.1002/app.28624

Published online 13 June 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The lithium-8-hydroxyquinolate functionalized polycation copolymers with quaternary ammonium-type linkage have been prepared by reaction of 5-chloromethyl-8-quinolinol hydrochloride (CHQ) with the copolymer (CPA) of methacrylic ester and 2-(dimethylamino)ethyl methacrylate (DM), followed by metalation with lithium. Two kinds of copolymers with each containing 9.69 and 16.29 wt % of the DM content (CPA<sub>1</sub> and CPA<sub>2</sub>) were involved in the study. The structures of these polymers were characterized by Fourier transform infrared techniques and gel permeation chromatography. The multilayer films were prepared by alternate electrostatic layer-by-layer self-assembly (ESA) of CPA with polyanion electrolyte. The UV-vis and fluorescence spectra of the films

showed a red shift compared to those in tetrahydrofuran solutions. The intensity in UV-vis increased and that of fluorescence decreased linearly with the number of film layers. Atom force microscope (AFM) results of the multilayer films demonstrated presence of compact films on the surface after chelating metal ions. The experimental results indicated that these kinds of materials have applied potential in organic light-emitting diodes (OLEDs). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 124–133, 2008

**Key words:** electrostatic self-assembly; 8-hydroxyquinoline; luminescence materials; the copolymerization of methacrylic ester; quaternary ammonium polymer; polyelectrolyte

## INTRODUCTION

Supramolecular chemistry as a highly interdisciplinary field is advancing so rapidly that it actually penetrates into every corner of research involving intermolecular noncovalent interactions since the Nobel laureate J.M. Lehn first expounded the conception.<sup>1,2</sup> Along this line is the development of supramolecular studies on macrocyclic chemistry, molecular assembly, molecular diode, and new function material. In polymer science, polyelectrolytes are excellent models for studies on supramolecular assembly. The most recent of the self-organization techniques is the alternating physiosorption of oppositely charged polyelectrolytes, the so-called layer-by-layer method or “electrostatic self-assembly” (ESA).<sup>3,4</sup> However, a practical method for ESA was not developed until the early 1990s by the group of Decher<sup>5,6</sup> although the self-assembly by alternating adsorption of oppositely charged polyions was

observed 22 years ago.<sup>7</sup> This technique has been intensely attractive in terms of its simplicity and controllability compared to other means.<sup>8,9</sup> It provides a way to control the construction of ultrathin films (e.g., thickness and composition) at nanoscale, and a long-term stability of the film can be obtained easily. Besides, this technique could be applied to many systems, not only polyelectrolytes, but also inorganic nanoparticles,<sup>10</sup> dyes,<sup>11,12</sup> and biological macromolecules such as DNA<sup>13</sup> and proteins.<sup>14</sup> ESA technique have already become an advanced and popular subject in chemistry research field.<sup>15–17</sup>

The design of next-generation organic light-emitting diodes (OLEDs) is focused on polymers containing electroluminescent functionality with efficient charge-transport capability. Because the first efficient OLED based on aluminum quinolate (AlQ<sub>3</sub>)<sup>18</sup> was reported by Tang and Van Slyke, these types of metal-chelating materials have been extensively studied especially in its application in conductible and luminous devices and delinear optical materials. Among them, the complex of 8-hydroxyquinoline and aluminum (AlQ<sub>3</sub>) stood out in serving as electron transporting emitting materials together with outstanding thermal stability and high luminescence efficiency. This kind of diode basically settles

Correspondence to: A. Zhong (zhongany@sina.com.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50573050.

the problem that there are the higher driving voltage, lower EL efficiencies, and badly brightness in OLEDs.

However, metaloquinolates experienced some drawbacks in that isomerizations or oligomerizations occur upon high temperature sublimation,<sup>19</sup> because the layers made of small molecular organic transport materials are usually amorphous thin solid films, which are prepared by using vacuum deposition method. At the same time, crystallizations may take place at the function time resulting in the decrease of work time. It is desirable to find materials that displayed both the excellent fluorescent properties of 8-hydroxyquinoline metal chelates and the processing properties of polymers. One of the resolution to these problems by utilizing a mixture of 8-hydroxyquinoline metal chelates and polymers<sup>20</sup> failed due to the limited solubility of the 8-hydroxyquinoline metal chelates and phase separation, leading to the poor optical properties and short work-time.<sup>21</sup> Researchers have recently reported two kinds of soluble metaloquinolate-containing copolymers. Lu et al. prepared a polymer fully functionalized with AIQ<sub>3</sub> in a postpolymerization step,<sup>22</sup> and Meyers and Weck's synthetic method was based on a fully functionalized monomer, which was polymerized in a controlled fashion and eliminated the crosslinking.<sup>23</sup> However, the solubility of these polymers was still not good enough. Herein, we report the lithium-8-hydroxyquinolate functionalized polycation copolymers whose solubility is better due to the presence of the hydroxy in the copolymer chains. To our knowledge, 8-hydroxyquinoline as side chains to a polymer with covalent bond in literature<sup>24,25</sup>; however, there is no report on quaternary ammonium polymers with positive charge.

LiQ is an efficient blue emitter, which has strong PL at 470nm that has also been examined as an interface material in combination with AIQ<sub>3</sub> and ZnQ<sub>2</sub> to lower the driving voltage.<sup>26-28</sup> 8-Hydroxyquinoline lithium-containing copolymers (CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li) were successfully synthesized by the 8-hydroxyquinoline-containing polymer chelated with metal ion Li<sup>+</sup>. The quaternary ammonium PDM was used as the cation first adsorption layer to obtain flexible substrate. The sulfonated fluoropolymer (Nafion 117) was used as the anion hole electron transport, 8-hydroxyquinoline lithium-containing copolymers were used as cation luminescent layers, and then the multilayer thin films were obtained by ESA. The relationship between side luminescent groups and photoelectricity and UV-vis properties of thin polymer films were investigated, which made a foundation of polymer thin luminescent device of preparation and mensurating its properties and also discovering and developing of overthin display.

## EXPERIMENTAL

### Materials

Reagent-grade acrylic resin monomers including *n*-butyl acrylate (BA), styrene (St), 2-hydroxypropyl acrylate (HPA), methyl methacrylate (MMA), and 2-(dimethylamino)ethyl methacrylate (DM) were purchased from Beijing Chemical Co. (Beijing, China). Nafion 117 solution was obtained from Fluka, Buchs, Switzerland. PDM was prepared by reaction of BA with DM. Other chemicals and solvents were used as received unless stated otherwise, including initiator 2,2'-azobis-isobutyronitrile (AIBN, Shanghai No.4 Reagent and H. V. Chemical Co.), Na<sub>2</sub>CO<sub>3</sub> (Tianjin Chemical Reagents Factory) ethanol, dilute ammonia solution (25%), isopropyl alcohol (IPA, Chengdu Changlian Chemical and Technology Reagents Co.), 8-hydroxyquinoline, anhydrous tetrahydrofuran (THF), sulfuric acid, hydrogen peroxide (30%) (Chengdu Kelong Chemical and Technology Reagents Co.), and LiOH · H<sub>2</sub>O (Sichuan Nike Guorun New Materials Co.). THF was refluxed with cuprous chloride for 1 h and distilled before use.

