We demonstrate highly-efficient solution processed small molecule solar cells with the best power conversion efficiency (PCE) of more than 5%. The active layer consists of a diketopyrrolopyrrole based donor molecule (DPP(TBFu)₂) and a fullerene derivative (PC₇₁BM) that is spin cast and subsequently treated with solvent vapor annealing (SVA) in air. We find not all solvent vapors leads to the best PCE. Solvents of high vapor pressures and medium donor solubilities, such as tetrahydrofuran or carbon disulfide, are most suitable for SVA in the context of organic solar cell application. On the other hand, acceptor solubility plays an insignificant role in such a treatment. Active layer treated with ideal solvent vapors develops desirable phase separation in both lateral and vertical directions, as revealed by AFM, TEM and TEM tomography. The SVA also leads to enhanced hole mobility. We believe the fast SVA treatment performed in air is a viable way to tune the active layer morphology for printed solar cells.

1. Introduction

Organic photovoltaics (OPVs) based on bulk heterojunction (BHJ) concept have been studied extensively over the past decade due to many promising merits including low fabrication cost, light weight, high mechanical flexibility, tunable chemical and physical properties via molecular design, and fast module installation rate.¹⁻⁵ By controlling the morphology of the active layer, modifying the interfaces, and building tandem cells, power conversion efficiencies (PCE) beyond 9% have been demonstrated, pushing this technology closer to commercialization.²⁻⁸ In order to fabricate OPVs in large scale, it is preferred to print active layer using solution techniques in ambient condition.⁹⁻¹³ In an easy and fast manner.¹⁴, ¹⁵ Unfortunately, most of the optimal active layer morphologies as well as the high PCEs are achieved in an inert atmosphere which is obviously not ideal for large scale printing processes.

Meanwhile, conjugated polymers have been the work horse donor material for high performance OPVs. A main drawback of the polymer donor material is the batch to batch variations which often makes the solar cell performance unpredictable. On the other hand, small molecules offer great advantages in terms of ease of purification, discrete molecular weight, small batch-to-batch material and device variation, strong tendency for self-assembly and potentially high charge carrier mobility, etc. The challenge for solution processed small molecule BHJ OPVs is to enhance molecular order for better charge carrier mobility, and at the same time, to restrict the domain size due to limited exciton diffusion length. Strategies such as thermal annealing, solvent additives or solid additives have been reported.¹⁶⁻²¹ It has also been realized that solvent vapor annealing (SVA), which is suitable for ambient condition process, helps to form crystalline domains.²²⁻²⁶ Solvent vapor can penetrate into the film allowing the molecules to re-organize for more ordered packing. A few groups successfully used SVA to treat the active layer and demonstrated improved OPV performance.²⁷⁻²⁹ However, the mechanism is still not fully understood and no solvent selection rule has been identified.³⁰

In this contribution, a range of solvents with different solvent properties are used to vapor-anneal the active layer, which consists of a small molecule donor, 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP(TBFu)₂), and a common fullerene derivative [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM). Their chemical structures are shown in Figure 1a. It is found that SVA of only a few seconds can change the morphology drastically, which is clearly observed in transmission electron microscopy (TEM) tomography analysis. The optimum morphology shows improved hole mobility, as well as solar cell device parameters.

![Fig. 1](image-url) (a) Chemical structure of DPP(TBFu)₂ donor and PC₇₁BM acceptor and (b) OPV cell architecture.
including short-circuit current density ($J_{sc}$) and fill factor (FF). Furthermore, solvents with high vapor pressure and medium solubility for the donor molecules are the ideal SVA solvent for OPV application. DPP(TBFu)$_2$:PC$_7$BM films that are vapor-annealed by tetrahydrofuran (THF) or carbon disulfide (CS$_2$), produce the highest PCE of 5.2%. We note that all the fabrication and treatment of the active layer are done at room temperature in air, suggesting the fast SVA is potentially compatible with large scale production of OPVs.$^{37}$

2. Experimental Section

2.1 Materials & solvents

DPP(TBFu)$_2$ was synthesized by following literature methods.$^{31}$ PC$_7$BM was purchased from Nano-C. All the solvents were ACS reagent grade and supplied by Sigma-Aldrich.

