Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

E-mail:

Solvent Annealing

Four solvents with different P3HT and PCBM solubility and vapor pressure were used as the solvent in the solvent annealing process; Bromobenzene (BB), Chlorobenzene (CB), Toluene (TL), 2-Chlorophenol (2-CP). A schematic of the solvent annealing apparatus is shown in Figure S1, where the total length of the vapor gradient L_0, i.e., the distance from column opening to solvent surface is 100 cm. The solvent vapor pressure gradient is allowed to reach equilibrium after solvent is added into the column.

For all solvent annealing procedures, the P3HT:PCBM mixture is positioned at L/L_0=0.9. This results in the vapor pressure of the solvent during annealing being 90% of the pure solvent vapor pressure. Table S1 lists the saturated vapor pressure of the four solvents used in this study at 20°C, as well as the vapor pressure of the solvent at the surface of the annealed sample (surface vapor pressure).

Table S1: Measured solubility of P3HT and PCBM in solvents for SVA and saturated and surface vapor pressure of each solvent.

Solvent	Vapor Pressure 20°C (mmHg)		Measured Solubility (mg/ml)	
	Saturated VP	Surface VP	P3HT	PCBM
Bromobenzene (BB)	3.3	2.97	107.9	33.4
Chlorobenzene (CB)	8.8	7.92	33.8	39.4
Toluene (TL)	22	19.8	1.4	16.3
2-Chlorophenol (2-CP)	2.2	1.98	<0.1	128.3

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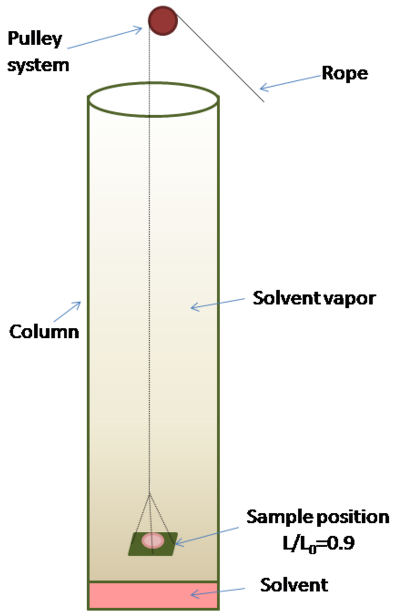


Figure S1: Schematic of the solvent vapor annealing apparatus: Variation in solvent vapor pressure during annealing is achieved by changing the position of wafer surface with respect to the solvent surface. $L/L_0 = 0.90$ is used in our experiment.

Solubility Measurements

The solubility of P3HT and PCBM in the solvents of interest was determined via UV-Vis spectroscopy using Thermo Scientific Evolution 600 UV-Visible spectrophotometers. In this experiment, the absorbance of solutions with known concentration is monitored at 600 nm. According to the Beer-Lambert Law,

$$A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon \cdot c \cdot L \tag{S1}$$

where A is the measured absorbance, I_0 is the intensity of the incident light, I is the transmitted intensity, L is the pathlength (1mm), c is the concentration of the absorbing species, and ε is the extinction coefficient. Plotting the absorbance as a function of known concentration provides a measure of the extinction coefficient, ε. With knowledge of ε, the measured absorbance of a solution with unknown solute concentration provides a method to determine the solute concentration.

This UV-Vis method was used to determine the solubility of P3HT and PCBM in all four solvents, and presented in Table S1. These results show that BB has the highest P3HT solubility, followed by CB, TL, and 2-CP; while the PCBM solubility is 2-CP > TL > CB > BB.

To further investigate the effect of P3HT solubility on the change in crystallinity during SVA, pure P3HT thin films, formed by spin coating from an ODCB solution (10 mg/ml), were solvent annealed in CB, TL, and 2-CP and characterized. The GIWAXS experiments show that the evolution of P3HT crystallinity is similar in these thin films to the P3HT/PCBM thin films when solvent annealed in CB and TL, (see Figure S2). However, there is little change in the crystallinity of the P3HT thin film that is annealed in 2-CP vapor, which can be attributed to the insolubility of P3HT in 2-CP. These results also exemplify that the high solubility of PCBM in 2-CP induces P3HT crystallization in the BHJ during SVA.

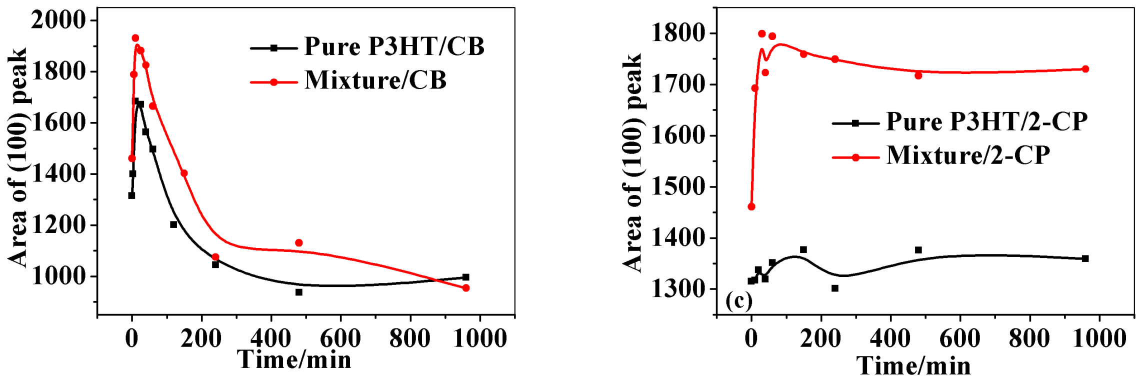


Figure S2: Comparison of P3HT the area of (100) peak for solvent annealed P3HT/PCBM and pure P3HT samples. Left: CB; Right: 2-CP. The curves are merely a guide for the eye.

Utilizing the 3-phase model for P3HT:PCBM mixtures,[1,2] the absorbed 2-CP solvent vapor penetrates the miscible amorphous P3HT:PCBM phase, increasing the mobility of PCBM. The increased PCBM mobility in the mixed phase will also allow P3HT chain movement, therefore permitting the P3HT to form crystals as well. The absorbed 2-CP solvent does not destroy previously formed P3HT crystals, due to its insolubility. Consequently, the P3HT crystallinity increases in the P3HT/PCBM mixture thin film; but the crystallinity of the P3HT is not altered in the pure P3HT thin film.

AFM Data

Figure S3 shows the AFM height and phase contrast images of the P3HT:PCBM thin film during solvent vapor annealing in CB and TL. In these figures, the bright dots in the phase contrast images are ascribed to PCBM domains, as a consequence of the higher modulus of PCBM than P3HT. The root mean square (RMS) roughness for each annealed film is presented in Figure S4.

