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POLYMER SOLAR CELLS AND INFRARED LIGHT EMITTING DIODES: DUAL FUNCTION LOW BANDGAP POLYMER

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Conjugated Polymers with a HOMO-LUMO transition < 2 eV, i.e. a low bandgap, respectively, have interesting and desired properties for some thin film optoelectronic devices like light emitting diodes and solar cells.

In this contribution we present the implementation of the novel copolymer PTPTB, consisting of alternating electron-rich N-dodecyl-2,5-bis(2′thienyl)pyrrole (TPT and electron-deficient 2,1,3-benzothiadiazole (B) units, in light emitting diodes (LEDs) and photovoltaic devices. The LEDs show emission in the near infrared region, peaking at 800 nm. The electroluminescence yield can

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be significantly enhanced by blending with the wide bandgap polymer poly (para-phenylene-vinylene) derivative MDMO-PPV. Bulk heterojunction devices of PTPTB blended with the C_{60} derivative PCBM shows AM 1.5 efficiencies around 1%. The low bandgap of PTPTB allows collecting photons up to 750 nm.

Keywords: low bandgap polymer; plastic solar cells; light emitting diodes; luminescence

1. INTRODUCTION

Several optoelectronic devices using conjugated organic materials have been demonstrated in the last decade [1–8]. Among this class of materials, conjugated polymers are of special interest because of their wide range chemical tunability and their low cost processability [5–8]. Polymer light emitting diodes (LEDs) are entering the display market already [5–6]. Whereas many materials have been reported to emit in the visible, conjugated polymers with suitable low bandgap for near infrared emission are rare [9–10].

Polymer photovoltaic devices using conjugated MDMO-PPV [poly-(2-methoxyl, 5-(3,7-dimethyloctyloxy)] para phenylene-vinylene)/PCBM ([6,6]-phenyl C_{61}butyric acid methylester) blends have been demonstrated with efficiencies up to 3% [11–13]. The corresponding internal quantum efficiency, absorbed photons to electrons, is estimated to be nearly 100% in the short circuit case. The main limiting factor towards higher efficiencies is the spectral mismatch of the active layer absorption, with a maximum around 500 nm, to the terrestrial solar spectrum with a maximal photon flux between 600 and 800 nm [13–14]. Therefore, the use of low bandgap polymers is a viable route to increase the amount of absorbed photons and consequently the power efficiency of solar cells.

In this contribution we present LEDs from the new conjugated polymer PTPTB as well as photovoltaic devices from PTPTB/PCBM blends. The electroluminescence is observed in the near infrared region. The yield of electroluminescence can be significantly enhanced by sensitization of PTPTB with admixture of MDMO-PPV. Photovoltaic devices of PTPTB/PCBM blends show AM1.5 efficiencies of 1%. The photovoltaic action spectrum of the device shows the contribution of photons up to 750 nm, which is the absorption edge of PTPTB.

2. EXPERIMENTAL

The synthesis of PTPTB has been described previously [15]. The structure is presented together with MDMO-PPV and PCBM in Figure 1. Polymer films are spincoated from chlorobenzene solution for PTPTB and

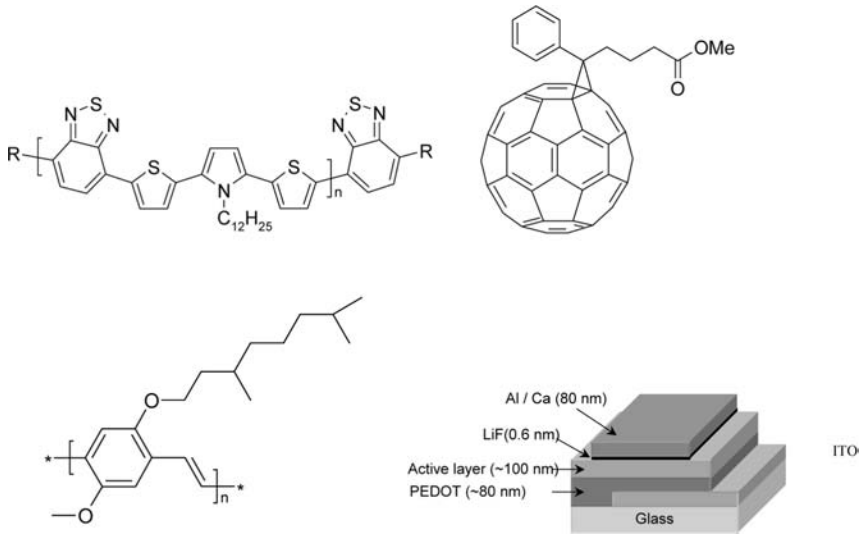

FIGURE 1 Chemical structure of PTPTB, PCBM, MDMO-PPV and the geometric structure for the photovoltaic devices and light emitting diodes.