2.2 Solvent vapor annealing (SVA)

SVA was conducted in ambient condition at room temperature. The respective vapor pressures were summarized in Table 1. Respective solvent (2 mL) was injected into a 30 mm glass Petri dish. The Petri dish was closed for 5 min to let the vapor saturate the treatment chamber. Then as-cast film was attached on the back side of a second Petri dish lid, which was quickly swapped with the lid covering the solvent containing Petri dish. The film was about 1 cm above the solvent level during the SVA. After certain duration, the film was removed from the treatment chamber.

2.3 Film characterizations

UV-vis-NIR spectra were recorded by a Varian Cary 50 Spectrometer. TEM bright field images were obtained by a FEI Tecnai TF30 TEM equipped with beam blank function. For electron tomography, tilt series were acquired using the Xplore 3D software (FEI Company). Tomograms were recorded between -65 and +65 degrees at 2° intervals and aligned with IMOD.$^{38}$ 3D model rendering employed 3dmod software.$^{39}$ Each model was generated from the aligned tomogram. The DPP(TBFu)$_2$ donor phase was rendered in golden color, while the PC$_7$BM acceptor phase was represented by empty space in SI movies except movie 2, in which the acceptor was rendered in green color to show the flake-like structure of PC$_7$BM. The scale bar is 50 nm in the model movies and 100 nm in the tomogram movies. AFM images were acquired with an Asylum Research Cypher scanning probe microscope operated in tapping mode. To obtain hole mobility using SCLCs, hole-only devices were constructed using a cell architecture as ITO/PEDOT:PSS/DPP(TBFu)$_2$:PC$_7$BM/Au. Their dark currents were recorded by a computer programmed Keithley 2400 source meter, and then fitted by Mott-Gurney equation.$^{40, 41}$ Film thickness was determined by Veeco Dektak 150+ Surface Profiler.

2.4 OPV fabrication & characterizations

All the fabrication and characterization processes were carried out in air. Patterned ITO glasses were washed sequentially by detergent, deionized water, acetone, and 2-propanol in an ultrasonication bath and UV/ozone-treated. PEDOT:PSS (Clevios P VP Al 4083) was spin-coated at 8000 rpm and then baked at 150 °C for 10 min in air. After cooling down to room temperature, a solution comprising 8 mg DPP(TBFu)$_2$ and 5.3 mg PC$_7$BM in 1 ml of chloroform was spin coated at 65 °C at 1500 rpm on top of the substrate. The films were solvent vapor annealed by respective solvent at various durations. Then they were transferred to a thermal evaporator where 1 nm LiF and 100 nm aluminum were deposited through a shadow mask (active area was 0.10 cm$^2$) at base pressure of 1 × 10$^{-6}$ torr. Film thicknesses were determined by a Veeco Dektak 150+ Surface Profiler. The thickness of the photoactive layers was optimized and was typically between 100 and 120 nm. The solar cells were illuminated at 100 mW/cm$^2$ using a 1 kW Oriel solar simulator with an AM 1.5G filter in air and J-V curves were measured using a Keithley 2400 source meter. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PVmeasurements Inc.) certified by the National Renewable Energy Laboratory.

3. Results and Discussion

The solvent vapor annealing was carried out by filling 2 ml of the solvent into a glass Petri-dish of 30 mm in diameter. The closed Petri-dish was held in ambient conditions (22 °C) for 5 min to let the solvent vapor saturate the chamber. The as-cast DPP(TBFu)$_2$:PC$_7$BM blend film without and with SVA by THF for 20 s. Inset of Fig. 2(b) is a digital picture of the films before (left) and after (right) the treatment.
PC71BM film was attached at the back of the Petri-dish lid and exposed to the vapor for various durations. The SVA treated films were assembled into OPVs with a device architecture of ITO/PEDOT:PSS/DPP(TBFu)$_2$:PC$_{71}$BM/LiF/Al, as illustrated in Figure 1b. The active layer deposition, treatment and OPV characterization were all completed in air.