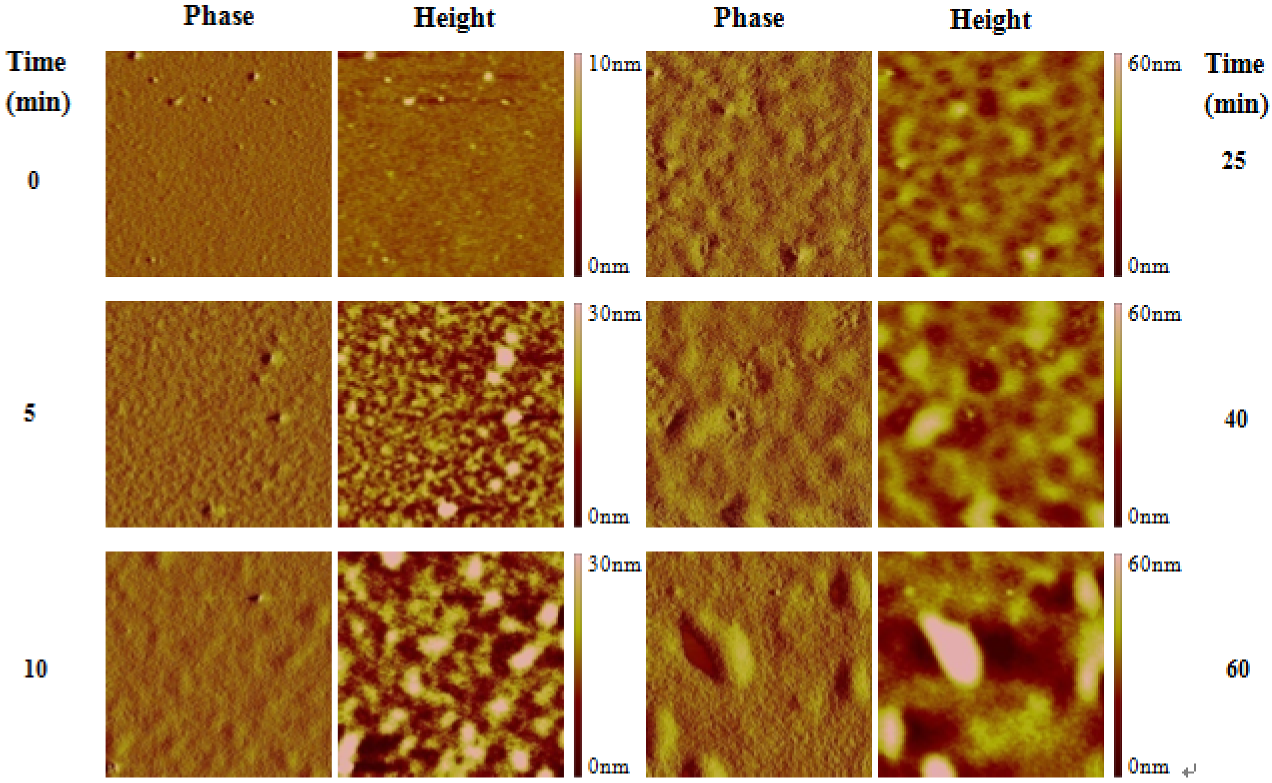
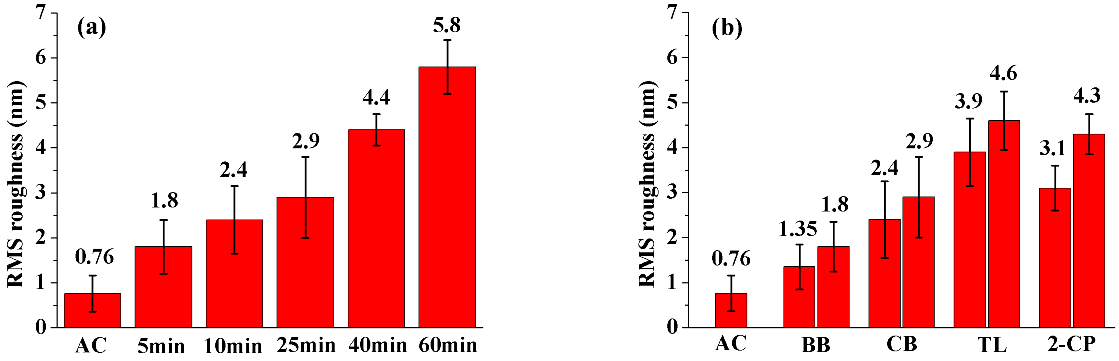


Figure S3: AFM image of CB annealed thin film at different annealing times of 0, 5, 10, 25, 40 and 60 min. In each column, left: 5μm×5μm phase image; right: 5μm×5μm height image.



(a) RMS roughness for CB at various times.

(b) RMS roughness for various solvents at times 1 and 2.

Figure S4: RMS roughness measurements corresponding to Figures S3 and **??**. RMS surface roughness continues to increase with increased SVA time.

References

(1) W. Yin and M. Dadmun, *ACS Nano*, 2011, **5**, 4756–4768.

(2) H. Chen, R. Hegde, J. Browning and M. D. Dadmun, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5635–5641.