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Synthesis and light emitting properties of polymeric metal complex dyes based on hydroxyquinoline moiety

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Abstract

Two kinds of polymeric metal complex dyes, Al(PHQ) **6** and Zn(PHQ) **7**, have been prepared. New polymeric dyes were examined as an light emitting material in organic EL devices. The forward bias turn-on voltage for the EL devices is 8 V for Al(PHQ) **6**.

Keywords: Metal complex dye; 8-Hydroxyquinoline; Electroluminescence; Photoluminescence

1. Introduction

An appreciable amount of research has been carried out in the field of organic electroluminescence (EL) based optoelectronic devices during the last decade. A variety of organic materials have been investigated as active layers for optimizing device performances.

Since the first discovery of the double organic layer EL devices [1] consisting of diamine hole-transport layer and a 8-hydroxyquinoline aluminium (Alq_3) complex emitting layer in 1987, EL devices have been studied due to their practical application as a full-colour flat panel displayers

After Tang's research work, other 8-hydroxyquinoline derivatives metal complexes were also used as emitters [2]. In order to obtain the high performance organic light-emitting diodes, organic materials are required to have good thermal stability and the ability to form amorphous thin films. Organic electroluminescent devices consist of one or more organic layers sandwitched between two electrodes, one of which must be transparent. A wide range of organic materials have been used in such devices, with these being typically divided into low-molecular-weight materials deposited by vacuum sublimation, and conjugated polymers deposited by spin coating.

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In this paper, we wish to report the new synthesis of polymeric metal complex dyes containing hydroxyquinoline moiety. Further, EL properties of multi-layered EL device using polymeric metal complex dye as the emitting material were report.

2. Experimental

Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. UV-visible spectra were recorded on a Shimadzu 2100 spectrometer. IR spectra were measured with a Nicolet Magna 550 IR spectrometer. Melting points were determined using an Electro-thermal IA 900 apparatus and are uncorrected.

2.1. Material

8-Hydroxyquinaldine, zinc chloride and aluminum sulfate octadecahydrate, were purchased from Aldrich Chemical Company. Terephthalaldehyde, triethylamine and acetic anhydride were purchased from Tokyo Kasei Kogyo Co. All chemicals were of the highest grade available and were used without further purification.

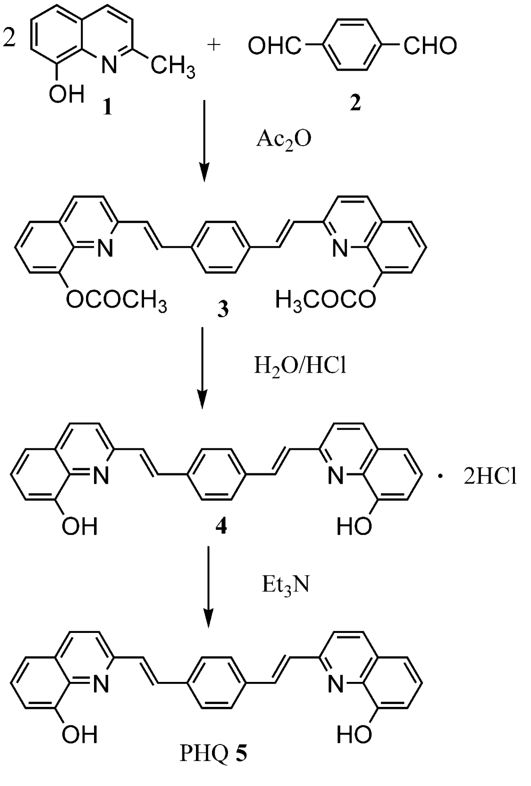
2.2. Synthesis of 2,2′-(1,4-phenylenedivinylene)bis-8-hydroxyquinoline (PHQ, 5) (Scheme 1)

2,2′-(1,4-Phenylenedivinylene)bis-8-hydroxyquinoline (PHQ, **5**) was synthesized according to the method in Ref. [3].

