APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 952–957
Main Group Metal Compounds **AOC**

The characteristic of photoluminescence of tris-(7-substituted-8-hydroxyquinoline) aluminum complexes and polymeric complexes

Yeh-Fang Duann[1]*, Yu-Jung Liao[1], Wenjeng Guo[1] and Shu-Mei Chang[2]

[1]Department of Chemical Engineering, National Taipei University of Technology, Taipei, Taiwan
[2]Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei, Taiwan

Received 4 February 2003; Revised 28 February 2003; Accepted 8 August 2003

The 7-allyl- and 7-(2-methylvinyl)-functionalized derivatives of 8-hydroquinoline are synthesized by Claisen rearrangement and double bond rearrangement respectively. Then 7-allyl-8-hydroquinoline (C) and 7-(2-methylvinyl)-8-hydroquinoline (D) are reacted with aluminum chloride to afford the corresponding tris-(7-allyl-8-hydroxyquinoline) aluminum complex (F) and tris-(7-(2-methylvinyl)-8-hydroxyquinoline) aluminum complex (G). The photoluminescence of complex (F) or (G), compared with that of tris-(8-hydroxyquinoline) aluminum complex (E), all showed a red shift in emission wavelengths in different solvents, such as chloroform, hexane and ethanol. For two substituents containing an external double bond, the 2-methylvinyl group gives a larger red shift in the emission wavelength than the allyl group. The X-ray crystal structure indicates that 7-(2-methylvinyl)-8-hydroxyquinoline (D) is a trans-isomer. The styrene and 7-allyl-8-hydroxyquinoline copolymer, and the styrene and 7-(2-methylvinyl)-8-hydroxyquinoline copolymer are also reported. Further reactions of the copolymer are then performed by adding aluminum(III) chloride and ligands 8-hydroxyquinoline. The spectroscopic characteristics of these aluminum(III) polymeric complexes are discussed. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: aluminum complex; Claisen rearrangement; differential scanning calorimetry (DSC); organometallic polymer; photoluminescence; thermogravimetric analysis (TGA); tris-(8-hydroxyquinoline) aluminum(III) complex

INTRODUCTION

The work of Tang and Van Slyke[1] demonstrated efficient electroluminescence in two-layer sublimed molecular film devices. The development of these devices has made substantial progress in recent years. Now, these devices are called organic light-emitting diodes.[2] They are highly luminescent, highly efficient, easy to fabricate and the possibility exists to create flexible devices.

At present, many methods are known to activate the organic material. The methods include radioluminescence, cathodoluminescence, X-ray luminescence, triboluminescence, electroluminescence and photoluminescence, etc.[3] Many papers have been dedicated to the development of organic light-emitting material, and many organic light-emitting materials have been synthesized and studied. The emission light wavelength of organic light-emitting material depends on the characteristics of the material. Typically, organic light-emitting devices can be tuned by means of applying different voltages, which then modifies the emission wavelength. Most work has been focused on understanding the charge transport mechanisms of the device, and tuning the organic light-emitting diodes emission wavelength.[4,5] Two different approaches are frequently employed to change the emission wavelength of organic light-emitting material. One approach involves doping the existing light-emitting material with various dopants and results in a red shift of the emission wavelength. The other approach is changing the substituents on the light-emitting material.

The light-emitting material tris-(8-hydroxyquinoline) aluminum (AlQ_3) is a stable aluminum-chelated complex that is one of the most successful organic materials used in organic

---

*Correspondence to: Yeh-Fang Duann, 1, Sec.3, Chung-Hsiao E. Rd, Taipei 106, Taiwan, ROC.
E-mail: f10421@ntut.edu.tw
Contract/grant sponsor: National Science Council, Taiwan.

electroluminescent devices,[6–9] owing to its high brightness, efficiency and ease of purification. AlQ_3 is suitable for commercial applications. The emission wavelength of AlQ_3 is about 520 nm. Many reports show that it is possible to shift the emission wavelength of the complex, 8-hydroxyquinoline, by changing the central metal.[10,11]

In the present work, two tris-(7-substituted-8-hydroxyquinoline) aluminum complexes were synthesized from 7-substituted-8-hydroxyquinoline. We substituted the seventh position of 8-hydroxyquinoline with an isolated double bond by O-allyl–C-allyl Claisen rearrangement of 8-quinoline allyl ether (**B**) or a conjugate double bond by the double bond rearrangement of 7-allyl-8-hydroxyquinoline. The emission spectra of these samples showed the influence of inductive and resonance effects.

