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Enhancement in fluorescence quantum yield of MEH-PPV:BT blends for polymer light emitting diode applications

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ABSTRACT

We have investigated the effect of blending electron deficient heterocycle Benzothiadiazole (BT) on the photo-physical properties of conjugated polymer Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). Quantum yield (QY) value has been found to increase from 37% for pure MEH-PPV to 45% for an optimum MEH-PPV:BT blend ratio of 1:3. This can be attributed to the efficient energy transfer from the wide bandgap BT (host) to the small bandgap MEH-PPV (guest). The FTIR spectrum of MEH-PPV:BT blended thin film indicates suppression of aromatic C-H out-of-plane and in-plane bending, suggesting planarization of the conjugated polymer chains and, hence, leading to increase in the conjugation length. The increase in conjugation length is also evident from the red-shifted PL spectra of MEH-PPV:BT blended films. Single layer MEH-PPV:BT device shows lower turn-on voltage than single layer MEH-PPV alone device. Further, the effect of electrical conductivity of PEDOT:PSS on the current-voltage characteristics is investigated in the PLED devices with MEH-PPV:BT blend as the active layer. PEDOT:PSS with higher conductivity as HIL reduces the turn on voltage from 4.5 V to 3.9 V and enhances the current density and optical output in the device.

1. Introduction

Since the first report on organic/polymer light emitting diodes [1,2], there have been continuous efforts to improve the device efficiency and lifetime by employing novel device architectures and synthesizing new efficient organic materials [3–12]. Organic semiconductors (OSCs) are well suited for thin, light-weight, flexible and large area flat panel displays and solar cells. Organic Light Emitting Diodes (OLEDs), Solar Cells, Sensors and Lasers are some of the explored applications of OSCs [13–15]. Polymer light-emitting diodes (PLEDs) are of particular interest since they can be fabricated by low temperature solution processing and scalable technologies, such as inkjet printing, on large area flexible substrates [16,17]. Recent applications of PLEDs include flexible displays, solid-state lighting and short-range indoor optical communication [18–20].

Efficient charge injection, balanced charge transport, exciton formation and recombination within the active layer are the basic processes involved in the operation of a PLED [21]. However, it is well documented in the literature that the magnitude of hole transport in OSCs are a few orders greater than that of electron mobility, which is hindered by omnipresent electron traps at 3.6 eV [22]. The imbalance of charge carrier transport in the OSCs invariably results in poor device efficiency and performance. This problem has been partly addressed by the design and synthesis of new materials with balanced charge carrier transport and, also, by blending active layer material with electron transport material [23]. A multilayer device includes hole injection layer (HIL), hole transport layer (HTL), electron blocking layer (EBL) on one side of the electroluminescent (EL) layer and, hole blocking layer (HBL), electron transport layer (ETL), electron injection layer (EIL) between the EL layer and the cathode. Such devices show improved device performance [24]. However, a serious problem in such multilayer devices is the dissolution of pre-deposited polymer layer by the solution for the subsequent layer [25]. Hence, there is great interest in fabricating few-layer devices using blended polymer materials with good device efficiency [26].

Poly [2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), a well-investigated electroluminescent conjugated polymer and Benzothiadiazole (BT), an electron deficient small molecule, have been widely used in the field of organic optoelectronics [27,28]. Recently, Bidgoli et al. have explored the possibility of blending these materials and applying it as a single electroluminescent layer in the polymer light emitting diodes [29,30]. The motivation behind this was to balance the charge carrier mobilities within the active layer and thereby avoiding the complexity of multilayer device structure. They could observe a reduction in the turn on voltage and an increase in the lifetime of these devices. However, an extensive study of the photo-

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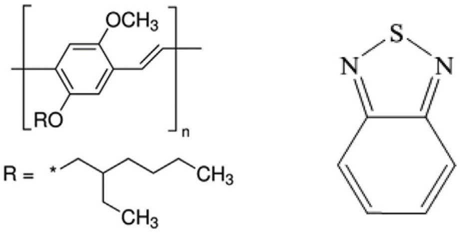

Fig. 1. Chemical structure of MEH-PPV and BT respectively (from Sigma-Aldrich website).

physical properties and different interaction mechanisms of these materials are still lacking in the literature. Here we report the enhancement in fluorescence quantum yield of MEH-PPV by the addition of BT. Fluorescence quantum yield (Φ_f), a measure of the efficiency of conversion of absorbed light into emitted light, is the key parameter for comparison of fluorophore efficiency. Relative fluorescence quantum yield can be easily measured using a UV–Vis spectrometer and a spectro-fluorometer.

2. Experimental details

MEH-PPV with a number averaged molecular weight (Mn) of 40000–70000 and with a polydispersity index (PDI) of around 6 and BT with a purity of 98% were purchased from Sigma Aldrich. Their chemical structures are shown in Fig. 1. Two varieties of PEDOT:PSS, one of conductivity (1 S/cm) grade (referred to as PEDOT:PSS1) and another with high-conductivity (> 200 S/cm) grade (PEDOT:PSS2) were also purchased from Sigma Aldrich. All these materials were used as received and without any further purification. Indium Tin Oxide (ITO) patterned glass substrates with sheet resistance of 15Ω/□ and thickness of 150 nm was sourced from Kintech, Taiwan, and used as the anode for the device fabrication. MEH-PPV and BT were separately dissolved in 1,2-dichlorobenzene (DCB) to obtain solutions with a concentration of 1 mg/ml each. These two solutions were mixed together in different ratios to get appropriate weight percentages and subjected to the absorption and emission spectroscopy to investigate the effect of BT on the optical properties of MEH-PPV. Fluorescence quantum yields were calculated from the absorption and fluorescence spectra using a comparative method in which Fluorescein used as the standard.