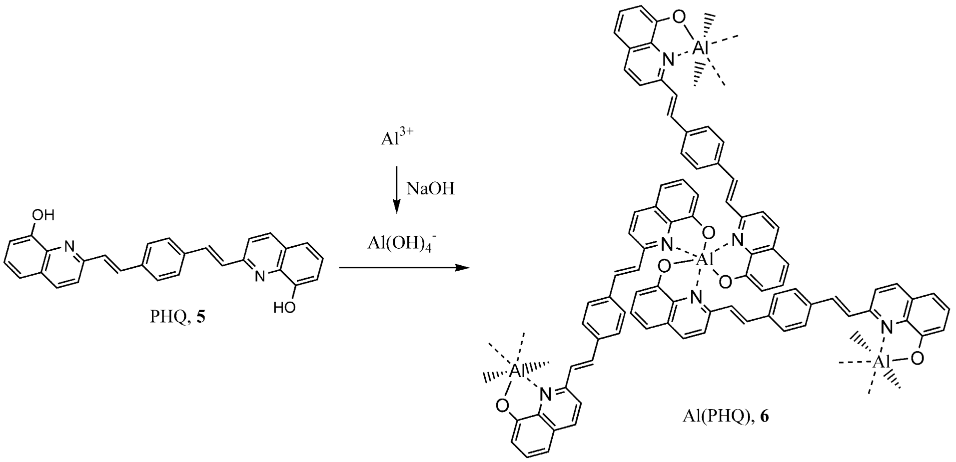
A mixture of 8-hydroxyquinaldine **1** (0.10 mol, 15.9 g), terephthalaldehyde **2** (0.05 mol, 6.7 g) and acetic anhydride (35 ml) was stirred and heated at 125 °C for 40 h under nitrogen. After cooled, it was subsequently poured into ice water (300 ml) and stirred overnight. The yellow solid obtained was filtered and washed with water and acetone. Yield 21.2 g, 85%. A purified sample was obtained by recrystallization from DMF and had a melting point of 261–263 °C. Elemental analysis: found C: 76.64, H: 4.38, N: 5.55 (%), calculated for $C_{32}H_{24}N_2O_4$ C: 76.78, H: 4.83, N: 5.60 (%). UV (in DMF): $\lambda_{max} = 386$ nm. MS: 500 (M^+).

2,2′-(1,4-Phenylenedivinylene)bis-8-acetoxyquinoline **3** (0.03 mol, 15.0 g) was dissolved in DMF (100 ml) by heating at 120 °C. Aqueous hydrochloric acid (35%, 70 ml) was added to the solution and the mixture was heated at 120–130 °C for 2 h. The precipitated orange solid was filtered off, washed with water, and dried to afford PHQ dihydrochloride **4**, yield 14.4 g, 97%.

A flask was charged with a mixture of PHQ dihydrochloride **4** (0.02 mol, 9.8 g) and DMF (100 ml). Triethylamine (0.04 mol, 4.1 g) was added to the solution at the boiling point and a red solution was obtained. It was subsequently poured into ice water (300 ml). The yellow solid obtained was filtered off, washed with water and dried to afford to PHQ **5** (7.2 g 87%). A purified PHQ was obtained by recrystallization from toluene and had a melting point of 225–227 °C. Elemental analysis:



Scheme 1.



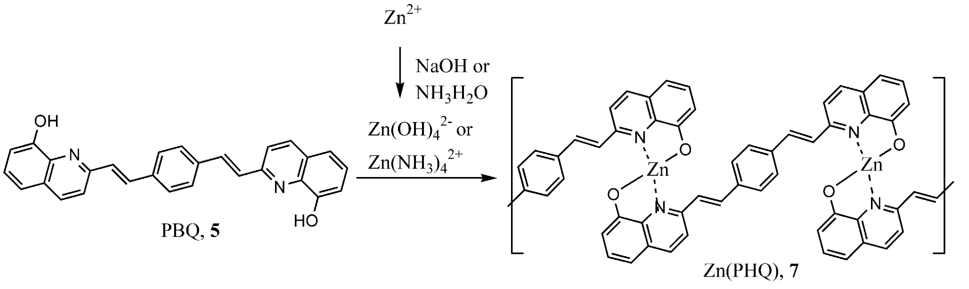
found C: 80.93, H: 4.55, N: 6.83 (%), calculated for $C_{28}H_{20}N_2O_2$ C: 80.76, H: 4.86, N: 6.72 (%). UV (in DMF): $\lambda_{max} = 388$ nm. MS: 416 (M^+, 100%). ^1H NMR in $(CD_3)_2CO$ (ppm): 7.12 (d, 2H, $J = 1.3$ Hz), 7.40 (m, 4H), 7.56 (d, 2H, $J = 16.2$ Hz), 7.79 (d, 2H, $J = 7.7$ Hz), 7.80 (s, 4H), 8.19 (d, 2H, $J = 16.2$ Hz), 8.31 (d, 2H, $J = 8.6$ Hz), 9.62 (s, 2H).