The synthesis and spectroscopic characteristics of tris-(7-substituted-8-hydroxyquinoline) aluminum complexes are investigated, as is the influence of the external double bond on the photoluminescence excitation spectra. Finally, tris-(7-substituted-8-hydroxyquinoline) complexes are polymerized with styrene and the photoluminescence emissions of these polymeric complexes are examined.

EXPERIMENTAL

Figure 1 outlines the synthesis procedure of the tris-(7-allyl-8-hydroxyquinoline) aluminum (**F**) and tris-(7-(2-methylvinyl)-8-hydroxyquinoline) aluminum (**G**) metal complexes.

The reactants, allyl bromide and 8-hydroxyquinoline, were purchased from Lancaster Chemical Co. Aluminum chloride was purchased from Aldrich Chemical Co. All were used without further purification.

^{1}H NMR spectra were measured on a Bruker AV-400 MHz FT-NMR spectrometer. IR spectra were recorded on a Perkin–Elmer (SPECTRUM 2000) FT-IR spectrometer. UV–visible absorption spectra were recorded on a UNICAM UV500 spectrometer. Photoluminescence emission spectra were recorded on a Perkin–Elmer L-55 spectrometer. Melting points were determined on MEL-TEMP capillary melting point apparatus and were uncorrected. X-ray crystallography was performed at 295 K on a Nonius Kappa CCD diffractometer for a block $0.30 \times 0.30 \times 0.35\ \mathrm{mm}^3$. $C_{12}H_{11}NO$, $M = 185.22$, orthorhombic, $Pbca$, $a = 7.4750(2)$ Å, $b = 15.8320(3)$ Å, $c = 16.6010$ Å, $V = 1964.63(8)$ Å^3, $Z = 8$, 1714 unique data ($\theta_{\max} = 25.0$), 1590 data with $I > 2\sigma(I)$. $R_1 = 0.061$, $wR_2 = 0.179$, $\rho_{\max} = 0.14\ \mathrm{e}^-$ Å^3. Programs used: SHELXL and ORTEP. The glass transition temperature was measured by a differential scanning calorimeter (Du Pont DSC 10). Dry nitrogen was used as a purge gas. Samples of approximately 5 mg were enclosed in aluminum differential scanning calorimetry (DSC) capsules. The thermal decomposition of epoxy resins have been studied by thermogravimetric analysis (TGA, Du Pont 951 instrument coupled to a Thermal Analyst 2000) in a flowing (60 ml min^{-1}) nitrogen atmosphere. Samples of about 9–12 mg were used. Four different heating rates were investigated: 2.5, 5, 10 and 15 °C min^{-1} from 50 to 800 °C.

