Supplementary information

The development of nanoscale morphology in polymer:fullerene photovoltaic blends during solvent casting

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1. A schematic cartoon of *in-situ* ellipsometry and GI-XS system.

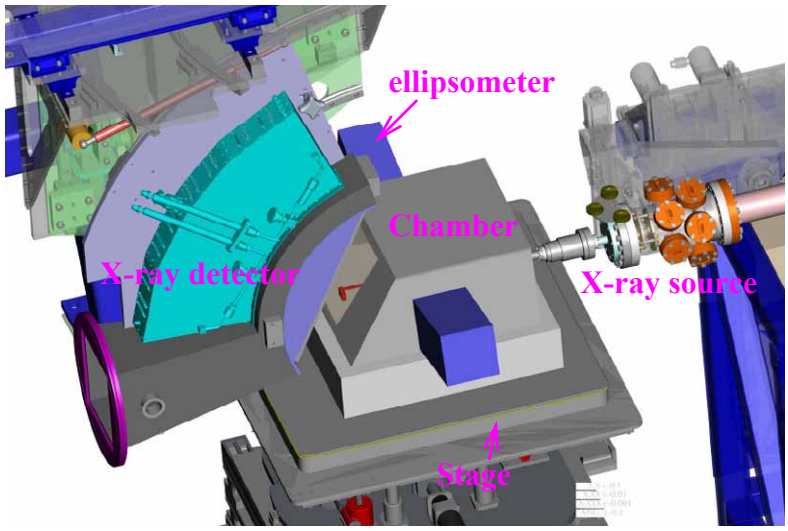

Figure S1 3D cartoon of the *in-situ* system setup.

2. Spectroscopic data recorded during the drying of a P3HT/PCBM blend cast from a solution of TCB.

Figure S2 shows typical ellipsometry data recorded as a function of time during the drying of a P3HT:PCBM film. Here, the film was cast using a doctor blade from a TCB (50 mg/ml) solution onto a Si wafer onto a substrate held at 30 ^{o}C.

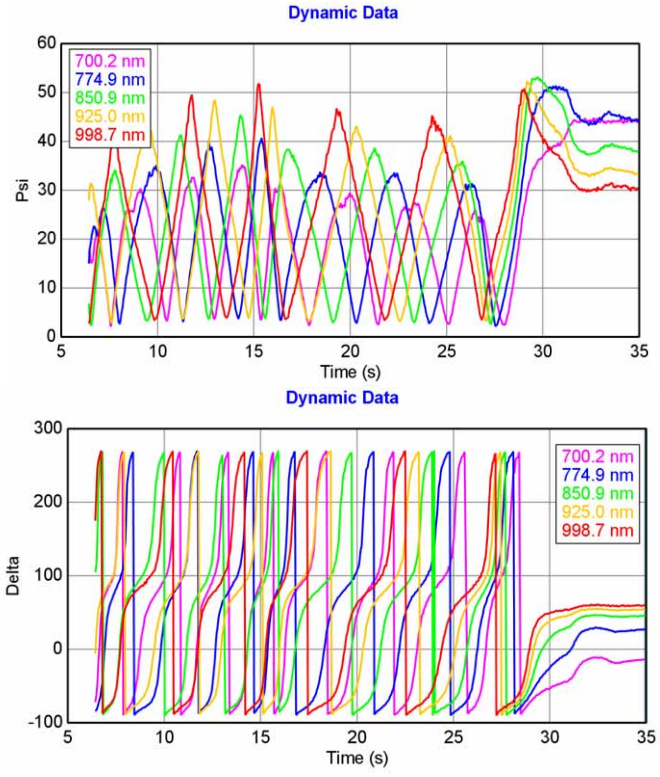

Figure S2 Spectroscopic data recorded during the drying of a P3HT/PCBM blend cast from a solution of TCB at a substrate temperature of 30 ^{o}C. Interference resulting from the passage of the doctor blade through the ellipsometer beam path is not shown.

3. Calculating the change in film thickness using a Cauchy model.

The change in film thickness during drying was determined using a Cauchy model that was fit to ellipsometry data over the wavelength-range 700 to 1000 nm, where the film has negligible absorbance. The Cauchy model has been utilized to describe the dispersion of the complex refractive index (refractive index n, and extinction coefficient k) in a transparent dielectric. In a transparent spectral region, the extinction coefficient is zero, whereas the refractive index is represented by a slowly varying function of wavelength λ as:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \ldots$$

Where A, B and C are fit parameters.