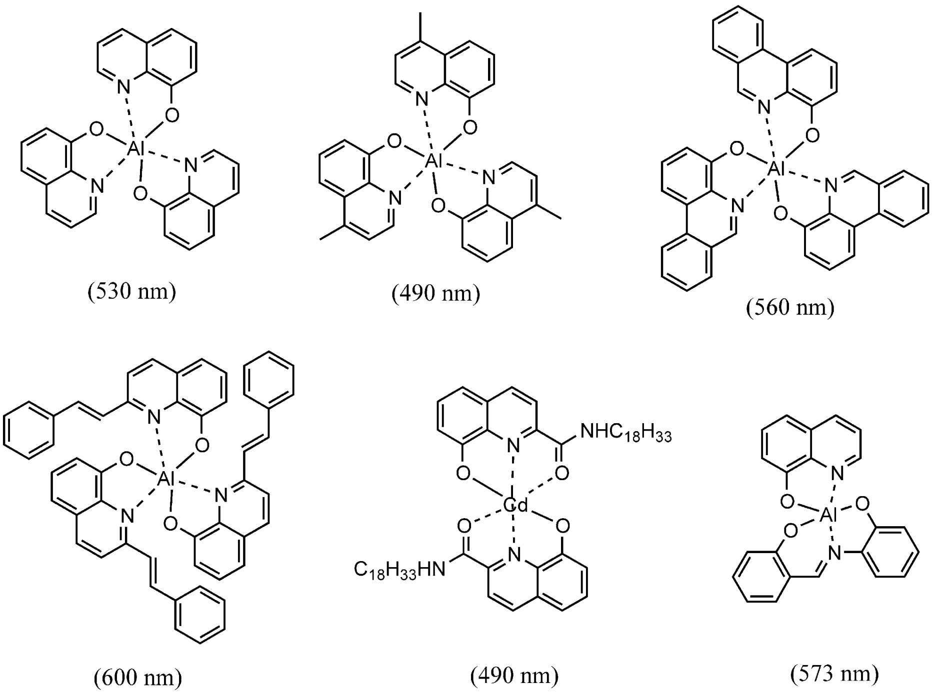
2.3. Preparation of aluminum complex of PHQ: (Al(PHQ), 6)

Al(PHQ) was prepared from PHQ and $Al_2(SO_4)_3 \cdot 18H_2O$ in DMF. Aqueous solution of sodium hydroxide was dropped into the solution of $Al_2(SO_4)_3 \cdot 18H_2O$ (0.001 mol, 0.666 g) in water (10 ml) until the precipitated solid was dissolved completely, and then DMF (50 ml) was added to the solution of Al(III). The Al(III) solution obtained was added dropwise into the solution of PHQ (0.003 mol, 1.25 g) in DMF (100 ml) while stirring, and keep stirring for 24 h. The yellow precipitate obtained was filtered off, washed with DMF 3 times and then water 3 times, and dried at 50 °C overnight. Yield 1.1 g, 90%. Melting point is higher than 300 °C. Elemental analysis: found C: 77.13, H: 4.35, N: 6.23 (%), calculated for $Al_2(C_{28}H_{18}N_2O_2)_3$ C: 77.77, H: 4.20, N: 6.48 (%).

2.4. Preparation of zinc complex of PHQ: (Zn(PHQ), 7)

Zn(PHQ) 7 was prepared from PHQ 5 and $ZnCl_2$ in DMF. Aqueous solution of sodium hydroxide (or aqueous solution of ammonia, 25%) was dropped into the solution of $ZnCl_2$ (0.002 mol, 0.272 g) in water (10 ml) until the precipitated solid was dissolved completely, and then DMF (30 ml) was added to the solution of Zn(II). The Zn(II) solution obtained was added dropwise into the solution of PHQ 5 (0.002 mol,





(530 nm) (490 nm) (560 nm)

(600 nm) (490 nm) (573 nm)

Fig. 1.

0.832 g) dissolved in DMF (70 ml) while stirring, and keep stirring for 24 h. The orange precipitate obtained was filtered off, washed with DMF 3 times and water 3 times, and dried at 50 °C overnight. Yield 0.85 g, 87%. Melting point is higher than 300 °C. Elemental analysis: found C: 69.17, H: 3.82, N: 5.66 (%), calculated for $Zn(C_{28}H_{18}N_2O_2)$ C: 70.09, H: 3.78, N: 5.84 (%).