Solvents with different vapor pressures, DPP(TBFu)$_2$ donor solubilities and PC$_{71}$BM acceptor solubilities were selected for SVA, including chloroform (CHCl$_3$), acetone, 1,2-dichloroethane (DCE), THF, CS$_2$, chlorobenzene (CB) and 1,2-dichlorobenzene (oDCB). The solvent properties, photovoltaic performance parameters and the optimal treatment duration are listed in Table 1. Figure 2a displays the current density ($J$) – voltage ($V$) curves of OPVs at optimized SVA conditions. The optimization process for each solvent can be found in Figure S1 and Table S1 in Supporting Information. Compared with the untreated OPV, SVA led to significant improvement in $J_{oc}$ and $FF$, but a slight drop in open-circuit voltage ($V_{oc}$). The overall effect was a more than four fold enhancement in PCE. The best photovoltaic performance was achieved by using THF or CS$_2$ vapors, with $V_{oc}$ around 0.8 V, $J_{oc}$ above 11 mA/cm$^2$, high $FF$ of 0.56 and PCE of 5.2%. The results were reproducible within two material batches and five device batches by two researchers (Figure S2 and Table S2, Supporting Information). Both THF and CS$_2$ have high vapor pressure and the donor material DPP(TBFu)$_2$ has medium solubility in both solvents. Interestingly however, PC$_{71}$BM exhibits much better solubility in CS$_2$ (142 mg/ml) compared with THF (3.45 mg/ml). These results suggest that the combination of high vapor pressure and medium solubility of the donor material implies fast vapor penetration into the active layer, moderate solvent-solid interaction and rapid dissipation of the solvent vapor after the treatment, all of which we believe play critical roles in SVA for OPV application. On the other hand, the acceptor solubility appears to have little effect on the photovoltaic performance, thus not important in SVA treatment.

Further evidence for this hypothesis was obtained when solvents with similar DPP(TBFu)$_2$ solubility but low vapor pressure, such as CB and oDCB, were tested for SVA. With decreasing vapor pressure, $V_{oc}$ and $FF$ remained almost constant while $J_{oc}$ reduced. Likely, the low vapor pressure solvent vapors remained inside the films for much longer duration even after the films were removed from the treatment chamber, which caused over-growth of the donor crystals. Solvents with high vapor pressure but different DPP(TBFu)$_2$ solubilities were also investigated. DPP(TBFu)$_2$ has the highest solubility in CHCl$_3$ (15.3 mg/ml), followed by DCE (0.59 mg/ml) and is least soluble in acetone (< 0.5 mg/ml). Table 1 suggests that too high or too low solubility does not produce good OPV performance. Donor solubilities in the range between 0.5 and 5 mg/ml are suitable. Presumably, solvents of high donor solubility result in fast donor crystal growth, leading to large average domain size and wide domain size distribution. In contrast, solvents of low donor solubility can hardly dissolve the donor phase and then penetrate into the film. In fact, the optimum treatment duration for acetone SVA is much longer than any other solvents (Table 1), which we attribute to a much slower film penetration and diffusion rate.

The SVA process can be monitored by color change of the DPP(TBFu)$_2$:PC$_{71}$BM film. Figure 2b shows the respective UV-Vis-NIR spectra and a digital picture of the films before and after THF SVA for 20 s. Upon exposure to these vapors, the film color changed from dark green to purple (Inset of Figure 2b). The absorption profile changed drastically as well. Due to aggregation of the DPP(TBFu)$_2$ molecules, the spectrum was blue-shifted after SVA. The intensity of the peak at 660 nm was reduced while those at 595 and 560 nm were enhanced. The intensity ratio between peak at 595 nm and that at 660 nm increased from 1.1 to 2.6 after the treatment. SVA by other solvents induced similar change in absorption profile (Figure S3, Supporting Information). The appearance of more prominent peaks at 595 and 560 nm is likely related to strong inter-molecular interaction, which enhances intermolecular π-π* transition. A similar phenomenon was observed for the same material system after thermal annealing and dichloromethane vapor annealing by other research groups. Such a change in absorption profile was related to improved crystallinity of DPP(TBFu)$_2$ donor phase, as suggested by their XRD results.

