

Studies on Printing Inks Containing Poly[2-methoxy-5-(2-ethylhexyl-oxy)-1,4-phenylenevinylene] as an Emissive Material for the Fabrication of Polymer Light-Emitting Diodes by Inkjet Printing

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Three solvent systems, chlorobenzene (ink 1), chlorobenzene/*o*-dichlorobenzene (ink 2) and chlorobenzene/tetrahydronaphthalene (ink 3), were compared as printable inks for the fabrication of polymer light-emitting diodes (PLEDs) using poly[2-methoxy-5-(2-ethylhexyl-oxy)-1,4-phenylenevinylene (MEH-PPV) as an emissive material and an inkjet printer (Fujifilm Dimatix DMP-2831). Ink 1 clogged the printer's nozzle and gave non-uniform film. Inks 2 and 3 were used to fabricate PLEDs with ITO/PEDOT:PSS/MEH-PPV/LiF/Al configurations. The best performance (turn-on voltage, 3.5 V; luminance efficiency, 0.17 cd/A; luminance, 1,800 cd/m) was obtained when ink 3 was used to form the emissive layer (thickness, 49 nm), attributable to the better morphology and suitable thickness of the MEH-PPV layer.

Key Words : Inkjet printing, Polymer LED, MEH-PPV, Printing ink

Introduction

Recent developments of printed electronics have been achieved through screen printing, roll to roll printing and inkjet printing for the fabrication of various devices such as polymer light-emitting diodes (PLED),¹ polymer solar cells² and organic thin film transistors.³ Of these, inkjet printing has many advantages, such as simple fabrication, compatibility with various substrates and flexibility. It also allows simultaneous deposition and patterning of materials. The deposition does not require the expensive masks employed in conventional photo-resist processes and the patterning does not require any chemical processes. Therefore, inkjet printing is attractive for PLED fabrication when compared with spin coating.⁴ However, there is little published research about the fabrication and properties of inkjet-printed PLEDs. Recently, Schubert *et al.* reported PLEDs fabricated by inkjet printing using printable inks containing poly[2-methoxy-5-(2-ethylhexyl-oxy)-1,4-phenylenevinylene (MEH-PPV) as an emissive material.⁵ Toluene was found to be the best solvent for the formulation of inks containing MEH-PPV from among chlorobenzene, *o*-xylene, toluene and tetrahydrofuran, as the resulting films were of largely uniform thickness. However, they only measured the current-voltage (I-V) properties of the printed films and characterized them by atomic force microscopy (AFM). Therefore luminance and conversion efficiency data were not available.

Schubert *et al.* attempted to fabricate PLEDs with MEH-PPV emissive layers using inks prepared from toluene or chlorobenzene, but the inks were unsuitable for the inkjet

printer (Fujifilm Dimatix DMP-2831), which is different from their Autodrop system (Microdrop Technologies, Norderstedt, Germany). The solvents caused some problems such as clogging the nozzle, unstable printing and non-uniformity of resulting films. The problems are likely caused by physical differences between the two printers. For example, Schubert *et al.*'s printer had micropipette nozzles of 70 μm and was capable of printing solutions with viscosities up to 20 cP. On the other hand, the nozzle diameter of the Fujifilm Dimatix DMP-2831 is only 21 μm , and has a recommended viscosity range of printable inks of 10-12 cP. The printings and morphologies of the resulting films were significantly different due to the nozzle's diameter that can greatly influence the volume of the ejected drops and consequently affect the drying rate of the deposited inks.^{5,6}

In this research, MEH-PPV-based printing inks in various one or two-component solvents were prepared, and then used in the fabrication of PLEDs using the Fujifilm Dimatix DMP-2831 inkjet printer. The performances of the resulting devices, such as turn-on voltage, luminance and efficiency were studied. PLEDs were also fabricated by spin coating for comparison of the devices' performances.

