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Efficient flexible devices using a statistical copolymer of oxadiazole containing PPV

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Abstract

Flexible light-emitting diodes, with simple device architectures, fabricated using a random copolymer of hole transporting dialkoxy-substituted phenylenevinylene (PV) with an electron transporting oxadiazole containing PV derivative as the emissive layer and higher work function aluminum cathodes have been examined and compared with control devices on glass substrates. In all devices poly(3,4-ethylenedioxythiophene) with poly(styrenesulfonate) (PEDOT:PSS) was used as the hole injection layer and a thin layer of cesium fluoride or lithium fluoride has been used at the polymer/cathode interface to aid electron injection. Devices on plastic substrates with a lithium fluoride interlayer performed the best, exhibiting an average external quantum efficiency (EQE) of 0.8% and luminance of 1600 cd/m^2 at 40 mA/cm^2 (7.8 V). Stability of this device and morphology of the emissive film have also been investigated.

Keywords: Light-emitting diodes; Electroactive organics; Flexible substrates; Oligomers; Conjugation; Poly(*p*-phenylenevinylene)

1. Introduction

Great progress has been made in developing conjugated polymeric materials for applications in optoelectronic devices, such as light-emitting diodes (LEDs) [1–3]. They exhibit good luminous efficiency, have low turn-on voltages and are solution processible. Additionally, these devices can be made on plastic substrates, such as poly(ethylene terephthalate) (PET), to make flexible displays, which are thin, lightweight, formable and durable [4,5].

Heeger and coworkers were the first to report on the fabrication of flexible polymer LEDs on a PET substrate using a poly(phenylenevinylene) (PPV) derivative [6]. In these devices they obtained a high 1% external quantum efficiency with calcium cathodes. Since then, others have reported results on LEDs made with both evaporated small molecules [7–11] and polymers [12–14] on plastic substrates. Devices made with small molecules such as tris-(8-hydroxyquinoline) aluminum (Alq_3) and α-napthylphenylbiphenyl diamine (NPB) have a luminance efficiency of 4.4 cd/A, however, the disadvantages of these devices are their complicated fabrication and structure, which include planarizing and insulating layers [10]. Polymer LEDs made with a novel ITO anode deposition technique and a PPV derivative exhibit luminance efficiency as high 5.8 cd/A; however, the drawback of these is the employment of low work function reactive cathodes such as calcium which must be capped with silver to improve cathode stability [12]. Since the use of such low work function metals places stringent requirements with regard to the encapsulation of the device, this work focuses on the development of polymers that will operate with higher work function cathodes such as aluminum, making encapsulation less problematic and device structure simpler. To this end, we have designed and used a random copolymer containing PV with solubilizing dialkoxy groups and a PV derivative with oxadiazole moieties (RC30) (Fig. 1) for the emissive layer. Based on prior work, it is known that oxadiazoles, when incor-

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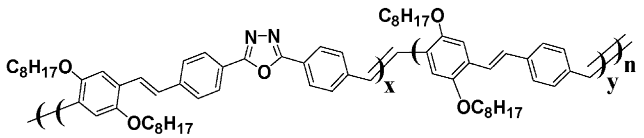

Fig. 1. Structure of the statistical copolymer (RC30), which has on average 70% oxadiazole containing PPV monomer and 30% PPV monomer.

porated into a PPV backbone, improve electron injection and hence result in a better balance of charges in the emissive semiconducting layer [15]. Also, these moieties are electron deficient and pull electron density away from neighboring vinyl bonds, rendering them less vulnerable to degradation upon exposure to oxygen [15]. The polymer RC30 was specifically chosen since, even in a single layer LED without additional hole and/or electron injecting layers and with aluminum as the cathode, this copolymer showed an EQE of 0.15% and a luminance of 544 cd/m^2 was obtained at a current density of 160 mA/cm^2 (20 V) [16].

2. Experimental

The synthesis, structural characterization, and photophysical properties of RC30 are reported elsewhere [16]. It is a random copolymer of 70% oxadiazole substituted PPV and 30% PPV as determined by NMR and has a M_n and M_w of 2490 and 4160, respectively, as determined by GPC. The M_n of this polymer was deliberately kept low to control energetic disorder associated with polydispersity in conjugation length which has been shown to influence device efficiency [17].