PTPTB/PPV films and from toluene for PTPTB/PCBM films. Absorption spectra are measured on a HP spectrometer. The Photoluminescence is measured on a homemade setup, exciting the film with the 514 nm line and a beam spot of approximately 10 mm^2 of an Ar^+ laser and detecting the luminescence with a silicon diode. Spectra are corrected for the diode sensitivity.

LED and photovoltaic devices are made in sandwich geometry, presented in Figure 1. On precleaned ITO, a layer of PEDOT: PSS, Baytron P, is spincoated from an aqueous solution and dried afterwards in vacuum. The active polymer layers are spincoated from toluene, giving a thickness of ~60 nm for the PTPTB and PTPTB/PCBM devices and ~100 nm for the PTPTB/MDMO-PPV blends. As top electrode, 6 Å LiF and 60 nm Al is evaporated under a vacuum better than 10^{-5} mbar.

All device testing is done in an Argon glovebox. Electroluminescence is measured with an Avantes diode array detector. I–V curves are recorded with a Keithley 2400 source measuring unit. AM 1.5 illumination is simulated with a Steuernagel solar simulator with 80 mW cm^{-2}.

IPCE is detected with a lock in amplifier after monochromatic illumination.

3. RESULTS

The optical bandgap of PTPTB, estimated from the onset of the absorption spectrum in Figure 2, is approximately 1.6 eV. Electron voltage spectroscopy shows reversible oxidation and reduction peaks. The onset for the oxidation is at +0.5 V vs. NHE, for the reduction at –1.2 V vs. NHE, leading to an electrochemical bandgap of approximately 1.7 eV in good agreement with the optical data.

The photoluminescence as well as the electroluminescence peaks at 800 nm, also presented in Figure 2.

Figure 3 shows the photoluminescence of MDMO-PPV and PTPTB and several blends. The luminescence at 800 nm, originating from PTPTB, is greatly enhanced by mixing a few percent of the low bandgap material in the wide bandgap polymer; coincidently the MDMO-PPV luminescence at 600 nm is quenched. The similar effect is observed for the electroluminescence of devices with the same blends, shown in Figure 4.

Thin film devices of PTPTB/PCBM show a rectification of ~100 at +/– 2 V and a clear photoeffect, I–V curves are shown in Figure 5. Under simulated AM1.5 conditions, a power conversion efficiency of 1% is

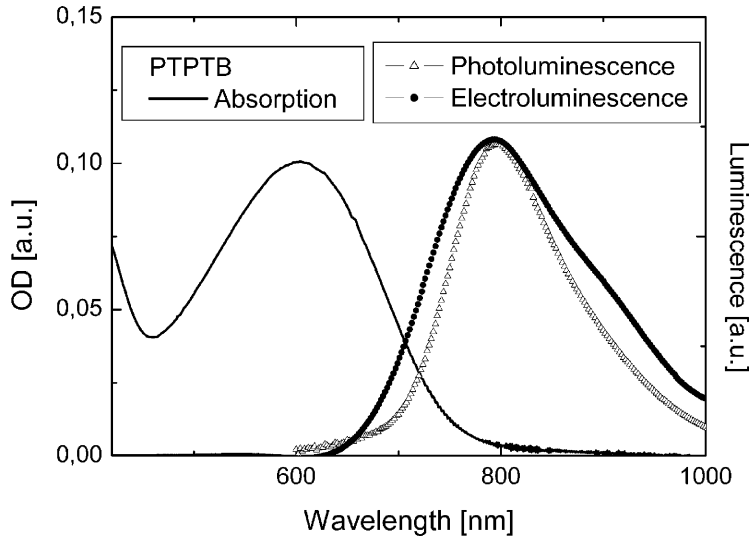

FIGURE 2 Optical absorption and photoluminescence, excited at 514 nm with 400 mW cm^2, of a spin cast PTPTB film; electroluminescence (-•-) at +5 V of a PTPTB with comparable thickness in a sandwich device.