To improve the fit, a non-uniformity parameter was added to the Cauchy model. The best fit was identified by minimizing the mean square error (MSE) defined by the following equation:

$$MSE = \frac{\sum \left[\frac{\left| \tan(\Psi_{\exp} - \tan(\Psi_{cal}) \right|}{\sigma_{\tan(\Psi)}} \right]^2 + \left[\frac{\left| \cos(\Delta_{\exp} - \cos(\Delta_{cal}) \right|}{\sigma_{\cos(\Delta)}} \right]^2}{N - M - 1}.$$

Here, Ψ and Δ are the ratios of the amplitude of light and its relative-phase before and after reflection from the film/substrate respectively with the subscripts *exp* and *cal* signifying experimentally and calculated values. The terms *N* and *M* represent the number of wavelengths at which measurements were performed and the number of parameters used in the fitting process, respectively. Values of Ψ and Δ recorded at

three different times during the drying process (1.8, 10.3 and 25.3 s after the film been cast) plotted as a function of wavelength are shown in Figures S3**a** to **c**. In each case, the dashed curves plotted over the range 700 to 1000 nm are fits to the data using the Cauchy model.

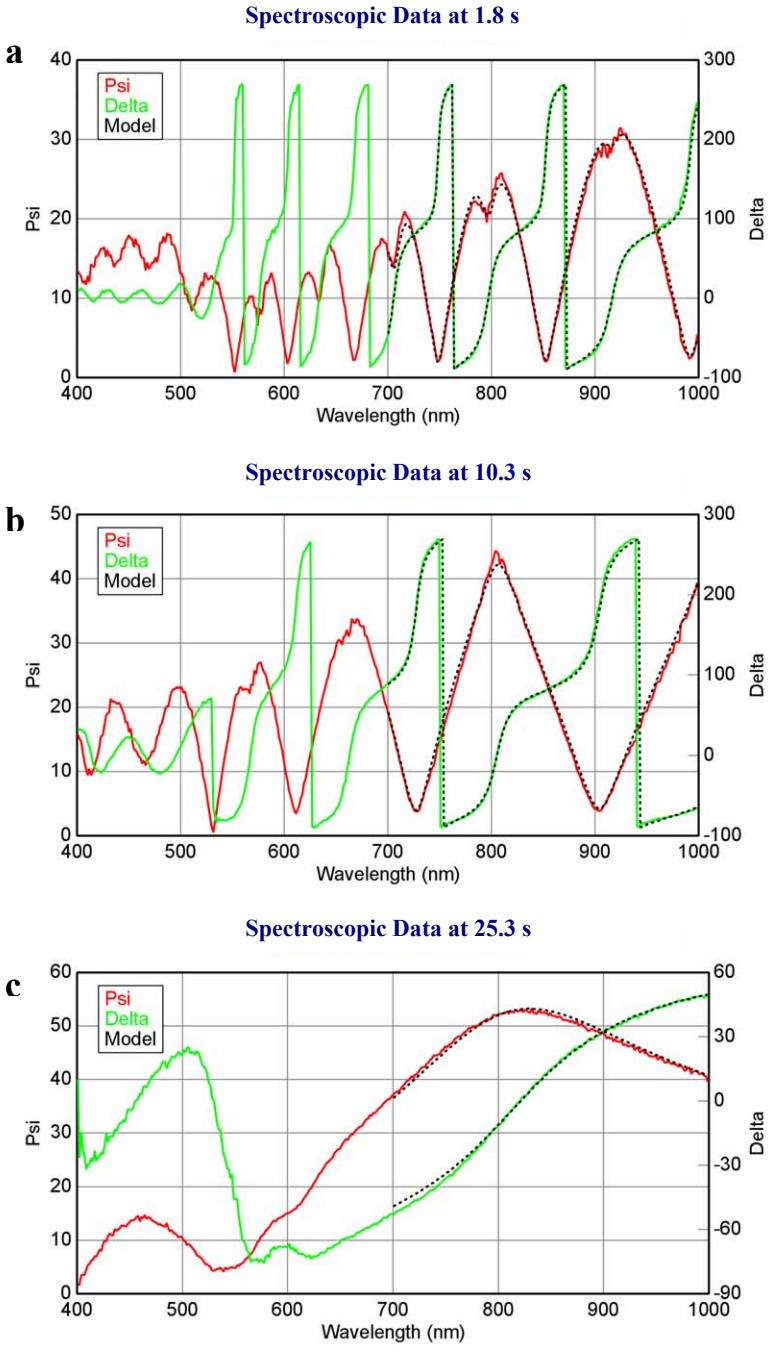

Figure S3 Ellipsometry data (Ψ and Δ; red and green respectively) as a function of wavelength at different drying times. Curves fits over the range from 700 nm to 1000 nm using a Cauchy model are shown as a dashed line.

