Efficient and saturated blue organic polymer light emitting devices with an oxadiazole containing poly(fluorene) polymer emissive layer

Shu-jen Lee,[a,b] Joseph R. Gallegos,[c] Julien Klein,[a] M. David Curtis,[b,c] and Jerzy Kanicki*[a,b]

[a] Organic and Molecular Electronics Laboratory, Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI 48109
[b] Macromolecular Sci. & Eng. Center, University of Michigan, Ann Arbor, MI 48109
[c] Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

ABSTRACT

A new series of organic light emitting copolymers, poly(dioctyl fluorene -co - diphenyl oxadiazole)s P(DOF-DPO), are reported in this paper. We found organic polymer light emitting devices with comparable device efficiency and more saturated blue color based on this new series of copolymers with less than 10% DPO moiety when compared with poly(dioctyl fluorene) P(DOF) devices. The device structures used in this study were indium tin oxide (ITO) anode / PEDOT-PSS layer / emissive layer / calcium (Ca) / aluminum (Al) cathode, while the emissive layer was P(DOF) or P(DOF-DPO) copolymer with different DOF and DPO ratio. The AFM data shows that the emissive layer has a smooth surface with RMS roughness of about 0.5 ± 0.2 nm over a 2 µm by 2 µm area. The photo-luminescence quantum efficiency of the P(DOF-DPO) copolymer decreases with increasing DPO moiety. Both the photo-luminescence spectra and electro-luminescence spectra are slightly blue shifted when adding less than 10% DPO moiety into P(DOF). Both the emission efficiency (~0.3-0.6 cd/A at 100 cd/m^2) and power efficiency (~0.1-0.2 lm/W at 100 cd/m^2) of the P(DOF-DPO) based PLEDs with less than 10% DPO moiety are comparable to the P(DOF) based PLEDs.

Keywords: Organic polymer light-emitting devices (PLEDs), poly(dioctyl fluorene -co - diphenyl oxadiazole), quantum efficiency

1. INTRODUCTION

Balanced electron and hole injection is the key to achieving organic polymer light emitting devices (PLEDs) with high efficiency and long lifetime. Poly(dioctyl fluorene) P(DOF) based organic light emitting devices have achieved high efficiency for commercial application; however, the lifetime of the poly(fluorene) PLEDs is still limited for commercial application.[1, 2] Poly(dioctyl fluorene) is known as a highly fluorescent blue light emitting material, and oxadiazole containing molecules have widely been used as the electron transporting and hole blocking materials because of its relatively high electron affinity when compared with P(DOF) polymer.[3] Polymers containing DPO include poly(p-phenylene vinylene) (PPV) copolymers with DPO in the backbone with a 4,-4'-phenyl linkage and occasionally as a 4-phenyl linkage when in a pendant arrangement.[4,5] Both these mainchain and pendant arrangements of DPO-PPV copolymers have been shown to exhibit appreciable quantum efficiencies as well as showing good molecular stability during performance.[5] Although the literature is abundant with DPO-PPV copolymer studies, there seems to be none describing DPO and fluorene copolymers. The rationale for synthesizing poly(dioctyl fluorene diphenyloxadiazole) P(DOF-DPO) is two-fold. The first potential advantage is that the high device efficiency could be achieved by covalently combining the emissive property of the poly(dioctyl fluorene) and the electron transport property of the diphenyloxadiazole component without micro phase separation between two components. The second reason is to adjust the emissive color by the molecular design. In this paper, we report on the performance of bi-layer PLEDs fabricated on flexible plastic substrates from these new light emitting materials.