The SVA influence on the morphology of DPP(TBFu)$_2$:PC$_{71}$BM blend film was studied by transmission electron microscopy (TEM) and tomography, which is a most relevant technique to study the morphology in three dimension, but has been rarely employed in OPV research. Especially in small molecule based OPVs. Figure 3 shows the TEM bright field images and 3D computer models of the films before and after SVA by different solvents at their best OPV performance. The video clips of the tomograms and constructed models can be found in Supporting Information (SI movies). Before SVA treatment, TEM bright field images (Figure 3a) showed a few dark structures homogeneously distributed in the bright background. Its angle-tilt tomogram suggested that the dark structures were flakes that were embedded inside the film and

### Table 1 Solvent properties, OPV performance parameters and optimal treatment durations of different solvents used in solvent vapor annealing of the active layer.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Vapor pressure 20°C [mm Hg]</th>
<th>Donor solubility a) [mg/ml]</th>
<th>Acceptor solubility a) [mg/ml]</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{oc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>Treatment duration [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No SVA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.95</td>
<td>2.08</td>
<td>28</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>THF</td>
<td>150</td>
<td>4.41</td>
<td>3.45</td>
<td>0.78</td>
<td>11.72</td>
<td>56</td>
<td>5.15</td>
<td>20</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>300</td>
<td>4.46</td>
<td>142</td>
<td>0.82</td>
<td>11.15</td>
<td>56</td>
<td>5.16</td>
<td>7</td>
</tr>
<tr>
<td>CB</td>
<td>9</td>
<td>3.39</td>
<td>60.6</td>
<td>0.82</td>
<td>8.29</td>
<td>55</td>
<td>3.72</td>
<td>10</td>
</tr>
<tr>
<td>oDCB</td>
<td>1.2</td>
<td>4.45</td>
<td>203</td>
<td>0.8</td>
<td>5.41</td>
<td>56</td>
<td>2.44</td>
<td>20</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>15.3</td>
<td>15.3</td>
<td>61.1</td>
<td>0.79</td>
<td>8.18</td>
<td>55</td>
<td>3.57</td>
<td>10</td>
</tr>
<tr>
<td>Acetone</td>
<td>180</td>
<td>0.5</td>
<td>0.5</td>
<td>0.81</td>
<td>10.40</td>
<td>43</td>
<td>3.64</td>
<td>120</td>
</tr>
<tr>
<td>DCE</td>
<td>64</td>
<td>0.59</td>
<td>3.47</td>
<td>0.83</td>
<td>10.48</td>
<td>56</td>
<td>4.85</td>
<td>25</td>
</tr>
</tbody>
</table>

a) Solubility parameters for all solvents were adapted from reference 44.
Fig. 3 (a-h) TEM bright field images of DPP(TBFu)2:PC71BM blend film (a) before and after SVA by (b) CHCl3, (c) acetone, (d) DCE, (e) THF, (f) CS2, (g) CB and (h) oDCB. The scale bar is 200 nm. The defocusing is typically between 3 and 5 μm. (i-l) Reconstructed 3D models from the tomograms of thin films (i) before and after SVA by (j) acetone, (k) CS2 and (l) oDCB. DPP(TBFu)2 donor phase is rendered in golden color while PC71BM acceptor phase is rendered in green. The scale bar is 50 nm.

occasionally protruded out of the front surface (Figure 3i and SI movie 1 & 2). Since PC71BM is denser than DPP(TBFu)2, the dark phases can be interpreted as PC71BM acceptors, which form very large aggregates. After SVA treatment, the film morphology changed considerably. Figure 3b-h shows that fiber-like structures appear in the films upon SVA. These fiber-like structures can be attributed to DPP(TBFu)2 crystallites. Different solvents resulted in DPP(TBFu)2 crystalline fibers of different sizes, with CHCl3, CB and oDCB producing bigger fibers (Figure 3b, g and h), while acetone, DCE, THF and CS2 gave much finer fibers (Figure 3c-f). This observation was further confirmed by tomography and 3D models (Figure S4 and Figure 3j-l). The difference in fiber size is mainly determined by the solvent-DPP(TBFu)2 interaction strength and duration, which are governed by solvent vapor pressure and DPP(TBFu)2 solubility. The surface texture and roughness were examined by tapping-mode atomic force microscopy (AFM) to gather additional information on the morphology change induced by SVA. Figure 4a-h depicts the AFM topographic images of the DPP(TBFu)2:PC71BM blend film before and after SVA by different solvents. Without SVA (Figure 4a), large parts of the film surface were smooth and featureless with a root-mean-square roughness (Rrms) of 0.39 nm, which was in good agreement with previous report. SVA induced significant changes to the surface texture, with fiber-like structures visible and an increase in Rrms. Films treated by CHCl3, CB and oDCB (Figure 4b, g and h) exhibited extremely large domains ranging between 50 and 300 nm. The Rrms values of the three films were all above 3 nm. Domain sizes larger than 50 nm are detrimental to charge carrier generation due to the limited exciton diffusion length. This result explains the reduced Jsc observed in CHCl3, CB and oDCB treated OPVs. Films treated by acetone, DCE, THF and CS2
Fig. 4 (a–h) AFM topographic images of DPP(TBFu)$_2$:PC$_{71}$BM blend film (a) before and after SVA by (b) CHCl$_3$, (c) acetone, (d) DCE, (e) THF, (f) CS$_2$, (g) CB and (h) oDCB. The root-mean-square roughness of the films is (a) 0.39, (b) 4.75, (c) 1.50, (d) 2.28, (e) 2.72, (f) 1.39, (g) 3.28, and (h) 3.83 nm, respectively. The scale is 2 x 2 μm and height bar is 8 nm. (i–l) Slides of TEM tomograms of films treated by (i, j) acetone and (k, l) CS$_2$. (i) and (k) are the top surface in contact with LiF/Al cathode while (j) and (l) show the bottom surface in contact with PEDOT:PSS/ITO anode. The scale bar is 100 nm. The arrows in (j) indicate the presence of PC$_{71}$BM phase on the bottom surface.

