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Supplementary Material: Solvent Vapor Annealing on Perylene-Based Organic Solar Cells

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I. XRD

To investigate the crystallinity of the annealed DBP layer, X-ray diffraction (XRD) measurements are performed and compared to XRD measurements of pristine DBP layers. Out-of-plane X-ray reflection (XRR), however, yield no peaks indicating a well-ordered crystalline structure, neither for the annealed nor for the pristine material. This data is shown in Fig. 1(a). Therefore, in-plane (grazing incident X-ray diffraction) measurements were recorded, but also in this configuration no peaks indicating DBP crystallinity are observable (Fig. 1(b)). Actually, three peaks appear, however, they appear for both the annealed and the pristine film and can clearly attributed to the ITO substrate.

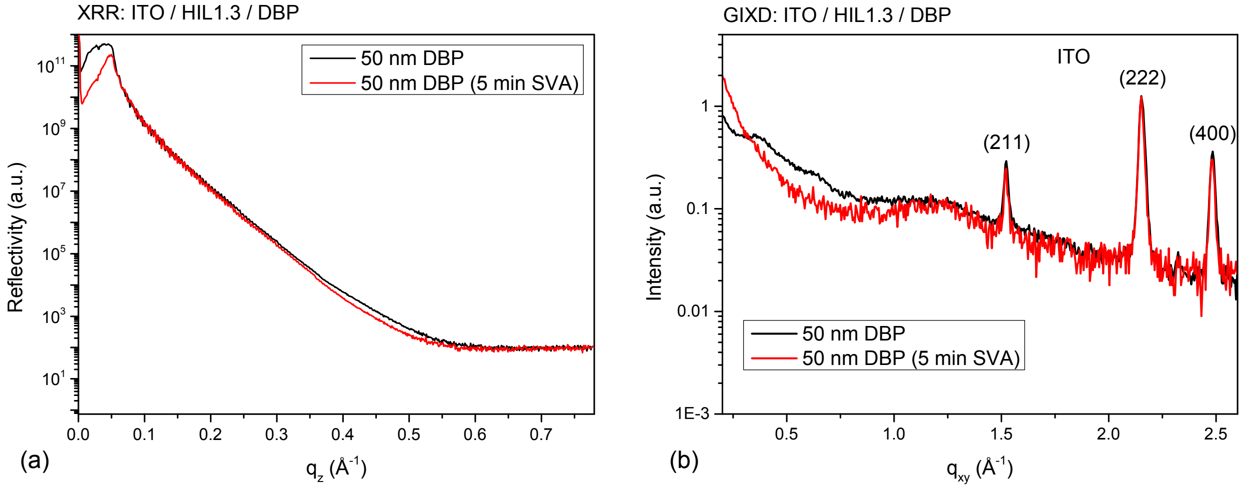

FIG. 1. In-plane ((a), GIXD) and out-of-plane ((b), XRD) X-ray diffraction measurements of pristine and annealed (5 minutes) DBP layers. The architecture of the samples is always ITO/HIL1.3/DBP (50 nm). Peaks indicating DBP crystallinity can not be observed for annealed layers for both configurations. The peaks visible in (a) can be clearly attributed to the ITO substrate.

Also for DIP films, XRR measurements do not reveal any change in the out-of-plane crystallinity due to SVA on 50 nm thick DIP layers. For the pristine as well as the SVA-treated sample, both the $\sigma(001)$ and the $\sigma(002)$-peak appear at $q_z = 0.38\,\text{Å}^{-1}$ and $q_z = 0.75\,\text{Å}^{-1}$ respectively. No additional peaks appear and also no broadening of the peaks occurs. A broadening would indicate a change of the vertical extent of the crystalline domains. However, it has already been shown in literature[1–3], that the vertical extent of DIP crystallites is determined by the layer thickness. This could also be observed here by calculating the crystallite sizes via Scherrer equation. An increase of the lateral domain size, as indicated by AFM images, is not possible to measure by out-of-plane XRD measurements.

