

Alternative selection of processing additives to enhance the lifetime of OPVs

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Abstract

The use of processing additives is known to accelerate the degradation of Organic Photovoltaics (OPVs) and therefore, this paper studies the impact of selecting alternative processing additives for PCPDTBT:PC₇₁BM solar cells in order to improve the stability. The use of naphthalene-based processing additives has been undertaken, which is shown to reduce the initial power conversion efficiency by 23%-42%, primarily due to a decrease in the short-circuit current density, but also fill factor. However, the stability is greatly enhanced by using such additives, with the long term stability ($T_{50\%}$) enhanced by a factor of four. The results show that there is a trade-off between initial performance and stability to consider when selecting the initial process additives. XPS studies have provided some insight into the decreased degradation and show that using 1-chloronaphthalene (CIN) leads to reduced morphology changes and reduced oxidation of the thiophene-ring within the PCPDTBT backbone.

1. Introduction

Organic Photovoltaics (OPVs) provide the possibility of low cost, solution processible solar electricity generation. Whilst performances have steadily improved over the past 10 years, OPVs still exhibit poor lifetimes. This is exasperated by the use of 'processing additives;' as shown in two recent reports of the stability of solar cells made with Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl}) (abbrev.: PTB7) and poly[{4,4-bis(2-ethylhexyl)-cyclopenta-[2,1-*b*;3,4-*b'*]dithiophene)-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl] (abbrev.: PCPDTBT) as well as other materials [1-3]. Processing additives

based on alkanethiols, halogenated naphthalenes or similar co-solvents are used in almost all reports of high efficiency OPVs and acts as a non-reacting solvent [4-5]. It has been shown that the incorporation of a few volume percent of 1,8-octanedithiol (ODT) into the blend improves the Power Conversion Efficiency (PCE) by about a factor of two. It does this by modifying the morphology and controlling the phase separation between the donor and acceptor components [6]. Reports indicate that ODT leads to enhanced connectivity of PC₇₁BM networks [7], a small increase in polymer crystallinity [8], reduced charge recombination and reduced charge carrier loss [9]. However, recent data indicates that inclusion of additives has a detrimental effect on the stability of the solar cell. Under stability measurements, solar cell devices made with processing additives tend to degrade quicker than devices made without additives. The likely reason for this is related to the high boiling point of the processing additive; typically greater than 150°C. From the analysis of active layer material systems, it is assumed that the processing additive remains in the film after processing, or creates an initially unstable morphology, and continues to detrimentally alter the active layer morphology.

In this paper the use of alternative processing additives is reported to identify if efficiency can be increased without compromising device lifetime. In particular, the work is targeted at lower boiling-point additives, as these are more likely to evaporate than alkanethiols. OPVs are fabricated with a range of additives and tested for efficiency and lifetime. In addition, the material changes are studied using X-ray Photoelectron Spectroscopy (XPS)

2. Experimental

2.1 Device fabrication

Initially, indium tin oxide (ITO) coated glass substrates ($R_s = 16 \Omega/\text{square}$) were cleaned using solvents. Subsequently, a 40nm PEDOT:PSS layer was deposited using spin coating and dried at 120°C for 30 minutes. PCPDTBT was synthesised in-house and possesses 2-ethylhexyl solubilising side chains [10]. Three blends were prepared whereby the polymer was mixed with a fullerene derivative. The PCPDTBT and PC₇₁BM blends were mixed with weight ratios 1:3 with chlorobenzene solvent using a concentration of 30mg/mL. Three different processing additives were trialled for this work; ODT, both 1-bromonaphthalene (BrN) and 1-chloronaphthalene (ClN) w/w of 2.5%. The additives, BrN and ClN, were selected due to their low boiling points of 119°C and 139°C, respectively and effectiveness when applied to blends of other active layer materials such as P3HT:PCBM [10]. For all blends, the same batch of PCPDTBT and PC₇₁BM were used, so the data

obtained compares only the changes in process additives. The parameters such as film thickness (as a function of spin-casting speed) and annealing temperatures were optimised for each blend. Prior to coating, all blends were allowed to dissolve for 24 hours on a hot plate stirrer and filtered using a 0.45 μm PTFE filter. All coatings were undertaken in a glovebox and annealed to remove any residual solvent; a procedure optimised for device fabrication [10]. Finally, the cathode electrode was deposited, which consisted of 8nm calcium (Ca) followed by 100nm of Aluminium (Al), to define an active area size of 0.5cm². A schematic of the device setup is shown in Figure 1.