* Contact: Jerzy Kanicki; kanicki@eecs.umich.edu; http://www.eecs.umich.edu/omelab/; phone) 1-734-936-0972; fax) 1-734-615-2843; Organic & Molecular Electronics Lab. 1049 BIRB, 2360 Bonisteel Blvd. Ann Arbor, MI48109

2. EXPERIMENT

Synthesis of 2,5-(4-bromophenyl)-1,3,4-oxadiazole, 2,7-dibromo-9,9'-dioctylfluorene, and poly(dioctyl fluorene - co- diphenyl oxadiazole) will be reported elsewhere.[6] Polaroid plastic substrates coated with ITO were used in this work. The ITO layer was used as a transparent anode in PLEDs with a sheet resistance of ~ 10 ohm/□ and a transparency higher than 80% over the visible range (400 – 800 nm). The ITO covered substrates were cleaned in an ultrasonic bath of isopropanol for 20 minutes and exposed to UV-ozone for 10 minutes before polymer spin coating. First, a hole-transport layer (HTL, 300~400 Å), poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS), was spin coated from solution and thermally cured at 90°C for 20 minutes. Then, an emissive layer (EL, ~1000 Å) was spin-coated from the solution in xylene and cured at 90°C for one hour. A calcium cathode (~400 Å) and then an aluminum cathode (~2000 Å) as a capping layer were evaporated through shadow masks in a thermal evaporation system under a high vacuum (~10^{-7} torr).

The absorption spectra, photoluminescence (PL) spectra, and the film thickness were measured with a CARY 5 UV-Visible spectrophotometer, FluoroMax-2, and Dektak 3 surface profiler, respectively. The emissive layers used in these measurements were prepared on quartz substrates by spin coating (~1600 rpm, 10 seconds) with the same solution concentration (1.2 % wt/volume), resulting in a consistent film thickness of ~1000 Å. The cyclic voltammetry (CV) data were measured with a CHI 660A model from the CH Instruments. Tapping mode atomic force microscopy images were carried out using a Digital Instruments NanoScope III Atomic Force Microscope. The photo-luminescence quantum efficiency measurements were performed using the integrating sphere method.[7, 8] The electro-luminescence (EL) was measured in the air by a CCD spectrum system with optical fibers, which has been calibrated by a Labsphere USS -600 Uniform Source System with a light source and a programmable attenuator. An integrated system consisting of an INS250 integrating sphere coated with barium sulfate from the International Light, a programmable Keithley 617 electrometer, and a 230 voltage source was used for simultaneously collecting the optical and electrical data controlled by a home made program written in the Labview language. The integrating sphere was calibrated to measure the total flux into the sphere system. Therefore, the current-voltage-luminous flux (I-V-L) relationship was obtained. We then derived the luminous intensity from the measured data by assuming a Lambertian angular distribution of the emission.[9] The power efficiency is defined as the total output of optical power (lumen) over the input electrical power (watt), and the emission efficiency is defined as the output light intensity (candela) over the input current density (Ampere). The power and emission efficiencies could be derived from the I-V-L characteristics. The effects of the substrates and interfaces between different layers were not included in this calculation.

3. RESULTS AND DISCUSSION

Material Properties

Fig. 1 shows the chemical structure of the copolymers used in this work. We are interested in getting high device efficiency by covalently combining the emissive property of the poly(dioctyl fluorene) (DOF) and the electron transport property of the diphenyloxadiazole (DPO) molecule without micro phase separation between the two components, and in adjusting the emissive color by the molecular design. To optimize the ratio between the fluorescent and electron transport segments of the P(DOF-DPO) copolymers, we synthesized three copolymers with **98:02**, **90:10**, and **80:20** DOF to DPO ratios and compared their material properties with P(DOF) polymer as listed in Table 1. Table 1 summarizes the properties of the polymers, including the molecular weight, ionization potential, electron affinity, CIE coordinates of the photo-luminescent spectra, CIE coordinates of the electro-luminescent spectra, and photo-luminescent quantum efficiencies. As can be seen in Table 1., the number average molecular weights of the polymers are above 100,000, suggesting that these polymers could have good film-forming properties by the spin-coating technique. The polydispersity index is ~1.7 for the light emitting polymers used in this work. We further investigated the surface topography of the polymer films by the atomic force microscopy (AFM) as shown in Fig. 2. The root-mean-square (RMS) roughness (Rq) of all studied emissive polymer films is 0.5 ± 0.2 nm over a 2 μm × 2 μm scan area, suggesting that the light emissive layer has a smooth surface.

