

EFFICIENT DEEP-RED ORGANIC LIGHT-EMITTING DIODES BASED ON BLENDING MEH-PPV WITH A SMALL MOLECULE COMPOUND*

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Abstract Efficient deep-red organic light-emitting diodes (OLEDs) were investigated based on the blend of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with 4,7-bis(5-(7-(9H-carbazol-9-yl)-9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (compound **1**). By optimizing the blend ratio, the turn-on voltage of the devices was significantly reduced from 4.9 V to 2.4 V. A highest external quantum efficiency of 2.56% was achieved at a blend ratio of 95:5 (wt) for compound **1**: MEH-PPV. The CIE coordinate was measured to be (0.70, 0.30), with the luminescence peak at around 680 nm. Based on experimental observations the improvement mechanism is described.

Keywords: MEH-PPV; Organic light-emitting diodes; Red electroluminescence; Soluble small molecule.

INTRODUCTION

Organic light-emitting diode (OLED) has attracted increasing attention in the past decades due to its potential application in low-cost, large-area and flexible display^[1–4]. For mass commercialization, full-color organic electroluminescent materials with high efficiency and long lifetime should be developed. Many attempts have been made and numerous electroluminescent materials including polymers as well as small molecules have been reported^[5–11]. Red material is one of the bottlenecks for fulfilling the commercialization of full-color OLED display due to its low efficiency and poor color purity^[12]. To improve the efficiency of OLED, balance in the transport and high possibility in radiative recombination of charge carriers, *i.e.* holes and electrons, should be achieved^[13–16]. For facile injection of holes and electrons from each electrode, energy level of each layer in the device architecture should match. Low work-function metals are commonly used as the cathode. The purity of the materials is also important since the impurity would act as charge traps which would influence the transport and recombination of carriers. High color purity and ease in synthesis are the superiorities of small molecules while solution processibility, high stability and efficiency are the merits of polymers. Blend system of polymer and small molecule was applied in order to combine both advantages.

We have reported a soluble red small molecule, compound **1**, as shown in Fig. 1. Such material emits deep-red luminescence with the spectrum peak at 680 nm. However the efficiency of the devices made of pure compound **1** was as low as 0.66%, and a high turn-on voltage of 4.9 V was needed^[17].

In order to enhance the efficiency of compound **1**, we applied the blend system of MEH-PPV (shown in Fig. 1) and compound **1** to fabricate deep-red OLED. Due to the lower hole injection barrier of MEH-PPV than

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compound **1** and more balanceable carriers of the device, the external quantum efficiency (QE_{ext}) was improved to 2.56% with a low turn-on voltage of 2.4 V.

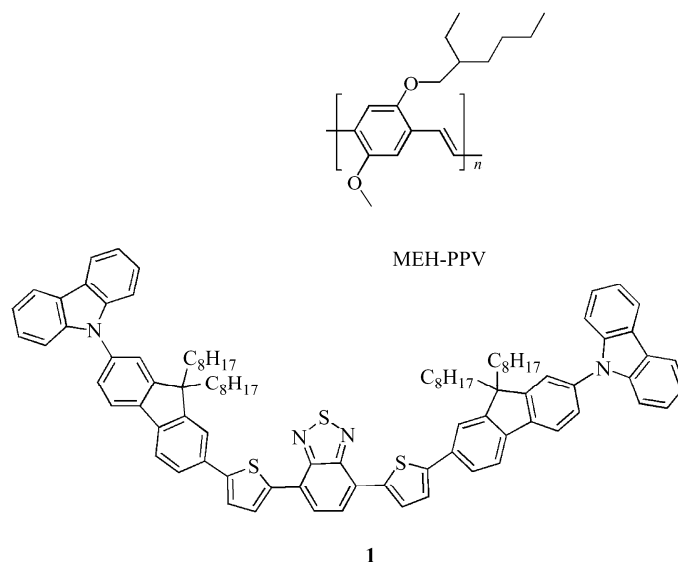


Fig. 1 Chemical structures of compound **1** and MEH-PPV

EXPERIMENTAL

Compound **1** and MEH-PPV were synthesized in our lab as published elsewhere^[17, 18]. Poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate) (PEDOT:PSS, Baytron P 4083) was purchased from Bayer AG. Commercial indium-tin oxide (ITO) glass substrates, with a sheet resistance of 10–20 ohm square⁻¹, were cleaned ultrasonically in solvent bath of acetone, detergent, deionized water and 2-propanol in sequence. After the pretreatment by oxygen plasma for 5 min, the ITO substrate was spin-coated with a 50 nm layer of PEDOT:PSS and transferred into an oven to remove the moisture at 80°C for 8 h under vacuum. Compound **1** and MEH-PPV were dissolved in toluene at a concentration of 14 and 3.5 mg/mL, respectively. The solutions were passed through a 0.45 μm filter before usage. Spin-coating of the solutions on top of the PEDOT:PSS-covered ITO substrate was performed inside the glove box under nitrogen atmosphere. The film thickness was controlled at around 70 nm by a calibrated surface profiler (Tencor Alfa-Step 500). Then the substrates were transferred into the evaporation chamber where the evaporation of the cathode of Ba/Al was conducted under a high vacuum below 3×10^{-4} Pa. Ba and Al were evaporated at a rate of 0.02 and 0.5 nm/s, respectively with the thickness of each layer set to 4 and 200 nm. The evaporation rate and film thickness were monitored by a calibrated quartz oscillator (Model STM-100, Syscon Instrument, Inc). The active device area was measured to be 0.17 cm².

The current-luminance-voltage data were measured on a semiconductor testing system consisting of a Keithley 236 sourcemeter and a calibrated Si photodiode. QE_{ext} was obtained by measuring the total light output in all directions inside an integrating sphere (Model IS-080, Labsphere) at a specific current. UV-Vis absorption spectra were collected by a spectrophotometer (Model HP8453). Photoluminescence (PL) spectra were taken by a spectrofluorometer (Model JY Fluorolog-3). The HOMO energy level was derived from the onset of the oxidation wave, determined by cyclic voltammetry on the dip-coated films on Pt electrodes in CH₃CN in the presence of *n*-Bu₄NPF₆ as electrolyte, using a saturated calomel reference electrode. The LUMO energy level was calculated based on the optical band gap in the solid film along with the HOMO energy level.

RESULTS AND DISCUSSION

Intrinsic Electroluminescence of Compound **1**

The charge injection and transport properties of solution-processed compound **1** were investigated, and the electroluminescent data are listed in Table 1. The single-layer bulk red emitting device with the structure of ITO/PEDOT:PSS (50 nm)/compound **1** (80 nm)/Ba (4 nm)/Al (200 nm) (defined as D1) showed a peak QE_{ex} of 0.66% and a turn-on voltage of 4.9 V. With incorporation into the emissive layer of an electron-transporting component of PBD, the device (Its structure is ITO/PEDOT:PSS (50 nm)/compound **1** + PBD (10 wt%, 80 nm)/Ba (4 nm)/Al (200 nm), defined as D2) showed an increase of QE_{ext} by about 50% and a lowered turn-on voltage by 1.7 V with respect to D1, implying that compound **1** is probably limited by the electron traps at the compound **1**/cathode interface and bulk electron transport, and yet dominated with hole transport, which is commonly observed in other related structures^[19,20]. As expected, the introduction of a vacuum-deposited TPBI hole-blocking layer resulted in a further increase of QE_{ext} up to 1.36%, strongly supporting the above assumption (Its device structure is ITO/PEDOT:PSS (50 nm)/compound **1** (80 nm)/TPBI (40 nm)/Ba (4 nm)/Al (200 nm), defined as D3).

Table 1. EL performances of the devices of D1–D3

Device structure	Turn-on voltage ^a (V)	Maximum QE_{ext}			$J = ca. 32 \text{ mA cm}^{-2}$		
		Bias (V)	L (cd m^{-2})	QE_{ext} (%)	Bias (V)	L (cd m^{-2})	QE_{ext} (%)
D1	4.9	6.1	23.8	0.66	6.3	28.1	0.61
D2	3.2	4.4	18.1	0.99	4.7	30.1	0.93
D3	7.0	8.2	22.4	1.36	8.8	44	1.14

^a Defined as a brightness of 1 cd m^{-2}

Light-emitting Devices Based on the Compound **1**:MEH-PPV Blends

MEH-PPV is a well studied yellow electroluminescent polymer^[21]. The EL device ITO/PEDOT:PSS/MEH-PPV/Ba/Al was shown to possess a turn-on voltage of slightly above 2.0 V, which is close to the band-gap of MEH-PPV, implying that holes and electrons can be injected from the respective electrodes (Fig. 2)^[22]. On the other hand, the bulk device D1 showed a much higher turn-on voltage of 4.9 V (Table 1), which can apparently be attributed to less efficient hole injection of compound **1** with respect to MEH-PPV. The overlap of the emission spectrum of MEH-PPV with the optical absorption of compound **1** suggests that an efficient energy transfer from MEH-PPV to compound **1** is expected (Fig. 3). By utilization of an emissive binary blend based on compound **1** and MEH-PPV, hole injection can thus be facilitated. Furthermore, a minor amount of MEH-PPV might act as a potential hole trap in the blended devices as shown in Fig. 2.

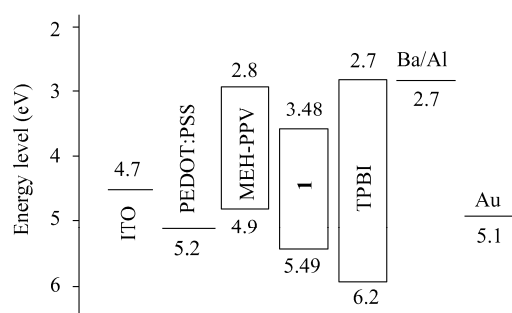


Fig. 2 Schematic illustration of energy level diagram

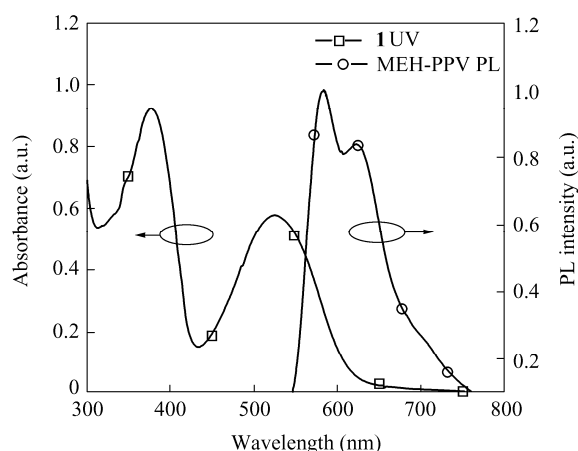


Fig. 3 UV-Vis absorption spectrum of compound **1** and PL spectrum of MEH-PPV in the solid films on quartz substrates

A series of single-layered blended light-emitting diodes was thus studied with concentration of 3, 5, 10, 20 and 80 wt% of MEH-PPV. The diode characteristics are shown in Table 2. When the MEH-PPV concentration was upon 10 wt%, improved external device efficiencies were achieved with decreased turn-on voltages against the D1. At the blend composition of compound **1**:MEH-PPV (95:5, *W/W*), a highest QE_{ext} of 2.56% was obtained with a turn-on voltage of 2.4 V (Fig. 4). The electroluminescence wavelength is centered at 675 nm in the deep red region with CIE coordinates of (0.70, 0.30), as shown in Fig. 5.

In the device with blend emitters, under low voltage, MEH-PPV accounts for the majority of hole injection. The injected holes captured by MEH-PPV may be released (detrapped) and subsequently transported by compound **1** to the other electrode when the devices with MEH-PPV less than 20 wt%. At this stage, the hole current seems to be controlled by the potential hole trap densities at the PEDOT:PSS/EML interface. With increase of the concentration of MEH-PPV up to 20 wt%, the hole current increases rapidly, implying that a hole conductive passage made of MEH-PPV would possibly be in place. Because MEH-PPV is a more efficient hole transporter with respect to compound **1**. Hence, the hole trapping by MEH-PPV is benefit of the balance of holes and electrons in the blend emitters.