### Characterization

The melting point of the 5-chloromethyl-8-quinolinol hydrochloride (CHQ) was recorded on XRC-2 microscope melting point apparatus (The Sichuan University Excercitation Plant). The Fourier transform infrared (FTIR) spectra were carried out with a Nicolet 1700SX spectrometer (all samples grounded in KBr). The UV-vis absorption measurements were performed on a TU-1901 UV spectrometer (Beijing Puxi Universal Devices Co.). Differential scanning calorimetry (DSC) was performed under nitrogen using a PerkinElmer 200PC at a heating rate of 10°C/min. The number-average molecular weights ( $\bar{M}_n$ ), the weight-average molecular weights ( $\bar{M}_w$ ), and distribution of the polymers were measured by gel permeation chromatography (GPC, Agilent 1100 chromatograph) at 35°C. THF was used as the eluent at a flow rate of 1.0 mL/min and standard polystyrene as the reference. Film samples were prepared on a quartz glass. Photoluminescence (PL) spectra of the polymer multilayer films were recorded on a Hitachi 850 fluorescence spectrophotometer. The surface structures on the films were observed by atomic force microscope (AFM, Scanning Probe Microscope System Series SPA-400, Japan Spiritus and Work Company, with DFM Model).

### Synthesis

The following is the synthetic route to the LiQ-containing copolymers:

Synthesis of 5-chloromethyl-8-hydroxyquinolinol hydrochloride (I) and 5-chloromethyl-8-hydroxyquinolinol (II, CHQ)

5-Chloromethyl-8-hydroxyquinolinol hydrochloride (I) was synthesized according to the literature<sup>29</sup> in a yield of 87.0%.

5-Chloromethyl-8-hydroxyquinolinol (II, CHQ) was synthesized by dropping  $\text{NH}_3 \cdot \text{H}_2\text{O}$  into I till pH of the mixture solution approached 7. The precipitate was washed with acetone three or four times, collected by filtration, and dried at 40°C *in vacuo* for 12 h to afford 15.94 g (87.0% yield) of a brown solid.

Synthesis of the copolymerization of methacrylic esters (III, CPA<sub>1</sub> and CPA<sub>2</sub>)

The copolymers of methacrylic esters (CPA<sub>1</sub> and CPA<sub>2</sub>) were synthesized according to the literature<sup>30</sup>: MMA (25 mL), St (13 mL), BA (38 mL), HPA (18 mL), DM (10 mL), IPA (70 mL), and AIBN (1.8 g) were mixed. The solvent IPA was heated to reflux, and the mixture of monomers and initiator were added at reflux to a 250-mL two-necked flask equipped with a stirrer and isobarically dropping funnel in 2 h. More other than 3.5 h was required to make the copolymer. After cooling, the product was purified by reverse precipitation by the slow addition of petroleum ether into the THF solution. The insoluble solid left in the solution was removed by centrifugation. The resulting polymer was redissolved in THF and further purified by reprecipitation in petroleum ether. The precipitate was filtered off and dried at 40°C in vacuum for 12 h to afford CPA<sub>1</sub> (9.69 wt %).

CPA<sub>2</sub> with a higher weight content of DM (16.29 wt %) was prepared by an analogous method.

Synthesis of the copolymer-containing 8-hydroxyquinoline ligands (IV, CPA<sub>1</sub>-HQ, and CPA<sub>2</sub>-HQ)

A 250-mL single-necked flask equipped with a magnetic stirrer and a condenser was charged with ethanol (100 mL), anhydrous  $\text{Na}_2\text{CO}_3$  (300 mg), CPA<sub>1</sub> (4.113 g), and 5-chloromethyl-8-hydroxyl-quinolinol (1.614 g). The reaction mixture was heated to reflux and kept at reflux for 24 h. The mixture was filtered through a G1 funnel to remove residual insoluble solids, and the filtrate was distilled to get rid of most alcohol and dried at 40°C for 12 h in vacuum. Then, the product was dissolved in THF, and the residual insoluble solids in the solution were removed by centrifugation, and the filtrate was reprecipitated by petroleum ether and washed by THF for several times. The precipitate was filtered off and dried at 40°C in vacuum for 12 h to provide CPA<sub>1</sub> (9.69 wt %) as a deep-brown solid (66.44% yield).

To increase the mass fraction of 5-chlorine-8-hydroxyquinoline in the CPA's side chains, CPA<sub>2</sub>-

HQ (19.37 HQ wt %) was prepared by an analogous method (70.54% yield).

Synthesis of the LiQ-containing polymers (V, CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li)

LiQ-containing polymer V was synthesized from the dehydration reaction of lithium hydroxide and polymer IV containing 8-hydroxyquinoline ligands. THF was used as solvent. CPA<sub>1</sub>-HQ (g, 13.2 mmol) were added to 20 mL of anhydrous THF in a three-necked flask equipped with a nitrogen inlet and a magnetic stirrer, and then the solution of LiOH (0.316 g, 13.2 mmol) in anhydrous THF was dropped into the flask until pH of the mixture solution reached 8–11. A yellow-green color appeared immediately. The mixture was stirred at room temperature for 48 h. Upon completion of the reaction, the precipitate was separated by filtration. The solution CPA<sub>1</sub>-HQ-Li was reprecipitated by petroleum ether and washed by THF for several times, and the insoluble solids left in the solution was removed by centrifuge. The reprecipitate was filtered off and dried at 40°C in vacuum for 12 h to give the product as a yellow-green solid (CPA<sub>2</sub>-HQ-Li, 11.66 LiQ wt %) (69.52% yield).

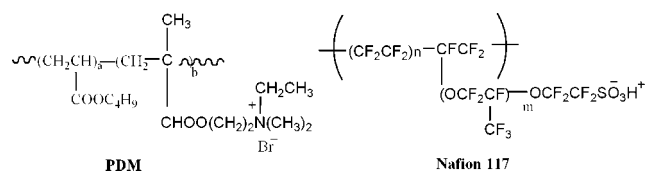
The CPA<sub>2</sub>-HQ-Li (19.59 LiQ wt %) was prepared by an analogous method (71.36% yield).

#### Multilayer fabrication of CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li/polyelectrolytes

Quartz slides (35.0 × 12.4 × 1.6 mm) were used as substrates for UV-vis spectroscopy and PL spectra, quartz slides were pretreated to render a net negative surface charge by a method previously described.<sup>31</sup> These slides were placed in glass weighing bottles and covered with a solution of concentrated  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  (7/3 v/v). After the mixture was heated at 90°C for 0.5 h, it was cooled to room temperature and the liquid was decanted. Quartz slides were immediately rinsed with deionized water and then decanted the liquid. This process was repeated five times, and the slides were rinsed twice with deionized water, dipped into  $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$  solution (v/v/v 5/1/1), and heated for 0.5 h at 40°C. Then, the liquid was decanted, the slides were rinsed five times with deionized water, and finally dried at 40°C in vacuum for 1 h.