Devices were tested for current density-Voltage (J-V) using a Newport solar simulator with 100 mWcm⁻² AM1.5G output (calibrated using a silicon reference cell from RERA in the Netherlands). For ageing of devices, light soaking was conducted using a halogen light soaking system. Devices were kept at open circuit in between measurements and J-V measurements were made every 30 minutes. This was conducted in accordance with ISOS-L-2 standards [11].

2.2 XPS experiments

The XPS data were acquired using a bespoke ultra-high vacuum system fitted with a Specs GmbH Focus 500 monochromated Al K α X-ray source, Specs GmbH Phoibos 150 mm mean radius hemispherical analyser with 9-channeltron detection, and a Specs GmbH FG20 charge neutralising electron gun. Survey spectra were acquired using Al K α radiation at 1486.6 eV over the binding energy range 1100 – 0 eV using a pass energy of 50 eV, and high resolution scans were made over the C 1s, O 1s and S 2p lines using a pass energy of 15 eV. In each case, the analysis was an area-average over a region approximately 2 mm in diameter on the sample surface. The energy scale of the instrument is calibrated according to ISO standard 15472, and the intensity scale is calibrated using an in-house method traceable to the UK National Physical Laboratory.

3. Results

3.1 Solar cell performance

Initially, optimising of the process conditions for OPVs with different additives was conducted. The optimum active layer thickness was found to be 160nm and 155nm for ClN and BrN, respectively. This compares closely to the optimal thickness for OPVS made with 1,8-octanedithiol (ODT) additive which was 140nm. In addition to optimising the spin-speed, annealing temperature and drying conditions were also investigated. After extensive optimisation in other papers [12,13], many groups have shown that PCPDTBT:PC₇₁BM including ODT additive operate best with 80°C annealing. This

was also found to be the optimum temperature for active layer annealing when using BrN and CIN additives also. Annealing was trialled at higher temperatures, but led to a decrease in Power Conversion Efficiency (PCE). For example, annealing at 140°C led to a relative decrease in PCE of 20%, as a result of decrease of in all performance parameters, namely short-circuit current density (J_{sc}), Fill Factor (FF) and open-Circuit Voltage (V_{oc}).

A summary of the optimum performance of PCPDTBT:PC₇₁BM OPVs manufactured with each processing additive and measured under AM1.5G conditions is shown in Table 1, with the J-V characteristics shown in Figure 2. It is clear that using the conventional additive, ODT, leads to the best PCE. As can be seen with data in Table 1, the difference in PCE between additives is primarily due to lower FF and J_{sc} , suggesting large morphological variance between the active layers and a reduced photo-generation in active layers containing BrN and CIN solvents. Interestingly, a correlation exists between boiling point of the processing additive and final device performance; BrN has the lowest boiling point and also the lowest PCE, whereas ODT possesses the highest boiling point and PCE. As OPV cells made with ODT possessed a higher J_{sc} and FF than those that include CIN or BrN, it can therefore be assumed that BrN led to the least optimal morphology, due to its lower boiling temperature. It is worth noting that the performances of these cells are slightly lower than the previous devices from the group due to the larger active area sizes used for these tests. AFM analyses were conducted on the surfaces of PCPDTBT-PC₇₁BM based films, which had been cast with CIN, BrN or ODT. Figure 3 shows topographical images of these films for scan areas of 5µm x 5µm. It can be seen from Figure 3 (a) that films made with BrN exhibit the greatest surface roughness and largest aggregates, whereas a much smoother film and lower aggregation is observed with the films processed with the ODT additive. This would explain the lower PCE of cells made with BrN; it is evident that the use of this additive leads to a worse initial morphology as such large aggregates are shown to reduce significantly performance [1], which explains the lower initial PCE of these cells.

3.2 Solar cell lifetime

In addition to optimising fabrication conditions, OPV cells of PCPDTBT-PC₇₁BM with ODT, CIN or BrN were tested for stability. **Figure** Figure 4 shows how the V_{oc} , J_{sc} , FF and PCE changed with time for cells made using ODT, CIN or BrN. It appears that layers made with BrN leads to the greatest stability. Unfortunately, this also showed the lowest initial PCE (see table 1). A good measure of the stability is to consider the time taken for the device to fall to 50% of the original value ($T_{50\%}$). The $T_{50\%}$

for the best performing cells made with CIN and BrN was measured to be 90 hours and 115 hours. Cells made with ODT possess $T_{50\%}$ of 25 hours. Interestingly, the data for improved $T_{50\%}$ appears to be correlated to lower additive boiling temperature.

From the data in figure 4 and Table 1, it is evident that the cells made with ODT possess substantially worse stability. Although ODT shows reduced stability, its initial PCE is at least twice that of cells using either CIN or BrN. Therefore, when comparing the relative performance of an OPV over its lifetime, a better indicator is the total power generated over the devices' lifetimes. This takes into account both the different initial PCE as well as the longer term stability of the device. The cell lifetime is defined as between the period of 0 hours until $T_{10\%}$ is reached and this data is shown in Table 2. From the data in Table 2, it is observed that devices made with CIN exhibit the best power generating capabilities, with greater than 2-fold increase in power generation observed over the lifetime when compared to a device made with ODT. Whilst devices made with BrN have a greater stability and those made with ODT possess higher PCE, the use of CIN appears to give the best trade-off between stability and performance.

Previous work in the area has supposed that the high boiling point of processing additive is likely to lead to the additive remaining in the active layer after processing, or leads to an unstable initial morphology [1]. This residual solvent/unstable morphology continues to dynamically alter the morphology with time, leading to enhanced degradation. The data in this section indicates that by using a more volatile additive, which evaporates quicker, the morphological changes that occur from the dynamically altering of the active layer can be reduced, enhancing the stability. Whilst the data is not shown, the authors found that the most stable devices for all additives was obtained by annealing at 80°C. This is an interesting conclusion and shows that 'over-annealing' at higher temperatures (up to 140°C was trialled) to remove as much of the additive as possible in the active layer doesn't necessarily lead to improved stability. The likely cause of this is that the higher temperature annealing might instigate a new degradation mechanism such as a less stable morphology. However, the work cannot rule out the possibility that ODT could react with the calcium interface layer, which could also account for the increased degradation rate.

3.3 Analysis of morphological and chemical changes using XPS measurements

Data was collated from the active layers of PCPDTBT-based solar cells using XPS to better understand the chemical and morphological changes. Two layers were used; PCPDTBT:PC₇₁BM with the processing additive, ODT, and PCPDTBT:PC₇₁BM with the CIN. Active layers made with BrN were

excluded from this study as the CIN showed the most promise. All blends were prepared with 75% fullerene content, in keeping with the optimal performance in device active layers and applied onto PEDOT-coated glass substrates. As both films contain a 75% fullerene content, we can expect the molecular structures of PCPDTBT:PC₇₁BM to possess a stoichiometry of 96.1% C, 2.1% O, 1.0% S and 0.8% N, but both layers exhibit higher S and N content. From Table 3, it is found that the relative % of PCPDTBT at 0 hours is higher for both films if the polymer and fullerene content was homogeneously distributed; one should expect 25% relative PCPDTBT if this was the case. However, the measured concentration of PCPDTBT is 58% for films with ODT and 48% for films with CIN. This indicates that both layers exhibit an enrichment of PCPDTBT at the surface; however, a greater enrichment occurs at the surface for blends with ODT. Cl was not detected in the sample produced using CIN. This suggests that either the CIN is evaporated when the samples were transferred into a UHV environment or that it is present in lower concentration than the typical detection limit for XPS

On ageing, both samples show an expected trend i.e. much higher O, higher N, lower S and correspondingly lower C. Carbon appears as an oxygen-containing hydrocarbon with little evidence of aromatic species (the curve fitting of this data is not shown). Oxygen increases in intensity and shows two broad components attributable to C=O and C-O with the C=O greater in relative proportion. Table 3 shows the peak area ratios of the S 2p and C 1s peaks for the top surfaces. The changes in concentration of oxygen between the samples made with ODT and CIN is relatively small. However, subtle differences can be observed in the individual spectra.