Experimental

Materials. MEH-PPV was purchased from Sigma-Aldrich Co. ($M_n = 40,000\text{--}70,000$ g/mol). Poly[3,4-ethylenedioxythiophene]:poly[styrene sulfonic acid] (PEDOT:PSS) was purchased from Bayer (Baytron P AI4083). Chloroform (99%), chlorobenzene (CB, 99%), *o*-dichlorobenzene (*o*-

DCB, 99%), toluene (99%), mesitylene (1,3,5-trimethylbenzene 99%), and tetrahydronaphthalene (THN, 99%) were purchased from Sigma-Aldrich Co. and used without further purification. Three inks (ink 1, ink 2, and ink 3) containing MEH-PPV were prepared using different solvents. Before inkjet printing, the inks were filtered using a syringe filter with 0.45 μm pore size.

Measurements. The solvents' and inks' viscosities were measured using a viscometer (LV DV-II + PRO, Brookfield). The thicknesses and morphologies of the polymer films, dots and lines were determined using a 2D surface profiler (KLA-Tencor P-16+ surface profiler), a 3D surface profiler (SNU Precision SIS3747), and a scanning probe microscope (SPM) (*n*-Tracer, Nanofocus, Inc). Current-voltage-luminance (I-V-L) and current-voltage characteristics of the PLEDs were measured using an I-V-L system (Mescience, Inc) with a Keithley 236 source measurement unit and a PR670 spectroradiometer (Photo Research Corp.).

Fabrication of PLEDs. PLEDs were fabricated with ITO/PEDOT:PSS/MEH-PPV/LiF/Al configuration. Patterned ITO glass was cleaned with isopropyl alcohol and deionized water using ultrasonication, and then treated with UV-ozone. After cleaning, the substrate was spin-coated with PEDOT:PSS and dried for 20 min at 140 $^{\circ}\text{C}$ in air. Emissive MEH-PPV layers were formed on the conductive layer (PEDOT:PSS) by inkjet printing using the Fujifilm Dimatix DMP-2831 printer. Each device was dried at 120 $^{\circ}\text{C}$ for 20 min under nitrogen. Emissive layers were also formed by spin coating for comparison using MEH-PPV ink in CB and dried under similar conditions as above. LiF was evaporated on the emissive layer to *ca.* 0.5 nm thickness, and Al was then evaporated to *ca.* 100 nm thickness under vacuum (10^{-7} torr).⁷ Each PLED was encapsulated and its performance was measured.

Results and Discussion

For the fabrication of PLEDs by inkjet printing, the emissive polymer should be completely dissolved in the ink solvent as the aggregation of polymer molecules can impede printing. Therefore the solubility of MEH-PPV was tested in various solvents: chloroform, CB, *o*-DCB, toluene, mesitylene and THN. Each solvent (1.0 mL) was added to MEH-PPV (20 mg), and after 5 min the resulting solution was visually examined (Fig. 1). Solubility appeared to decrease gradually in the order chloroform, *o*-DCB, CB, toluene, mesitylene, THN.

The printer's manual states that the viscosity and surface tension of inks are required to be 10–12 cP and 28–33 dynes/cm, respectively, for optimum performance.⁶ Each solvent's physical properties are listed in Table 1, with only viscosities measured as part of this experiment. Any ink with unsuitable viscosity cannot be used with the printer. The ink should have a relatively high boiling point, low vapor pressure, and low surface tension to minimize clogging of nozzle, unstable printing, and non-uniformity of the resulting printed films. However, solvents with too high boiling points are not

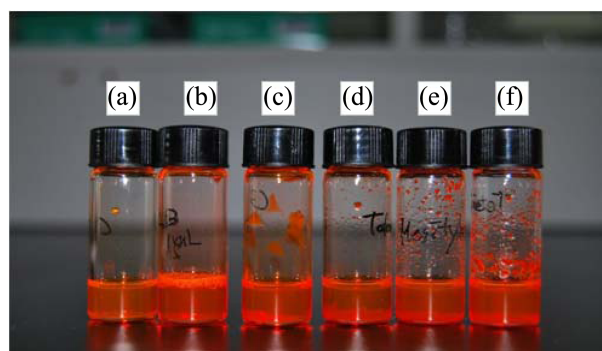


Figure 1. MEH-PPV in various organic solvents (conc. 2 mg/mL): (a) chloroform, (b) *o*-DCB, (c) CB, (d) toluene, (e) mesitylene, and (f) THN.

