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Electronic Supplimentary Information

Understanding the Morphology of Solution Processed Fullerene-Free Small Molecule Bulk Heterojunction Blends

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1. Materials and Methods

1.1. Reagents

Bis-furandiketopyrrolopyrrole (DPPFu$_2$) was synthesis are previously reported.[1] 1,8-diiodooctane (DIO), chloroform (CHCl$_3$), acetone and ethanol were purchased from Sigma-Aldrich. Pre-patterned indium tin oxide (ITO) coated glass was purchased Lumtec (15 Ω/sq) Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was purchased from Heraeus Precious Metals GmbH & Co. KG. Glass substrates cut from microscope slides were cleaned prior to use by scrubbing the surface with lab detergent, rinsed thoroughly with deionized water, acetone and ethanol then placed in a UV/ozone cleaner for 20 minutes

1.2. Thin-Film Preparation

Unless otherwise stated, neat and blend films were spun from CHCl$_3$ solutions with concentration of 10 and 20 mg/mL, respectively. The solutions were heated gently for 10 minutes under stirring and then allowed to stir overnight at room-temperature to fully dissolve the materials. On cleaned glass substrates neat and blend solutions were spin-coated at 1000 rpm for 90 seconds. Drop-casted films were prepared by depositing 200 μL of the precursor solution onto the center of clean galss substrate. The solvent was allowed to evaporate until a film of material remained.

1.2.1. Thermal Annealing

The as-cast films neat and blend films were placed on the surface of a pre-heated hotplate to a given temperature for 10 minutes and covered with an aluminum foil. Afterwards, the substrates were left to cool at room temperature.

1.2.2. Solvent-Vapour Annealing (SVA)

In a glass Petri dish, 2 mL of $CHCl_3$ was placed into the bottom-half of the dish. The solvent vapor was allowed to saturate the interior of the dish for 10 minutes. Then, a film coated substrate was stacked to the upper-half of the dish. The vapor was allowed to penetrate the film for a set amount of time before removal. The film was dried for 2 minutes before any measurements.

1.2.3. Solvent Additives

A stock solution of 4% (v/v) of DIO was prepared in $CHCl_3$. Precursor solutions were prepared by dissolving the solid compound(s) in appropriate volumes of the DIO solution and $CHCl_3$. Neat and blend films were prepared as descried before.

1.3. Thin-Film Characterization

1.3.1. UV-Vis and Photoluminescence (PL) Spectroscopy

All UV-vis spectra were acquired with an Agilent Cary 60 spectrophotometer operating at room temperature. Solution UV-Vis experiments were run using $CHCl_3$ as a solvent in 1 mm quartz cuvettes. For acquisition of thin-film spectra, the coated substrates were mounted vertically into the instrument and scanned from 900 to 300 nm. The film emission profiles were recorded using a Cary Eclipse spectrophotometer operating at room temperature. The excitation wavelength (λ_{ex}) was the maximum absorption wavelength obtained from the UV-Vis experiments of thin-films.

1.3.2. Cyclic Voltammetry (CV)

CV measurements were performed using a BASi Cell Stand instrument and BASi Epsilon EC software. Measurements were performed in a three-electrode, one compartment configuration equipped with silver/silver chloride electrode, platinum wire, and glassy carbon electrode (3 mm diameter) as a pseudo reference, counter electrode, and working electrode, respectively. The glassy carbon electrodes were polished with alumina. The measurements were performed using 0.1 M solution of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) dissolved in an anhydrous dichloromethane as a supporting electrolyte. All solutions were purged with nitrogen and then scanned at 50, 100 and 150 mV/s as-is and at 100 mV/s after the addition of a ferrocene (Fc) standard. The resulting voltammograms were referenced to the oxidation potential of Fc/Fc^+ which was defined as 0.48 V. The values of the HOMO levels (relative to vacuum) were obtained by comparing the onset of oxidation to the standard hydrogen electrode (SHE), assuming that the HOMO of Fc/Fc^+ is 4.80 eV below the vacuum level.

1.3.3. Thin-Film X-ray Diffraction (XRD)

The XRD study was performed using Rigaku Ultima IX diffractometer, equipped with a conventional Cu/Ka source. The XRD measurements were performed between 3 to 22° angular range at a rate of 1° per minute.

1.3.4. Atomic Force Microscope Imaging (AFM)

AFM images of blend film were obtained using Innova® AFM (Bruker Corporation). Intermittent contact imaging ‘‘Tapping Mode’’ was used to collect topographical images. Samples were typically imaged with a scan size of 5×5 μm, a scan rate of 0.30 Hz and a resolution of 256 pixels per line.

1.4. Organic Solar Cell Fabrication and Photovoltaic Performance

Organic photovoltaic (OPV) devices were fabricated on 25×25 mm pre-patterned ITO-coated glass substrates. Substrates were cleaned by gently scrubbing the surface with a solution lab detergent solution using a soft toothbrush followed by ultrasonic agitation in detergent solution, acetone and ethanol. The substrates placed in a UV/ozone cleaner for 20 minutes. The PEDOT:PSS solution was spin-coated at 2000 rpm for 45 seconds on the pattered and cleaned ITO coated glass substrate and baked at 140°C in air for 10 minutes. After cooling the substrates to room-temperature, the active layer was spin coated as described before.

The top metal contact was deposited using a custom-built thermal evaporator connected to the glovebox and equipped with two evaporation sources. Calcium (Ca) was loaded into an alumina crucible as the first source and Aluminum (Al) pieces were secured to a tungsten filament as the second source. Once the substrates were transferred into the evaporation chamber, the system was pumped down to $< 1\times10^{-6}$ torr. The metal cathode was formed by sequential thermal evaporation of 7.5 nm of Ca and 100 nm of Al. The chamber was allowed to cool for 30 minutes under vacuum before the substrates were transferred directly into the glovebox where they were promptly tested using a Keithley 236 Source-Measure Unit under 100 $\mathrm{mAcm^{-2}}$ illumination (AM 1.5G).

2. References

(1) Areephong, J.; Hendsbee, A. D.; Welch, G. C. *New J Chem* **2015**, *39* (9), 6714–6717.