The curve-fitted XPS data for the S 2p peaks is shown in figure 5. The curve-fits are constrained to a physical model whereby the all S 2p_{3/2} – 2p_{1/2} doublet separations are fixed at 1.13 eV, and all S 2p_{3/2} – 2p_{1/2} doublet intensity ratios are fixed to the ratios of the calculated Hartree-Slater cross sections for photoemission from these levels at the Al K-alpha X-ray energy [14]. Based upon this physical model, the % of S in an oxidised state can be calculated. This gives 43.5% of the S in the oxidised state for the sample prepared with ODT, and 30.86% of the S in the oxidised state for the sample prepared with Cl-N. It is clear that the S component of the PCPDTBT in the sample made with ODT shows a greater susceptibility to oxidation than the one prepared with CIN. This indicates samples made with ODT are more susceptible to oxidation, possibly due to the increased enrichment of PCPDTBT at the air facing surface, which is confirmed by the relative % of PCPDTBT at the surface data in table 3. The level of oxidised S is increased after light soaking when using ODT, however the magnitude of this effect does not correlate to the loss of performance observed between the two cells in working OPV cells. It can, therefore, be concluded that processing additives impair the performance of OPV cells via a combination of chemical and physical changes.

Conclusion

PCPDTBT:PC₇₁BM solar cells are normally made with the inclusion of the processing additive, ODT, which is known to lead to enhanced initial PCE, due to improved morphology. However this additive is known to increase the degradation rate, so this paper has investigated the selection of alternative naphthalene-based processing additives in order to improve the stability. By using a less volatile processing additive such as BrN or ClN, a greater surface roughness is observed with aggregation observed from AFM topographic scans. Such morphology leads to lower initial PCE due to the worse active layer morphology. However, the stability by using these additives is shown to be enhanced by a factor three, though the initial PCE is reduced as a result. By considering this trade-off between initial PCE and stability, it has been shown that the output power generated in the first 1000 hours is about a factor two greater.

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Table 1: Mean and standard deviation value for PCPDTBT-PC₇₁BM based cells cast with 1-chloronaphthalene (CIN) and 1-bromonaphthalene (BrN) additives respectively. PCPDTBT-PC₇₁BM cast with ODT was included as a control. Characterised under AM1.5G conditions (100mW.cm⁻²).

	CIN	BrN	ODT
V _{oc} (V)	0.64 ± 0.01	0.63 ± 0.01	0.62 ± 0.00
J _{sc} (mA.cm ⁻²)	-7.71 ± 0.29	-7.20 ± 0.28	-9.05 ± 0.38
FF (%)	46.53 ± 1.04	38.00 ± 2.78	51.05 ± 0.88
PCE (%)	2.30 ± 0.07	1.72 ± 0.20	2.95 ± 0.10
Boiling point			

Table 2: The sum of the electrical power generated over the first 1000 hours of PCPDTBT-PC₇₁BM cells, made with 1-chloronaphthalene, 1-bromonaphthalene and ODT respectively. Also included are the approximate times until the OPV performance is 50% of the original value (T_{50%}), and additive boiling temperatures (B.T.).

Additive	Electrical Power (mWh.cm ⁻²) [T _{100%} -T _{10%}]	Time to reach 50% of initial PCE (T _{50%}) (hours)	B.T. (°C)
1-bromonaphthalene	260.58	121.47	119
1-chloronaphthalene	292.56	88.63	139
ODT	130.93	24.75	270

Table 3: The relative atomic concentrations in PCPDTBT:PC71BM blends at 0 and 300 h when blended with the processing additives 1,8-octanedithiol (ODT) or 1-chloronaphthalene (CIN) w/w of 2.5%

	Atom % concentration			
	PCPDTBT:PC ₇₁ BM with CIN		PCPDTBT:PC ₇₁ BM with ODT	
Name	0 hours	300 hours	0 hours	300 hours
C 1s	91.50	71.88	90.84	69.48
O 1s	1.61	22.58	1.26	23.48
N 1s	2.41	2.90	2.56	3.73
S 2p	3.39	2.64	5.34	3.31
C:S	20.38	27.23	17.01	20.99
Relative % of PCPDTBT	48.0	42.1	58.0	52.8