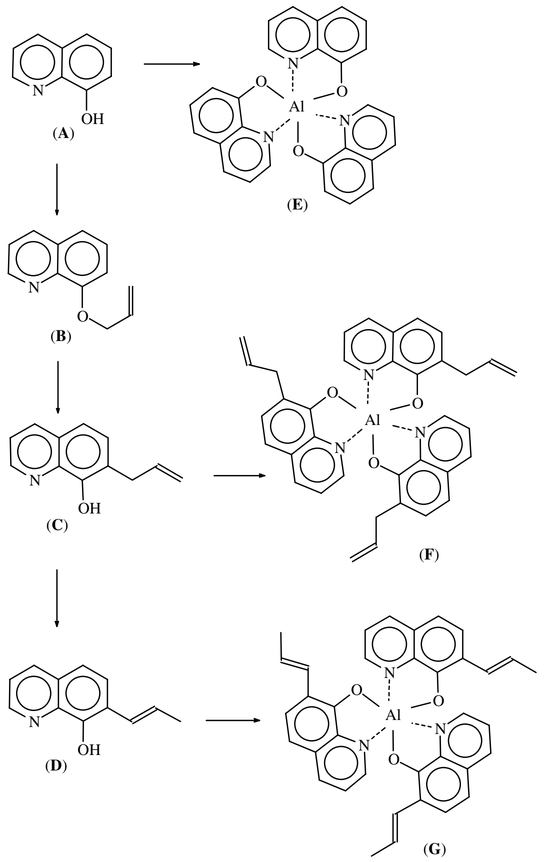

Figure 1. The structure and synthesised process of tris-(7-substituted-8-hydroxyquinoline) aluminum.

SYNTHESIS

8-Quinoline allyl ether (B)

A mixture of 1.45 g (0.01 mol) of 8-hydroxyquinoline (**A**), allyl bromide 1.32 g (0.01 mol), 1.40 g of anhydrous potassium carbonate (0.01 mol), and 25 ml of dry acetone was placed in a 250 ml three-necked round-bottomed flask fitted with a condenser, refluxed overnight and cooled. The mixture was then filtered. The resulting liquid was next washed with 50 ml of water and extracted with two 20 ml portions of diethyl ether. The combined extracts were washed with two 10 ml potions of 10% sodium hydroxide and dried with anhydrous potassium carbonate. After removal of the solvent, the residual oil was used as a reactant for a Claisen rearrangement reaction. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 4.83 (d, 2H), 5.32 (d, 1H), 5.46 (d, 1H), 6.23 (m, 1H), 7.03 (d, 1H), 7.36 (m, 3H), 8.07 (d, 1H), 8.93 (d, 1H). ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 69.77 ($-CH_2-$), 109.25, 117.31, 119.72, 121.56, 126.56, 129.47, 133.16, 135.88, 147.80, 149.26, 154.27.

7-Allyl-8-hydroxyquinoline (C), by Claisen rearrangement

The 8-quinoline allyl ether (**B**) 1.85 g (0.01 mol) was cautiously brought to boiling in a 50 ml round-bottomed flask at 160 °C, left overnight, and cooled. The reaction mixture was dissolved in 25 ml of diethyl ether, and the solution was then extracted with three 20 ml potions of 10% sodium hydroxide. Next, the combined alkaline extracts were acidified with 10 ml of concentrated hydrochloric acid diluted with 25 ml of water. Subsequently, the mixed extracts were dried with 10 g of anhydrous sodium sulfate and evaporated, after which the residual was crystallized with hexane. The yield of 7-allyl-8-hydroxyquinoline (**C**) was 1.21 g (65%); m.p.: 38–39 °C.^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 3.64(d, 2H), 5.11 (m, 2H), 6.08 (m, 1H), 7.35 (m, 3H), 8.11 (d, 1H), 8.75 (d, 1H). ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 33.98 ($-CH_2-$), 115.73, 117.34, 121.07, 121.69, 127.12, 129.65, 136.08, 136.45, 138.07, 147.75, 149.16.

7-(2-Methylvinyl)-8-hydroxyquinoline (D)

The 7-allyl-8-hydroxyquinoline (**C**) 27.75 g (0.15 mol) and a saturated solution of potassium hydroxide in 100 ml of methanol was mixed in a 250 ml round-bottomed flask fitted with simple distilling equipment. 70 ml of methanol was distilled, then the simple distilling equipment was removed and a condenser was attached to the flask. After boiling the reaction mixture gently under reflux at 180 °C for 12 h, the reaction mixture was cooled. Next, the reaction mixture was poured into 100 ml of water, acidified with concentrated hydrochloric acid, and then the organic and aqueous layers were separated by extraction with three 100 ml portions of diethyl ether. The organic layer was dried over anhydrous potassium carbonate. Subsequently, the diethyl ether was removed with a rotary evaporator and the residue was crystallized with hexane. Finally, the product was collected, obtaining a yield of 14 g (50%); m.p.: 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.98 (d, 3H), 6.46 (m, 1H), 6.92 (d, 1H), 7.24 (d, 1H), 7.33 (m, 1H), 7.58 (d, 1H), 8.05 (d, 1H), 8.72 (d, 1H). ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 19.10 ($-CH_3$), 117.51, 120.03, 121.09, 125.28, 125.69, 127.26, 127.38, 135.90, 138.61, 147.86, 147.91.