Table 1. Physical properties of various solvents

	Boiling point ^a ($^{\circ}\text{C}$)	Surface tension ^a (dyne/cm)	Vapor pressure ^a (mmHg at 20 $^{\circ}\text{C}$)	Viscosity ^b (cP)
Chloroform	61.2	27.5	160	1.14
<i>o</i> -DCB	180.5	36.6	1.2	1.44
CB	131	33.6	9	1.11
Toluene	110.6	28.5	21.8	0.79
Mesitylene	166	28.8	2.1	0.85
THN	207	33.2	0.18	2.05

^aobtained from the literature.^{3,8} ^bmeasured at room temperature

Table 2. Formulation details and measured viscosities of three inks

	MEH-PPV (g)	CB (mL)	<i>o</i> -DCB (mL)	THN (mL)	Viscosity (cP)
Ink 1	0.040	5.0	-	-	4.46
Ink 2	0.040	2.5	2.5	-	5.48
Ink 3	0.040	2.5	-	2.5	8.16

recommended either because evaporation of the solvents can cause thermal damage to the devices. Based on these considerations, CB (ink 1), CB/*o*-DCB (ink 2) and CB/THN (ink 3) were selected as solvent systems for the formulation of printing inks (Table 2): CB had a good solubility and proper surface tension; *o*-DCB had a good solubility and high boiling point; and THN had a low solubility but high boiling point and appropriate viscosity. All inks had viscosities ranging from *ca.* 4–8 cP.

The inks were tested in inkjet printing. Ink 1 performed poorly. It clogged the nozzle and had poor directivity of drops, likely because only CB was used as the solvent. Even though its surface tension (33.6 dynes/cm) is near the range required for the printer, CB had the highest vapor pressure and lowest boiling point of the solvents used in this study.^{6,8} Its high vapor pressure and low boiling point may have contributed to the clogging of the nozzle because fast evaporation of the solvent can leave the polymer (MEH-PPV) on the surface of the nozzle, interfering with ink jetting, and causing poor directivity of the drops. Ink 2 performed better, and the problems associated with the clogging of the nozzle and the directivity of drops were significantly reduced. This