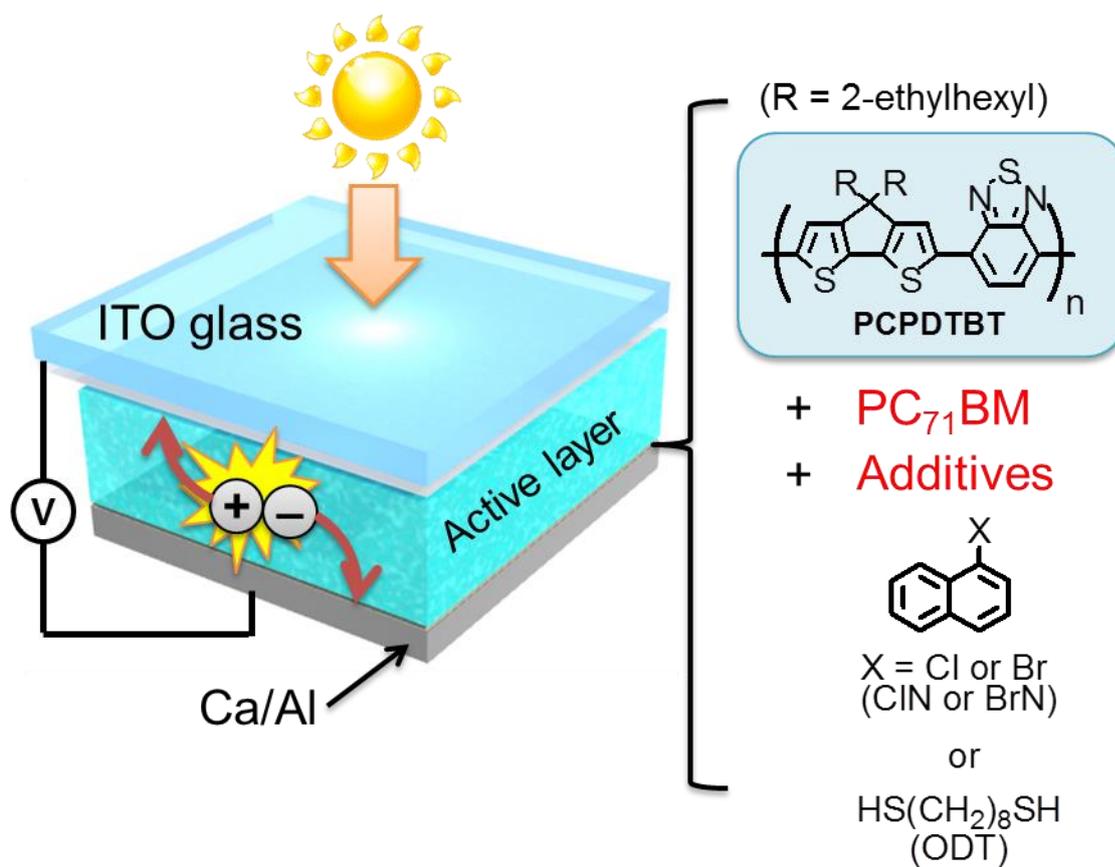


Figure 1: Schematic of device architecture used for these tests consisting of and ITO electrode, PEDOT:PSS hole transport layer, active layer and calcium/Aluminium cathode.

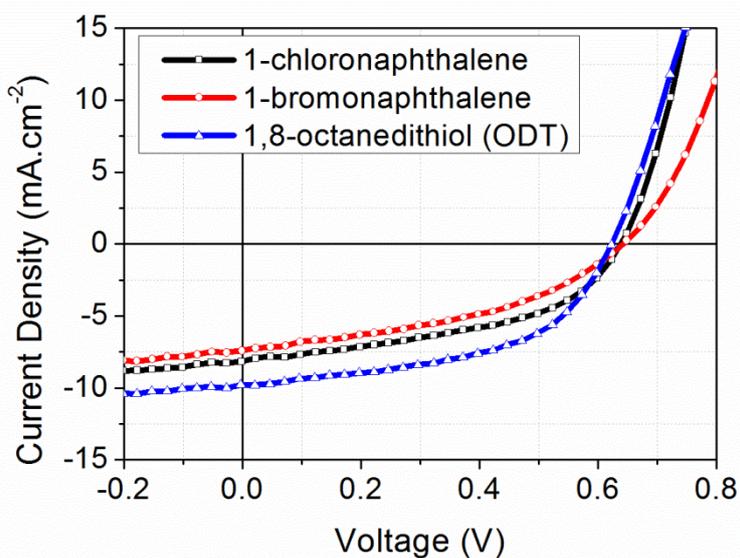


Figure 2: IV characteristics of the PCPDTBT:PC71BM solar cells made with ODT, CIN and BrN additives and tested under Am1.5G irradiation