Tris-(7-allyl-8-hydroxyquinoline) aluminum (F)

The tris-(7-substituted-8-hydroxyquinoline) aluminum complexes (7-substituted-AlQ_3, **F** and **G**) powder was prepared as follows: 7-substituted-8-hydroxyquinoline was dissolved in acetic acid, and then an $AlCl_3$ aqueous solution was slowly dropped into the 7-substituted-8-hydroxyquinoline solution while the solution was stirred. After the mixed solution was adjusted to pH 5 using potassium hydroxide aqueous solution, the 7-substituted-AlQ_3 complex precipitate was deposited. Finally, the 7-substituted-AlQ_3 precipitate was filtered and washed with methanol and water and dried under vacuum; m.p.: 206–208 °C.

Tris-(7-(2-methylvinyl)-8-hydroxyquinoline) aluminum (G)

The procedure is as described in the synthesis of tris-(7-allyl-8-hydroxyquinoline) aluminum (**F**); m.p.: 160–164 °C.

Polymerization

Poly(7-allyl-8-hydroxyquinoline-alt-styrene) and poly(7-(2-methylvinyl)-8-hydroxyquinoline-alt-styrene) were prepared as follows: 7-substituted-8-hydroxyquinoline and styrene were dissolved in tetrahydrofuran (THF), and then a trace amount of benzoyl peroxide was added to the mixture while the solution was stirred under nitrogen at 70 °C. After the mixed solution was reacted overnight, the polymer was poured into methanol solution and deposited. Finally, the copolymer was filtered and washed with methanol and vacuum dried.

Polymeric aluminum(III) complexes

The polymeric aluminum(III) complexes were prepared as follows. The ligands poly(7-allyl-8-hydroxyquinoline-alt-styrene) or poly(7-(2-methylvinyl)-8-hydroxyquinoline-alt-styrene)) were dissolved in THF and 8-hydroxyquinoline was dissolved in acetic acid; then, $AlCl_3$ aqueous solution was dripped into the ligand-containing solution, which was simultaneously stirred. After adjusting the mixed solution to pH 6 using potassium hydroxide aqueous solution, the polymeric aluminum(III) complex precipitates were deposited. Finally, the precipitate was filtered, washed with chloroform, methanol and water and then vacuum dried.

RESULTS AND DISCUSSION

Interestingly, an O-allyl–C-allyl Claisen rearrangement reaction can be used to introduce a double bond (a functional group) into 8-hydroxyquinoline. The double bond can be polymerized. Such a synthesis process can make a polymeric complex luminescent. The 7-substituted side chain on 8-hydroxyginoline ring can change into another functional group, such as carboxylic acid, ester or amide, following oxidization of further reaction. Consequently, the AlQ_3 is clearly functional. In this work we introduced a double bond into 8-hydroxyquinoline. Crystallographic data of compound **D** are presented in Table 1.

The length of the external double bond is 1.301(4) Å and the $C_7-C_{10}-C_{11}$ and $C_{10}-C_{11}-C_{12}$ angles are 127.9(2)° and 126.0(3)° respectively. The structure shows a trans-geometry, as shown in Fig. 2.

The maximum photoluminescent emission wavelengths of the aluminum complexes shown in Fig. 1 are listed in Table 2.

Three different kinds of solvent have been used in measuring the photoluminescent spectra. The position of maximum emission of each band λ_{max} corresponds to the tris-(7-substituted-8-hydroxyquinoline) aluminum complex shown under the influence of the isolated double bond and conjugated double bond.