Poly(dioctyl fluorene-co-diphenyl oxadiazole), P(DOF-DPO)

DOF (dioctyl fluorene)
highly fluorescent material

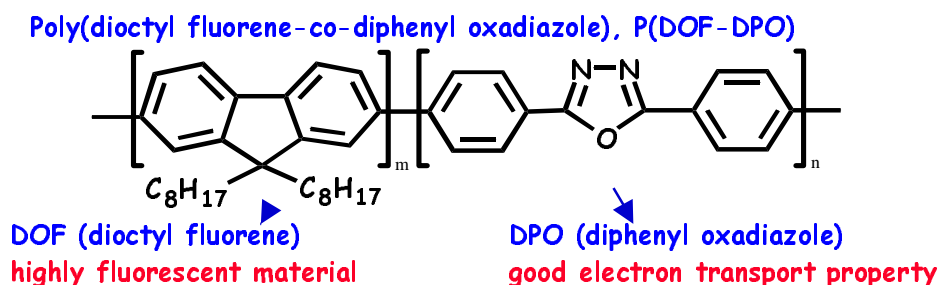DPO (diphenyl oxadiazole)
good electron transport property

Figure 1. The chemical structure of the copolymers used in this work

Table 1. The molecular weight, ionization potential, electron affinity, CIE coordinates of the photo-luminescent spectra, CIE coordinates of the electro-luminescent spectra, and photo-luminescent quantum efficiency of the P(DOF-DPO) copolymers with different compositions

Sample	DOF	DPO	Molecular weight (Mn)	I_p (eV)	E_{a_1} (eV)	E_{a_2} (eV)	PL CIE	EL CIE	PL quantum efficiency
P(DOF)	1	0	>100,000	5.8	2.1	2.3	0.178, 0.127 (a)	0.234,0.264 (A)	$21 \pm 3\%$
98:2	0.98	0.02	>100,000	5.8	2.1	2.3	0.158, 0.060 (b)	0.184, 0.205 (B)	$18 \pm 3\%$
90:10	0.9	0.1	>100,000	5.8	2.1	2.3	0.170, 0.091 (c)	0.216, 0.225 (C)	$17 \pm 3\%$
80:20	0.8	0.2	>100,000	5.7	2.1	2.3	0.182, 0.139 (d)	0.228, 0.249 (D)	$13 \pm 3\%$
DPO	0	1	<10,000	N/A	N/A	N/A	0.177, 0.103 (e)	N/A	N/A

*I_p is the ionization potential derived from the oxidation potential obtained by the cyclic voltammetry measurement
*E_{a_1} is the electron affinity derived from the reduction potential obtained by the cyclic voltammetry measurement
*E_{a_2} is the electron affinity obtained by a combination of the oxidation potential derived from the cyclic voltammetry measurement and the optical energy band gap derived from the UV-vis absorption spectroscopy
*PL CIE is the CIE coordinate of the photo-luminescent spectra
*EL CIE is the CIE coordinate of the electro-luminescent spectra
*PL quantum efficiency is the measured photo-luminescent quantum efficiency of the polymer films using an integrating sphere method
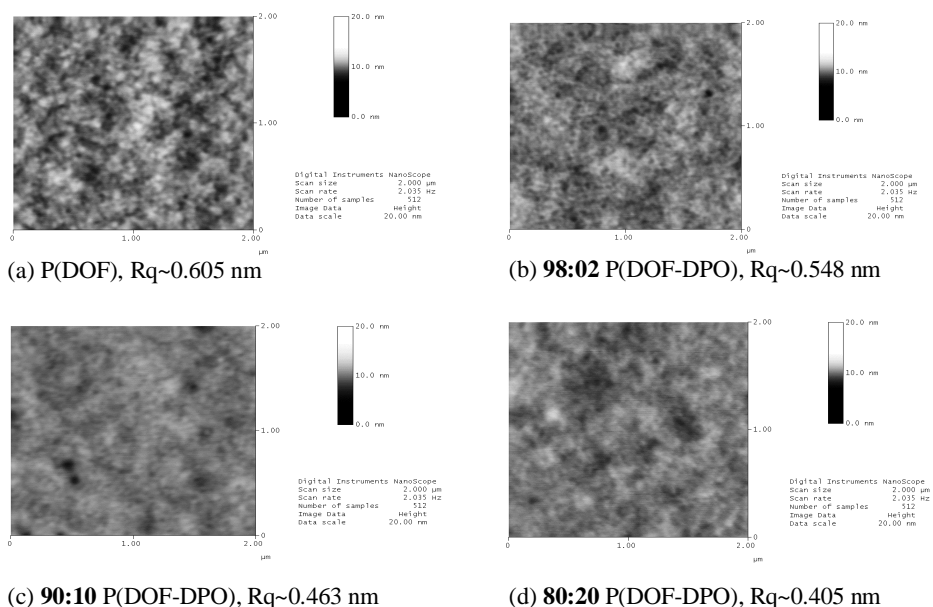

