Gaining Further Insight into the Effects of Thermal Annealing and Solvent Vapor
Annealing on Time Morphological Development and Degradation in Small Molecule
Solar Cells

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Figure S1. Current density-voltage ($J$-$V$) characteristics of the relevant cells evaluated under illumination with a solar simulator.

Table S1. Photovoltaic parameters of DRCN5T:PC$_{70}$BM BHJ solar cells fabricated under different processing conditions. Cells were tested in air without encapsulations, illumination intensity was 100 mW cm$^{-2}$.

<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>$PCE_{max}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO</td>
<td>982</td>
<td>7.53</td>
<td>48.24</td>
<td>3.57</td>
</tr>
<tr>
<td>TA</td>
<td>932</td>
<td>12.27</td>
<td>58.81</td>
<td>6.73</td>
</tr>
<tr>
<td>SVA</td>
<td>952</td>
<td>12.58</td>
<td>55.45</td>
<td>6.64</td>
</tr>
</tbody>
</table>

Figure S2. Absorption spectrum of films without any treatments and with TA and SVA treatments, respectively.
Figure S3. AFM images (5×5 μm²; 1×1 μm²) of DRCN5T:PC_{70}BM BHJ layers without and with TA and SVA treatments.

Figure S4. Circular 1D GIWAXS profiles of DRCN5T:PC_{70}BM films under various annealing conditions. The curves are vertically shifted for better comparison about PC_{70}BM scattering peak around 1.3 Å⁻¹.
Figure S5. Lorentz-corrected and thickness normalized circular RSoXS profiles of DRCN5T:PC$_{70}$BM films with different processing conditions. All data were taken under 284.2 eV, which maximizes inter-domain scattering and eliminates fluorescence background.

Figure S6. Multi-peak fitting results of films with various processing conditions, implemented to all RSoXS profiles.

Figure S7. Quantitative comparison between RSoXS and AFM images. The power spectral density (PSD) of AFM images is converted from FFT of the direct images, weighted by $q^2$. The low-q peak from 270 eV RSoXS originates from mass-thickness variation, while the high q peak in 270 eV RSoXS correlated well with the dominant peak of 284.2 eV RSoXS. The PSD of AFM phase images match well with 284.2 eV RSoXS, indicating that the phase images reflect the material contrast between donor-rich domains and acceptor-rich domains within the bulk of the films. The AFM height images exhibit large discrepancy with RSoXS results due to the fact that AFM height measurement is only sensitive to the topography of films.
Figure S8. Schematic illustration of the experimental chamber for in situ measurements of thin film drying from the side view; the horizontal purple line on the sample represents the X-ray; the red line indicates the measurement sequence of PL and LS.

Figure S9. Schematic of fitting model used for the thickness calculation of swollen films.

A layer ($d_{\text{total}}$) under a solvent vapor which is a good solvent for one or all components in the layer would induce a swelling behavior. The vapor starts to be absorbed by the film surface, and creates a ‘second’ layer ($d_{\text{blend+solvent}}$) on the dry film ($d_{\text{blend}}$). This solvent-soaked layer can be modelled with effective medium approximation (EMA). Three assumptions were made for
the thickness calculations: (1) the effect of re-evaporation is omitted. (2) Constituent molecules are randomly distributed and are smaller than the wavelength. (3) It is assumed that the EMA layer has high fraction of solvent molecules. Hence, the fraction of solvent molecules in the EMA layer is taken as 90 v% and kept at this value for all calculations. The film optical constants were determined by NIKA software,[2] which is a calculation method based on the reflection and transmission behavior of a flat layer. Since SVA has induced changes in crystallinity (i.e. change in refractive index), 2 sets of film optical constants were used in the EMA and d_{blend} layer modelling: (1) optical constants from the film without any treatment and (2) optical constants from the film with SVA treatment. Hence, the optical constants were changed accordingly for the thickness calculation when reflection spectrum of the layer has indicated crystallinity changes. The optical constants for chloroform molecules used in EMA layer were modelled with a Cauchy dispersion[3] due to their transparency.
Here Figure S10a is the EMA model as mentioned in Figure S9. Absorption peak (right column) fits much better as compared to the other three models. As shown in Figure S10b, optical
constants of the model without any chloroform in film layer does not fit to the measured reflectometry data of SVA 60th second. Absorption peak is blue-shifted, while n and k data of the dray layer do not fit to that of SVA treated layer. We also used another model, showing that the DRCN5T:PC\textsubscript{70}BM layer is swelled completely with 5\% chloroform after 60 seconds SVA. Theoretically, a dry non-porous layer with 111 nm dry thickness would be 116 nm after soaking 5\% chloroform. Further checking the corresponding graph shows that the absorption peak fits good from the position, but the intensity is too different between fit spectrum and reflectometry data (see Figure S10c). In addition, when the film layer is swelled completely with 10 vol.\% chloroform, the thicknesses of swelled layer changes from 111 nm to 122 nm after soaking. Compared with the reflectometry data, the absorption peak from the fit starts to red shift with this model (see Figure S10d). In short, we selected this bilayer model (Figure S9) to analysis the in situ PL data, resulting from the better fitting curve as compared to the other three models.

![Figure S11](image_url)

**Figure S11.** The reflection spectra of TA film are plotted from 0 seconds till 120 seconds. The inset is a zoom to the wavelength range of 550-750 nm for a better clarity of the spectral changes.
**Figure S12.** The reflection spectra of SVA film are plotted from 0 seconds till 240 seconds. The inset is a zoom to the wavelength range of 575-725 nm for a better clarity of the spectral changes.

**Figure S13.** SIMS ion yield as a function of sputtering time for (a) WO sample, (b) TA sample and (c) SVA sample, the depth distribution of DRCN5T molecules is shown here. The blue dashed line is an indicator for the bottom interface between active layer and cathode.
Figure S14. The dark $J$-$V$ characteristics of devices with TA and SVA treatments, including hole-only devices and electron-only devices, respectively. The inset mobility data are average values of each sample within 6 devices.

Figure S15. Changes of normalized (a) $V_{oc}$, (b) $J_{sc}$, (c) FF and (d) PCE losses over illumination time for TA and SVA treated solar cells.
Figure S16. Changes of normalized absorption spectra over illumination time for TA and SVA treated films.

Figure S17. SIMS ion yield as a function of sputtering time for (a) fresh sample without any treatments, (b) aged sample without any treatments, (c) fresh sample with TA treatment, (d) aged sample with TA treatment, (e) fresh sample with SVA treatment and (f) aged sample with SVA
Figure S18. SIMS ion yield as a function of sputtering time for (a) fresh and (b) aged samples without any treatments, the depth distribution of DRCN5T molecules is shown here. The blue dashed line is an indicator for the bottom interface between active layer and cathode.

References:

