

Electroluminescent properties of a Schiff-base aluminum complex in single layer polymer light-emitting diodes

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The Schiff-base ligand aluminum complex, [AlMe₂] [L = *ortho*-C₆H₄(NC₆H₃Me₂-2,6)(CH=NC₆H₃Me₂-2,6)], has been synthesised and characterised; its electroluminescent properties are reported. Electroluminescent devices were fabricated by doping [AlMe₂] in a polymer host of poly (vinylcarbazole) (PVK) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) using a simple solution spin-coating technique. The single-layer polymer organic light-emitter devices exhibited green emission, showed maximum current efficiency of 1.4 cd/A and maximum luminance of near 1000 cd/m².

Keywords: electroluminescence, Schiff-base ligand, aluminum complex

Following early reports^{1,2} organic and polymer light-emitting diodes (LEDs) have received considerable attention due to their potential applications in various displays.³⁻⁶ These devices are able to produce all emission colours in accordance with a wide selection of organic emitting materials. In recent years fluorescent organometallic- and coordination-complexes have attracted extensive attention, many luminescent complexes of main group and transition metals, such as Al(III),⁹⁻¹³ B(III),^{12,13} Be(II),¹⁴⁻¹⁷ and Zn(II)¹⁸ complexes, have been designed, synthesised and applied in OLEDs. Particularly, chelate aluminum complexes have attracted much attention due to their low cost, good luminescent and electron-transporting properties. Leung *et al.* reported the AlMq₂OH complex to achieve a blue OLED with luminance of 14000 cd/m² at 480 mA/cm² and a current efficiency of 5.03 cd/A.¹⁸ An oxadiazole aluminum complex (AlPOP) was reported to exhibit strong blue emission with high external quantum efficiency and brightness in two-layers devices.¹⁹ Anzenbacher *et al.* reported Al(q)₃ complexes in which the 5-position of the 8-hydroxyquinoline (q) ligand is modified with electron-withdrawing or electro-donating groups (EWG/EDG) that can be tuned to wavelengths across the visible spectrum.⁹⁻¹³ However, organic light-emitting devices with fluorescent organometallic complexes as the emitting layer are generally fabricated by vapour-deposition technology, which requires increased amounts of dyes and requires an expensive device. Fortunately, spin-coating of blended polymer solutions to fabricate single-layer polymer devices is easy and offers a promising low-cost technique for large-area display application.²⁰⁻²² Nevertheless, polymer light-emitting devices obtained by doping the fluorescent complex are still scarce.^{23,24}

Complexes with Schiff-bases are interesting for their simple synthesis, easily tunable properties by changing the substituents on the Schiff-base ligands, and good stability in electroluminescent (EL) devices.²⁵⁻²⁷ We have recently focussed our attention on the photoelectric properties of coordination complexes.²⁸⁻³¹ Previously, we reported a series of luminescent aluminum complexes with chelating anilido-imine ligands that produce bright fluorescence in both solution and the solid state, and the emission colour in solution can be tuned by the *ortho*-substituents on the rotatable aryl rings of the ligands.²⁸ As a continuation of studies on the luminescent aluminum complexes, herein we report here

the electroluminescent characterisations of [AlMe₂{*ortho*-C₆H₄(NC₆H₃Me₂-2,6)(CH=NMe₂C₆H₃-2,6)}] ([AlMe₂L]).

Experimental

Materials

Toluene and hexane were dried by refluxing over sodium and benzophenone and distilled under nitrogen gas prior to use. C₆D₆ was dried over activated 4 Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. AlMe₃, poly (vinylcarbazole) (PVK) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) were purchased from Aldrich and used as received. *ortho*-C₆H₄(NHC₆H₃Me₂-2,6)(CH=NMe₂C₆H₃-2,6) was prepared according to published literature.²⁸ NMR spectra were measured using a Varian Mercury-300 NMR spectrometer.

Physical measurements

The elemental analyses were performed on a Perkin-Elmer 2400 analyser. UV-Vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with a RF-5301PC instrument.