(a) P(DOF), Rq~0.605 nm

(b) **98:02** P(DOF-DPO), Rq~0.548 nm

(c) **90:10** P(DOF-DPO), Rq~0.463 nm

(d) **80:20** P(DOF-DPO), Rq~0.405 nm

Figure 2. The AFM images of (a) P(DOF), (b) **98:02** P(DOF-DPO), (c) **90:10** P(DOF-DPO), and (d) **80:20** P(DOF-DPO) light emitting polymer films The root-mean-square (RMS) roughness (Rq) is less than 1 nm over a 2 μm × 2 μm scan area.

The ionization potential (Ip) and electron affinity (Ea_1) in table 1 are derived from the oxidation and reduction potential edges obtained by cyclic voltammetry measurements, respectively. In our case, we observed two oxidation peaks and thus, two oxidation potentials. (The CV spectra are not shown in this paper.) However, since we believe that the first oxidation potential (E_{ox} ~ 1.1 V vs. Ferrocene/Ferrocenium (Fc/Fc+) couple) represents the triggering point of oxidation process, we used this value to define highest occupied molecular orbital (HOMO) level of our emissive polymer. The reduction potential (E_{red} ~ -2.6 V vs. Fc/Fc+) was used to calculate the lowest unoccupied molecular orbital (LUMO) level of the polymer. It is usually assumed that the Ferrocene/Ferrocenium (Fc/Fc+) oxidation potential ($E_{1/2}$ ~ 0.12 V) corresponds to 4.8 eV versus the vacuum.[10] Hence, this factor may be used to estimate the Ip and Ea of the polymeric materials, thus defining the HOMO and LUMO levels (table 1). As can be seen in table 1, no significant changes on the ionization potential and electron affinity were observed when increasing DPO amounts in the P(DOF-DPO) copolymers, therefore the electron and hole injection barriers do not change significantly for our studied polymers. We further calculated the optical band gap energy value (E_G~3.5 eV) from the Tauc plot of absorption spectra,[11] and extracted the electron affinity 2 (Ea_2) by using the HOMO level as the reference level. Since the optical band gap and HOMO level of the studied polymers do not change significantly with increasing DPO amount, no significant changes on the electron affinity 2 were observed. It should be noted that values of Ip and Ea obtained by these methods represent a weighted average, so that no large changes are expected for relatively small amounts of DPO in the copolymer. However, on a microscopic level, the presence of DPO units could facilitate electron injection and transport.

