

Preparation and Characterization of High Efficient Blue-Light Emitting Materials with a Secondary Ligand for Organic Electroluminescence

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In this paper, a blue-light emitting material, bis(2-methyl-quinolinolato)(phenolato) aluminum(III) ($\text{Alq}'_2\text{OPh}$), was synthesized. Organic electroluminescent (EL) devices have been fabricated with the homemade organometallic compound as the emitting layer and N,N' -diphenyl- N,N' -di(m-tolyl)benzidine (TPD) as the hole transport layer, blue light emission with a high efficiency was obtained. Compared with tris (8-hydroxyquinoline) aluminum (Alq_3), the presence of the phenolato ligand shifts the light emission to the blue region of the spectrum. The maximum wavelength of the EL is at around 495 nm and the brightness is up to 4000 cd/m^2 with the maximum efficiency up to 1.4 lm/W . Two new compounds have also been prepared in order to investigate the effect of the secondary ligand. The comparison study indicates that the organometallic compound with a secondary ligand, not only the sterical effect but also some other effect would be responsible for the change of the emission wavelength.

KEYWORDS: organic electroluminescence, thin film, organometallic compound, emitting material, electroluminescent device, flat panel display

1. Introduction

Organic electroluminescence (EL) is a new display technology. It is attractive for its high efficiency, low cost application as a result of the high luminance yields and simple flat structure. Great improvements have been made since 1987.¹⁾ Many new materials have been synthesized and used in organic EL devices.^{2–4)} But the blue-emitting materials with high efficiency remain rare. 1,2,4-triazole derivatives,⁵⁾ distyryl arylene derivatives⁶⁾ and some metal-chelate complexes^{7,8)} have also been examined to act as the blue-emitting EL materials.

8-hydroxy-quinoline is a steady ligand for tris (8-hydroxyquinoline) aluminum (Alq_3), which is an excellent green light emitting material used in organic EL devices. 2-methyl-8-hydroxy-quinoline is a derivative of 8-hydroxy-quinoline. Different from 8-hydroxy-quinoline, it has a sterical block group, which prevents it from forming stable complex with aluminum ion directly.⁹⁾ There are two ways for 2-methyl-8-hydroxyquinoline to form organometallic compounds with aluminum. One is combining two aluminum atoms with an oxygen-bridge bond,¹⁰⁾ the other is using a phenolato as a secondary ligand.¹¹⁾

In this paper, a blue-emitting material, an aluminum chelate containing a phenolato ligand and two 2-methyl-8-quinolinolato ligands, bis(2-methyl-quinolinolato)(phenolato) aluminum(III) ($\text{Alq}'_2\text{OPh}$), was synthesized. With $\text{Alq}'_2\text{OPh}$ as the light emitting layer, organic EL devices with a double-layer or three-layer structure have been fabricated. $\text{Alq}'_2\text{OPh}$ has been used in organic EL matrix device and three-color device research,^{12,13)} but there is no detailed report on the material itself. In order to investigate the effects of the secondary ligand, two new derivatives have also been synthesized and characterized.

2. Experimental

$\text{Alq}'_2\text{OPh}$ was prepared according to the following steps. A solution of phenol (0.5 M) in 10 ml toluene was added to a solution of aluminum isopropoxide (0.5 M) in 10 ml toluene

with intensive stirring. After about 10 min, a solution of 2-methyl-8-hydroxy-quinoline (1.0 M) in 10 ml toluene was added slowly. The mixture was continuously stirred for about 1 h, during which time a light yellow precipitate was formed. Then the mixture was cooled to room temperature and kept in dark for about 10 h. The product was collected by filtration and washed with toluene. The materials were further purified by the train sublimation method. Based on similar procedure, two derivatives of $\text{Alq}'_2\text{OPh}$, bis(2-methyl-quinolinolato)(4-chloro-phenolato) aluminum(III) ($\text{Alq}'_2\text{OPh-Cl}$) and bis(2-methyl-quinolinolato)(4-methoxy-phenolato) aluminum(III) ($\text{Alq}'_2\text{OPh-OMe}$), have also been synthesized and purified. $\text{Alq}'_2\text{OPh-Cl}$ and $\text{Alq}'_2\text{OPh-OMe}$ are two new materials, which have not been reported before. The molecular structures of the synthesized materials are shown in Fig 1.

The EL devices were fabricated using conventional vacuum vapor deposition under a $2 \times 10^{-3} \text{ Pa}$ vacuum at room temperature. There are two device structures for $\text{Alq}'_2\text{OPh}$: ITO/TPD (40 nm) / $\text{Alq}'_2\text{OPh}$ (80 nm) / MgAg (10 : 1) (A) and ITO/TPD (40 nm) / $\text{Alq}'_2\text{OPh}$ (60 nm) / Alq_3 (20 nm) / MgAg (10 : 1) (B). The device structures for $\text{Alq}'_2\text{OPh-Cl}$ and $\text{Alq}'_2\text{OPh-OMe}$ are the same as structure A.

