

Novel bis(8-hydroxyquinoline)phenolato–aluminum complexes for organic light-emitting diodes

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Abstract

A novel series of emitting aluminum complexes containing two 8-hydroxyquinoline ligands (q) and a phenolato ligand (p) were synthesized and characterized. Double layer organic light-emitting diodes (OLEDs) were fabricated using these complexes as luminescent layers, and strong electroluminescence (EL) was observed. It was found that their emitting wavelengths were mainly determined by the first ligands (q). Cyclic voltammograms revealed a partially irreversible n-doping process and indicated that these complexes show excellent electron-transporting ability.

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1. Introduction

The interest in organic molecular materials for the use in light-emitting devices (organic light-emitting diodes, OLEDs) began with the report of efficient green electroluminescence (EL) from aluminum tris(8-hydroxyquinoline) (Alq_3) [1]. Since then, many metal complexes [2–4] have been developed. The emission color and charge-transporting properties of complexes can be changed by varying the central metal ion, the ligand structure and the number of ligands. Many pentacoordinated complexes [5–7] have different charge transport and emission properties from hexacoordinated complexes. The emissive wavelength in pentacoordinated bis(2-methyl-8-hydroxyquinoline)phenolato–aluminum complexes [6,7] shifts from green of Alq_3 to blue, and the authors attributed the shifts to the phenolato ligand. In those complexes, the stereo-hindrance of the methyl group in the 2-position of 8-hydroxyquinoline was in favor of the formation of pentacoordination. To further investigate the effect of first (q) and second ligands (p) on emissive wavelength and efficiency, series bis(8-hydroxyquinoline)phenolato–aluminum complexes (Alq_2p), as shown in Fig. 1, were synthesized.

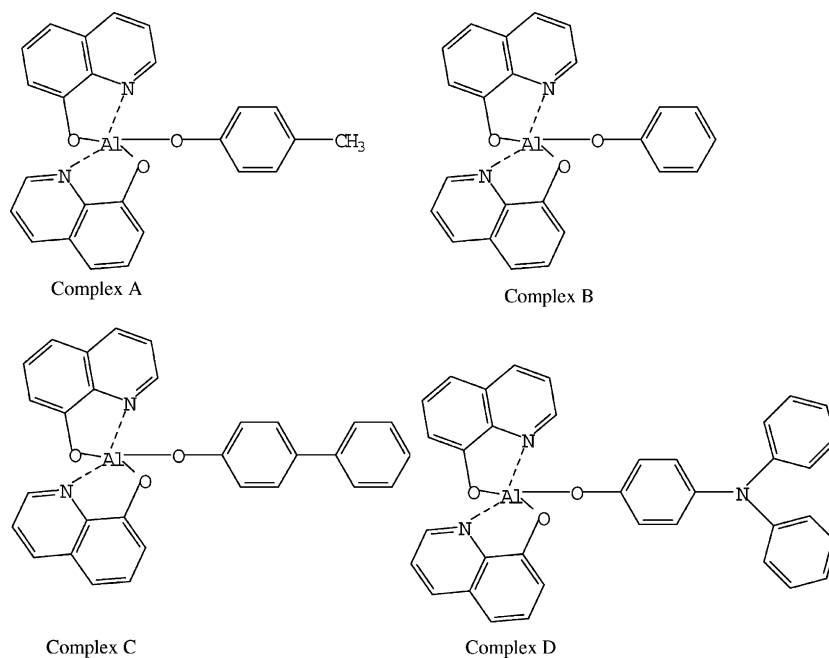
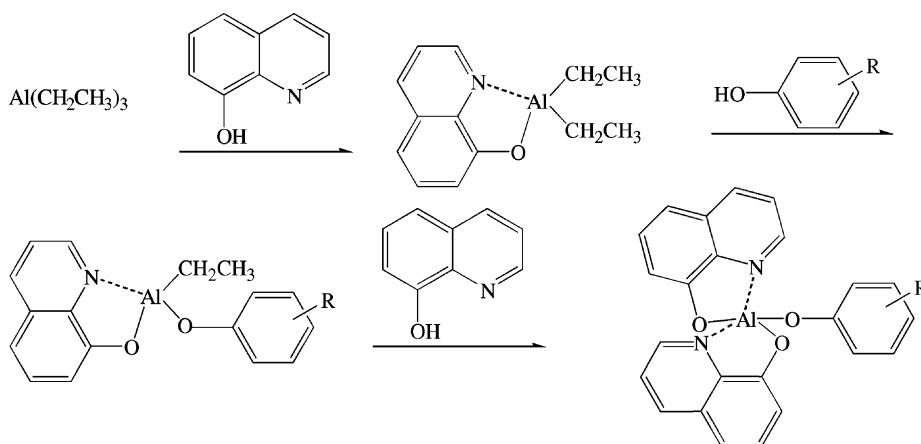
As depicted in Fig. 1, a series of novel pentacoordinated aluminum complexes (Alq_2p) containing two 8-hydroxyquinoline ligands (q_2) and one phenolato ligand (p) were synthesized. The introduction of phenolato with different hole-transporting ability substituents is to investigate the influence of phenolato on the luminescent efficiency of designed complexes.