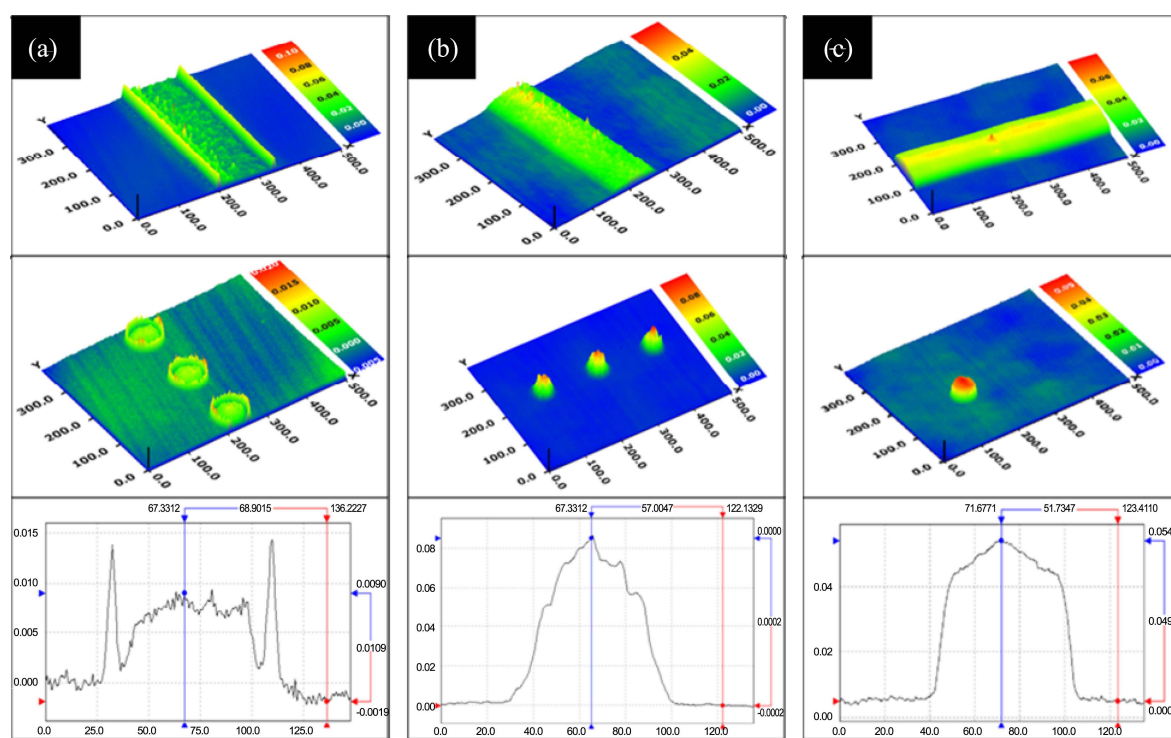


Figure 2. Three-dimensional images of lines (top), drops (middle), and cross sections of drops (bottom) on PEDOT:PSS layers, printed using inks (a) 1, (b) 2 and (c) 3.

was attributed to the higher viscosity of the ink (5.48 cP) as well as the higher boiling point and lower vapor pressure of *o*-DCB compared with CB. Ink 3 showed the best results among the three inks, probably because its viscosity (8.16 cP) was the closest to the range (10–12 cP) recommended for the printer, and THN had the lowest vapor pressure and highest boiling point of the three solvents.^{2,6}

The morphologies of printed dots and lines were investigated using 2D and 3D surface profilers (Fig. 2). Ink 1 printed dots and lines that were much thicker at their edges because most of the solute (MEH-PPV) was deposited in a ring marking the original contact line in a ‘coffee-drop effect’. This effect can occur through the pinning of the contact line of the droplet combined with increased evaporation at the edges. Pinning of the contact line involves liquid evaporating at the edges being replenished by liquid from the interior, with the resulting outward flow carrying most of the dispersed material to the edge.^{5,9} In contrast, inks 2 and 3 produced mountain-shaped drops, due to the Marangoni flow. The convective flow that transports the solute to the

contact line can be counterbalanced or enhanced, depending on the solvent, by Marangoni flow (surface-tension-driven flow) induced by the surface tension gradient between the periphery and the interior of the droplet from low surface tension regions to regions with high surface tension. Cho *et al.* recently reported that the addition of dodecane, with high boiling point (216 °C) and low surface tension, to CB resulted in recirculating flow in the droplets during drying. The

Table 3. Widths and thicknesses of printed dots and lines, and thicknesses of printed films

	Dot ^a		Line ^a		Film ^b
	Width (μm)	Thickness (nm)	Width (μm)	Thickness (nm)	Thickness (nm)
Ink 1	87	<15	100	<25	-
Ink 2	74	85	160	77	58
Ink 3	92	34	118	44	49