exhibited smaller domain sizes of 20–50 nm. These observations were consistent with TEM and tomography results. The $R_{\text{rms}}$ values of these films were between 1.4 and 2.7 nm, which agreed well with the optimal roughness determined by other groups,$^{30,31}$

We note that due to limited donor solubility and much longer treatment duration, acetone-treated films show a large number of well defined DPP(TBFu)$_2$ crystalline fibers on the front surface of the film (Figure 4c). On the other hand, TEM tomograms revealed PC$_{71}$BM, i.e. dark elongated structures indicated by arrows in Figure 4j, aggregating at the bottom of the film. In comparison, donor and acceptor phases distributed more homogeneously in CS$_2$ treated films (Figure 4k and l). Any accumulation of donor material at the cathode interface or acceptor material near the anode would increase the bimolecular recombination rate, which may be the reason for the observed low FF in acetone-treated OPV devices but will require further investigations in the future.$^{32,52,53}$

Thermal annealing is the most popular way to improve the morphology and OPV performance. Nguyen and coworkers reported the highest efficiency of 4.8% for the same donor:acceptor system after thermal annealing at 110 °C.$^{36}$ We compared SVA with thermal annealing side-by-side, using the same OPV cell architecture and fabrication conditions. Thermal annealing also leads to great changes to absorption profile and surface texture of the active layer (Figure S5 and S6). However, we recorded a slightly lower efficiency of 3.8% when fabricating in inert atmosphere and a much worse efficiency of 2.2% when thermally annealed in air (Figure S7).

Finally, the hole mobility of donor-acceptor blend films was determined from the space charge limited currents (SCLC, Figure S8 and Table S3). The as-cast film showed a hole mobility of $2 \times 10^{-4}$ cm$^2$/V·s. SVA improved the hole mobility but thermal
annealing did not, which was consistent with previous report.31 More specifically, SVA almost tripled the hole mobility to 5.7 × 10^{-4} \text{cm}^2/(\text{V} \cdot \text{s}). We attribute the improved mobility to more ordered donor phase after SVA, enabling the observed enhancement in $J_{sc}$ and FF.

4. Conclusions

In summary, a solvent vapor annealing (SVA) method was demonstrated to improve photovoltaic performance of DPP(TBU)2:PC70BM based OPVs through changes in blend film morphology that was revealed in 3D by TEM tomography. A range of solvents were tested and compared. Solvents with high vapor pressure and medium donor solubility were found to produce changes in morphology leading to higher solar cell efficiency, while acceptor solubility in these solvents played an insignificant role in determining the photovoltaic performance. The best efficiencies were achieved by SVA using THF or CS2, both yielding a PCE of 5.2%, which was the highest PCE for DPP(TBU)2:PC70BM material combination. To the best of our knowledge, this is the first demonstration of highly efficient air-processed small molecule OPVs, and is comparable with the best polymer-based OPVs fabricated in air.54,55 As the treatment is rapid and takes place in ambient condition, it has great potential to be incorporated into large-scale continuous OPV fabrication processes.

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Notes and references

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