2.5. *Measurement of electrical and luminescent characteristics*

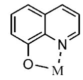
Al(PHQ) or and TPD(*N*,*N*′-diphenyl-*N*,*N*′-di(*m*-tolyl)benzidine) used as an emitting layer and a hoe transporting layer in EL devices. The structures of organic EL devices was ITO/PEDOT/TPD/Al(PHQ)/Al.

Poly(3,4-ethylenedioxythiophene)(PEDOT) as a hole conducting buffer layer was spin coated on the patterned pre-cleaned indium-tin oxide(ITO)-coated glass substrates. In device with Al(PHQ), all organic TPD and Al(PHQ) dye layers and Al cathode were deposited by vacuum thermal evaporation on PEDOT layer under a vacuum of about 2×10^{-6} Torr. The thicknesses of Al(PHQ) film and Al cathode were about 50 and 100 nm, respectively, which measured by a quartz crystal thickness monitor placed near the substrate. The active area of devices is 3.0×3.0 mm^2.

The electrical and luminescent characteristics of EL devices were analyzed by using a sourcemeter 2400 (Keithley) and an optical power meter 1830S (Newport). Photoluminescence (PL) spectra were measured using a Spectra Pro-300I (Princeton Instruments).

3. Results and discussions

8-Hydroxyquinoline (1) and its derivatives have been found extensive application as analytical reagents for examples, for example, in solvent extraction, absorption spectrophotometry and fluorometry, because of their ability to form complesex with many metal ions [4]. Many metal ions react with electropair donors to form coordination compounds or complexions. 8-Hydroxyquinoline combines with metal ions regardless of the charge on the cation. 8-hydroxyquinoline forms N,O-bidentate complexes with virtually all cations, most of which are sufficiently stable to form the basis of a volumetric analysis.



Mg^{2+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} (yellow ppt), Fe^{3+} (greenish black), Fe^{2+} (red ppt)

The most common emitter used in organic EL devices, aluminium tris(8-hydroxyquinoline) (Alq_3) and some of its derivatives are shown in Fig. 1.

In the EL diode with Alq_3, high external quantum efficiency and brightness are achievable at a low driving voltage. EL emission is centered 530 nm, but by varying either the central metal or surrounding ligands it is possible to tune the