2. Experimental

Alq_2p were synthesized from triethylaluminum, 8-hydroxyquinoline and phenol-compounds. In our designed complexes, without 2-methyl group on 8-hydroxyquinoline hinders us to use the same synthetic method as published pentacoordinated bis(2-methyl-8-hydroxyquinoline)phenolato–aluminum complexes [6,7]. Hence, a new route of synthesis, as shown in Scheme 1, was selected. At room temperature, a solution of triethylaluminum (1.14 g, 0.01 mol) in 20 ml of dried benzene was placed in a 100 ml three-necked flask under an atmosphere of nitrogen. The solution of 8-hydroxyquinoline (1.45 g, 0.01 mol) in 15 ml dried benzene was added dropwise into the above solution with stirring at such a slow rate that a gentle reflux of the solvent was maintained ($\sim 37^\circ\text{C}$). The yellow-green precipitate appeared, this precipitate was a diethyl aluminum-compound [8–10]. The

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Fig. 1. Molecular structures of Alq₂p complexes.Scheme 1. Synthesizing route of Alq₂p.

reaction was allowed to continue for 1 h, and then a solution of phenol-compound (0.01 mol) in 15 ml dried benzene was added dropwise. The precipitate disappeared gradually. The mixture was continuously stirred for about 2.5 h. Afterwards, another solution of 8-hydroxyquinoline (1.45 g, 0.01 mol) in 15 ml dried benzene was added dropwise, the precipitate appeared again. The reaction mixture was continuously stirred for 15 h. The product was collected by filtration and washed with benzene. The materials were further purified by sublimation in a glass-tube oven. The phenol-compounds can be added directly into the reactor if it cannot be dissolved in benzene.

These complexes are evaluated as emitting layers in bilayer-type devices ITO/NPB (50 nm)/complex (50 nm)/Mg/Ag (10:1), having a hole transport layer NPB inserted between the anode and the emitter (Alq₂p or Alq₃) layers.

The organic layers are successively deposited onto an ITO-coated glass substrate at 1.0×10^{-5} Torr. The Mg/Ag top electrode is finally codeposited at 7.0×10^{-6} Torr.

¹H NMR spectra were recorded on a BRUKER AC-80 spectrometer with TMS as internal standard. The elemental analysis was carried out on Elemental Analysis System from Gmbh Varioel. Photoluminescence (PL) and EL spectra were recorded on a luminance meter RF-5000. The cyclic voltammograms were recorded with a computer-controlled model 283 potentiostat/galvanostat from EG&G parc.

3. Results and discussion

The ¹H NMR spectra of the complexes prepared were measured in CDCl₃, the related data are given in Table 1.