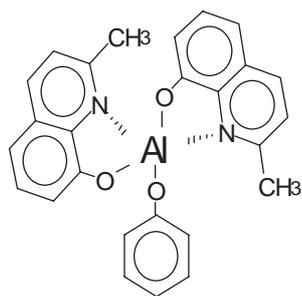
In order to measure the photoluminescence (PL) and absorption spectra, Pure films of $\text{Alq}'_2\text{OPh}$, $\text{Alq}'_2\text{OPh-Cl}$ and $\text{Alq}'_2\text{OPh-OMe}$ on quartz glass have also been prepared by vacuum vapor deposition.

3. Results and Discussion

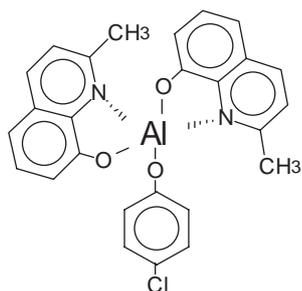
In our experiment, it was found that with $\text{Alq}'_2\text{OPh}$ as the emitting layer, the maximum wavelength of EL emission was at around 495 nm (Fig. 2.). The maximum brightness of the structure A was up to 2000 cd/m^2 and that of the structure B was up to 4000 cd/m^2 (Fig. 3.). The maximum efficiencies were up to 1.0 lm/W (A) and 1.4 lm/W (B), respectively (Fig. 4). It was also found that the devices exhibit good stability. Obviously, device B showed better performance than device A. That was due to the shift of the light emitting one away from the cathode, thus avoiding the possible exciton quenching occurring at the organic film-metal film interface.

Compared with Alq_3 , the advantage of using $\text{Alq}'_2\text{OPh}$ as light emitting material is that almost all the desirable physi-

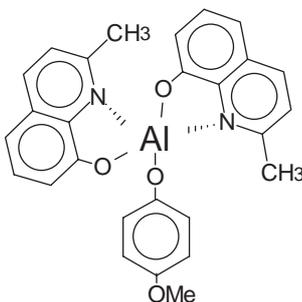
*E-mail: qiuy@mail.tsinghua.edu.cn



(a)



(b)



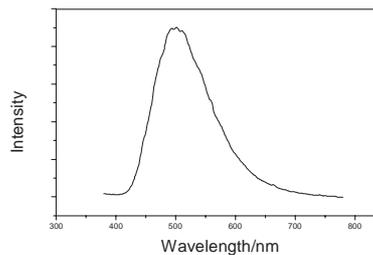
(c)

Fig. 1. The molecular structure of compounds. (a) $\text{Alq}_2'\text{OPh}$, (b) $\text{Alq}_2'\text{OPh-Cl}$, (c) $\text{Alq}_2'\text{OPh-OMe}$.

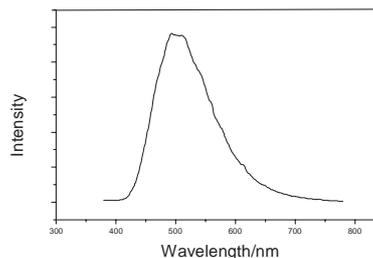
cal properties of Alq_3 are retained while emission was shifted to the blue region of the spectrum. It is reasonable to think that the presence of the phenolato ligand is responsible for the shift.

In the molecular structure of $\text{Alq}_2'\text{OPh}$, $-\text{OPh}$ is regarded as a secondary ligand. In order to further investigate the effect of the secondary ligand, we prepared $\text{Alq}_2'\text{OPh-Cl}$ and $\text{Alq}_2'\text{OPh-OMe}$. Similarly, $\text{Alq}_2'\text{OPh-Cl}$ and $\text{Alq}_2'\text{OPh-OMe}$ exhibited good stability as $\text{Alq}_2'\text{OPh}$. There was no distinct difference among the absorption spectra of these compounds.