Synthesis of the complex

[AlMe₂{*ortho*-C₆H₄(NC₆H₃Me₂-2,6)(CH=NMe₂C₆H₃-2,6)}].²⁸ A solution of *ortho*-C₆H₄NH(C₆H₃Me₂-2,6)(CH=NC₆H₃Me₂-2,6) (0.20 g, 0.61 mmol) in *n*-hexane (10 ml) was slowly added to a solution of AlMe₃ (0.61 mmol) in *n*-hexane (15 ml) at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min, and at room temperature for additional 2 h, then was concentrated to about 10 ml and kept at -20 °C overnight to let the product crystallise. The product was obtained as orange-green crystals (0.21 g, 90%). Anal: Calcd for C₂₅H₂₉N₂Al (384.49): C, 78.09; H, 7.60; N, 7.29. Found: C, 78.21; H, 7.51; N, 7.37%. ¹H NMR (C₆D₆, 293 K): δ -0.50 (s, 6H, Al(CH₃)₂), 2.15 (s, 6H, Ph-CH₃), 2.29 (s, 6H, Ph-CH₃), 6.31 (t, 1H, Ph-H), 6.73 (d, 1H, Ph-H), 6.80–7.16 (m, 8H, Ph-H), 7.32 (s, 1H, HC=N) ppm.

Device fabrication.³⁵

Indium-tin-oxide (ITO)-coated glass with a sheet resistance of <50⁻¹ was used as substrate. The substrate was pre-patterned by photolithography to give an effective device size of 4 mm². Pre-treatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. Active layers were spin-coated from chloroform solutions containing 20 mg/ml of x% by weight [AlMe₂L] in polymer on ITO substrates to give film thickness of 80–100 nm. The cathode barium Ba was deposited (50 nm) by thermo-evaporation, followed by a thick Al capping layer. The electroluminescence and luminance were recorded on a PR65-spectrometer. Current voltage and light intensity measurements were made at room temperature and ambient conditions.

Results and discussions

Photoluminescent properties

Figure 1 shows the chemical structures of the Schiff-base aluminum complex and polymer hosts used in this study. The UV-Vis absorption and fluorescence spectra of [AlMe₂L] in chloroform solution are in

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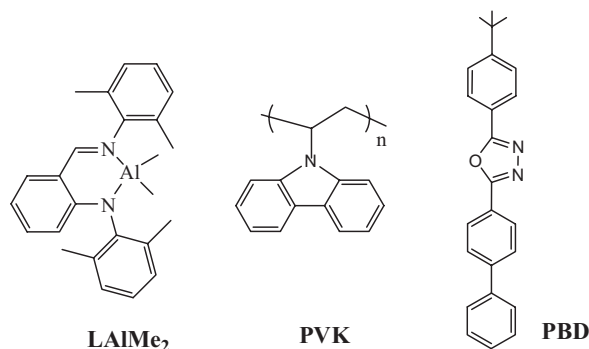


Fig. 1 The molecular structures of relevant compounds used in this study.

Fig. 2. The absorption and emission peaks of $[\text{AlMe}_2\text{L}]$ are at 456 nm and 520 nm in chloroform, respectively. The Stokes shift is 64 nm and the overlapping area between the absorption and emission peak is small. However, $[\text{AlMe}_2\text{L}]$ in the solid state emit bright fluorescence with an emission maximum of 531 nm (Fig. 2), which are red shifted in comparison with the emission maximum in solution. This is attributed to the π - π stacking of aromatic rings in the molecules in the solid state. The polymer blend PVK-PBD (40 wt.%) was selected as the host to facilitate Förster energy transfer because its emission band overlaps the absorption spectrum of $[\text{AlMe}_2\text{L}]$ as shown in Fig. 2.

Electroluminescent properties

To understand the EL properties of $[\text{AlMe}_2\text{L}]$, single layer polymer light-emitting devices using it as the dopant emitter were fabricated and examined. Use of PVK and PBD as the mixture host material for phosphorescent emitters in electroluminescent devices has been well documented previously.^{32,33} PVK is known as a good hole-transporting material and PBD is an electron-transport material. In fact PVK-PBD was employed as the mixture host to enhance the balance of carriers in the light-emitting layer and enhance the emitting efficiency of the device. The device's structure was as follows: ITO/PVK-PBD (40 wt.%): x wt.% $[\text{AlMe}_2\text{L}]/\text{Ba}/\text{Al}$. The emitting layer, $[\text{AlMe}_2\text{L}]$ -doped polymer PVK-PBD (40 wt.%), was spin-cast onto the surface of ITO from the chloroform solution. The thickness of the doped PVK-PBD films was approximately 80 nm. In previous experiments it was proved that Ba/Al is a more suitable cathode than LiF/Al for PVK-PBD devices because of the low work function of Ba of 2.48 eV (4.36 eV for LiF/Al).³⁴