Table 1. The crystal data of X-ray analysis of compound **D**

O(1)–C(8)	1.359(3)	N(1)–C(1)	1.316(3)
N(1)–C(9)	1.365(3)	C(1)–C(2)	1.394(4)
C(2)–C(3)	1.352(4)	C(3)–C(4)	1.408(4)
C(4)–C(5)	1.404(4)	C(4)–C(9)	1.414(3)
C(5)–C(6)	1.366(5)	C(6)–C(7)	1.415(4)
C(7)–C(8)	1.378(3)	C(7)–C(10)	1.474(4)
C(8)–C(9)	1.418(3)	C(10)–C(11)	1.301(4)
C(11)–C(12)	1.471(4)		
C(1)–N(1)–C(9)	116.9(2)	N(1)–C(1)–C(2)	124.6(2)
C(3)–C(2)–C(1)	118.6(3)	C(2)–C(3)–C(4)	120.2(2)
C(5)–C(4)–C(3)	124.6(2)	C(5)–C(4)–C(9)	118.6(3)
C(3)–C(4)–C(9)	116.8(2)	C(6)–C(5)–C(4)	120.3(2)
C(5)–C(6)–C(7)	122.7(2)	C(8)–C(7)–C(6)	117.3(3)
C(8)–C(7)–C(10)	120.1(2)	C(6)–C(7)–C(10)	122.6(2)
O(1)–C(8)–C(7)	118.7(2)	O(1)–C(8)–C(9)	119.7(2)
C(7)–C(8)–C(9)	121.6(2)	N(1)–C(9)–C(4)	122.9(2)
N(1)–C(9)–C(8)	117.6(2)	C(4)–C(9)–C(8)	119.6(2)
C(11)–C(10)–C(7)	127.9(2)	C(10)–C(11)–C(12)	126.0(3)

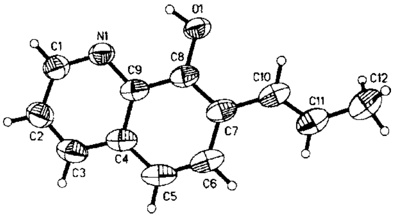

Figure 2. The trans-structure of compound **D**. Key geometric parameters: C_7–C_{10} 1.474(4), C_{10}–C_{11} 1.301(4), C_{11}–C_{12} 1.471(4) Å; C_7–C_{10}–C_{11} 127.9(2), C_{10}–C_{11}–C_{12} 126.0(3), C_6–C_7–C_{10} 122.6(2), C_8–C_7–C_{10} 120.1(2)°.

Table 2. The maximum photoluminescence emission wavelength λ_{max} of aluminum complexes E–G

	λ_{max} (nm)		
	Chloroform	Hexane	Ethanol
E	510	506	511
F	535	515	528
G	546	540	544

When chloroform was used as a solvent in measuring photoluminescence spectra, the λ_{max} for complex **E** was about 510 nm, whereas λ_{max} for complex **F** was 535 nm and for complex **G** was 546 nm. In complex **F**, the double bond was not conjugated with the quinoline ring. The emission was of lower energy than complex **E**. In complex **G**, the double bond was conjugated and the emission wavelength was the longest. As the conjugated system exists, the π orbitals interact to form a new set of bonding and anti-bonding orbitals in which the energy difference between the highest occupied energy level and the lowest unoccupied energy level decreases. In complex **G**, this energy difference must correspond to low energy. The lowest unoccupied molecular orbital (LUMO) state can be stabilized to a greater extent because it has more polarity than the highest occupied molecular orbital (HOMO) state. The energy difference between LUMO and HOMO becomes small. The emission will shift toward a longer wavelength with a polar solvent. It has a bathochromic effect (red shift). Therefore, chloroform will stabilize the LUMO state to a greater extent than the HOMO state.

