



# Organic photovoltaic devices with enhanced efficiency processed from non-halogenated binary solvent blends



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## ABSTRACT

The development of processing routes to fabricate organic photovoltaic devices (OPVs) using non-halogenated solvents is a necessary step towards their eventual commercialisation. To address this issue, we have used Hansen solubility parameter analysis to identify a non-halogenated solvent blend based on a mixture of carbon disulphide and acetone. This solvent blend was then used to deposit a donor–acceptor polymer–fullerene thin-film that was then used as the active layer of bulk-heterojunction OPV. For the benchmark polymer:fullerene system PCDTBT:PC<sub>70</sub>BM, a power conversion efficiency of 6.75% was achieved; a 20% relative improvement over reference cells processed using the chlorinated-solvent chlorobenzene. Improvements in device efficiency are attributed to an increase in electron and hole conductivity resulting from enhanced fullerene crystallisation; a property that leads to enhanced device efficiency through improved charge extraction.

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## 1. Introduction

Bulk-heterojunction organic photovoltaic devices (BHJ OPVs) have seen rapid improvements in power conversion efficiency (PCE) over the past few years, resulting from improvements in the design of new semiconductors and the optimisation of device architectures. Current record PCE's for single junction OPVs have seen dramatic leaps with the polymer PTB7 capable of exceeding 9% and most recently a PCE of 10.8% has been achieved using the polymer PffBT4T-2OD, these values are approaching the value deemed viable for commercial adoption [1–4]. We note however that most work on the development OPV devices has concentrated on the use of halogenated solvents (e.g. chlorobenzene) to solubilise and deposit the active semiconducting layer. Whilst such solvents enable uniform thin-films to be cast having a BHJ nanomorphology that is optimised for efficient photocurrent generation, environmental concerns place restrictions upon the use of halogenated solvents in an industrial environment; an issue that is problematic for the commercialisation of high-performance OPVs [1,5,6]. Unfortunately, many organic semiconductors have poor solubility in non-halogenated solvents; a property that results

in the formation of non-uniform thin-films that have poor photocurrent generating properties when fabricated into an OPV.

To address this, attention has focussed on the synthesis of high-performance organic semiconductors having improved solubility in non-halogenated solvents such as alcohols or water. Unfortunately the presence of additional solubilising side-groups can both increase the density of charge traps and result in the formation of a non-optimal active-layer morphology leading to a reduction in PCE [7–10]. An alternative approach is to use blends of non-halogenated solvents to mimic the solubility characteristics of a halogenated solvent. Here, the solubility of a material can be estimated by matching the Hansen solubility parameters (HSPs) of a blend of solvents to a specific solvent that is able to solubilise the desired material [11]. The HSP of a solvent consists of three components; the energy of the dispersion forces between molecules ( $\delta_d$ ), the energy resulting from permanent dipole moments ( $\delta_p$ ), and the energy of hydrogen bonds ( $\delta_h$ ). This powerful technique has been previously used to determine the solubility of a number of material systems including small molecule organic semiconductors [12]. HSP analysis has also been used to develop non-halogenated solvent blends to process a mixture of the polymer P3HT (poly(3-hexylthiophene-2,5-diyl)) and the fullerene acceptor PC<sub>60</sub>BM ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) with

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PV devices created having a PCE of up to 3.4% [13–15]. In other work, non-halogenated solvent systems have been developed to solubilise OPV active-layers based on the polymers PIDT-phanQ, PIDTT-DFBT, and PBDT-DTNT. Here, a solvent blend based on a mixture of the solvents toluene:1-methylnaphthalene and o-xylene:1,2-dimethylnaphthalene, with the devices created having a PCE of 6.1%, 7.2% and 6.1% respectively. It was however found that these systems required strict control over solvent blend composition to optimise device efficiency [16,17].

Here, we report the use of a blend of carbon disulphide and acetone to cast the active semiconducting layer of an OPV consisting of a blend of the polymer PCDTBT ((poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4,7'-di-2-thienyl-2',1',3'-benzothiadiazole)])) and PC<sub>70</sub>BM ([6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester). Average PCEs of 6.6% are achieved (peak 6.75%); a value that exceeds the efficiency achieved for reference devices cast from chlorobenzene (5.5%). In comparison to previous work on the use of HSP to develop non-halogenated solvent blends for OPV active layers [13], the replacement non-halogenated solvent blend we have developed here results in improved performance compared to its halogenated counterpart. Indeed, the PCEs values we have obtained using a non-halogenated solvent blend are close to the largest values that have been demonstrated for this donor:acceptor system using devices based on a ITO/Molybdenum (VI) Oxide anode and a Ca/Al cathode. We also show that this solvent system can be used to deposit a related polymer:fullerene system based on PFDT2BT-8 (poly[9,9-dioctylfluorene-4,7-alt-(5,6-bis(octyloxy)-4,7-di(2,2-bithiophene-5-yl)benzo[c]thiadiazole)-5,5-diyl]) and PC<sub>70</sub>BM [18]. Here PCEs of 6.81% are achieved using the non-halogenated solvent blend compared to reference literature values of 5.8% achieved using chlorinated solvents. To understand such improvement in device performance, we apply a range of structural and optoelectronic probes to study the thin-films deposited including the use of grazing-incidence X-ray scattering to probe film structure at angstrom length scales. We demonstrate that films cast from non-halogenated solvents have improved electron- and hole-carrier conductivity that we speculate results from enhanced PCBM crystallisation; properties that are likely to reduce efficiency losses through geminate and non-geminate recombination.