To test the efficiency of the Förster energy transfer, films contain PVK-PBD (40 wt.%) with different concentrations of $[\text{AlMe}_2\text{L}]$ were prepared and excited optically at 325 nm radiation. Figure 3(a) shows normalised photoluminescence (PL) spectra of $[\text{AlMe}_2\text{L}]$ -doped PVK-PBD devices with doping concentrations of 0.3%, 1% and 3% (w/w). The PL profile contains two peaks: one is centred at ~ 425 nm from emission of the PVK-PBD host; the other peak is of lower energy and is due to $[\text{AlMe}_2\text{L}]$ emissions. The lower energy emission peaks occur at 519 nm and are not red-shifted with increasing doping concentration. The host emission at 425 nm decreased

significantly with increasing doping concentration, 1% (w/w) $[\text{AlMe}_2\text{L}]$ was required to completely quench the host PL. Figure 3(b) shows the corresponding EL spectra obtained from the devices made from the same solutions. The emission at 430 nm disappears at doping concentration higher than 1% (w/w). The EL emission spectra dominated by $[\text{AlMe}_2\text{L}]$ have a central wavelength at 513 nm and a full width at half maximum of 76 nm. In $[\text{AlMe}_2\text{L}]$ doping devices the maximum emission peaks do not vary with doping concentration. The decrease in host emission and simultaneous increase in $[\text{AlMe}_2\text{L}]$ emission are consistent with Förster energy transfer from the PVK-PBD to $[\text{AlMe}_2\text{L}]$ [Fig. 3(a) and 3 (b)].^{35,36}

In Fig. 4 (supporting information held by author) the EL spectra of doping concentration 3 wt% $[\text{AlMe}_2\text{L}]$ in the PVK-PBD device with applied voltage from 10 V to 14 V, shows a stable green emission from $[\text{AlMe}_2\text{L}]$ with a peak at 513 nm. The Commission Internationale de l'Éclairage (CIE 1931) coordinates remained nearly constant from (0.2822, 0.5867) at 10 V to (0.2869, 0.5861) at 14 V. The performance parameters of PLEDs based on the concentrations 0.3, 1.0, 3.0 wt% $[\text{AlMe}_2\text{L}]$ and 3.0 wt% Alq_3 in PVK-PBD blends of the devices are listed in Table 1. It was found that the 3.0 wt% $[\text{AlMe}_2\text{L}]$ doping concentration is most suitable for obtaining high EL efficiency (1.41 cd/A). At the same doping concentration (3.0 wt%), the EL efficiency of the $[\text{AlMe}_2\text{L}]$ device is two times that of Alq_3 , this could be attributed to stronger intermolecular π - π interaction for Alq_3 in the solid state.³⁷ The current density (J) and luminance (L) versus applied voltage (V) characteristics of the 3% $[\text{AlMe}_2\text{L}]$ -doped PVK-PBD device is shown in Fig. 5 (supporting information held by author). The turn-on voltage of this device is 7.5 V (at brightness of 1 cd/m^2). The device has a luminance of 404 cd/m^2 at voltage of 12 V and current density of 16.54 mA/cm^2 , and the luminance reaches near 1000 cd/m^2 at voltage of 17 V and current density of 75.13 mA/cm^2 . Figure 6 (supporting information held by author) shows the luminous efficiency (LE) as a function of the current density (J) of the

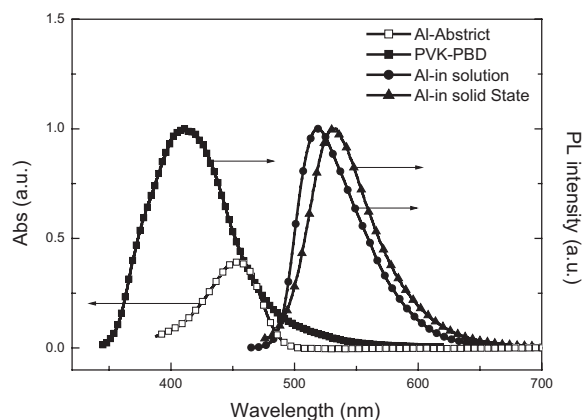
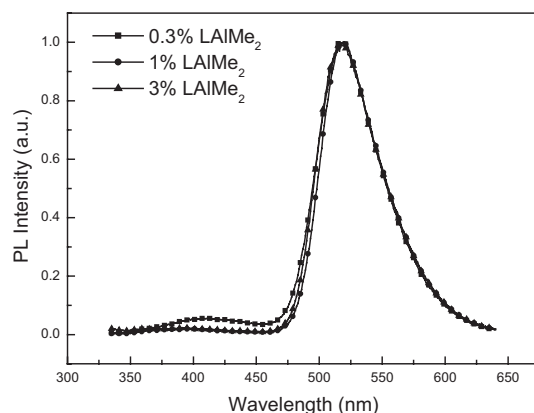
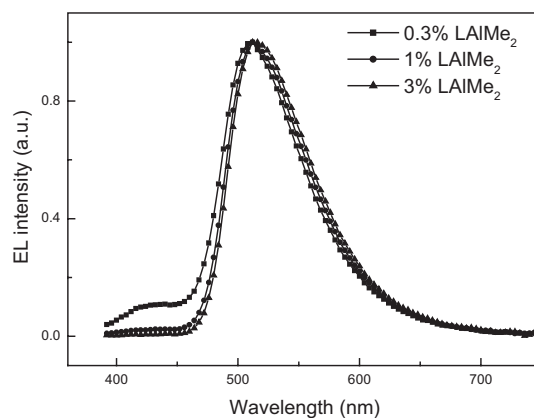


Fig. 2 The absorption, emission spectra of $[\text{AlMe}_2\text{L}]$ and emission spectra of PVK-PBD (40 wt.%).



(a)



(b)

Fig. 3 (a) PL spectra of $[\text{AlMe}_2\text{L}]$ doped PVK-PBD (40wt%) film with different concentrations. (b) EL spectra of single layer device ITO/PVK-PBD: x % $[\text{AlMe}_2\text{L}]/\text{Ba}/\text{Al}$. (The concentration of $[\text{AlMe}_2\text{L}]$ used were 0.1%, 1% and 3% by weight).

Table 1 The performances for the single-layer polymer devices. The devices structure is ITO/PVK–PBD: x% [AlMe₂L] or Alq₃/Ba/Al

Compound	Concentration/wt%	Turn-on /V	LE _{max} /cd/A	PE _{max} /lm/W	B _{max} /cd/m ²
[AlMe ₂ L]	0.3	5.0	0.63	0.26	528
[AlMe ₂ L]	1.0	5.5	0.82	0.42	1197
[AlMe ₂ L]	3.0	7.5	1.41	0.49	908
Alq ₃	3.0	10.0	0.71	0.20	84

device made from PVK–PBD with 0.3, 1.0 and 3.0 wt% [AlMe₂L]. The efficiencies of the devices increase as the current densities increase at first and then decrease after reaching the maximum value. The LE_{max} is from 0.63 cd/A to 1.41 cd/A for 0.3–3% doping concentration of [AlMe₂L] in PVK–PBD. For larger doping concentration (>5%) the device efficiency decreases significantly (not shown). We consider that this LE_{max} (1.41 cd/A at 3.78 mA/cm²) for the single-layer polymer electroluminescent devices by the doped fluorescent complex is acceptable. In addition, at the larger current density (33 mA/cm²) for the device of doped 3% [AlMe₂L], a good LE (0.90 cd/A) was obtained. Such decreasing of LE is slow in these PLEDs, which is possibly due to the bulky Schiff-base ligand suppressing aggregation of the dopant aluminum complex.

Conclusion

We have investigated the electroluminescent properties of an aluminum complex that has an anilido-imine conjugated Schiff-base ligand. Single layer polymer light-emitting devices were fabricated by doping the Schiff-base aluminum complex in a polymer host using a simple solution spin-coating technique. The Förster energy transfer is the dominant electroluminescence mechanism in these devices. The doping concentration 3 wt.% in the single-layer polymer light-emitting device achieved a maximum current efficiency of 1.4 cd/A and with maximum brightness of 908 cd/m².

This work was supported by the National Natural Science Foundation of China (No. 20674024) and Ministry of Science and Technology of China (No. 2002CB6134003). One of the authors (Dr X. Liu) is grateful for financial support from Jilin University.

Received 17 March 2008; accepted 5 August 2008

Paper 08/5163 doi:10.3184/030823408X354758

Published online: 10 October 2008

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