This trend is also indicated in the other measurements in Table 2. Hexane is a non-polar solvent. The maximum emission of each band λ_{max} is shorter in hexane. That means the LUMO state is more polar than the HOMO state. Interactions of solvents with molecules result in lower states (HOMO), and the energy difference becomes large. Therefore, the maximum emission λ_{max} is shorter in hexane. Ethanol is a polar solvent and creates a hydrogen bond. Molecules with non-bonded electrons are able to interact with hydrogen-bonding solvents to a greater extent in the HOMO state than in their LUMO state. As a result, the emission will shift toward a shorter wavelength as the hydrogen-bonding ability of the solvent increases. Ethanol is a polar solvent and creates a hydrogen bond, but the maximum emission wavelength list in Table 1 indicates that there is no hydrogen bonding between ethanol and complexes **E**, **F** and **G**, since the maximum emission wavelength is not short enough. The nitrogen atom in the quinoline ring is coordinated with aluminum, and steric hindrance excludes the formation of a hydrogen bond. Thus, there is no hydrogen bonding between the solvent and the quinoline ring.

Figures 3 and 4 illustrate the synthetic procedure of 7-substituted-8-hydroxyquinolines copolymerized with styrene.

The polymeric aluminum(III) complexes **J** and **M** are cross-linked copolymers for which aluminum chloride is the cross-linking agent. Polymeric aluminum(III) complexes **I** and **L** are both AlQ_3-containing polymers. Table 3 lists the photoemission wavelengths of polymeric aluminum(III) complexes **I**, **L**, **J** and **M** under excitation at $\lambda_{max} = 300$ nm.

Interestingly, the polymeric aluminum(III) complexes **I** and **J** emitted at the same wavelength, i.e. $\lambda_{max} = 522$ nm. Meanwhile, the photoemission wavelengths of polymeric aluminum(III) complexes **M** and **L** are $\lambda_{max} = 525$ nm and $\lambda_{max} = 529$ nm respectively, and thus are longer than those of **J** and **I**. DSC indicated that all of the above complexes had a glass transition temperature T_g of over 300 °C. Table 4 lists the results of thermogravimetric analysis (TGA) of the polymeric aluminum(III) complexes **I**, **J**, **L** and **M** in nitrogen at a 10 °C min^{-1} heating rate.

TGA indicates that the degradation temperatures of polymeric aluminum(III) complexes **L** and **M** are lower than for complexes **I** and **J** respectively. The structures in

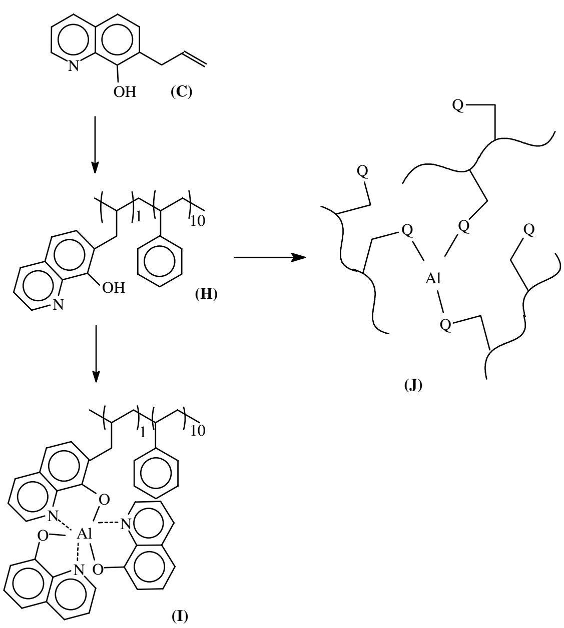

Figure 3. The synthesis procedure of copolymer **H** and polymeric aluminum(III) complexes **J** and **I**.