CPA<sub>1</sub>-HQ-Li was dissolved in 30 mL of anhydrous THF. The purchased Nafion 117 (120 mg) was added to a container containing 30 mL of water (2 mg/mL). PDM/ammonia solution (2.0 mg/mL, pH = 11.47) was added to a container containing ammonia 30 mL of water by the same method. The molecule structures of PDM and Nafion 117 are shown in Figure 1.

The multilayer films were prepared by a layer-by-layer adsorption method. The quarternary ammo-



**Figure 1** The molecule structure formulas of PDM and Nafion 117.

anium PDM was used as the first positively charged adsorption layer to obtain flexible substrate. The polyelectrolyte (CPA<sub>1</sub>-HQ-Li) synthesized above and Nafion 117 were used as polycation and polyanion, respectively, to assemble multilayer thin films.

A negative-charged quartz slide was first immersed into 2 mg/mL PDM aqueous solution for 20 min. After rinsing five times in deionized water and dried at 40°C in vacuum for 30 min, the quartz slide was inserted into the solution of Nafion 117 and CPA<sub>1</sub>-HQ-Li alternately. This process was repeated until the desired number of bilayers of CPA<sub>1</sub>-HQ-Li/Nafion 117 was obtained. After each deposition, the slide was washed with deionized water for 1 min and dried at 40°C in vacuum for 30 min. Here, a layer of CPA<sub>1</sub>-HQ-Li and a layer of Nafion 117 are entitled a double layer. The adsorption process of CPA<sub>1</sub>-HQ-Li/Nafion 117 multilayers was monitored by the UV-vis spectrometer and fluorescence spectrometer. All adsorption procedures were carried out at room temperature.

The ESA multilayer films of CPA<sub>2</sub>-HQ-Li (2 mg/mL)/Nafion 117 were obtained by the same method.

Multilayer of CPA<sub>1</sub>-HQ-Li/Nafion 117, CPA<sub>1</sub>-HQ/Nafion 117, and single-layer fabrication of CPA<sub>1</sub> were fabricated by an analogous method with three pieces of clean quartz slides (30.0 × 30.0 × 1.6 mm), and the surfaces of film were studied by AFM.

The following are the molecule structure of PDM and Nafion 117.

## RESULTS AND DISCUSSION

### Synthesis and ESA

In preparing the copolymers of CPA<sub>1</sub> and CPA<sub>2</sub>, it is essential to manipulate the addition speed and to choose the way of addition. If AIBN was added too fast, an explosive polymerization would result owing to high temperature and release of a great deal of heat in local region of polymerization. So, AIBN was dropped slowly through isobarically dropping funnel. In addition, powdered AIBN was more favorable allowing for the low solubility in isopropyl alcohol.

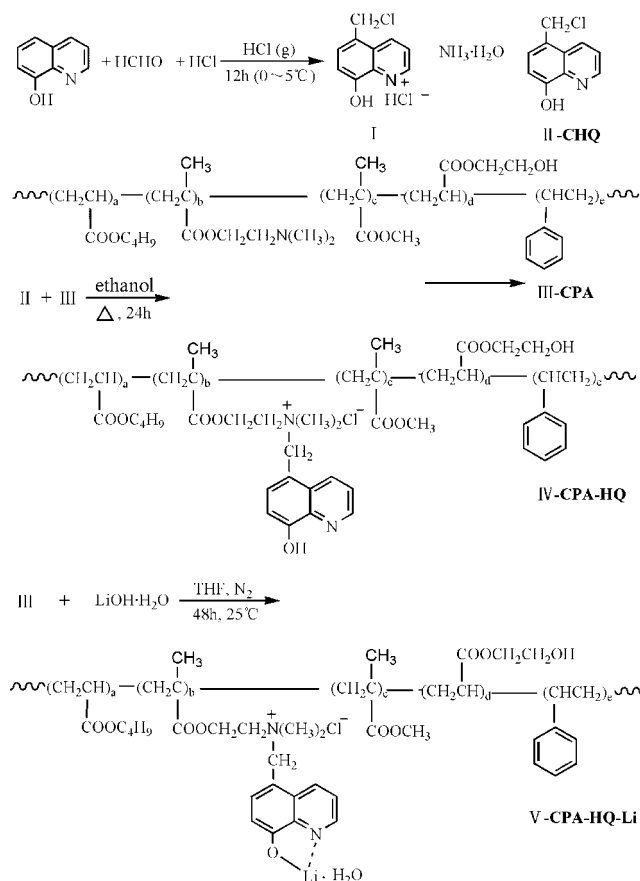
Ethanol was chosen as solvent for attaching CHQ to CPA<sub>1</sub> and CPA<sub>2</sub> in the reaction, because both CHQ and copolymers (CPA<sub>1</sub> or CPA<sub>2</sub>) are soluble in it, and it is more polar and CHQ gives better solubil-

ity in it, which facilitates the reaction between CHQ and tertiary amine in the polymer backbone. Also, excessive CHQ can ensure the high yields of CPA<sub>1</sub>-HQ and CPA<sub>2</sub>-HQ.

The synthetic scheme of preparation of the LiQ-containing polymer V(CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li) is shown in Scheme 1. The dropping sequence of the reactants, pH of the mixture solution (8–11) and the dry atmosphere were very important. A classical lithium complex was formed with the possible structure LiQ · ×H<sub>2</sub>O. Fully anhydrous complexes could not be obtained because of the highly hygroscopic nature. The details of synthesis are given in the Experimental section. Compound V was directly obtained from the reaction of compound IV and LiOH (1 : 1). The lithium complex was a hygroscopic material.

Qualitative evaluation of solubility of CHQ and the copolymers mentioned above was done for ensuring absence of unreacted small molecule CHQ.

CHQ could be dissolved well in water and ethanol, whereas but not in other common organic solvents such as THF, chloroform, benzene, toluene, DMF, and acetone. CPA<sub>1</sub>, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li could be dissolved well in the above solvents except water. Similar solubility was observed for CHQ in comparison with CPA<sub>2</sub>, CPA<sub>2</sub>-HQ, and CPA<sub>2</sub>-HQ-Li.



**Scheme 1** Synthetic route to the LiQ-containing copolymer.

TABLE I  
Solubility of CHQ in Comparison with CPA<sub>1</sub>-CPA<sub>1</sub>-HQ and CPA<sub>1</sub>-HQ-Li

Sample	Water	Ethanol	THF	Chloroform	Benzene	Toluene	DMF	Acetone
CHQ	+ <sup>a</sup>	+	–	–	–	–	–	–
CPA <sub>1</sub>	– <sup>b</sup>	+	+	+	+	+	+	+
CPA <sub>1</sub> -HQ	–	+	+	+	+	+	+	+
CPA <sub>1</sub> -HQ-Li	–	+	+	+	+	+	+	+

<sup>a</sup> Dissolve.