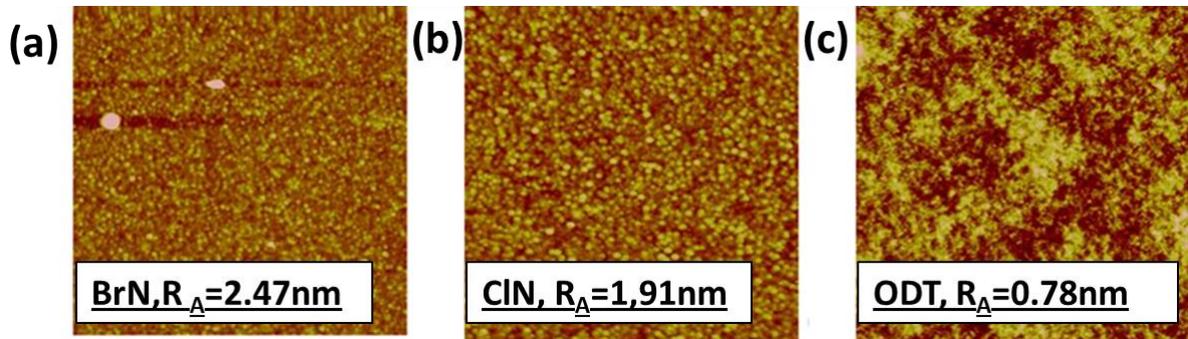


Figure 3: Topographic scans ($5\mu\text{m} \times 5\mu\text{m}$) using AFM for films of PCPDTBT-PC71BM with (a) 1-bromonaphthalene, (b) 1-chloronaphthalene or (c) ODT (c)