Table 2. EL performances of ITO/PEDOT/compound **1**:MEH-PPV/Ba/Al

Compound 1 : MEH-PPV (<i>W/W</i>)	Turn-on voltage (V)	Max <i>L</i> (cd m ⁻²)	Maximum QE_{ext}			$J = ca. 32 \text{ mA cm}^{-2}$		
			Bias (V)	<i>L</i> (cd m ⁻²)	QE_{ext} (%)	Bias (V)	<i>L</i> (cd m ⁻²)	QE_{ext} (%)
0:100	2.1	5689	3.4	2102	1.22	2.7	262	0.93
20:80	3.0	240	9.0	240	0.28	5.3	17	0.16
80:20	2.4	591	2.8	3.2	1.13	4.4	68	0.98
90:10	2.3	1105	2.3	1.6	1.95	4.2	90	1.58
95:5	2.4	1019	4.3	35	2.56	5.6	110	2.23
97:3	2.7	992	4.3	29.1	2.52	5.9	122	2.21
100:0	4.9	154	6.1	24	0.66	6.3	28	0.61

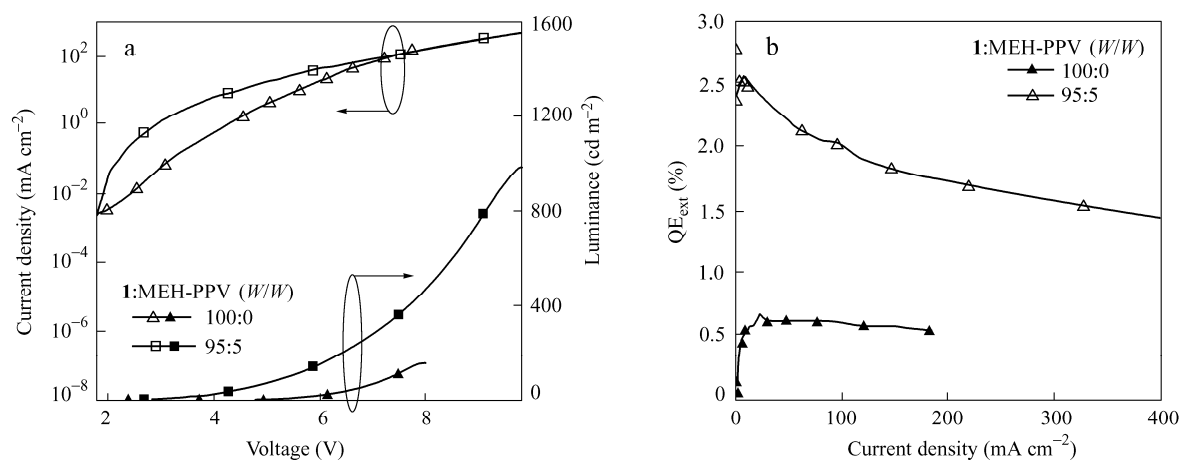


Fig. 4 J - V - L (a) and QE_{ext} - J (b) of the devices of compound **1** and compound 1:MEH-PPV blend (95:5, W/W)

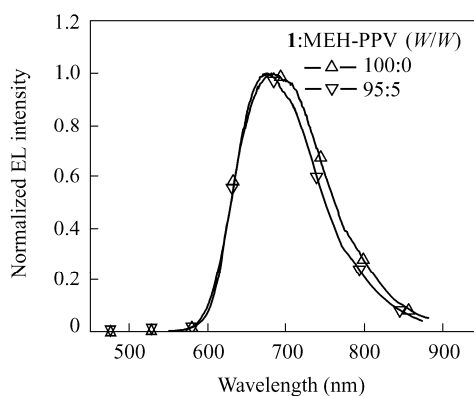


Fig. 5 EL spectra of device of compound 1:MEH-PPV blend (95:5, W/W) and bulk compound **1**

It is noted that, with MEH-PPV high above 20 wt%, a decreased QE_{ext} was observed. We suspect that significant holes and electrons would recombine on MEH-PPV since a continuous infinite network of MEH-PPV seems to have been completed. The excitons then undergo transfer to compound **1** (as noted, complete exciton transfer from MEH-PPV to compound **1** occurs at a concentration of compound **1** of *ca.* 20 wt% under optical excitation). Under this situation, the device efficiency can be limited.

CONCLUSIONS

We have achieved efficient deep-red organic light-emitting diodes by blending small molecules with MEH-PPV. MEH-PPV can facilitate the holes injection according to the turn-on voltage reduction of the devices. The optimum performance was attained at the weight ratio of 95:5 for compound **1**:MEH-PPV. The maximum QE_{ext} was achieved by 2.56%, which was four-time higher than that of pure compound **1**. A possible reason for the improvement of the EL efficiency in the device with the blend emitter is the hole trapping of MEH-PPV to balance the holes and electrons in the emitter under lower concentration of 10% of MEH-PPV.

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