4. Calculating the optical constants via a B-spline fit.

The film thickness at each time during film drying was determined using the Cauchy model as described in the above. This value was then put into a B-spline model to fit the optical constants (*n* and *k*) over the optical range corresponding to strong optical absorption of the P3HT / PCBM thin film (400 to 700 nm). This fitting was performed with a 10 nm wavelength resolution. We found that the MSE during the B-spline fit went from ~ 9 in a "wet" film to ~ 3 as the film dried. Figure S4**a** shows a typical plot of the extinction coefficient between 400 and 700 nm determined from a wet P3HT:PCBM film. A characteristic peak is observed at 460 nm that corresponds to the absorption of solvated (un-aggregated) P3HT molecules. Figure S4**b** shows a typical extinction coefficient plot of a dry (polycrystalline) P3HT:PCBM film. Characteristic P3HT absorption peaks at 517, 550 and 605 nm (the 0-2, 0-1 and 0-0 vibrational and electronic modes respectively) can be resolved.

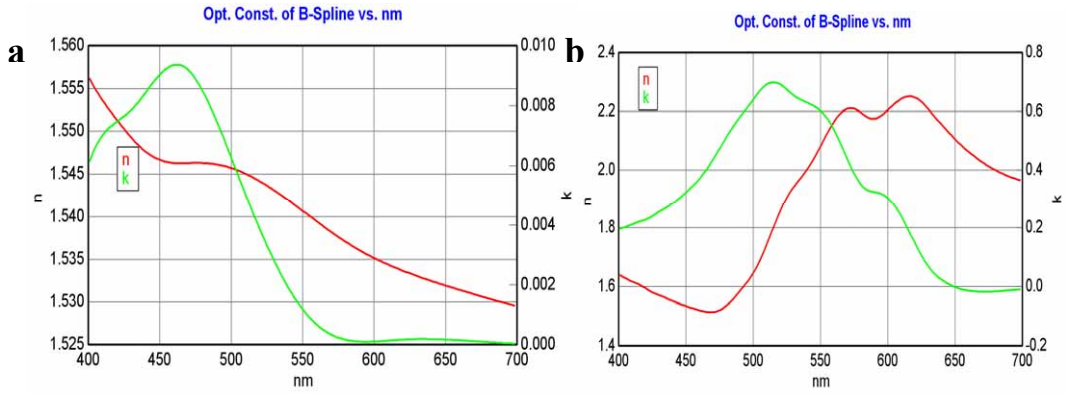

Figure S4 Extinction coefficient determined from a wet (S4**a**) and dry (S4**b**) P3HT/PCBM film.

5. The evolution of the extinction coefficient of a P3HT:PCBM film cast from a CB solution at a substrate temperature of 40 and 50 ^{o}C. The variation of extinction coefficient as a function of $\varphi_{P3HT:PCBM}$.