Table 1
¹H NMR chemical shift of the complexes in CDCl₃

Complex	Chemical shifts (ppm)
A	2.2 (s 3H), 6.6–7.6 (m 13H), 8.1–8.3 (m 2H), 8.7–8.8 (m 1H)
B	6.2–6.5 (m 4H), 6.6–7.1 (m 6H), 7.3–7.9 (m 4H), 8.1–8.4 (m 2H), 8.6–9.4 (m 1H)
C	6.6–6.8 (d 3H), 7.1–7.3 (m 15H), 8.1–8.3 (m 2H), 8.6 (s 1H)
D	6.4–6.6 (m 4H), 6.9–7.5 (m 16H), 8.1–8.3 (m 4H), 8.7–8.8 (m 2H)

Table 2
 Elemental analysis data (%) of the complexes

Complex	C	H	N	Al
A	71.09 ^a	4.50	6.63	6.40
	70.87 ^b	4.59	6.21	6.38
B	70.59 ^a	4.17	6.86	6.62
	70.12 ^b	4.25	7.03	6.54
C	74.38 ^a	4.34	5.78	5.58
	74.05 ^b	4.41	6.01	5.62
D	75.13 ^a	4.52	7.30	4.70
	74.91 ^b	4.77	7.25	4.78

^a Calculated (%).

^b Found (%).

Synthesized complexes were confirmed by their ¹H NMR spectra. The elemental analyses also confirm the molecular structures as shown in Table 2, because the measured elemental compositions are in good agreement with the calculated ones. Although the complexes were prepared from the non-substituted 8-hydroxyquinoline, stable penta-coordination aluminum complexes were still obtained. This is due to our synthetic route: the two 8-hydroxyquinoline ligands (q) were attached to the aluminum ion before and after the introduction of phenolato ligands (p), respectively.

3.1. Electrochemical property

The electrochemical properties are investigated in order to determine the effect of the second ligand on the redox property of the complexes. The cyclic voltammograms were recorded at a constant scan rate of 50 mV/s in a solution of 0.1 mol/l tetrabutylammonium perchlorate dissolved in dichloromethane. A three-electrode cell was used: the working electrode was a Pt micro-electrode (Ø 0.8 mm), the counter electrode was a Pt wire and the reference electrode was SCE. The cyclic voltammograms for Alq₂p in 1 × 10⁻³ mol/l solution in dichloromethane are shown in Fig. 2. It is found that Alq₂p complexes have no oxidative process in the range of 0–2 V and show an irreversibly reductive process in the range 0 to –2 V. The peak positions shift from A (–0.36 V) to D (–1.89 V), indicating that the electron affinity of Alq₂p decrease from A to D, which is in parallel to their PL and EL efficiency. Therefore, Alq₂p

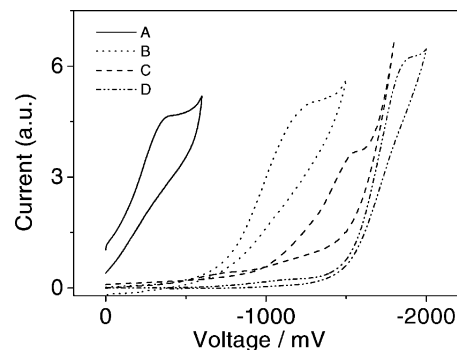


Fig. 2. The CV curves of Alq₂p complexes (A–D).

complexes have lower electron injection energy barriers and easily accept and transport electron. The electron-transporting ability decreases from A to D, probably due to the increase of hole-transporting ability of phenol-compound from A to D.