All three compounds exhibited strong fluorescence. But the PL and EL spectra were different from each other. The normalized EL spectra of $\text{Alq}_2'\text{OPh}$, $\text{Alq}_2'\text{OPh-Cl}$ and $\text{Alq}_2'\text{OPh-OMe}$ are shown in Fig. 5. Table I summarizes the PL and EL peak wavelengths, the device luminous efficiencies and the maximum brightnesses of these compounds. The EL spectra are all red shifted with respect to their PL spectra. It is noted that $\text{Alq}_2'\text{OPh-Cl}$ and $\text{Alq}_2'\text{OPh-OMe}$, as the light emitting

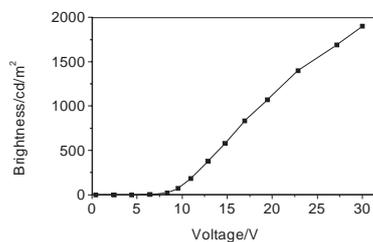


(a)

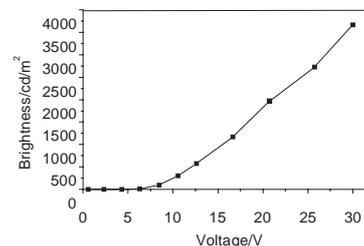


(b)

Fig. 2. The EL spectra of $\text{Alq}_2'\text{OPh}$. (a) ITO/TPD/ $\text{Alq}_2'\text{OPh}$ /MgAg, (b) ITO/TPD/ $\text{Alq}_2'\text{OPh}$ / Alq_3 /MgAg.



(a)

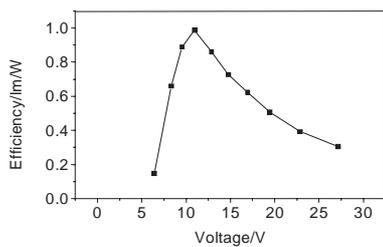


(b)

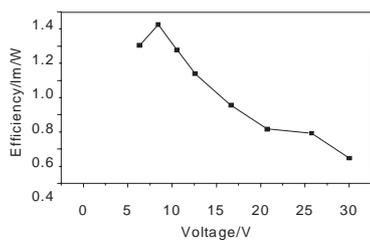
Fig. 3. The B - V curves of the devices. (a) ITO/TPD/ $\text{Alq}_2'\text{OPh}$ /MgAg, (b) ITO/TPD/ $\text{Alq}_2'\text{OPh}$ / Alq_3 /MgAg.

materials in the organic EL devices, did not show better performance than $\text{Alq}_2'\text{OPh}$.

Bryan *et al.*¹¹⁾ reported that as the phenolato group was replaced by 2-methylphenolato group, the additional steric effect introduced by the 2-methyl group would result in a further blue shift of the EL emission to 483 nm. In our work, however, compared with $\text{Alq}_2'\text{OPh}$, $\text{Alq}_2'\text{OPh-Cl}$ and $\text{Alq}_2'\text{OPh-OMe}$ with the secondary ligand, phenolato, being



(a)



(b)

Fig. 4. The efficiency curves of the devices (a) ITO/TPD/Alq₂'OPh/MgAg (b) ITO/TPD/Alq₂'OPh/Alq₃'/MgAg

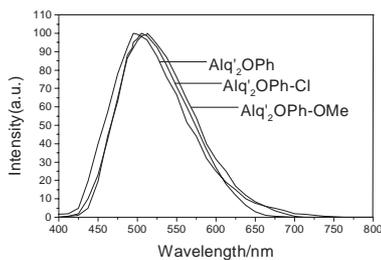


Fig. 5. The EL spectra of Alq₂'OPh, Alq₂'OPh-Cl, Alq₂'OPh-OMe.

replaced by 4-chlorophenoto and 4-methoxyphenolato, respectively, showed no additional blue shift both in PL and EL spectra. This might be attributed to the fact that the introduction of a 4-chloro group or 4-methoxy group led to insignificant change in the sterical effect of the secondary ligand. It is worth noting that, however, red shifts of PL and EL wavelengths with respect to Alq₂'OPh have been observed for Alq₂'OPh-Cl and Alq₂'OPh-OMe. It is known that -Cl is an electron-withdrawing group, while -OMe is an electron-donating group. It seems that for the organometallic compound with a secondary ligand, not only the sterical effect but

Table I. PL and EL characteristics of the organometallic compounds.

Compound	PL peak (nm)	EL peak (nm)	The maximum efficiency (lm/W)	The highest brightness (cd/m ²)
Alq ₂ 'OPh	470	495	1.4	4000
Alq ₂ 'OPh-Cl	485	505	0.6	2900
Alq ₂ 'OPh-OMe	486	513	0.3	1000

also some other effect would be responsible for the change of the emission wavelength.

4. Conclusions

A high efficient blue light emitting organic EL material, Alq₂'OPh, has been synthesized and characterized. The comparison study of Alq₂'OPh, Alq₂'OPh-Cl and Alq₂'OPh-OMe demonstrated that some unknown effect rather than the sterical effect can also influence the light emission. In summary, our work indicates that the introduction of a secondary ligand in the molecular structure opens a new route for exploring new organometallic compounds for organic EL. Such efforts, however, will depend on the understanding of the structure-property relationship regarding these compounds.

Acknowledgement

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