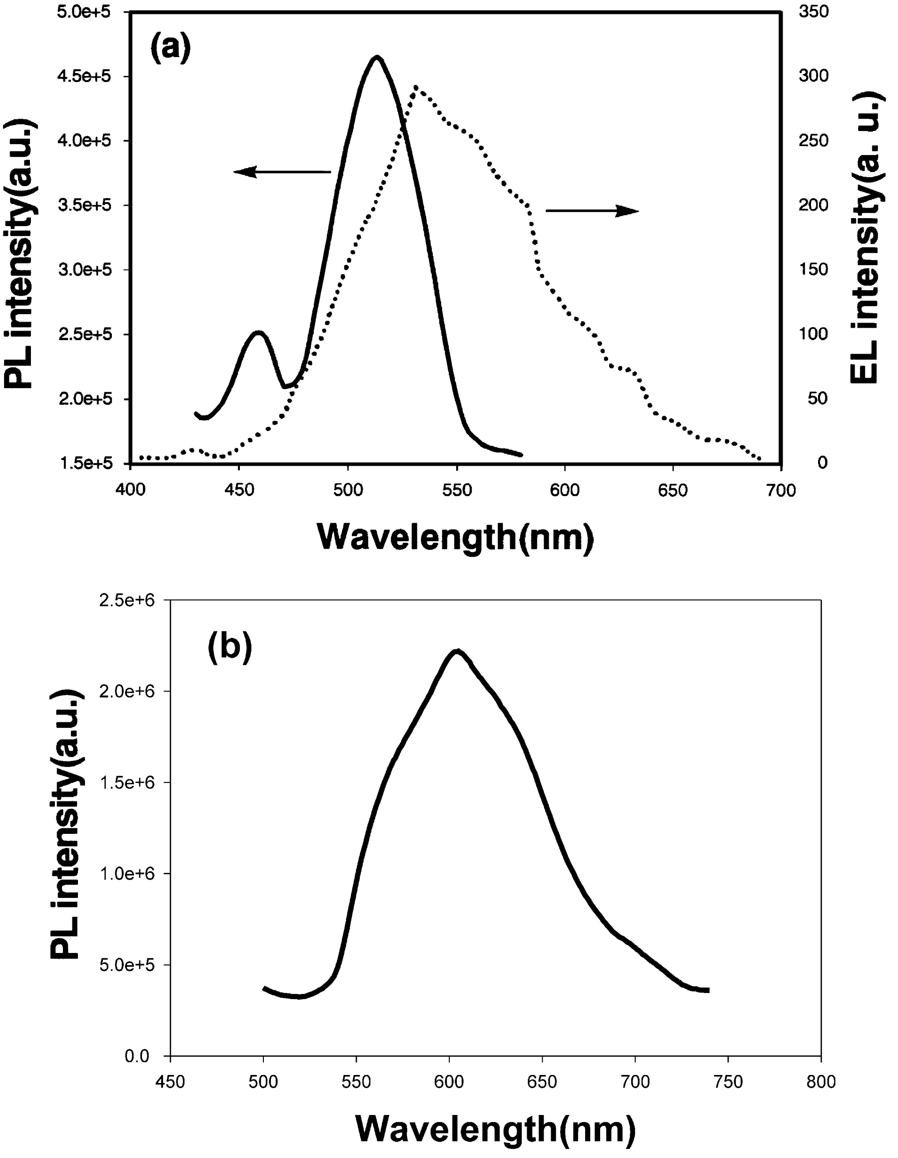


Fig. 2. Photoluminescence and electroluminescence spectra of the EL device with (a) Al(PHQ) 6 and (b) Zn(PHQ) 7.

emission wavelength Fig. 1 [2,5–7]. During the course of our investigation on the synthesis and light emitting property of Alq3 derivatives, we have found that PHQ **5** is a good candidate for polymeric metal complex dyes as emitters in organic EL devices. Diakoumakos Costanos and Mikroyannidis prepared polyesters, polyurethanes, and epoxy resins derived from 2,2′-(1,4′-phenylenedivinylene)bis-8-hydroxyquinoline (PHQ, **5**) [3].

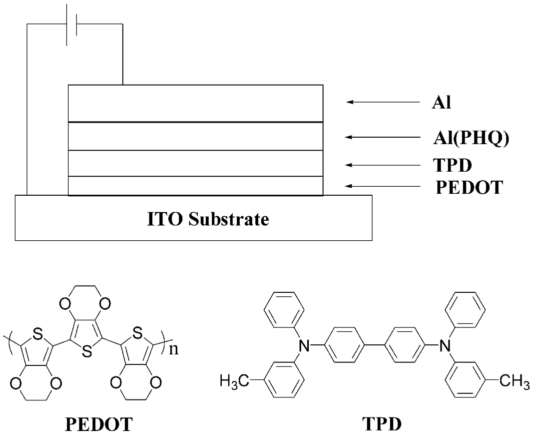


Fig. 3. Device configuration of LED and molecular structures of PEDOT and TPD.

2,2′-(1,4-Phenylenedivinylene)bis-8-hydroxyquinoline(PHQ, **5**) was used as starting material for the preparation of polymeric metal complex dyes for EL emitting material. 8-Hydroxyquinaldine (**1**) was condensed with a half molar amount of 1,4-dibenzenedicarbaldehyde **2** in the presence of acetic anhydride to give 2,2′-(1,4-phenylenedivinylene)bis-8-acetoxyquinoline **3**. The acetoxy groups of the product were hydrolized in DMF in the presence of aqueous hydrochloric acid to yield PHQ hydrochloride **4**. PHQ dichloride **4** was treated with triethylamine in DMF to yield PHQ **5**. Al(PHQ) **6** was synthesized from aluminium sulfate octadecahydrate and PHQ **5**. To a solution of PHQ **5** in DMF, a solution of aluminium sulfate octadecahydrate in DMF/water containing an equivalent of sodium hydroxide was slowly added. After stirring for 24 h, the yellow precipitate was obtained. Zn(PHQ) **7** was prepared by similar procedure. The PL spectra of Al(PHQ) **6** and Zn(PHQ) **7** film are shown in Fig. 2. The PL spectra of a Al(PHQ) **6** and Zn(PHQ) **7** single layered film show two sharp peaks at 458 and 514 nm for Al(PHQ) **6** and a broad PL band around 605 nm for Zn(PHQ) **7**, respectively.