<sup>b</sup> Insoluble.

The first layer film is key in preparing the multi-layer films; otherwise, the next film shall be affected. The PDM is used as flexible substrate, which is helpful to the success of the multilayer assembly.

### The solubility characteristic

Solubility of CHQ in comparison with CPA<sub>1</sub>, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li is summarized in Table I. The polarity of the CHQ, CPA<sub>1</sub>-HQ, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li could influence the solubility of them in common solvents. CHQ could dissolve well in water and ethanol, whereas could not dissolve in the other common organic solvents such as THF, chloroform, benzene, toluene, DMF, and acetone. CPA<sub>1</sub>, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li could be dissolved well in the common organic solvents except water.

Solubility of CHQ in comparison with CPA<sub>2</sub>, CPA<sub>2</sub>-HQ, and CPA<sub>2</sub>-HQ-Li is similar to the above Table I.

### The GPC results of CPA<sub>1</sub>-HQ, CPA<sub>2</sub>-HQ, CPA<sub>1</sub>-HQ-Li, and CPA<sub>2</sub>-HQ-Li

The GPC results of CPA<sub>1</sub>-HQ, CPA<sub>2</sub>-HQ, CPA<sub>1</sub>-HQ-Li, and CPA<sub>2</sub>-HQ-Li are shown in Table II. The number-average molecular weights ( $\bar{M}_n$ ) of CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li increase compared to those of CPA<sub>1</sub>-HQ and CPA<sub>2</sub>-HQ, which is opposite to  $\bar{M}_w$ ,  $\bar{M}_z$ , and  $\bar{M}_\eta$ . This is a more trenchant evidence of the polymer IV containing 8-hydroxyquinoline ligands chelated with metal ion Li<sup>+</sup>.

### The DSC results of CPA<sub>1</sub>, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li

Thermal analysis was done by DSC, and the results were shown in Figure 2. The samples (10 mg) were

placed in aluminum pans and run at a rate of 10°C/min, followed by cooling rapidly or by a controlled cooling rate of 10°C/min to form glassy state. The glass transition ( $T_g$ ) was measured from a second heating of the glassy state. The  $T_g$  of CPA<sub>1</sub> is 26.8°C, the  $T_g$  of 8-hydroxyquinoline lithium-containing copolymers increased from 42.9 to 62.9°C after the dehydration reaction of lithium hydroxide and polymer IV containing 8-hydroxyquinoline ligands. The  $T_g$  of CPA<sub>1</sub>, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li increased along with the introduction of the quinoline ring and metal ion Li<sup>+</sup>. In other words, its thermal stability can be improved, because the rigidity increases as the introduction of the quinoline ring and metal complex.

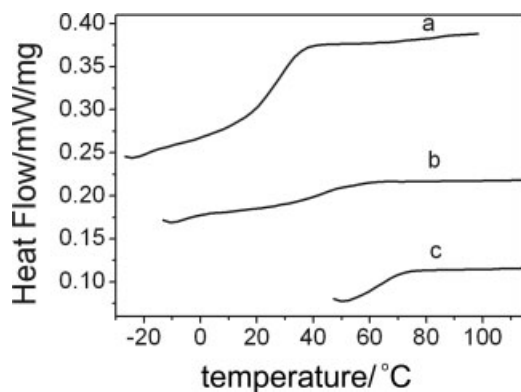
### The FTIR spectra of CPA<sub>1</sub>, CPA<sub>1</sub>-HQ, and CPA<sub>1</sub>-HQ-Li

From the FTIR measurements of CPA<sub>1</sub> (a) and CPA<sub>1</sub>-HQ (b) as shown in Figure 3, it was found that the strong peak at 3443 cm<sup>-1</sup> from O–H stretching vibration give a blue shift to 3422 cm<sup>-1</sup> due to the pendant of CHQ in CPA<sub>1</sub>. The vanishing of the peak at 696 cm<sup>-1</sup> in the CHQ (the stretching vibration of C–Cl) indicated the success of the graft reaction. The new absorbance at 1638 cm<sup>-1</sup> comes from the conjugation of lone pair electron of N atom of CHQ with benzene rings.

For CPA<sub>1</sub>-HQ (b) and CPA<sub>1</sub>-HQ-Li (c) as shown in Figure 3, the strong absorbance peak of 3421 cm<sup>-1</sup> from O–H stretching vibration and 1234 cm<sup>-1</sup> from O–H deformation vibration of 8-hydroxyquinoline were markedly weakened owing to the coordination of O–H and N with metal ion Li<sup>+</sup>. The distinct peaks at 1569 cm<sup>-1</sup>, 1593 cm<sup>-1</sup>, 1505 cm<sup>-1</sup>, and 1465 cm<sup>-1</sup> were characteristic of the absorption vibration of the aromatic ring skeleton. The intensity increase implied that the conjugated system is extended,

TABLE II  
The GPC Results of CPA<sub>1</sub>-HQ, CPA<sub>2</sub>-HQ, CPA<sub>1</sub>-HQ-Li, and CPA<sub>2</sub>-HQ-Li

Sample	DM%	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_\eta$	PDI
CPA <sub>1</sub> -HQ	11.52 (HQ%)	6,501	25,803	59,162	25,803	3.9692
CPA <sub>2</sub> -HQ	19.37 (HQ%)	10,047	26,781	50,163	26,781	2.6655
CPA <sub>1</sub> -HQ-Li	11.66 (LiQ%)	7,064	12,571	18,722	12,571	1.7795
CPA <sub>2</sub> -HQ-Li	19.59 (LiQ%)	10,574	20,341	33,409	20,341	1.9237



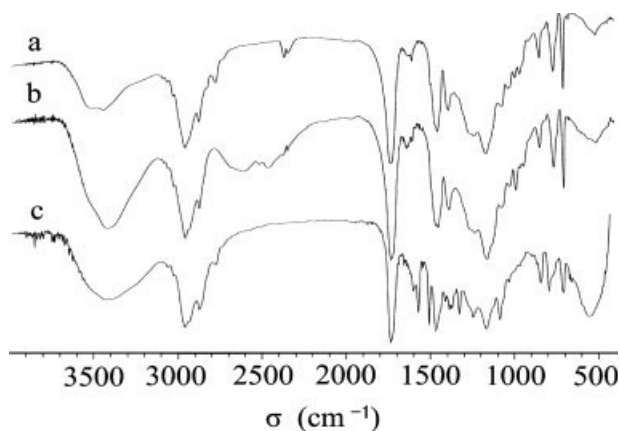
**Figure 2** DSC curves for CPA<sub>1</sub> (a), CPA<sub>1</sub>-HQ (b), and CPA<sub>1</sub>-HQ-Li (c).

which is the evidence of preformed LiQ group in polymer. Furthermore, the stretching vibration peak located initially at 1638 cm<sup>-1</sup> was blue shifted to 1603 cm<sup>-1</sup> nearby, which was ascribed to the reduction of electron density upon chelating of Li<sup>+</sup> with N and O, leading to the decrease of force constant of C—N bond and thus a blue shift of absorption frequency. The observation indicated the formation of the synthesized product as the desired copolymers.

