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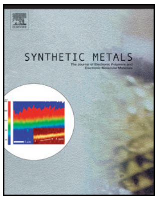

Enhanced electron extraction from solution processed organic solar cells employing rhodamine B doped fullerene layers

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ABSTRACT

Fullerene interlayers are a common approach to improve electron extraction in organic solar cells. In this work, we investigate n-doping of solution processed fullerene derivatives by the cationic dye rhodamine B (RhB), formerly known from vacuum device fabrication only. The doping efficiency under illumination is quantified by electron paramagnetic resonance yielding 0.3% for PCBM, and 0.02% for bis-PCBM and ICBA. Incorporated into nanoparticulate organic solar cells, n-doped fullerene layers enhanced the electron extraction and improved the devices' power conversion efficiencies.

1. Introduction

Common organic optoelectronic devices such as organic light emitting diodes (OLEDs) or organic solar cells (OSCs) comprise multi-layer thin-film architectures where layer interfaces often rule the device properties. Among the many interfaces, charge carrier extraction to and charge carrier injection from the electrodes are crucial to the device performance. Besides interfacial dipoles using alkali metal salts (such as lithium fluoride) [1–3] or polyelectrolytes (such as PFN, PEI, PEIE) [4–9], electrical doping can be employed to establish ohmic contacts. *p*-Doping can be achieved by adding strong acceptor molecules to a molecular hole transport matrix which leads to an electron depletion of the matrix molecules and hence to the generation of hole excess [10,11]. For n-doping, electron excess on the lowest unoccupied molecular orbital (LUMO) is generated, for example, by incorporating alkali metals with low work function [12–14] or cationic dyes such as rhodamine B (RhB) [15], leuco crystal violet (LCV) [16], pyronine B (PyB) [17] and acridine orange base (AOB) [18]. Alkali metals are known to often diffuse through the device, which can lead to quenching of excited states in light-harvesting or light-emission layers [19], whereas the diffusion of cationic dyes may be hampered by their size. To act as dopants, cationic dyes require activation by light or thermal energy to transform the dyes into their leuco form [16]. The underlying doping mechanisms have been investigated in detail for LCV and AOB [16,18]. When doping non-functionalized fullerenes (C_{60}) with LCV, the excited electron transfers from LCV to the LUMO of C_{60} ($LCV + C_{60} \rightarrow LCV^{+} + C_{60}^{-}$). The dye is then stabilized through oxidation by a transfer of a radical hydrogen atom to another fullerene ($2\ LCV + 3C_{60} \rightarrow 2\ CV^{+} + 2C_{60}^{-} + C_{60}H_2$) [16]. The reaction of two LCV with $3C_{60}$ forms two n-doped and one hydrogenated (reduced) C_{60} molecule.

Whereas the fabrication of n-doped thin-films using cationic dyes and their incorporation into organic semiconductor devices exclusively relied on vacuum deposition in the past, the prospect of future device printing will require solution processable layers.

In this work, we investigated cationic n-doping of three solution-processable fullerene derivatives that are commonly employed in organic solar cells: [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM), bis-phenyl C_{61}-butyric acid methyl ester (bis-PCBM) and indene-C_{60} bisadduct (ICBA). The physical properties of RhB doped fullerene layers were examined by electron paramagnetic resonance (EPR) spectroscopy and UV–vis absorption spectrometry. The layers were then implemented into organic nanoparticle solar cells that showed superior performance compared to non-doped electron extraction layers (EELs).

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2. Experimental details

PCBM (Solenne, 99%), bis-PCBM (Solenne, 99.5%) and ICBA (Luminescence Technology Corporation, >99%), were dissolved (20 g/L) in *o*-dichlorobenzene (DCB, Sigma Aldrich, anhydrous, 99%) under inert atmosphere. Rhodamin B (RhB, Acros, >99%) was dissolved (20 g/L) in Ethanol (EtOH, Rotipuran, Carl Roth, >99.8%). The solutions were mixed to yield fullerene:RhB solutions with a dopant concentration of 20 mol%.

A home-built X-band EPR spectrometer was used to record room temperature continuous wave electron paramagnetic resonance (cwEPR) spectra to detect unpaired spins in the doped layers. Therefore, 50 μL of the respective solutions were filled in EPR tubes. The tubes were filled with inert gas after removing the solvent in vacuo, and sealed using a blowtorch. The magnetic field strength was regulated by a controller (Bruker BH15), and a microwave bridge (Bruker ER 048 R) was used for microwave generation and detection. Magnetic field modulation in combination with lock-in detection was employed using a lock-in amplifier (Stanford Research SR810) and a modulation amplifier (Wangine WPA-120), resulting in derivative spectra. The sample was placed in a Bruker ER 4122 SHQ microwave resonator and illuminated with white light (Streppel halolux 110HI, 100 mW/cm^2) through a window in the resonator. The quality factor *Q* of the resonator loaded with the sample was determined from the mode picture before each EPR measurement was started. All measured spectra were background-corrected and double integration was performed to obtain the integrated EPR signal amplitude. By comparison of this intensity to the double integrated intensity of a reference sample with a known number of spins (4-hydroxy-TEMPO dissolved in toluene) and taking into account *Q*, as measured for the respective sample, and all experimental parameters that influence the signal intensity, this comparison yielded the absolute number of spins [20]. The uncertainty with respect to the absolute number of unpaired spins is less than 20% which is estimated based on the uncertainty of the sample volume when filling the tubes.