## 2. Experimental

### 2.1. Materials

Carbon disulphide (99.9% HPLC grade), acetone (99.5% HPLC grade) and chlorobenzene (99.95%) were purchased from Sigma Aldrich and used without any further purification. MoO<sub>3</sub> (99.95%) was purchased from Testbourne Ltd, vanadium (V) oxytriisopropoxide, aluminium (99.99%) and calcium (99%) were purchased from Sigma Aldrich. PCDTBT was synthesised according to previously reported methods [19,20], and had a  $M_w$  of 26.5 KDa, and PDI of 2.18. PFDT2BT-8 was synthesised according to a previously reported method [16], and had a  $M_w$  of 91.6 KDa, and PDI of 1.47. PC<sub>70</sub>BM was purchased from Ossila Ltd and had a purity of 95% (5% PC<sub>60</sub>BM).

### 2.2. OPV fabrication and measurement

For PCDTBT:PC<sub>70</sub>BM devices ITO substrates were coated with a (8 nm) layer of molybdenum (VI) oxide for use as a hole extraction layer via vacuum evaporation. For PFDT2BT-8 devices vanadium (V) oxide was deposited via spin coating in air at speed of 4000 rpm from a precursor solution of vanadium (V) oxytriisopropoxide dissolved in isopropyl alcohol at a concentration of

4 mg ml<sup>-1</sup>. The active layer was deposited from a solution of polymer:PC<sub>70</sub>BM dissolved in either chlorobenzene or a solvent blend of carbon disulphide and acetone (solvent blend ratio of 4:1) and with a polymer:fullerene blend ratio of 1:3.5 at an overall concentration of (25 mg ml<sup>-1</sup> for PCDTBT devices and 35 mg ml<sup>-1</sup> for PFDT2BT-8). Solutions were then spin coated at 4300 RPM for CS<sub>2</sub>:Acetone solutions and 1800 RPM for chlorobenzene solutions. Devices were then transferred into a vacuum chamber for the deposition of the top calcium (3 nm)/aluminium (100 nm) cathode via vacuum evaporation in order to enhance hole blocking and reflectivity at the electron extracting interface [21]. Devices were encapsulated under nitrogen using a glass slide fixed in place by an inert UV-setting epoxy. For each solvent system explored, we have fabricated 4 independent devices-substrates, each containing 6 individual pixels (having an area of 4.8 mm<sup>2</sup>) corresponding to a total of 24 devices per solvent-system. OPV devices were measured under ambient conditions using a Keithley 2400 source meter and a Newport 92251A-1000 AM1.5 solar simulator. A shadow mask was used to define the area of illumination as 4.5 mm<sup>2</sup>. An NREL calibrated silicon diode was used to calibrate the power output at 100 mWcm<sup>-2</sup> at 40 °C. In our data analysis, we have selected the top 50% of pixels having the highest efficiency from each deposition condition. This was done in order to remove any failed pixels and prevent any selection bias. EQE measurements were also recorded at  $J_{sc}$  for champion devices cast from the two different solvent blends.

### 2.3. Fabrication of devices having conductivity dominated by a single charge carrier

Devices were fabricated in which charge conductivity is assumed to be dominated by electrons. Electron-dominated devices were based on a ITO/CS<sub>2</sub>CO<sub>3</sub>/PCDTBT:PC<sub>70</sub>BM/Ca/Al architecture. J-V characteristics were measured in the dark over the voltage range 0–10 V. Data presented has been corrected for the built-in voltage of each device (estimated from the difference in electrode work functions). A total of 31 devices (for CB) and 14 devices (for CS<sub>2</sub>:Acetone) were fabricated to obtain average values.

### 2.4. GIWAXS

Wide-angle X-ray diffraction patterns were obtained for each thin-film in a grazing-incidence geometry at the I07 beam-line at the Diamond Light Source (Didcot, UK). PCDTBT and PCDTBT:PC<sub>70</sub>BM blend films were deposited via spin-casting onto silicon/native oxide substrates for measurement. Samples were measured within a custom-built cell containing a slight overpressure of helium to minimise background X-ray scatter. For measurement, an 8 keV X-ray beam was incident on the sample surface at a grazing-incidence angle of 0.2°. Data was collected using a Pilatus 2 M detector and analysed using the DAWN software package (<http://www.dawnsci.org>). Silver behenate powder was used as a calibrant. Out-of-plane X-ray scattering profiles were obtained from a 20° wide sector-integration of the 2D GIWAXS images, whereas azimuthal X-ray scattering profiles were obtained over the  $q$  range 1–1.71 Å<sup>-1</sup> for PCDTBT:PC<sub>70</sub>BM films, and from 1.21 Å<sup>-1</sup> to 1.89 Å<sup>-1</sup> for PCDTBT films. Data plots were normalised to  $q_z$  values of 0.9 for the polymer:fullerene blend films and at  $q_z = 2.3$  for the polymer films.

### 2.5. Photoluminescence measurements

PL measurements were recorded using a 532 nm CW laser having a power of approximately 100 mW as an excitation source, with photoluminescence imaged into a monochromator coupled

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