3.2. Photoluminescence property

The photoluminescence of the complexes Alq₂p are shown in Fig. 3. The spectra are measured on solid films prepared by deposited on a quartz substrate. Under the excitation of UV-light of wavelength 380 nm, all samples show a PL peak around 500 nm. Compared with the PL of Alq₃, the emission phenomena of Alq₂p complexes show a slightly blue shift about 20 nm from that of Alq₃ (520 nm). The tendency of shift is similar to that of bis(2-methyl-8-hydroxyquinoline)phenolato complexes [6,7]. Hence, it is suggested that penta-coordination is responsible for the blue-shift effect. Although complexes A through D have different second ligands, they all show almost the same PL position with each other. It is worth noting that though the slightly blue-shift effect is observed in designed complexes, the emission colors of these complexes are all similar to the PL of Alq₃. Therefore, this indicates that the second ligands (p) have no serious influence on the PL wavelength of the penta-coordinated aluminum complexes and the first ligands (q) are responsible for the PL wavelength. Perhaps, this is because the energy gaps between HOMO and LUMO

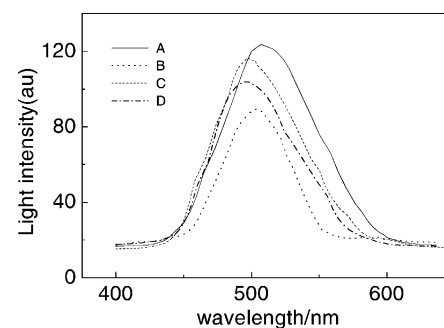


Fig. 3. Fluorescence spectra of Alq₂p in solid films excited by 380 nm UV-light.

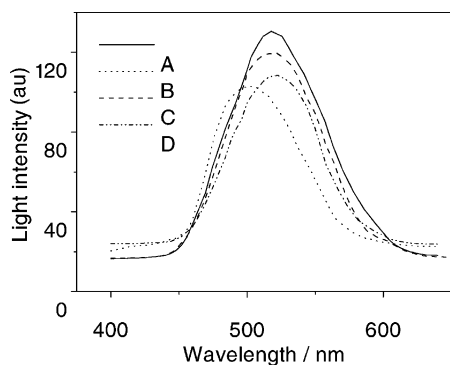


Fig. 4. EL spectra of Alq₂p (A–D) of ITO/NPB/complex/Mg:Ag devices.

in these complexes are mainly determined by 8-hydroxyquinoline ligands, while the phenolato ligands have less effect. This conclusion is reverse with the published works [6,7], where the phenolato ligand was regarded as the reason for the emission shifts of bis(2-methyl-8-hydroxyquinoline)phenolato complexes.

3.3. Electroluminescence property

To study the effect of the first and second ligands on the efficiencies of devices, respectively, we fabricate two-layer devices: ITO/NPB (50 nm)/complex (50 nm)/Mg/Ag (10:1). For the bilayer devices, bright green light is emitted at around 520 nm, as shown in Fig. 4. It is found that the EL peaks of complexes are all red shifted from the PL peaks about 20 nm, which indicates that the peak position of pentacoordinated complex does not depend on the structure of the second ligand. For the difference between EL and PL (20 nm shift), which is the common phenomena for this kind of pentacoordinated complexes [6,7], the real reason for this is still not clear. Comparing with Alq₃ and pentacoordinated 2-methyl-8-hydroxyquinoline aluminum complexes, it shows that the EL wavelengths of the complexes are mainly determined by the first ligands (q), and the second ligands (phenol-compounds) have minor influence on the EL color.

Typical brightness (*B*)–voltage (*V*), current (*I*)–voltage (*V*) and efficiency–voltage (*V*) curves for the ITO/PBD/