The absorbance spectra were measured on a Cary 5000 UV–vis-NIR absorption spectrometer from Agilent Technology in ambient conditions.

Solar cells were built on indium tin oxide (ITO) coated glass substrates ($R_{\square} = 13\ \Omega/\mathrm{sq}$) according to the device architecture shown in Fig. 1a comprising undoped or doped fullerene EELs or, for reference, a nanoparticulate ZnO layer. The substrates were successively cleaned in acetone and 2-propanol in an ultrasonic bath and treated with oxygen plasma before being transferred to a glovebox where they were kept in nitrogen atmosphere for the remaining fabrication and characterization process. 20 nm thick EELs were spin cast from solution (20 g/L, dichlorobenzene, 4000 rpm, 45 s). For reference, 30 nm zinc oxide (ZnO) was spin cast from nanoparticle isopropanol dispersion (Nanograde N-10, Nanograde Ltd., 1 wt%, 4000 rpm, 30 s) and thermally annealed on a hotplate (85 °C, 10 min). To avoid dissolution of the EEL, the photoactive layers comprising poly(3-hexylthiophene-2,5-diyl) (P3HT, Rieke Metals, $M_W = 57000$, $Đ_M = 2.4$, $RR = 91\%$) and ICBA (1:1, w:w, 10 g/L) were deposited from EtOH nanoparticle dispersion that had been synthesized according to processes described in the literature [21]. The particle size (diameter) $d = 176 \pm 84$ nm was measured by dynamic light scattering with a Malvern Instruments Zetasizer Nano-ZS. The active layer was deposited by three spin coating cycles from nanoparticle dispersion (10 mg/mL, 1000 rpm) and afterwards annealed (150 °C, 10 min). Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, HTL Solar, Heraeus) was diluted with water (1:1 v/v) and then spin coated (500 rpm, 5 s; 2000 rpm, 30 s; layer thickness 35 nm) on top. Then the samples were annealed on a hotplate (120 °C, 10 min). The Ag counter electrode (100 nm) was thermally evaporated through a shadow mask in a Lesker Spectros evaporation chamber (base pressure ~10^{-6} mbar), attached to the glovebox.

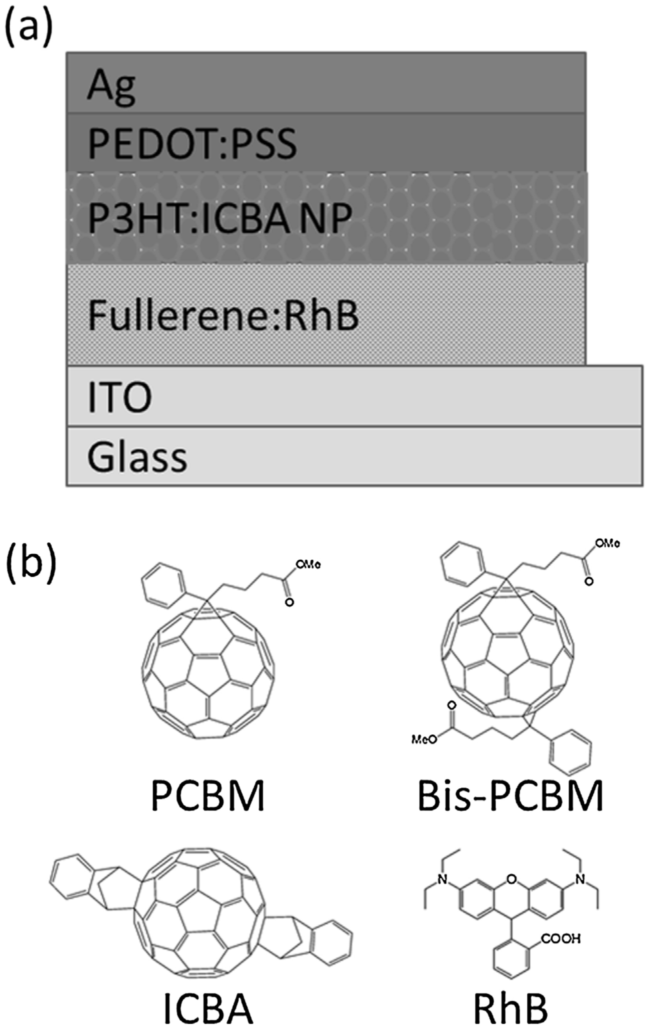

Fig. 1. (a) Device architecture and (b) chemical structures of PCBM, bis-PCBM, ICBA and the dopant RhB in its leuco form.

Current density-voltage (*J*–*V*) curves were recorded directly after fabrication with a source measurement unit (Keithley 238) under illumination from a spectrally monitored solar simulator (Oriel 300 W, 1000 W/m^2, ASTM AM 1.5G), calibrated with a KG5 filtered silicon reference cell (91150-KG5, Newport). We noticed a slight performance improvement after ten days due to shunt burning and henceforth discuss the performance data of the second measurement.

Film thicknesses were determined on a tactile stylus surface profiler (Bruker Dektak XT). Film thicknesses of the photoactive layers, processed from nanoparticle dispersion, were measured using atomic force microscopy in tapping mode on a Bruker Dimension ICON utilizing a TESP-HAR tip.

3. Results and discussion

Whereas electrical doping of C_{60} by cationic dyes has been widely employed in vacuum processed devices, the low solubility of C_{60} in most common solvents hampers layer deposition from solution. Due to their high solubility, PCBM, bis-PCBM and ICBA are the most often used functionalized fullerene derivatives in solution processable organic optoelectronic devices (Fig. 1b). The