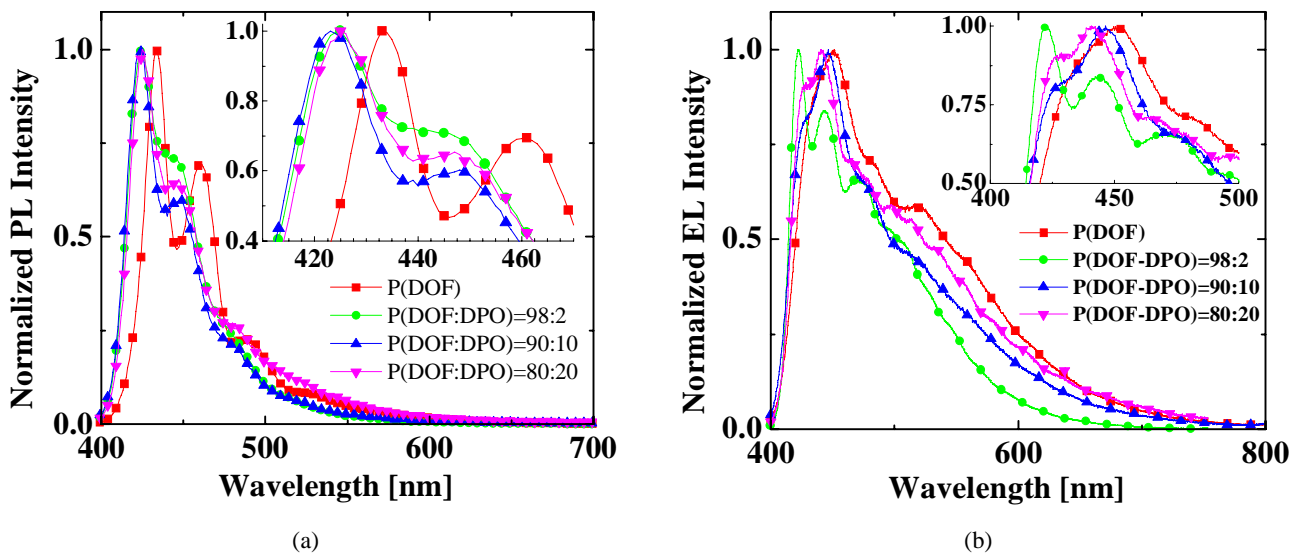(a)   (b)

Figure 3. The photo-luminescence (a) and electro-luminescence (b) spectra of P(DOF), **98:02** P(DOF-DPO), **90:10** P(DOF-DPO), and **80:20** P(DOF-DPO) light emitting polymers. The insets in both (a) and (b) are magnified figures for the ease of reading.

The normalized photo-luminescence (PL) and electro-luminescence (EL) spectra are plotted in Fig. 3(a) and Fig. 3(b), respectively. The PL spectra of the P(DOF) polymer shows three main peaks at ~434, ~461, and ~488 nm, while those of three copolymers with **98:02**, **90:10**, and **80:20** DOF to DPO ratios show three main peaks at ~424, ~447, and ~479 nm. The EL spectra of the P(DOF) polymer shows three main peaks at ~435, ~451, and ~483 nm, while those of three copolymers show three main peaks at ~426, ~442, and ~475 nm. As can be seen in Fig. 3(a) and Fig. 3(b), both the photo-luminescence and electro-luminescence spectra of the two copolymers with **98:02** and **90:10** DOF to DPO ratios are slightly blue shifted when compared with the poly(fluorene) polymer. The EL spectra of the studied polymers also show broadened emission spectra when compared with their PL spectra. This EL broadening phenomenon is probably induced by the change of the polymer film morphology caused by thermal annealing of the polymer film during