^aobtained from 3D surface profiler. ^bobtained from 2D surface profiler

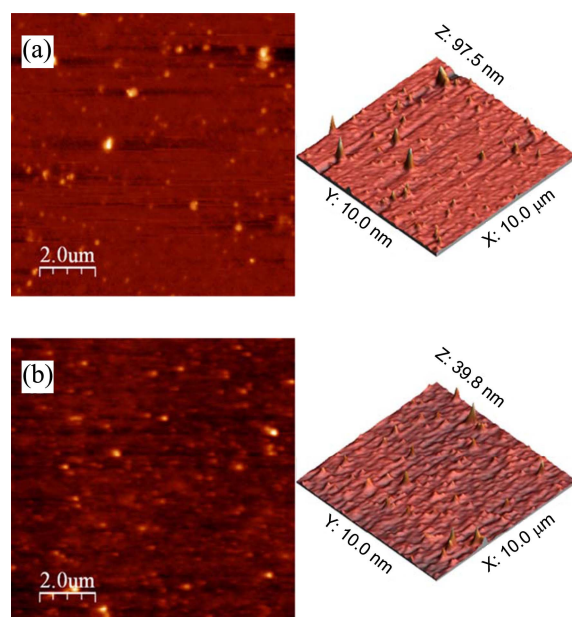


Figure 3. SPM images of inkjet-printed MEH-PPV films on PEDOT:PSS: (a) ink 2 and (b) ink 3.

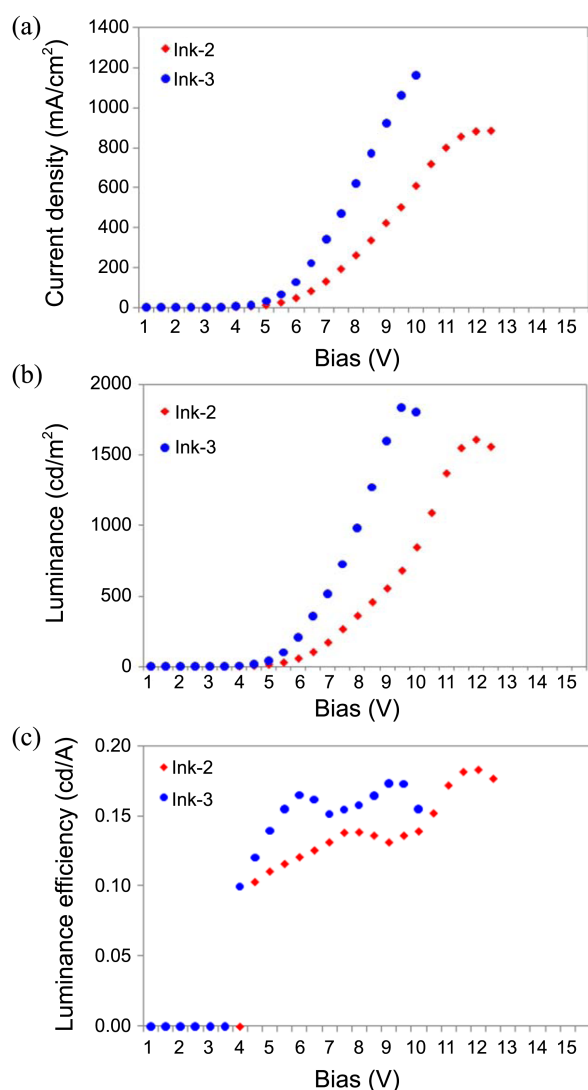


Figure 4. Characteristics of PLEDs with emissive layers inkjet-printed using inks 2 and 3: (a) current density-voltage, (b) luminance-voltage, and (c) luminance efficiency-voltage.

flow was induced by the Marangoni flow in the direction opposite to convective flow.^{3,10,11} The dimensions of the dots and lines and films' thicknesses were measured by 3D and 2D surface profilers, respectively (Table 3). Inks 2 and 3 produced drops and lines with better morphologies than ink 1. The film of ink 3 (49 nm) was thinner than that of ink 2 (58 nm) due to THN's lower surface tension compared with *o*-DCB, and the higher viscosity of ink 3.^{3,10-14,17} The surface morphologies of films printed from inks 2 and 3 were further studied by SPM (Fig. 3).^{15,16} The root-mean-square values of the inkjet-printed MEH-PPV films obtained from the inks were 4.6 nm and 1.8 nm, respectively, indicating that the film from ink 3 was much smoother than that from ink 2, similar to the results obtained from the surface profilers.