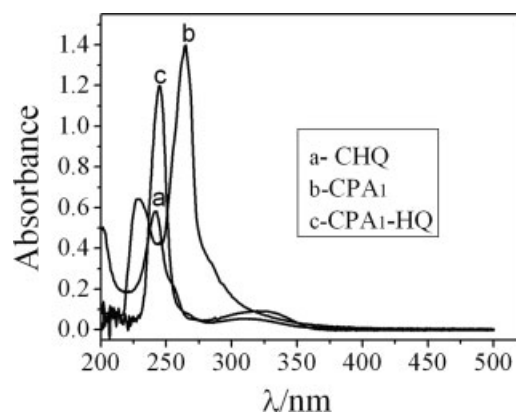
#### The UV-vis absorption spectra of CHQ, CPA<sub>1</sub>, CPA<sub>2</sub>, CPA<sub>1</sub>-HQ, CPA<sub>2</sub>-HQ in THF

It was found from Figures 4 and 5 that there are two uniform absorption peaks (229 and 265 nm) in UV-vis absorption spectrum of CPA<sub>1</sub> and CPA<sub>2</sub>, the similar trend was observed in CPA<sub>1</sub>-HQ and CPA<sub>2</sub>-HQ (248 and 320 nm), indicating that the concentration of copolymer and the content of DM in copolymer have a little influence on the UV-vis absorption spectra of CPA<sub>1</sub> and CPA<sub>2</sub> or CPA<sub>1</sub>-HQ and CPA<sub>2</sub>-HQ.

The UV-vis absorption spectra of CHQ, CPA<sub>1</sub>, and CPA<sub>1</sub>-HQ are shown in Figure 4. The narrow and strong absorption at 248 nm corresponds to the



**Figure 3** FTIR spectra of CPA<sub>1</sub> (a), CPA<sub>1</sub>-HQ (b), and CPA<sub>1</sub>-HQ-Li (c).



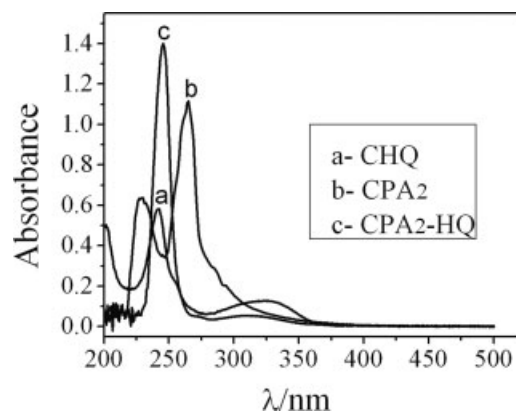
**Figure 4** UV-vis absorption spectra of CHQ, CPA<sub>1</sub>, and CPA<sub>1</sub>-HQ in THF.

$\pi \rightarrow \pi^*$  electron transition of CPA<sub>1</sub>-HQ, and the absorption at 320 nm is the  $n \rightarrow \pi^*$  electron transition caused by lone pair electron of N atom of CPA<sub>1</sub>-HQ. There is a wide and weak peak at 320 nm, because the energy of  $n$  orbit is so close with  $\pi$  and  $\pi^*$  orbit in the conjugated system of CPA<sub>1</sub>-HQ that the energy gap overlap occurs.<sup>32</sup> The absorption spectra provide the evidence for the graft of CHQ on the side chain of copolymer.

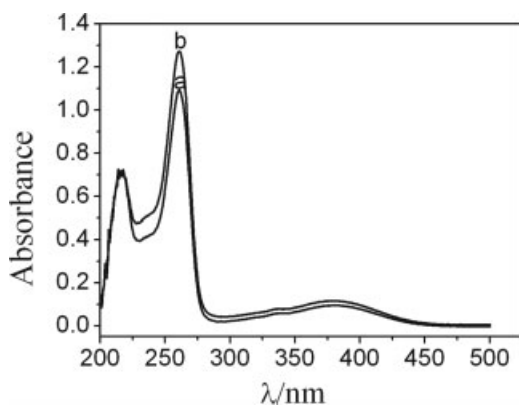
A similar conclusion could be drawn from the UV-vis absorption spectrum of CHQ, CPA<sub>2</sub>, and CPA<sub>2</sub>-HQ as shown in Figure 5.

#### The UV-vis absorption spectra of CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li in THF

The interaction between metal ion Li<sup>+</sup> and polymer V containing 8-hydroxyquinoline ligands was also supported by the UV-vis spectra. As can be seen from Figure 6, the intensity of UV-vis absorption spectra of CPA<sub>2</sub>-HQ-Li (b) is stronger than that of CPA<sub>1</sub>-HQ-Li (a). The absorption peak at 248 nm  $\pi \rightarrow \pi^*$  electron transition from quinoline was present, but it has already red shifted to 260 nm and the  $n \rightarrow \pi^*$  transition at 320 nm disappeared or was weakened. The lone pair



**Figure 5** UV-vis absorption spectra of CHQ, CPA<sub>2</sub>, and CPA<sub>2</sub>-HQ in THF.

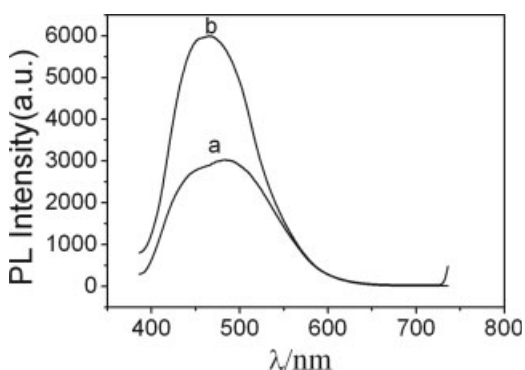


**Figure 6** UV-vis absorption spectra of CPA<sub>1</sub>-HQ-Li (a) and CPA<sub>2</sub>-HQ-Li (b).

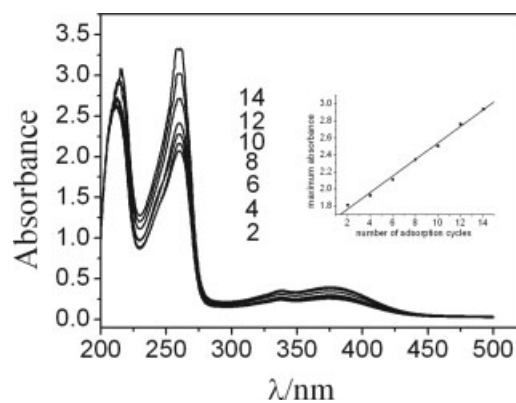
electrons of N do not conjugate with the empty orbit of metal ion Li<sup>+</sup> after O—H and isolated electron of N atom complexed with metal ion Li<sup>+</sup>, which reduce not only the energy of n orbit but also the energy of π orbit, the position, and the intensity change of  $n \rightarrow \pi$  and  $n \rightarrow \pi^*$ ,<sup>33</sup> a broad absorption at 367 nm, this is a strong evidence for the chelating of the polymer IV containing 8-hydroxyquinoline ligands with metal ion Li<sup>+</sup>. A shoulder at 340 nm can be seen, which is due to the plus of UV-vis of CPA<sub>1</sub>-HQ-Li and other polymers root in the V-containing 8-hydroxyquinoline ligands chelated partly with metal ion Li<sup>+</sup> only.

#### The fluoroscope spectra of CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li in THF

Figure 7 displays the PL emission spectra of CPA<sub>1</sub>-HQ-Li (a) and CPA<sub>2</sub>-HQ-Li (b) run in THF. According to the experiments and prediction made by molecular modeling, an electron-donating substituent at C-5 position of the phenoxide side of the quinolate ligand will cause a red shift of the luminescence of 8-hydroxyquinoline metal chelates.<sup>34,35</sup> We observed very strong luminescence CPA<sub>1</sub>-HQ-Li even at room temperature as shown in Figure 7. The blue luminescence was clearly visible with the naked eye even in good illuminated room. It confirmed the existence of



**Figure 7** Photoluminescence (PL) emission spectra of CPA<sub>1</sub>-HQ-Li (a) and CPA<sub>2</sub>-HQ-Li (b) in THF.



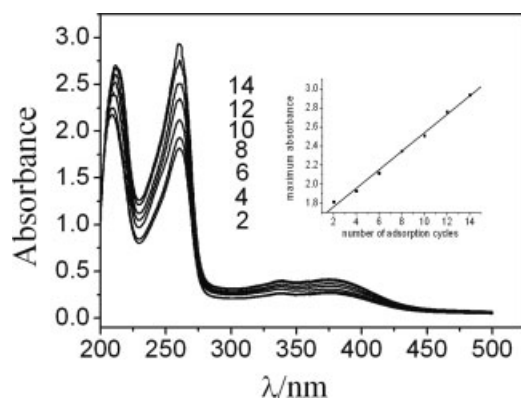
**Figure 8** UV-vis absorption spectra of CPA<sub>1</sub>-HQ-Li/Nafion 117 multilayer films with increasing number of layer pairs. The insert shows the relationship between the maximum absorbance of CPA<sub>1</sub>-HQ-Li/Nafion multilayer films and the number of layer pairs.

a fluorescent species formed between metal ion Li<sup>+</sup> and 8-hydroxyquinolinol. The chelated metal cations have an effect on system π-electronic cloud and lone-pair electron of N. The effect depends upon ionic polarization force, which has close relation to ionic radius, valency state, and covalent character. The less the ionic radius of chelated metal cations are, the higher valency state is, PL emission and excitation wavelength of the LiQ-pendant copolymers were the least.<sup>36</sup> The emission spectra of CPA<sub>1</sub>-HQ-Li ( $\lambda_{\text{max}} = 481$  nm) were collected from 386 to 736 nm with an excitation wavelength of 370 nm, which is consistent with the report.<sup>26</sup>

Figure 7 also displays the PL excitation and emission spectra run in THF of CPA<sub>2</sub>-HQ-Li. As shown in Figure 7, the emission spectra of CPA<sub>2</sub>-HQ-Li ( $\lambda_{\text{max}} = 489$  nm) were collected from 410 to 760 nm with an excitation wavelength of 372 nm.

#### The UV-vis absorption spectra of the self-assembly multilayer films

Figure 8 shows the UV-vis absorption spectra of CPA<sub>1</sub>-HQ-Li/Nafion 117 multilayer films with increasing number of layer pairs, containing sequentially deposited CPA<sub>1</sub>-HQ-Li and Nafion 117 layers with increased number of dipping cycles. A linear increase of absorbance was observed as the number of the layer pairs increased, which was maintained up to at least 10 layer pairs and proved to be a layer-by-layer assembly. It is well known that the UV-vis absorbance of CPA<sub>1</sub>-HQ-Li in solution were blue-shifted compared to those of their multilayer thin films. The reason may be excimer formation between adjacent lumophors in solid films and intermolecular processes that are greatly reduced in dilute solution, leading to a blue-shifted of the emission spectra.<sup>37-41</sup>

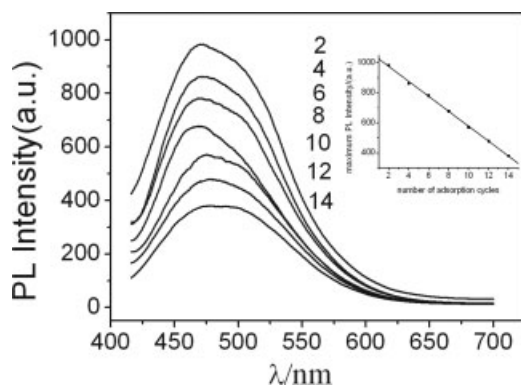


**Figure 9** UV-vis absorption spectra of CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films with increasing number of layer pairs. The insert shows the relationship between the maximum absorbance of CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films and the number of layer pairs.

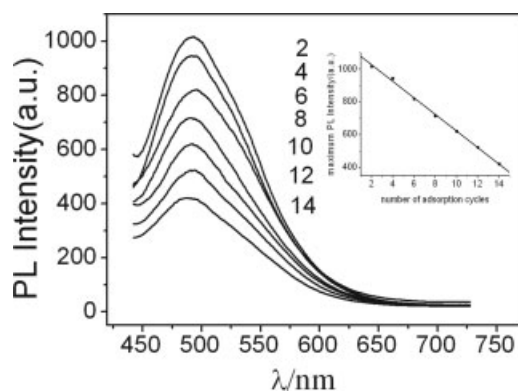
From Figure 9, we can see that the analogous rule in the UV-vis absorption spectra of CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films with increasing number of layer pairs and the relationship between the maximum absorbance of CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films and the number of layer pairs.

#### The fluorescence spectra of the self-assembly multilayer films

Figure 10 shows the PL emission spectra of the multilayer films, containing sequentially deposited CPA<sub>1</sub>-HQ-Li and Nafion 117 layers with increased number of dipping cycles. A linear reduction of PL was observed as the number of the layer pairs increased, which was maintained up to at least 10 layer pairs and proved a layer-by-layer assembly. The reason is quenching of fluorescence intensity along with increment of materials (CPA<sub>1</sub>-HQ-Li and



**Figure 10** Photoluminescence (PL) emission spectra of tCPA<sub>1</sub>-HQ-Li/Nafion 117 multilayer films through ESA. The insert shows the increase of ESA-films made from CPA<sub>1</sub>-HQ-Li/Nafion 117 in absorbance at 480 nm as a function of ESA-films cycles.