operation as a PLED. The effect of annealing is a partial crystallization, possibly assisted by the applied electric field. [12] Excimer emission at a longer wavelength usually happens in the more ordered regions within crystalline domains, thus resulting in the bandtailing phenomena seen in the EL spectra of our studied polymers. We further measured the PL spectra of the polymer layer within the PLEDs after device operation and found that the PL spectra are also broadened after device operation. We further calculated the PL and EL CIE (Comission Internationale de l'Éclairage) coordinates based on CIE 1931 chromaticity calculations. [13] These values are listed in Table 1 and plotted in Fig. 4. As can be seen in Fig. 4, both the PL and EL of P(DOF-DPO) copolymers with less than 10% DPO amount show more saturated blue color coordinate when compared with P(DOF) polymer, and in particular, the **98:02** P(DOF-DPO) shows the most saturated blue color. When the amount of DPO is above 20%, both the PL and EL spectra of the P(DOF-DPO) are broadened, thus shifting the CIE coordinate toward the center of the chromaticity diagram.
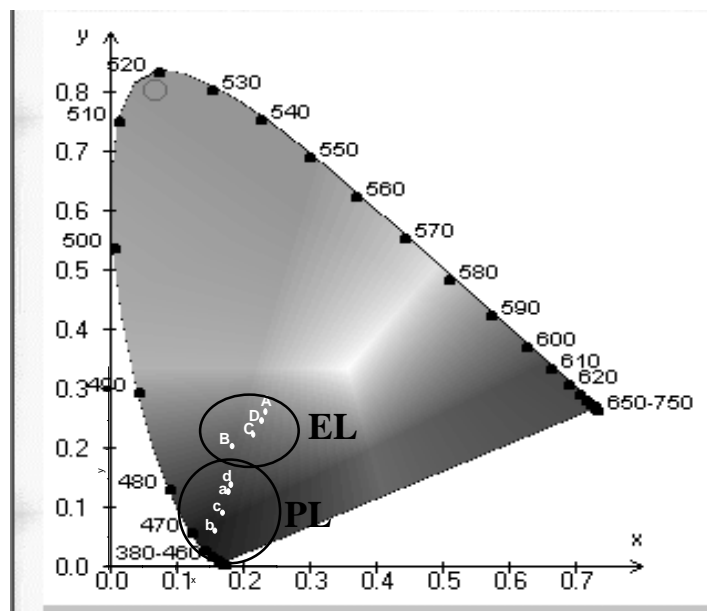

Figure 4. The CIE chromaticity diagram of photoluminescence CIE coordinates of (a) P(DOF), (b) **98:02** P(DOF-DPO), (c) **90:10** P(DOF-DPO), and (d) **80:20** P(DOF-DPO), and electro-luminescence CIE coordinates of (A) P(DOF), (B) **98:02** P(DOF-DPO), (C) **90:10** P(DOF-DPO), and (D) **80:20** P(DOF-DPO)

Opto-Electronic Characteristics

The photo-luminescence quantum efficiencies of the P(DOF), **98:02** P(DOF-DPO), **90:10** P(DOF-DPO), and **80:20** P(DOF-DPO) are $22 \pm 3\%$, $18 \pm 3\%$, $17 \pm 3\%$, and $13 \pm 3\%$, respectively. The PL quantum efficiency of the P(DOF-DPO) copolymers decreases with increasing DPO amount. The DPO component is less sterically hindered when compared with the DOF component, so more crystalline regions that decrease the quantum efficiency upon addition of DPO component might be formed. Therefore, the DPO molecules are probably introduced as the photo-luminescence quenching center. The current density and luminance versus applied voltage characteristics (J-L-V) are shown in Fig 5(a) for bi-layer copolymer PLEDs fabricated on flexible plastic substrates. Turn-on voltages at 1 cd/m^2 luminance level are ~3.8, ~5.9, ~4.6, and ~5.2 V and turn-on current densities at 1 cd/m^2 luminance level are ~4.6, ~5.1, ~9.6, and 35 mA/cm^2 for P(DOF), **98:02** P(DOF-DPO), **90:10** P(DOF-DPO), and **80:20** P(DOF-DPO) , respectively. As can be seen in Fig. 5(a), the turn-on voltage of P(DOF-DPO) based PLEDs is higher than that of P(DOF) based PLEDs, while the turn-on current density of P(DOF-DPO) based PLEDs is comparable with that of P(DOF) based PLEDs. Further study on the change of P(DOF) molecular orbital structure and carrier mobility upon addition of DPO molecule is needed for clarifying the factors contributing to higher turn-on voltage of the P(DOF-DPO) based PLEDs. The emission efficiency is defined as the output light intensity (candela) over the input current density (Ampere), and the power efficiency is defined as the total output optical power (lumen) over the input electrical power (watt). As can be seen in Fig. 5(b), the