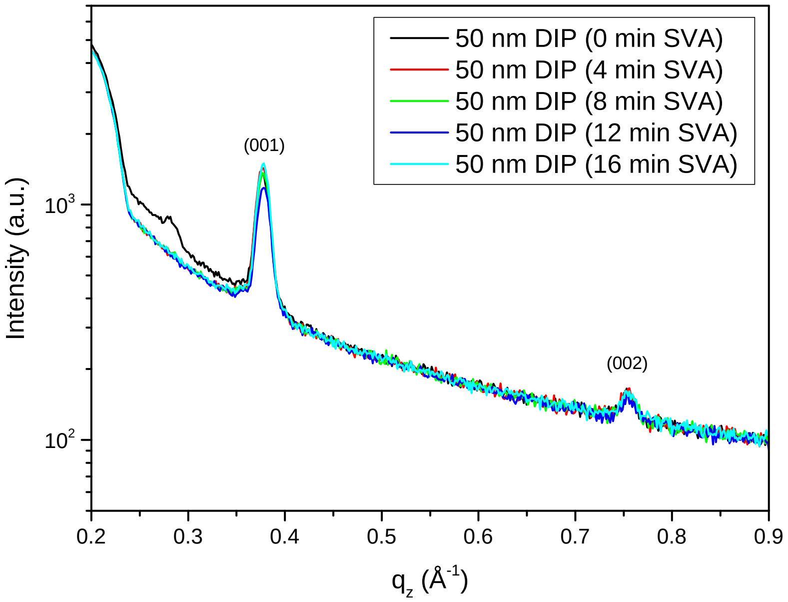

FIG. 2. Out-of-plane XRD measurements of samples consisting of ITO/HIL1.3/DIP (50 nm) either pristine or annealed for 4, 8, 12 and 16 minutes. For both samples the same peaks, (001) and (002), appear. They do not show any broadening due to SVA. Full width at half maximum (FWHM) of each peak was determined and crystallite sizes calculated via Scherrer equation. The results are nearly identical, yielding vertical coherence lengths close to the layer thickness of 50 nm. This means that the choice of the layer thickness already determines the vertical crystallite size, a fact that has already been shown in literature[1–3].

II. NEXAFS

Near edge X-ray absorption fine structure (NEXAFS) measurements of pristine and solvent annealed DBP films reveal a change in molecular orientation. Measurements on pristine films yield a higher intensity for low angles of incidence (θ) of the X-ray photons as compared to high values of θ in the low energy region which is related to the transition from the C1s core level to the LUMO level. This reveals a more flat lying perylene core. After 4 minutes of SVA, however, no angular dependence appears any more. This is indicative of a reorientation process which has started, leading to an intermediate configuration, similar to the results obtained by AFM and absorption measurements. Further annealing yields a reversed angular dependence indicating a change of molecular orientation due to solvent vapor annealing (Fig. 4). These results indicate a more upright oriented perylene core and even more upright oriented phenyl rings. In contrast to Fig. 4 in the manuscript, the omitted data for $\theta = 30°, 55°$ and $70°$ are also shown here.

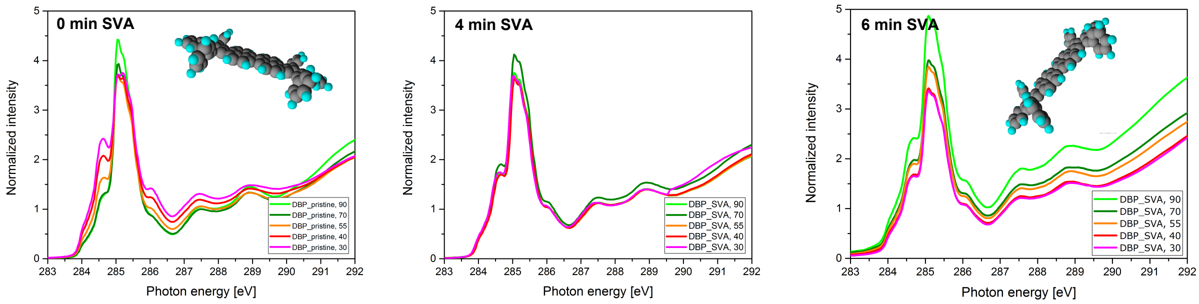

FIG. 3. NEXAFS data of a 15 nm DBP film annealed for 0 (a), 4 (b) and 6 minutes (c) at $30°, 40°, 55°, 70°$ and $90°$ angle of incidence (θ) of the X-ray photons. Comparing the data of the untreated sample and the sample annealed for 6 minutes a distinct change in dichroism is visible e.g. at about 284.6 eV. This indicates a change in molecular orientation from rather horizontal to more upright standing alignment.