**Figure 11** Photoluminescence (PL) emission spectra of the CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films through ESA. The insert shows the increase of ESA-films made from CPA<sub>2</sub>-HQ-Li/Nafion 117 in absorbance at 480 nm as a function of ESA-films cycles.

Nafion 117) concentration.<sup>42</sup> Possibly, the quenching process can be in two different ways which including dynamic and static quenching, there is not a single mechanism of luminescent quenching in the above actual system because of multifarious environmental factors (medium, temperature, concentration etc).<sup>43</sup> To illustrate this phenomenon ulteriorly, the polymer main chain structure was changed, that is, CPA<sub>2</sub>-HQ-Li was synthesized corresponding to 16.29% of DM added starting material, the result of control experiments shown in Figure 11.

Figure 11 also shows that it holds true for PL emission spectra of CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films with increasing number of layer pairs and the relationship between the maximum emission spectra of CPA<sub>2</sub>-HQ-Li/Nafion 117 multilayer films and the number of layer pairs.

It is also well known that the PL emission spectra of CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li in solution were blue shifted compared to those of their multilayer thin films.

#### The properties of copolymers and its films

The origin of 229 nm peak in CPA<sub>1</sub> and CPA<sub>2</sub> is disappeared in CPA-HQ compounds (see Figs. 4 and 5). The final products CPA-HQ-Li have a very strong peak at 218 nm (see Fig. 6). The 214/210 nm peaks of CPA<sub>1</sub>-HQ-Li/CPA<sub>2</sub>-HQ-Li in multilayer films become the strongest (see Figs. 8 and 9).

Figure 7 shows that CPA<sub>1</sub>-HQ-Li in THF has two shoulder peaks at 459 and 481 nm, which is due to the plus of the PL emission spectra of CPA<sub>1</sub>-HQ-Li and other polymers root in the V-containing 8-hydroxyquinoline ligands chelated partly with metal ion Li<sup>+</sup> only. CPA<sub>2</sub>-HQ-Li in THF has only one peak at 489 nm can be seen, which is clarified that the distribution of CPA<sub>2</sub>-HQ-Li (2.6655) is less than that of CPA<sub>1</sub>-HQ-Li (3.9692). The same difference is better



**TABLE III**  
The Properties of Copolymers and Its Films

Sample	UV-vis/ $\lambda_{\max}$ (nm)		PL and extent of half-peak ( $E$ )			
	Solution	Film	Solution		Film	
			PL Em	$E$ (nm)	PL Em	$E$ (nm)
CPA <sub>1</sub>	229/265	–	–	–	–	–
CPA <sub>2</sub>	229/265	–	–	–	–	–
CPA <sub>1</sub> -HQ	248/320	–	–	–	–	–
CPA <sub>2</sub> -HQ	248/320	–	–	–	–	–
CPA <sub>1</sub> -HQ-Li	260/367	375	481	134	488	117
CPA <sub>2</sub> -HQ-Li	253/369	377	489	130	494	–

appreciated in the PL spectra of the multilayer films, with a red shift of the three mentioned peaks compared with the solution ones (Figs. 10 and 11).

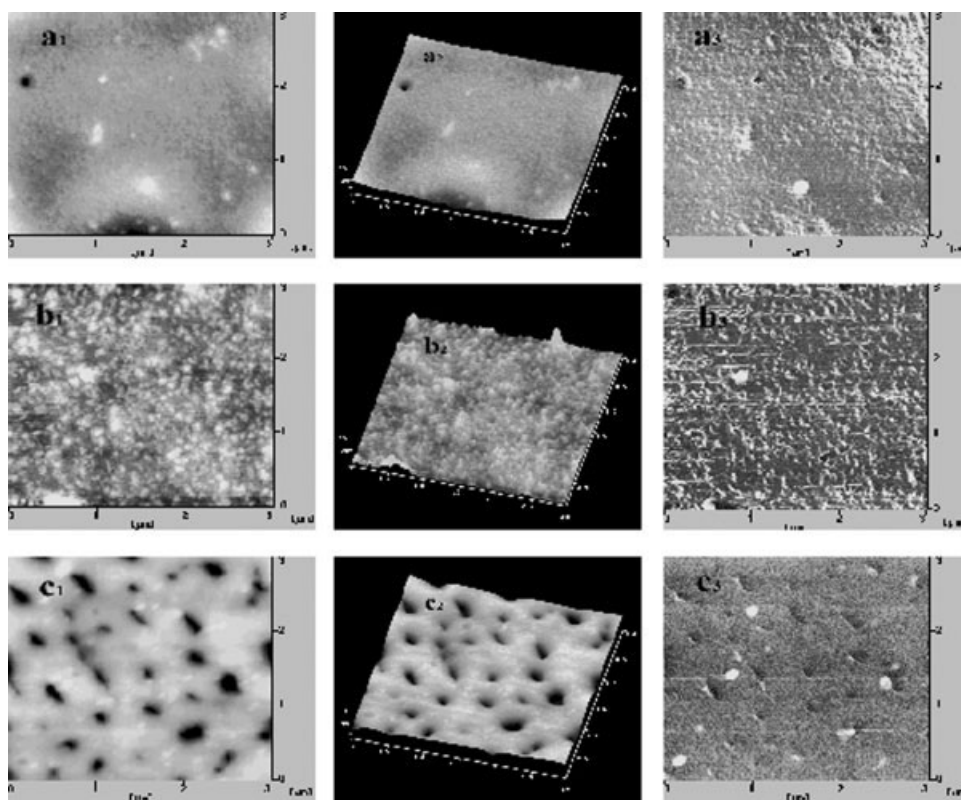
The UV-vis, PL, and extent of half-peak ( $E$ ) of copolymers and its films were shown in Table III. The  $E$  of CPA<sub>1</sub>-HQ-Li and CPA<sub>2</sub>-HQ-Li in the films corresponds to the THF solution. The  $E$  of CPA<sub>1</sub>-HQ-Li in the film is bigger than that of CPA<sub>2</sub>-HQ-Li in the THF solution.

#### Surface-relief on monolayer and multilayers films

The AFM image of CPA<sub>1</sub>, CPA<sub>1</sub>-HQ/Nafion 117 multilayers, and CPA<sub>1</sub>-HQ-Li/Nafion 117 multi-

layers were shown in Figure 12. The bright spots are protuberant particles, and the dark spots are holes. From the images, we can see that the surface of the films is rather smooth in Figure 12(a<sub>1</sub>–a<sub>3</sub>), and the particulates distribute uniformly in the surfaces Figure 12(b<sub>1</sub>–b<sub>3</sub>). However, the surface in Figure 12(c<sub>1</sub>–c<sub>3</sub>) is more compact, which was explained by the fact that the interaction force of chains or segments are stronger than those of CPA<sub>1</sub>-HQ after complexed with metal ion Li<sup>+</sup>, the pliability of copolymer chains is destroyed to form a big rigidity plane so that the polymer chain was puckered by static force.