P(DOF-DPO) based PLEDs with less than 10% DPO amount show comparable emission efficiencies and slightly lower power efficiencies when compared with the P(DOF) based PLEDs. This is because the P(DOF-DPO) based PLEDs has significant larger operating voltage and comparable current density at same luminance level when compared with P(DOF) based PLEDs.
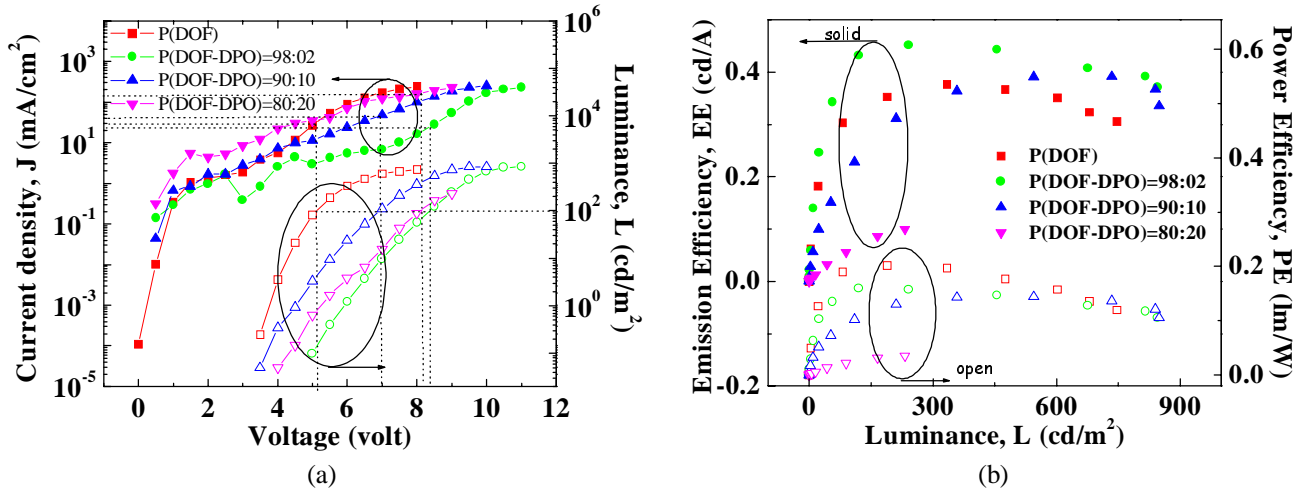

Figure 5.The J-L-V characteristics (a) and emission and power efficiency versus luminance (b) for bi-layer PLEDs based on P(DOF) ■ , **98:02** P(DOF-DPO) ● , **90:10** P(DOF-DPO) ▲, and **80:20** P(DOF-DPO) ▼ light emitting polymers The PLEDs structure is ITO anode / PEDOT-PSS layer (70 nm) / light emitting polymer layer (100 nm) / Ca (40 nm) /Al (200 nm) cathode.

4.   CONCLUSIONS

We have shown that the **98:2** P(DOF-DPO) based PLEDs have comparable emission efficiency ($\sim$0.55 cd/A at 100 cd/m^2) and power efficiency ($\sim$0.16 lm/W), and more saturated blue color (1931 CIE coordinate=0.184,0.205) when compared with P(DOF) based PLEDs. We have studied the copolymer characteristics and opto-electronic properties of copolymer based devices with different compositions. The AFM data suggested that the emissive layer has a smooth surface with RMS roughness about 0.5 ± 0.2 nm over a 2 μm by 2 μm area. The photo-luminescence quantum efficiency of the P(DOF-DPO) copolymer decreases with increasing DPO moiety. Both the photo-luminescence spectra and electro-luminescence spectra are slightly blue shifted when adding less than 10% DPO moiety into P(DOF). Both the emission efficiency ($\sim$0.3-0.6 cd/A at 100 cd/m^2) and power efficiency ($\sim$0.1-0.2 lm/W at 100 cd/m^2) of the P(DOF-DPO) based PLEDs are comparable to the P(DOF) based PLEDs when adding less than 10% DPO. We have shown the device characteristics of the P(DOF-DPO) PLEDs, and we plan to further investigate changes in the P(DOF) electronic structure and the electron and hole transport property upon addition of the DPO moiety.

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