**SUPPLEMENTARY MATERIAL**

**Relating Nanoscale Structure to Optoelectronic Functionality in Multiphase Donor-Acceptor Nanoparticles for Printed Electronics Applications**

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**1. Experimental Procedures**

**1.1 Optical Simulation:**

An optical modelling technique was utilized to identify and isolate the light absorption in the active layer of OPV devices based on UV-vis measurements. The simulation process started by determining the complex dielectric function of all materials that were used in the multilayer structure, using a Scout software package (M. Thesis, Aachen Germany) [1]. For this purpose, pure layers of each material were spun onto quartz, and their film thicknesses verified by profilometry before measuring their UV-vis spectra. The spectra were simulated by fitting dielectric functions to match the modelled and measured absorption. After extracting the dielectric function of each material, we applied the following two assumptions to model light interactions within the multi-layer OPV device structure: (1) the incident light (electromagnetic waves) propagate in one dimension through the device layers,(2) the layers of each organic material are isotropic, homogeneous, and have parallel and flat interfaces [2]. The modelled dielectric functions were then used as inputs into a custom MATLAB code that solved Maxwell’s equations using the Transfer Matrix Method (TMM) to identify the distribution of electric field in each successive boundary and bulk layer of the multilayer system. This process has been described in further detail in our previous work [3]. Once the electric field propagating in the individual device layers is known, the absorbance spectrum can be calculated from the negative derivative of the Poynting vector for one dimension [4].

|  |  |  |
| --- | --- | --- |
|  | $$Q\left(x\right)=\frac{1}{2} ω\_{ο}ε\_{ο}ε\_{2} \left|E(x)\right|^{2}$$ | (1) |

where $ε\_{ο}$ and $ε\_{2}$ are the vacuum permittivity and imaginary part of dielectric function, respectively.

**1.2. Materials:**

Indene-C60-bisadduct (ICBA) was supplied from Solenne BV, Netherlands and anhydrous chloroform and sodium dodecyl sulphate surfactant (SDS) were both purchased from Sigma Aldrich. Poly(3-hexylthiophene) (P3HT) was synthesised at the University of Newcastle as previously reported [5], with these synthesis conditions producing a polymer with a Mn of 22.7 kg mol−1, Mw of 32.6 kg mol−1, and a PDI of 1.44.

**1.3. Fabrication of OPV Devices:**

To formulate active layer solutions for BHJ devices, the photoactive layer solution was prepared from a P3HT:ICBA solution with a mixing ratio of 1:0.8. The mixed materials were dissolved together in chloroform with a total solids concentration of 18 mg/mL, followed by sonication for 1 hour to produce the blended active layer solution. To fabricate the NP dispersions, the mixed emulsion process [6] was used to prepare NP photoactive layer dispersions, with a 1:1 ratio of P3HT:ICBA and an initial total solids concentration of 53.6 mg/mL in chloroform. This material solution was then mixed with an aqueous solution of sodium dodecyl sulphate (SDS) (solids concentration of 10.7 mg/mL) to form a macroemulsion, and an ultrasound horn was used to form a miniemulsion. Chloroform was removed from the colloidal droplets via evaporation at 60 °C to convert the miniemulsion into a colloidal NP ink. The detailed experimental steps to isolate and purify blended P3HT:ICBA NP inks were performed according to routine procedures reported in our previous report [7].

In order to fabricate an OPV devices, a PEDOT: PSS layer was spin coated (4000 rpm) onto pre-cleaned patterned ITO substrates and baked on a hotplate at 140 °C for 35 min to remove residual water in the films. The active layer solutions were then spin coated on top of these PEDOT:PSS layers inside a glovebox, with conditions optimised to maintain the active layer thickness at 100±10 nm. Device thicknesses were confirmed using a stylus profilometer (Dektak) with 3 mg of force applied. The devices were dried inside the glovebox at 60 °C (BHJ) or 110 °C (NP) for 5 min. A calcium electron transport layer and aluminium cathode were subsequently evaporated onto the active layers under vacuum (2×10-6 Torr) to complete the devices and allow collection of the generated electrons.

**1.4. Characterisation of Devices**

*1.4.1. Device characterisation*

IV characterisation of OPV devices was conducted using a Newport AM1.5 solar simulator and Keithley 2400 source meter inside an N2 glovebox calibrated to 1 Sun light intensity with a silicon photodiode. A home-built external quantum efficiency (EQE) measurement system consisting of an Oriel Cornerstone 130 monochromator, a tungsten halogen lamp, and a Stanford Research Systems SR830 DSP digitising lock-in amplifier was used to measure EQE spectra of devices after the system was calibrated by a silicon photodiode in the wavelength range between 300-800 nm.

*1.4.2. UV–visible spectrophotometry*

The reflection and transmission of both individual films and complete devices were measured using a Varian Cary 6000i spectrophotometer. Thin films (100±10 nm) of active layers prepared from both the BHJ and NP structure were spun onto quartz slides for the computation of the active layer dielectric function. Film thicknesses were verified using a stylus profilometer (Dektak) with 3 mg of force applied. Complete devices were measured for verification of the modelling output for the complete layer stack. All measurements were performed using the diffuse and specular reflection accessories with an integrating sphere detector to ensure quantitative detection of photons in both transmission and reflection mode.

*1.4.3. Photoluminescence spectroscopy*

Pure P3HT, ICBA and blended P3HT:ICBA BHJ and NP films were spin coated onto quartz glass substrates and annealed for 4 min at 140 °C. Photoluminescence measurements of each of these films were acquired using a Varian Cary Eclipse fluorescence spectrophotometer with an excitation wavelength of 535 nm. The photoluminescence intensity was corrected for the relative absorbance of each film at the excitation wavelength, measured using a Varian Cary 6000i UV–visible spectrophotometer.