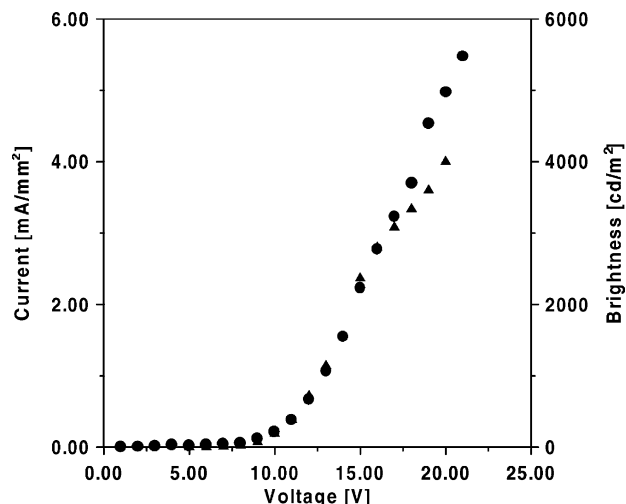


Fig. 5. Current (*I*)–voltage (*V*) and brightness (*B*)–voltage (*V*) curve for ITO/PBD/complex B/Mg:Ag device: (●) current; (▲) brightness.

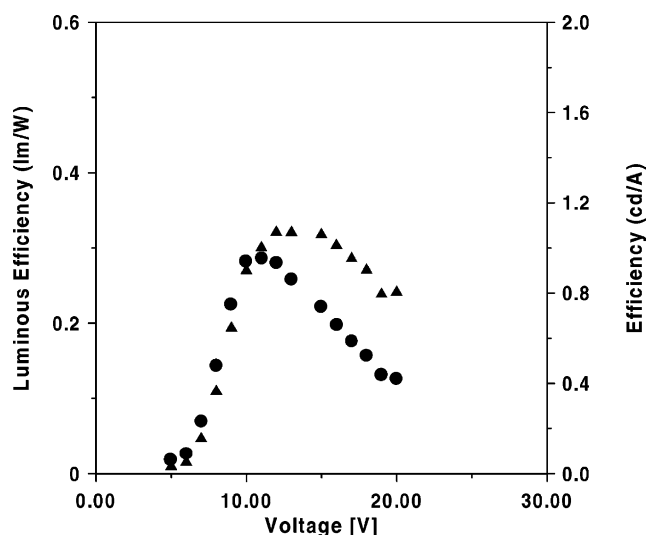


Fig. 6. Efficiency–voltage (*V*) curve for ITO/PBD/complex B/Mg:Ag device: (●) efficiency (lm/V); (▲) efficiency (cd/A).

complex B/Mg:Ag device are displayed in Figs. 5 and 6, the other devices have similar properties. Related spectra data are listed in Table 3. The turn-on voltages are around 10 V. The brightness and current intensity increases with

Table 3
Luminescent properties of Alq₂p complexes (A–D)

Complex	PL		EL		Brightness (cd/m ²) ^a	Device performance (maximum EL efficiency)			CV data (reduction potential, V)
	Peak (nm)	Half width (nm)	Peak (nm)	Half width (nm)		lm/W	cd/A	Turn-on (V)	
A	503	74	527	72	8000 (25)	0.3	1.2	4	–0.36
B	507	70	517	75	5300 (20)	0.3	1.1	9	–1.25
C	497	76	522	75	5080 (20)	0.25	0.8	8	–1.65
D	495	70	524	76	700 (20)	0.006	0.3	6	–1.89

^a The values in parentheses are in V.

the increasing of voltage. When the hole-transporting ability of the phenol-compound increases from A to D, the brightness of Alq₂p and the efficiency of devices decrease. The largest external quantum efficiency for these complexes is found for complex A (1.2 cd/A), and the smallest efficiency is obtained for complex D (0.3 cd/A). The maximum brightness among these devices is 8000 cd/m² at 25 V based on complex A. Obviously, the emitting color of the complexes are mainly determined by the first ligands, and the brightness and efficiency are affected by second ligands for devices.

4. Conclusion

A series of high efficient emitting organic EL materials of Alq₂p were synthesized and characterized. Their properties of PL, EL and CV show that Alq₂p are excellent electron-transporting materials as well as a strong green light emitter. The second ligands (p) in the complexes have small effect on the luminescent wavelength, but strongly influence the luminescent efficiency.

Acknowledgements

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