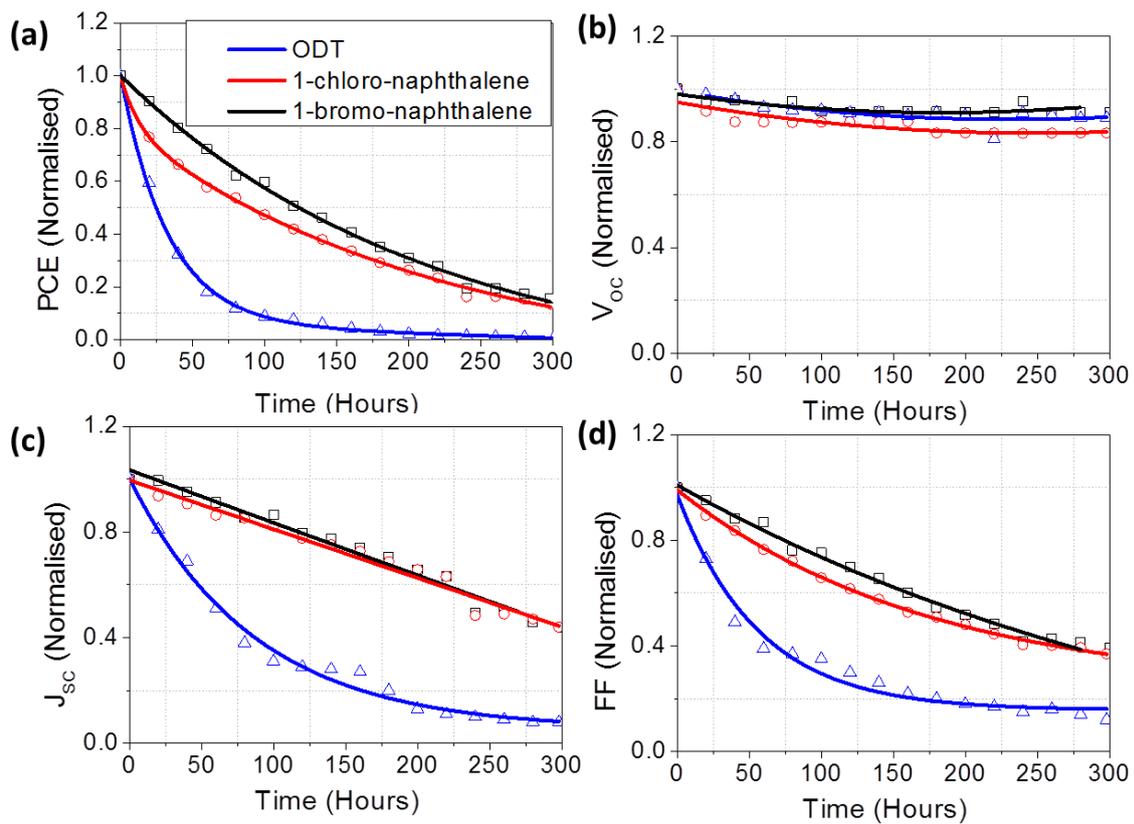


Figure 4: OPV cell characteristics for PCPDTBT:PC₇₁BM made with CIN or BrN processing additives. Shown are the variations of the PCE, V_{OC} , J_{SC} , and FF with time, all normalised from their starting values.

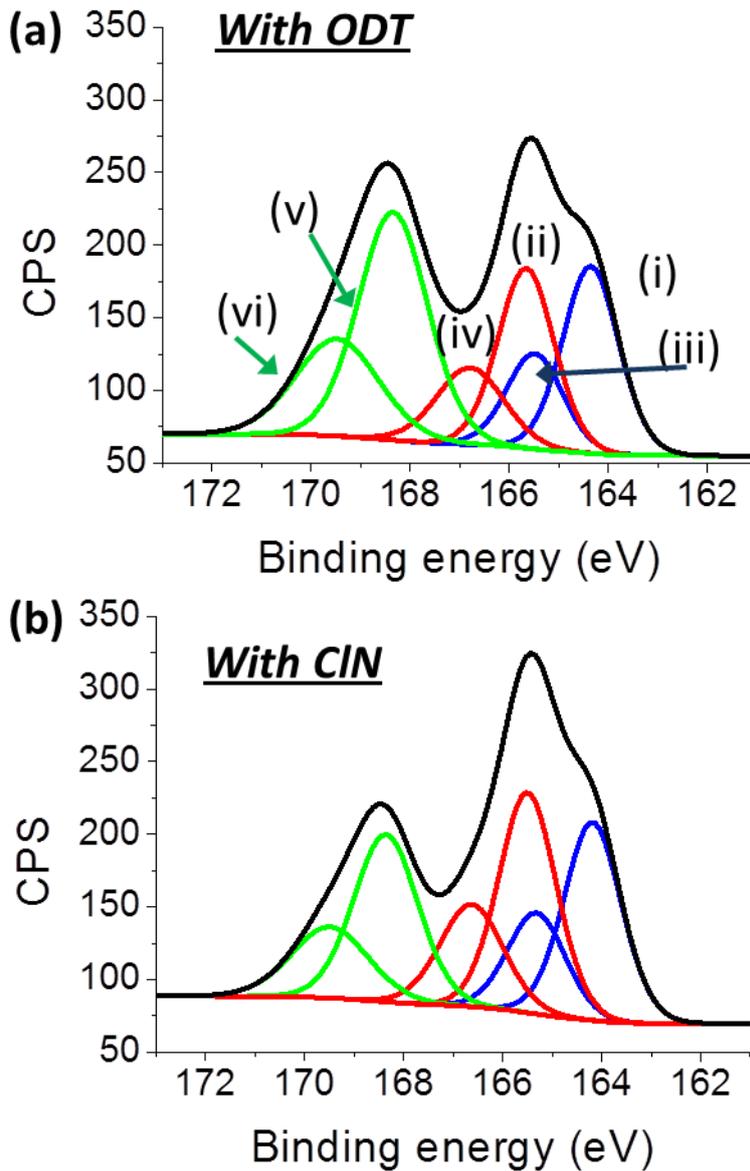


Figure 5: XPS spectra and curve fitting of PCPDTBT:PC₇₁BM OPVs made with (a) ODT additive and (b) CIN additive and aged for 300 h using ambient air light soaking facilities for the S2p peak only. In figure (a) only, the curved fitted positions of the (i) thiophene S 2p_{3/2} (ii) thiadiazole S 2p_{3/2}, (iii) thiophene S 2p_{1/2}, (iv) thiadiazole S 2p_{1/2}, (v) oxidised S 2p_{3/2} and (vi) oxidised S 2p_{1/2} peaks are shown.