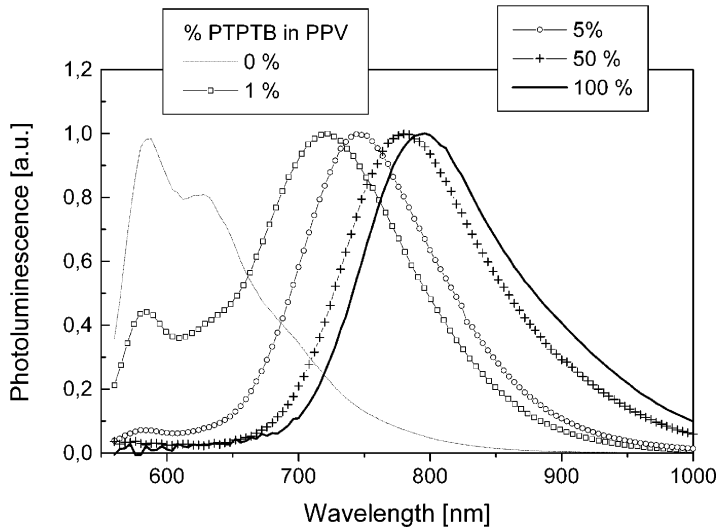

FIGURE 3 Photoluminescence of MDMO-PPV (dotted line), PTPTB (full line) and different blends with 1% (open square), 5% (open diamond) and 50% (crosses) PTPTB in MDMO-PPV, excited with 400 mW cm^{-2} at 514 nm, Photoluminescence is normalized at the peak maximum.

measured. The thickness of the active layer for the photovoltaic devices is measured with 60 nm, determined by AFM.

The indicent photon to electron IPCE peaks to a value of 600 nm with a quantum efficiency of 20%, shown in Figure 6. The IPCE spectrum matches the optical absorption spectrum well.

4. DISCUSSION

The low yield of electroluminescence of the pristine PTPTB device can be due to unbalanced charge injection or non-radiative recombination.

The spectral overlap of the MDMO-PPV luminescence with the PTPTB absorption around 600 nm allows for an energy transfer form the wide bandgap material to the lower one. The shift of the photoluminescence by mixing a few percent of PTPTB into MDMO-PPV shows the possibility of energy transfer from the wide bandgap to the low bandgap polymer.

Accordingly, a shift of the electroluminescence is observed for the LEDs. We assume that the charge injection and transport is done by the MDMO-PPV, but excitons formed on the MDMO-PPV chain are transferred to the PTPTB, where they decay radiatively. The electroluminescence yield is enhanced significantly by diluting PTPTB into MDMO-PPV.

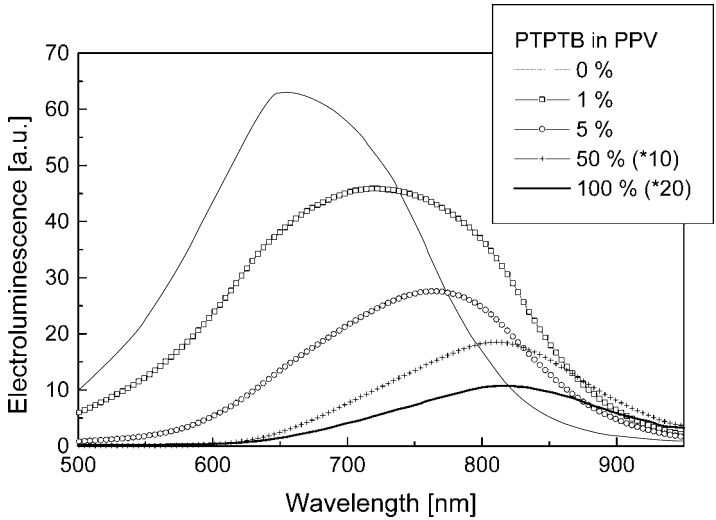

FIGURE 4 Electroluminescence of MDMO-PPV (dotted line), PTPTB (full line) and different blends with 1% (open squares), 5% (open diamonds) and 50% (crosses) PTPTB in MDMO-PPV; electroluminescence is measured in sandwich devices with ITO/PEDOT anode and LiF/Al cathode.