*1.4.4 Photo-CELIV measurements*

Photo-CELIV measurements were performed using the commercially available PAIOS 2 system (Fluxim AG). A light pulse from a white LED (Cree, xp-g) was used to generate charges whilst a compensating offset voltage held the device at open circuit. The end of the light pulse was simultaneous with the application of a linearly increasing voltage to extract photogenerated charges. The current transients were recorded by the integrated PAIOS hardware using a voltage ramp rate of 250 V ms-1 to a maximum voltage of -4V (BHJ) or 30 V ms-1 to a maximum voltage of -1 V (NP). The time resolution of the LED pulse rise was 100 ns, and the calculated RC constant of the devices and measurement system was ≈ 170 ns (BHJ) and 1 µs (NP OPV).

*1.4.5. Transient photovoltage measurements*

Transient photovoltage measurements were performed using the commercially available PAIOS 2 system (Fluxim AG). The device was illuminated with a high power white LED (Cree, xp-g), the intensity of which was altered by varying the drive current using the PAIOS software to generate various carrier densities. A compensating voltage was supplied to ensure the devices were at open circuit under illumination. A small optical perturbation was generated using a voltage pulse to vary the LED intensity such that the voltage transient had an amplitude of less than 5 mV. The relaxation of the transient voltage back to open circuit following the light pulse was fitted to a mono-exponential decay to determine the transient lifetime, which was subsequently adjusted by an experimentally determined factor to calculate the total charge carrier population lifetime as described previously [8].

*1.4.6 Scanning Transmission X-ray Microscopy and Transmission Electron Microscopy*

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements of P3HT and ICBA were performed on beamline 5.3.2.2 at the Advanced Light Source (ALS) synchrotron in Berkeley, California. Pristine films of P3HT and ICBA were prepared by spin coating chloroform solutions of each semiconductor material onto PEDOT:PSS (Clevios P VP AI 4083, purchased from H.C. Starck) coated glass substrates. 2 × 2 mm2 sections were scored on the films using a scalpel, followed by floating off the film sections onto a Milli-Q® filtered water surface, which was made possible by re-dissolving the PEDOT:PSS sacrificial layer under the semiconductor material films. 2 × 2 mm2 film sections were subsequently collected onto 300 mesh Cu grids (20 μm bar, 63 μm hole, 3 mm diameter, purchased from ProSciTech Pty Ltd) for NEXAFS measurements. The energy of the X-ray beam was varied between 270 and 340 eV, spanning the C K-edge region with an energy resolution of 0.1 eV. NEXAFS spectra were used firstly to identify key X-ray absorption peaks for the donor and acceptor materials (orthogonal energies), and then for singular value decomposition (SVD) fitting of the scanning transmission X-ray microscopy (STXM) data.

STXM measurements were performed on beamline 5.3.2.2 at the ALS synchrotron. Samples were prepared for STXM measurements by spin coating 2.5 μL of nanoparticle ink onto low stress silicon nitride (Si3N4) membrane windows with SiO2 coating at 3000 rpm, 1 min, low acceleration of 112 rpm/s. Si3N4 substrate specifications: window thickness 15 nm, window dimensions 0.25 × 0.25 mm2, silicon frame dimensions 5 × 5 mm2, purchased from Norcada, Canada. Samples were air dried at room temperature and loaded into the STXM sample chamber and rastered with respect to the X-ray beam. The STXM sample chamber was backfilled with helium (0.33 atm). Second- and third- order light was removed by an order sorting aperture and also N2 gas filter. Energy calibration at the C K-edge was performed using CO2 gas. The transmitted X-ray beam is detected by a scintillator and a photomultiplier tube. The STXM Fresnel zone plate had an outer most zone width of 25 nm, setting the spatial resolution limit of the measurement. SVD fitting was used to fit a sum of the pristine material NEXAFS spectra to the measured blend spectrum of the nanoparticles – at each pixel – in the STXM images. The aXis2000 package was used to perform image analysis of STXM data.

Transmission electron microscopy (TEM) was used to reimage the same nanoparticles for collecting position-matched images. The Si3N4 substrates with deposited nanoparticles were transported back to the University of Newcastle (Australia) to measure TEM on a JEOL 1200 EXII at an accelerating voltage of 80 kV at varying magnification ranges.

**2. Optical Modelling Results**

**(b)**

**(a)**

**Figure S1:** The complex dielectric function of P3HT:ICBA devices prepared with a (a) BHJ, and (b) NP active layer morphology.

**Figure S2:** The modelled spectral distribution of absorbance per unit area as a function of depth in the active layer for OPV devices with (a) a BHJ structure, and (b) a NP structure. 0 nm represents the PEDOT:PSS interface and 100 nm is the calcium interface.

**Incident Light**

**Incident Light**

**Cathode**

**Anode**

**Cathode**

**Anode**

(a)

(b)

**Table S1:** Comparison of the modelled and measured photocurrent generation data extracted from Figure 2 for OPV devices prepared with BHJ and NP active layer structures.

|  |  |  |
| --- | --- | --- |
| Parameter | BHJ | NP |
| Maximum *J*sc[1] (mA/cm2)  | 11.0 | 10.6 |
| Average IQE (375-600 nm) (%) | 72 | 43 |
| Computed *J*sc (mA/cm2) | 7.9 | 4.6 |
| Measured *J*sc[2] (mA/cm2) | 7.6 | 4.5 |
| *J*sc Mismatch (%)  | 6.8 | 4.5 |

[1] Calculated from the integrated overlap of the modelled active layer internal absorbance from 2(c) with the AM1.5 solar spectrum.

[2] Determined by integrating the overlap of the measured EQE spectra in Figures 2(a) and 2(b) with the AM1.5 solar spectrum.

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