UV–Vis absorption spectrum was recorded using Ocean Optics USB 4000 spectrophotometer with integration time of 30 ms. Fluorescence spectrum at room temperature was recorded using Horiba Jobin Yvon Fluoromax-4 spectrometer. Both the fluorescence reference standard and samples under the investigation were excited by light of wavelength 496 nm and the slit width of excitation and emission monochromators were kept 0.75 nm. FTIR spectrum of MEH-PPV and MEH-PPV:BT blend films were recorded by Perkin Elmer Frontier MIR spectrometer to investigate the structural changes and bond stretching or bending in MEH-PPV after blending with BT.

3. Results and discussions

3.1. Photo-physical studies of MEH-PPV and MEH-PPV:BT blends

Fig. 2 shows the normalized UV–Vis absorption curves for pure BT, pure MEH-PPV and for MEH-PPV:BT in a 1:3 blend in DCB solvent. The same curves were recorded for all other MEH-PPV:BT blend ratios (see the supporting information). The absorption spectrum shows characteristics absorption peak at 310 nm and 503 nm for solution of pure BT and MEH-PPV, respectively. The MEH-PPV:BT blend solution retains the absorption maxima at 310 nm, however, the absorption at 503 nm is much reduced. The absorption spectrum for 1:1 shows almost equal absorption for the constituent materials and is simply the linear combination of absorption spectrum of BT and MEH-PPV. As the weight percentage of MEH-PPV in the blend decreases, a similar reduction is seen in the absorbance. Optical bandgap of these materials was calculated by substituting the λ_{onset} value in the equation $E_g = \frac{1241.25}{\lambda_{onset}}$ eV, and found to be 3.55 eV and 2.18 eV for BT and MEH-PPV solutions, respectively. The calculated optical bandgap values are in good agreement with the values in the literature [31].

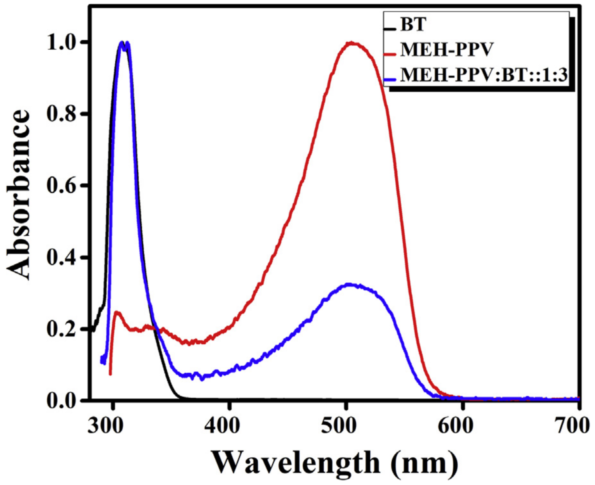

Fig. 2. Normalized UV–Vis absorption spectrum of MEH-PPV, BT and MEH-PPV:BT (1:3 ratio) solutions in DCB solvent.

For very dilute solution (absorbance < 0.1) of BT, the excitation wavelength was 310 nm, corresponding to absorption maximum in UV–Vis, and the fluorescence emission (Fig. 3) was recorded from 325 nm to 600 nm. BT shows a narrow emission spectrum ranging from 350 nm to 450 nm with an emission maximum at 380 nm. MEH-PPV and MEH-PPV:BT solutions were excited with light at wavelength of 496 nm and the emission was recorded from 506 nm to 800 nm. Both the solutions show almost identical emission spectra without any shift in the peak wavelength. This suggests that blending has little effect on the shape of the PL spectrum and the optical band gap of MEH-PPV. Therefore, BT can be a good alternative for inducing the charge carrier balance in MEH-PPV without modifying the optical characteristics of MEH-PPV. Both MEH-PPV and MEH-PPV:BT blend solutions show a dominant peak at 569 nm and a shoulder at 610 nm, and their corresponding energy values are 2.18eV, 2.03eV respectively. Another shoulder peak at 668 nm (1.86eV) is barely visible. The energy difference between the three peaks are equal and it follows the usual vibronic progression [32]. A red shifted PL spectrum was obtained for both

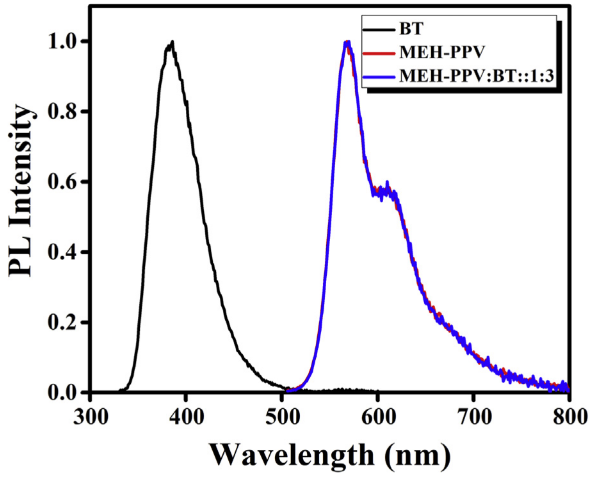

Fig. 3. Normalized fluorescence spectra of MEH-PPV, BT and MEH-PPV:BT (1:3 ratio) solutions in DCB solvent.