Fig. 3 shows the configuration of EL device fabricated in the present study and the structure of PEDOT and TPD. To facilitate hole injection

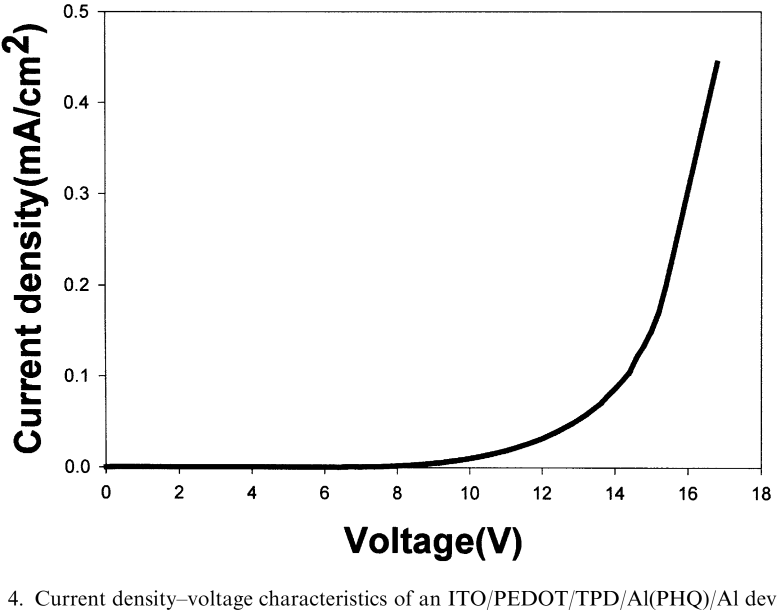


Fig. 4. Current density–voltage characteristics of an ITO/PEDOT/TPD/Al(PHQ)/Al device.

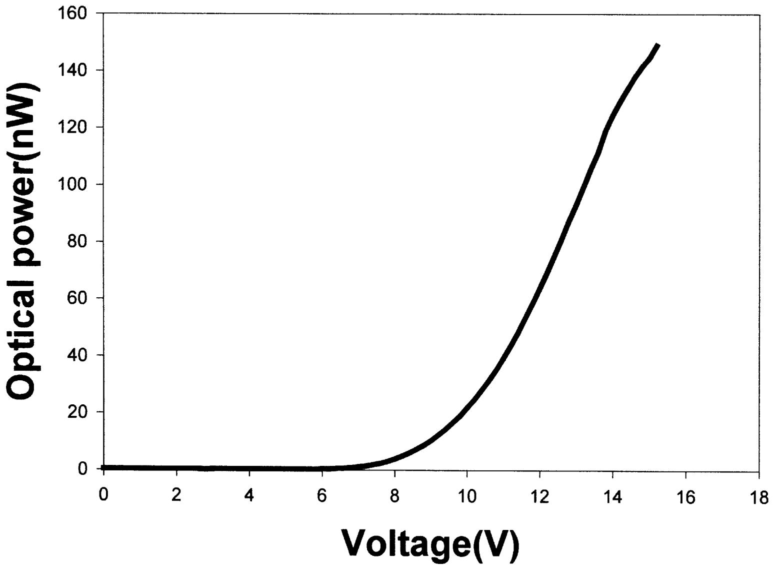


Fig. 5. Voltage–luminescence characteristics of the EL devices with Al(PHQ) **6**.

from anode, the hole injection layer, PEDOT was inserted between the hole injection electrode and TPD as the hole transport layer. Another advantage of the inserting of PEDOT are smoothened the anode surface and facilitated hole injection and reduced the probability for electrical shorts.

Fig. 4 shows the current density-voltage characteristics of the devices with Al(PHQ) **6**. The turn-on voltages of the devices with Al(PHQ) **6** is approximately 8V.

The luminescence versus applied voltage characteristics of the devices using Al(PHQ) **6** layer is shown in Fig. 5. The luminescence intensity was increased with increasing voltage in EL device. The maximum luminescence of the devices with Al(PHQ) **6** is about 149 nW/cm^2 at 15 V. However, the maximum luminescence of the devices with Zn(PHQ) **7** is still low as about 1.6 nW/cm^2 at 11 V. Although the maximum luminance was not satisfactory in EL device with Zn(PHQ) **7**, the performance of the EL devices with Zn(PHQ) **7** is expected to be improve by optimization of each layer.

Acknowledgements

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