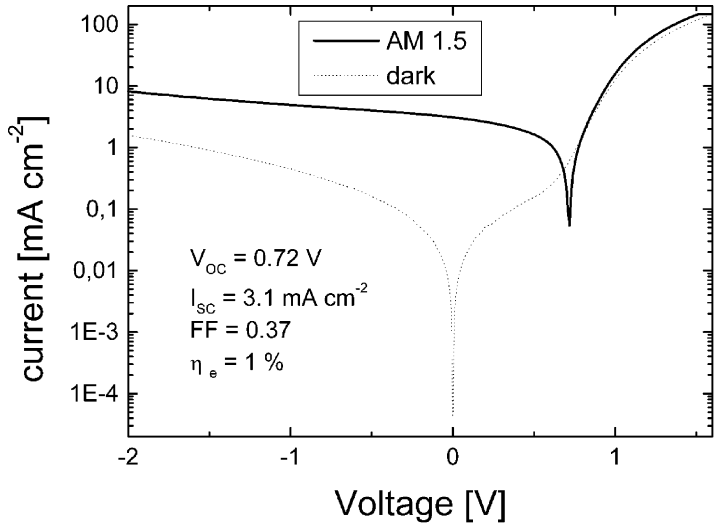

FIGURE 5 I–V curve of a PTPTB/PCBM 1/3 device under simulated AM 1.5 conditions (solid line) and in the dark (dotted line). Thickness of the active layer is ~60 nm.

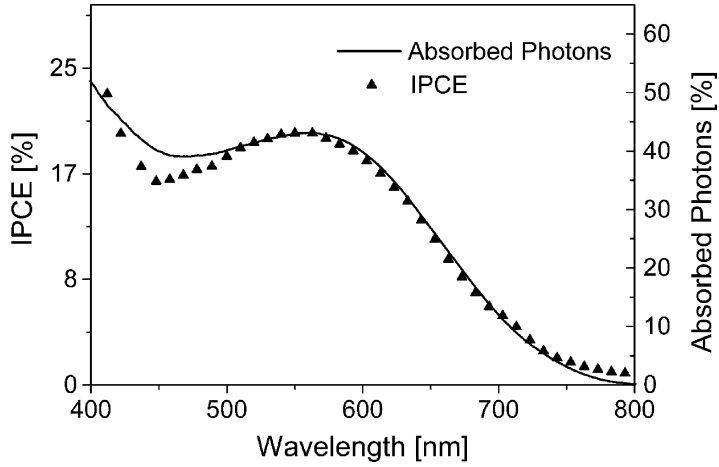

FIGURE 6 IPCE spectrum (triangle) of a PTPTB/PCBM 1/3 device in comparison with the percentage of absorbed photons (transmission) of a reference film of comparable thickness.

The reduction potential of PCBM with −0.69 V vs. NHE [16] and PTPTB with −1.17 eV vs. NHE show a clear offset. Photoinduced electron transfer from the conjugated polymer to the fullerene shall therefore be energetically favorable [17]. The occurrence of polaronic absorption in the photoinduced absorption spectrum as well as the quenching of the luminescence [15] in the blend shows clearly that charges are formed upon illumination. The high quantum efficiency of the solar cell as well as the high overall photocurrent is the direct effects of the efficient charge creation process. The IPCE spectrum shows symbatic behavior of the cell, i.e. the photocurrent spectrum follows the absorption spectrum. This shows that PTPTB contribute to the photovoltaic action.

The open circuit voltage of 0.72 V is lowered less than 0.1 V after reduction of the polymer bandgap of more than 0.6. The effective energetic splitting of the charges, i.e. the difference of the conjugated polymer HOMO and the fullerene LUMO, is similar in both cases since the onset for electrochemical oxidation as indication for the polymer HOMO is at the same values ($\sim$ +0.5 V vs. NHE) in both cases.

5. CONCLUSIONS

The PTPTB bandgap is determined by optical absorption and electrochemical voltage spectroscopy with 1.6–1.7 eV. The material shows

photoluminescence and electroluminescence in the near infrared region. Both processes can be enhanced by sensitization with MDMO-PPV. PTPTB shows photoinduced electron transfer to the fullerene acceptor PCBM. The created charges can be collected in a photovoltaic device with a power efficiency of 1%. The use of low bandgap polymers in bulk heterojunction solar cells is a viable route to improve the power efficiency.

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