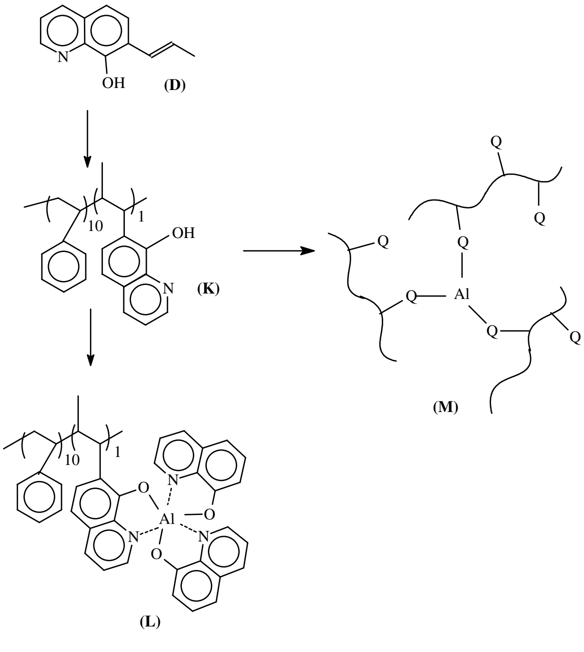

Figure 4. The synthesis procedure of copolymer **K** and polymeric aluminum(III) complexes **M** and **L**.

Figs 3 and 4 clearly illustrate that the main chain in polymeric aluminum(III) complexes **L** and **M** are more crowded than in the polymeric aluminum(III) complexes **I** and **J**. The differences in the degradation temperature are small. Another study is needed to clarify the relationship between the steric hindrance and the stability of these polymer or polymeric aluminum(III) complexes.

Table 3. The maximum emission λ_{max} of polymeric complexes

Compound	$\lambda_{abs,max}$	$\lambda_{abs,max}$	Compound	$\lambda_{ex,max}$	$\lambda_{ex,max}$
I	300	522	L	300	529
J	300	522	M	300	525

Table 4. TGA of polymeric aluminum(III) complexes **I**, **J**, **L** and **M**

Compound	Degradation temperature (°C)
I	421
J	425
L	415
M	419

CONCLUSIONS

The aim of this work is to investigate the influence of external double bonds on the photoluminescent excitation spectra of tris-(7-substituted-8-hydroxyquinoline) aluminum complexes, which have been synthesized by Claisen rearrangement and double bond rearrangement. The double bond can be polymerized. This synthesis process can make a polymeric complex luminescent. This double bond can change into another functional group. Consequently, the AlQ_3 is clearly functional. Compared with the emission wavelength of AlQ_3, the emission wavelength $\lambda_{max} = 510$ nm in chloroform), we found that the external double bond increased the wavelength of the photoluminescent emission light. Three different kinds of solvent, i.e. chloroform, hexane and ethanol, showed the same trend and there was no hydrogen bonding between the solvent and the quinoline ring when ethanol was used as a solvent. DSC indicated that all of the above complexes had a T_g of over 300 °C. TGA indicates that the degradation temperature of polymeric aluminum(III) complexes is in the range 415–425 °C.

Acknowledgements

We would like to thank the National Science Council, Taiwan, Republic of China, for financial support.

REFERENCES

1. Tang CW, Van Slyke SA. *Appl. Phys. Lett.* 1987; **51**: 913.
2. Dodabalapur A. *Solid State Commun.* 1997; **102**: 259.
3. Krasovitskii BM, Bolotin BM. *Organic Luminescent Materials*, Vopian VG (transl.). VCH Verlagsgesellschaft 1988.
4. Destruel P, Jolinat P, Clergereaux R, Farence J. *J. Appl. Phys.* 1999; **85**: 397.
5. Stampor W, Kalinowski J. *Phys. Lett.* 1997; **70**: 913.
6. Tang CW, Van Slyke SA, Cheng CH. *J. Appl. Phys.* 1989; **65**: 3610.

7. Kido J, Kimura M, Nagai K. *Science* 1995; **267**: 1332.
8. Kalinowski J, Di Marco P, Cammaioni N, Fattori V, Stampor W, Duff J. *Synth. Met.* 1996; **26**: 77.
9. Kalinowski J, Camaioni N, Di Marco P, Fattori V, Giro G. *Int. J. Electron.* 1996; **81**: 377.
10. Tao XT, Suzuki H, Wada T, Sasabe H, Miyata S. *Appl. Phys. Lett.* 1999; **75**: 1655.
11. Wang L, Jiang X, Zhang Z, Xu S. *Displays* 2000; **21**: 47.