PLEDs were fabricated using inks 2 and 3 and their performances were measured in air (Figure 4 and Table 4). Their turn-on voltages were 4.0 and 3.5 V, respectively; the turn-on voltage of the PLED fabricated using ink 3 was

Table 4. Performances of inkjet-printed PLEDs fabricated using inks 2 and 3

Ink	Turn-on voltage (V)	Efficiency ^{max} (cd/A)	Luminance ^{max} (cd/m ²)
Ink 2	4.0	0.18 (at 11.5 V)	1610 (at 11.5 V)
Ink 3	3.5	0.17 (at 9.0 V)	1850 (at 9.0 V)

Table 5. Characteristics of PLEDs fabricated by spin coating at three different spin speeds

Speed (rpm)	Film thickness (nm)	Turn-on voltage (V)	Efficiency ^{max} (cd/A)	Luminance ^{max} (cd/m ²)
700	47	3.5	0.30 (at 6.0 V)	1740 (at 9.5 V)
1000	38	3	0.23 (at 5.5 V)	2370 (at 9.0 V)
1300	33	3	0.30 (at 5.5 V)	2450 (at 8.5 V)

slightly lower than that of the PLED fabricated using ink 2. Ink 3 produced a PLED with better luminance than ink 2. Its luminance efficiency (0.17 cd/A) was higher than that of the PLED fabricated using ink 2 (0.13 cd/A) in the voltage range of 3.5–9 V. The improved performance of the PLED fabricated using ink 3 was perhaps due to the uniformity and thickness (49 nm) of the MEH-PPV film. In order to optimize the thickness of the MEH-PPV layer, several PLEDs were fabricated by spin coating, where the layer thickness was controlled by the spin speed. Spin speeds of 700, 1,000 and 1,300 rpm produced layers of 47, 38 and 33 nm thickness. Decreased thickness of the MEH-PPV layer resulted in reduced turn-on voltage and accordingly the maximum luminance increased from 1,740 cd/m² to 2,450 cd/m² (Table 5). This result indicates that the performance of the PLEDs was improved by decreasing the thickness of the active layer, with other conditions unchanged, due to decreasing bulk resistance.¹⁸⁻²⁰

Ink 3 produced thinner MEH-PPV films than ink 2 under similar printing conditions, which consequently improved the resulting PLEDs' performance. The turn-on voltage and maximum luminance of the PLED fabricated using ink 3 were 3.5 V and 1,850 cd/m² at 9.0 V, respectively, a slightly inferior performance compared with PLEDs fabricated by spin coating because the ink-jet printed MEH-PPV film was thicker than the spin-coated film (49 nm vs. 33 nm). Further decreases of the emissive layer's thickness are being sought.

Conclusions

Three inks containing MEH-PPV were prepared for the fabrication of PLEDs by ink-jet printing. Ink 1, formulated using only CB as solvent, clogged the printer's nozzle and gave non-uniform films. PLEDs fabricated using ink 3 performed better than those fabricated using ink 2: turn-on voltage 3.5 V, luminance efficiency 0.17 cd/A, luminance 1,800 cd/m². The improved performance resulted from smoother and thinner emissive MEH-PPV layers, due to the appropriate physical properties of the two-component solv-

ent, such as vapor pressure, surface tension and boiling point as well as an appropriate viscosity of the ink. The performances of the PLEDs were slightly inferior to those fabricated by spin coating due to their thicker emissive layers. This research suggests that further optimization of the printed emissive layers would improve PLEDs' performances to levels comparable to those of PLEDs fabricated by spin coating.

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