For DIP films, however, no change of molecular orientation could be observed via NEXAFS.

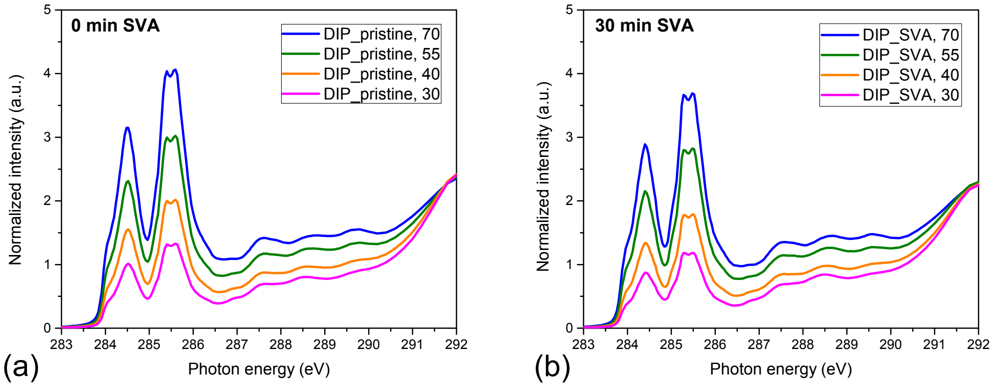

FIG. 4. NEXAFS data of a 15 nm DIP film annealed for 0 (a) and 30 minutes (b) at 30°, 40°, 55° and 70° angle of incidence (θ) of the X-ray photons. Comparing the data of the untreated sample and the sample annealed for 30 minutes no change in dichroism is visible, indicating that there is no change in molecular orientation.

III. SVA FOR DIP/DBP

By annealing DBP, which is evaporated on top of DIP, some changes occur compared to annealed DBP layers on HIL1.3. The strong aggregation of DBP sets in earlier, already for 4 minutes of SVA. We think that the acceleration of the DBP roughening effect is due to the rougher DIP surface compared to HIL1.3. As a consequence, it is easier for the solvent to impact on the DBP layer. Thus, the strong decrease of the absorption coefficient already starts for 4 minutes of SVA.

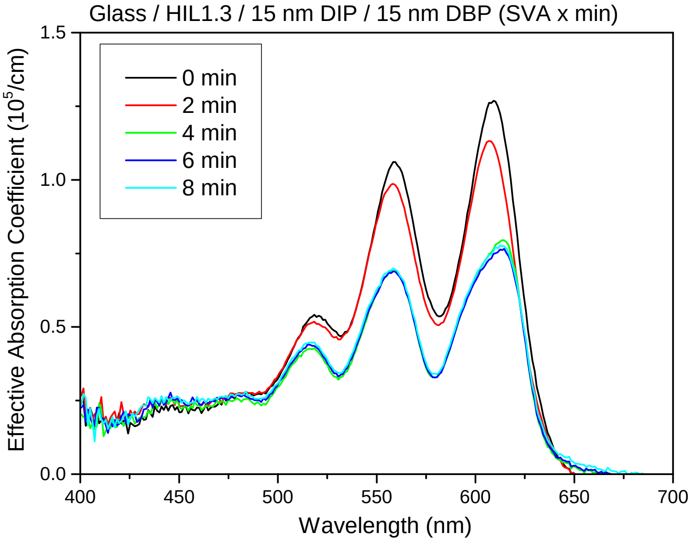

FIG. 5. Correlation between SVA time and absorption drop of an annealed DBP layer evaporated on top of an untreated DIP layer. Compared to HIL1.3/DBP (SVA) without DIP blocking layer (Fig. 3 in the document) the strong decline of absorption occurs earlier. As a result, 4 minutes of SVA are already too long. Note that the spectra are the sum of 15 nm of DIP and 15 nm of DBP, however, the absorption coefficient is calculated with the overall thickness of 30 nm.

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