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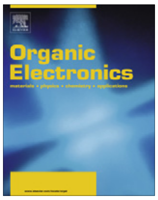

Solution processed small molecule organic interfacial layers for low dark current polymer photodiodes

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ABSTRACT

We demonstrate a small molecule solution processed hole interfacial layer approach to improve the dark current characteristics of polymer photodiodes. The two hole blocking materials under investigation 3-phenyl-4(1′-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) and 2-[3,5-bis(1-phenylbenzimidazol-2-yl)phenyl]-1-phenylbenzimidazole (TPBi) are spin-coated from ethanol as an orthogonal solvent on top of a P3HT:PCBM active layer. We reduce the dark current at a bias voltage of −1 V by a factor of 17.2 by introducing a TAZ interfacial layer while keeping the responsivity unchanged.

1. Introduction

Semiconducting polymers offer substantial advantages for photodetectors as compared to their inorganic counterparts. Devices can be fabricated on virtually any surface using low cost solution based processes like spincoating [1,2], spraycoating [3], doctor-blading [4] or inkjet printing [5]. The high absorption coefficient of organic semiconductors enables ultrathin devices with thicknesses in the sub-micron range. One challenge for the application of organic photodiodes is the reduction of the dark current under reverse bias, as the dark current limits the detection of low intensity signals. A major contribution to the dark current is the injection of charge carriers through the respective counter electrode, e.g. holes being injected through the cathode.

An analogous situation is well known from organic light emitting diodes (OLEDs) where charge carriers are supposed to recombine inside the emission layer of the device rather than recombining at the counter electrode. In order to reduce losses, interfacial layers that form an energetic barrier are added which hinder charge carriers from recombination at the electrode. This approach helps to confine the injected charge carriers to the emission zone [6] and can also hinder the generated excitons from diffusing to the electrodes [7]. The very same concept is used in organic solar cells to prevent the loss of photogenerated charges at the electrode accounting for a simultaneous enhancement of the fill factor and the device photo current [8]. While in both, organic photodiodes and organic solar cells, the aim is to reduce the recombination of excitons at the electrodes, the reduction of charge carrier injection in reverse bias is the main goal in photodiodes. Vacuum deposited small molecules have been successfully used as interfacial layers in organic solar cells and photodiodes [9–15]. Recently, solution-processed small molecule blocking layers have been used for multilayer OLEDs combining the advantages of solution processing with the low defect

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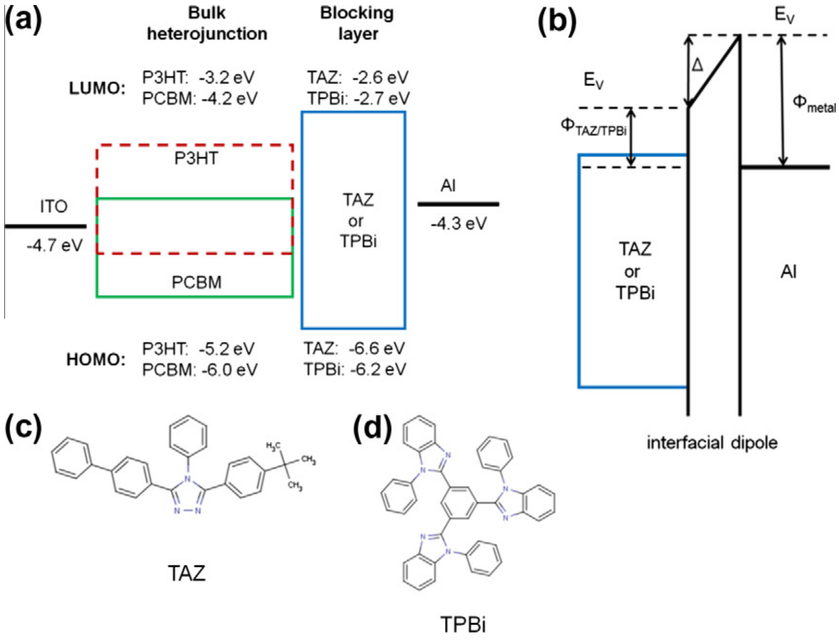

Fig. 1. (a) Proposed energy levels for the investigated organic materials. (b) Schematic energy diagram of an interfacial dipole formed at the TAZ/TPBi to aluminum interface.

density of small molecules [16,17]. With respect to a future low-cost solution device processing, blocking layers from inorganic nanoparticles [18], crosslinked polymers [19,20] or a combination of inorganic sol–gel materials and crosslinked polymers [21,22] have been incorporated into organic photodiodes in order to reduce the dark current of the device. In this work we present organic bulk heterojunction poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) photodiodes comprising hole interfacial layers from solution processed small molecules, i.e. 3-phenyl-4(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) or 2-[3,5-bis(1-phenylbenzimidazol-2-yl)phenyl]-1-phenylbenzimidazole (TPBi). TAZ and TPBi are commonly used as blocking layers in OLEDs [23] due to their energetically low highest occupied molecular orbital (HOMO) energy levels that were reported at $E_{HOMO} = -6.6$ eV and $E_{HOMO} = -6.2$ eV, respectively [24,25]. Hence, the HOMO energy levels of TAZ and TPBi are significantly lower than those of P3HT and PCBM at $E_{HOMO} = -5.2$ eV and $E_{HOMO} = -6.0$ eV, respectively, and it could be assumed that they act as efficient hole blocking layers as depicted in the energy scheme in Fig. 1 [26].

2. Materials and methods

The active layers of the devices were fabricated by spincoating onto indium-tin-oxide (ITO)-coated glass substrates. Regioregular P3HT (Rieke, 4002-E, RR = 91%) and PCBM (Solenne BV, 99%) were dissolved in o-dichlorobenzene in a 1:1 ratio at a concentration of 80 mg/ml. TAZ (Sensient, sublimated) and TPBi (Lumtec, sublimated) were dissolved in ethanol at varying concentrations ranging from 0.06 mg/ml to 3 mg/ml. All solutions were stirred for at least 12 h on a hotplate at 80 °C. ITO coated glass substrates (SNP, ITO thickness 125 nm) were cut to size (16×16 mm^2) and structured via standard photolithography and etching in hydrochloric acid. They were sequentially cleaned by scrubbing with detergent and ultrasonication in water, acetone and isopropanol. After blow-drying with a nitrogen gun the substrates were dehydrated at a temperature of 150 °C for 2 h. Before spincoating the functional layers, an oxygen plasma (100 W, 2 min) was applied to the substrates in order to remove any organic residue on the surface. All subsequent steps were carried out in nitrogen atmosphere. P3HT:PCBM was spincoated to a thickness of 450 nm directly onto the ITO electrodes intentionally omitting the commonly used hole transport layer poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS). Though PEDOT:PSS is a widely used hole injection layer for OLEDs, organic solar cells and photodiodes, the incorporation of PEDOT:PSS has been reported to increase the dark current [27] and to limit the device lifetime due to ion mobility [28]. After a thermal annealing step on a hotplate (135 °C, 10 min) TAZ and TPBi were spincoated onto the P3HT:PCBM layer with thicknesses below 3 nm for the 0.06 mg/ml solutions and 37 nm and 26.7 nm for the 3 mg/ml solutions respectively. As a reference we also vacuum deposited TAZ and TPBi layers via thermal evaporation (Lesker Spectros) at a rate of 0.3 Å/s – 0.5 Å/s and at a pressure of 1.1×10^{-6} mbar. 200 nm thick aluminum electrodes were thermally vacuum deposited from a ceramic crucible (2 Å/s, 2×10^{-6} mbar). The active device area was 2×2 mm^2 as defined by the overlap of the ITO and aluminum electrodes. We determined the J-V-characteristics using a source measurement unit (Keithley 238) and a solar simulator (Oriel,