The surface modulation and regular surface pattern can be gained through control of the film layers.



**Figure 12** Comparison of (a) the AFM image of the CPA<sub>1</sub> and (b) the AFM image of the CPA<sub>1</sub>-HQ/Nafion multilayers and (c) the AFM image of the CPA<sub>1</sub>-HQ-Li/Nafion multilayers.

We believe that easy control of the film thickness and composition through ESA process can be readily extended to a wide variety of polyelectrolytes for optical applications.

### CONCLUSIONS

In conclusion, the organic PL material 8-hydroxyquinoline lithium-containing copolymers have been synthesized and purified. The analysis of FTIR spectra explicated the bonding character of LiQ and the existence of quinoline rings. Fluorescence data confirmed the presence of a fluorescent species formed between  $\text{Li}^+$  and 8-hydroxyquinolinol. Furthermore, the multilayer films were studied through UV-vis, PL, and AFM.

The solution of CPA-HQ-Li and ESA films have strong fluorescence and concentration self-quenching. By adjusting the content of HQ on the side chains of polymers, we prepared ESA films that emit different lights. That may become a new method for the preparation of full-spectrum fluorescent polymers. This kind of materials might be interesting for practical applications in OLEDs. The method is suitable for most 8-hydroxyquinoline metal chelates. An in-depth study of the copolymerization mechanism and an investigation into application for the metaloquinolate-containing copolymers are currently under way.

The authors acknowledge Professor L. H. Yuan and master Y. F. Tian for their fruitful discussions and useful suggestions.

### References

1. Wang, K. *Chem Commun* 1997, 1.
2. Lehn, J. M. *Angew Chem Int Ed Engl* 1990, 29, 1304.
3. Laschewsky, A. *Eur Chem Chron* 1997, ECC2, 13.
4. Decher, G.; Eckle, M.; Schmitt, J.; Struth, B. *Curr Opin Colloid Interface Sci* 1998, 3, 32.
5. Lvov, Y.; Decher, G.; Sukhorukov, G. *Macromolecules* 1993, 26, 5396.
6. Ho, P. K. H.; Kim, J. S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. *Nature* 2000, 404, 481.
7. Tredgold, R. H.; Winter, C. S.; El-Badawy, Z. I. *Electron Lett* 1985, 21, 554.
8. Wu, T.; Zhang, X. *Chem J Chin Univ* 2001, 22, 1057.
9. Zhang, X.; Chen, H.; Zhang, H. Y. *Chem Commun* 2007, 1395.
10. Schmitt, J.; Decher, G.; Dressik, W. J.; Brandow, S. L.; Geer, R. E.; Shashidbar, R.; Calvert, J. M. *Adv Mater* 1997, 9, 61.
11. Zhong, A. Y.; Lin, X. J.; Chen, D. B.; Zhou, Z. H. *J Appl Polym Sci* 2003, 87, 1029.
12. Lin, X. J.; Zhong, A. Y.; Chen, D. B.; Zhou, Z. H.; He, B. B. *J Appl Polym Sci* 2003, 87, 369.
13. Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J Am Chem Soc* 1995, 117, 6117.
14. Caruso, F.; Mohwald, H. *J Am Chem Soc* 1999, 121, 6039.
15. Zhang, X. *Acta Polym Sin* 2007, 10, 905.
16. Zhang, X.; Chen, H.; Zhang, H. *Chem Commun* 2007, 1395.
17. Yan, X. J.; Deng, Y. H.; Wang, X. G. *Acta Polym Sin* 2007, 5, 440.
18. Tang, C. W.; Vanslyke, S. A. *Appl Phys Lett* 1987, 53, 913.
19. Ghedini, M.; La Deda, M.; Aiello, I.; Grisolia, A. *Synth Met* 2003, 138, 189.
20. Affinito, J. D.; Martin, P. M.; Graff, G. L.; Burrows, P. E.; Gross, M. E.; Sapochak, L. U.S. Pat. 6,228,436 (2002).
21. Uchida, M.; Ohmori, Y.; Noguchi, T.; Ohnishi, T.; Yoshino, K. *Jpn J Appl Phys* 1993, 32, L921.
22. Lu, J. P.; Hlil, A. R.; Meng, Y. Z.; Hay, A. S.; Tao, Y.; Diorio, M.; Mainron, T.; Dodelet, J. *J Polym Sci Part A: Polym Chem* 2000, 38, 2887.
23. Meyers, A.; Weck, M. *Macromolecules* 2003, 36, 1766.
24. Yu, H. H.; Chen, X. Y.; Hu, W. D.; Yang, E. Y.; Li, H. H.; Li, X. F. *Chin J Synth Chem* 2004, 12, 283.
25. Du, N. Y.; Mei, Q. B.; Lv, M. G. *Acta Polym Sin* 2005, 4, 507.
26. Schmitz, C.; Schmidt, H. W.; Thelakkat, M. *Chem Mater* 2000, 12, 3012.
27. Haskal, E. I.; Curioni, A.; Seidler, P. F.; Androni, W. *Appl Phys Lett* 1997, 71, 1151.
28. Hung, L. S.; Tang, C. W. *Appl Phys Lett* 1999, 74, 3209.
29. BurckhLiter, J. H.; Leib, R. I. *J Org Chem* 1961, 26, 4078.
30. Xiao, D. Q.; Chen, D. B.; Zhou, Z. H.; Zhong, A. Y. *J Appl Polym Sci* 2002, 83, 112.
31. Wasserman, S. R.; Tao, Y. T.; Whitesides, G. M. *Langmuir* 1989, 5, 1074.
32. Tsukruk, V. V. *Polym Sci* 1997, 22, 247.
33. Lee, H.; Kepley, L. J.; Hong, H. G.; Mallouk, T. E. *J Am. Chem Soc* 1998, 110, 618.
34. Pohl, R.; Anzenbacher, P. *Org Lett* 2003, 5, 2769.
35. Jang, H.; Do, L. M.; Kim, Y.; Zyung, T.; Do, Y. *Synth Met* 2001, 121, 1667.
36. Zhao, W. M.; Zhu, W. Q.; Zhang, B. X.; Jiang, X. Y.; Zhang, Z. L.; Xu, S. H. *Acta Opt Sin* 2000, 21, 78.
37. Bell, C. M.; Arendt M. F.; Gomez, L.; Schmehl, R. H.; Mallouk, T. E. *J Am Chem Soc* 1994, 116, 8374.
38. Cataldo, F. *Dyes Pigments* 1997, 34, 75.
39. Sun, L.; Kepley, L. J.; Crooks, R. M. *Langmuir* 1992, 8, 2101.
40. Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. *Langmuir* 1997, 13, 1385.
41. Gao, G.; Hong, H. G.; Mallouk, T. E. *Acc Chem Res* 1992, 25, 420.
42. Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol Rapid Commun* 2000, 21, 319.
43. Ariga, K.; Lvov, Y.; Kunitake, T. *J Am Chem Soc* 1997, 119, 2224.