2.1. Device fabrication

Devices were made, starting with ITO coated on glass or PET substrates. The flexible substrates were obtained from Innovative Specialty Films and had a sheet resistance of 100 Ω/□. The ITO was cleaned according to a protocol obtained from Bayer Chemicals [18]. A 120 nm thick PEDOT:PSS film (Baytron® P VP CH 8000 grade obtained from Bayer Chemicals) was spin-coated at a rate of 1500 rpm for 180 s on top of the ITO as the hole injecting/transporting layer. After deposition of this layer, the glass devices with PEDOT:PSS were dried in a vacuum oven for 5 min at 100 °C and the plastic substrate devices at 60 °C for 15 min. On flexible ITO substrates, where the oxide layer is rough, PEDOT:PSS also serves as a planarizing layer. The RC30 was dissolved in freshly distilled 1,1,2,2-tetrachloroethane at a concentration of 20 mg/mL and spin-coated onto the ITO layer at a rate of 900 rpm for 120 s resulting in a film of ca. 100 nm in thickness. Thickness values of the organic layers were measured with a DekTak Profilometer. To aid in electron injecting a thin 8–10 Å layer of either cesium fluoride (CsF) or lithium fluoride (LiF) was evaporated, at a rate of 0.1 nm/s, over the RC30 layer. Finally, a 200 nm thick aluminum cathode was shadow evaporated at a rate of 1 nm/s onto the substrate defining pixels of ca. 1 mm radius.

2.2. Electroluminance measurement

Current–voltage characteristics were measured using a HP 4155B Semiconductor Parameter Analyzer with a Newport 818UV silicon photodetector. Only light transmitted through the transparent substrate was collected on the detector. External quantum efficiencies were determined as the ratio of the photocurrent to device current, with a correction factor of 1.43 for detector sensitivity at 540 nm. No other corrections were made.

Brightness measurements were done using a calibrated TRI-COR Inc. Model 820 Video Photometer and analyzed using Eyeppearance 3.67 software.

All devices were tested and stored in a dry nitrogen filled glove box at room temperature where the water and oxygen levels were less than 1 ppm.

2.3. Morphological studies

AFM images were collected with a Digital Instruments Nanoscope IIIa AFM in tapping mode using BS-Tap300Al tips from Budget Sensors Inc. Height profiles were flattened to enhance image quality.

3. Results and Discussion

3.1. Device properties

The electroluminescent properties of the RC30 device with aluminum cathodes and either CsF or LiF interlayers are tabulated in Table 1 and illustrated in Fig. 2. Also, for comparison, efficiencies for devices on glass and plastic substrates with no fluoride interlayer are tabulated. As expected, performance of the diodes improved with the addition of the fluoride layers. The CsF devices showed average EQE of 0.6% (turn-on voltage 3.7 V) and 0.67% (turn-on voltage 3.6 V) on glass and plastic, respectively. Additionally, these devices also displayed a good brightness, with the flexible device having a luminance of 760 cd/m^2 at 40 mA/cm^2 (8.4 V). Diodes with LiF showed improved performance exhibiting average EQE of 0.8% on both glass and plastic and a turn-on voltage of 4.5 V, with the best diodes performing at an exceptional efficiency of 1%. At these efficiencies, the LiF devices showed a brightness of 1600 cd/m^2 at 40 mA/cm^2 (7.8 V). This translated to luminance and power efficiencies reaching 4 cd/A and 1.8 lm/W, respectively. These values compare well with device data obtained for other PPV

Table 1
Device efficiency and turn-on voltage values determined for PLEDs

Device configuration	External quantum efficiency (%)	Turn-on voltage (V)
Glass/ITO/PEDOT/RC30/Al	0.23	6
Plastic/ITO/PEDOT/RC30/Al	0.13	8
Glass/ITO/PEDOT/RC30/LiF/Al	0.80	4.5
Plastic/ITO/PEDOT/RC30/LiF/Al	0.80	4.5
Glass/ITO/PEDOT/RC30/CsF/Al	0.60	3.7
Plastic/ITO/PEDOT/RC30/CsF/Al	0.67	3.6