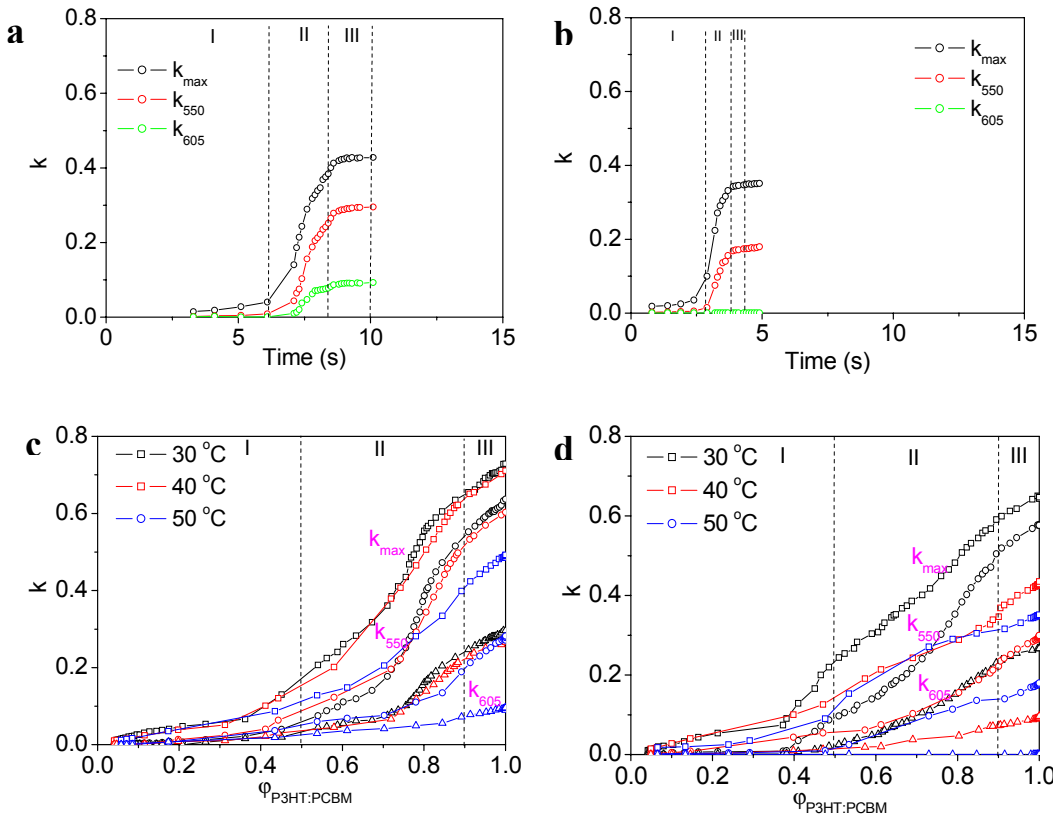

Figure S5**a** and **b** plots the change in the extinction coefficient of a P3HT:PCBM film cast from CB at a temperature of 40 and 50 °C respectively. Parts **c** and **d** show the evolution of *k* vs. $\varphi_{P3HT:PCBM}$ in films cast from TCB and CB respectively at a range of temperatures as indicated in the figure.

6. X-ray scattering of P3HT:PCBM

A 2D GIWAXS of a P3HT:PCBM film is shown in S6**a**. Here, the primary [100], secondary [200], and tertiary [300] scattering peaks of P3HT lamella are detected in the out-of-plane direction. An in-plane [010] peak corresponding to π-stacked P3HT molecules is also detected. The PCBM is apparent from the presence of a broad and diffuse ring. Smoothed [100] profiles obtained by GI-XS show the evolution of P3HT crystallization during the film growth process.

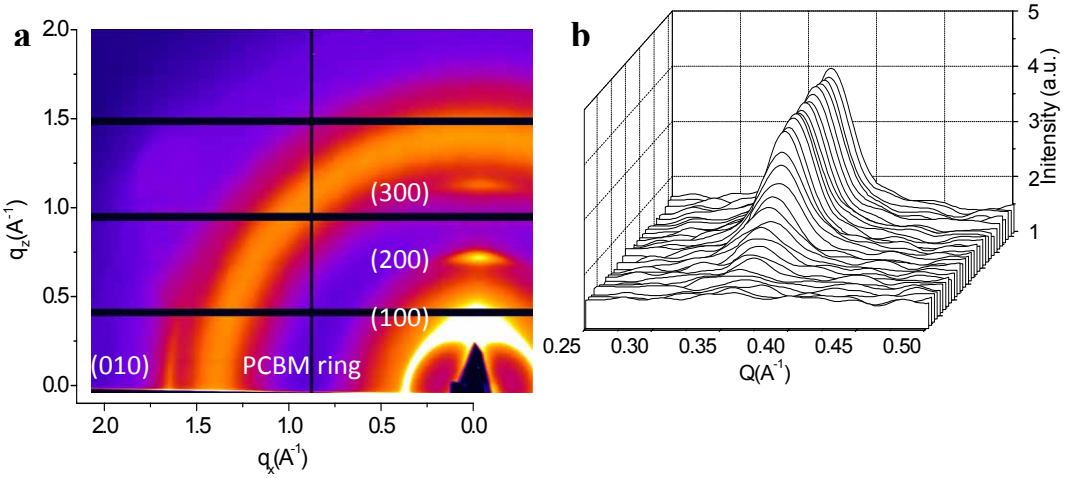

Figure S6 **a**, GIWAXS of a P3HT:PCBM blend measured at I16, Diamond Light Source. **b**, The evolution of the P3HT [100] X-ray scattering peak during drying of the film, after been smoothed to clearly show the growth of this feature.

7. Relation between the measured extinction coefficient and crystallinity

There is an approximately linear dependence of the extinction coefficient on the P3HT crystallinity as determined from the intensity of the [100] scattering peak. This data-set was constructed by performing X-ray scattering and ellipsometry measurements on *ex-situ* prepared P3HT:PCBM blend films cast using doctor blading. The films were cast using different solvents onto substrates at different temperatures, resulting in films having a range of crystallinities.

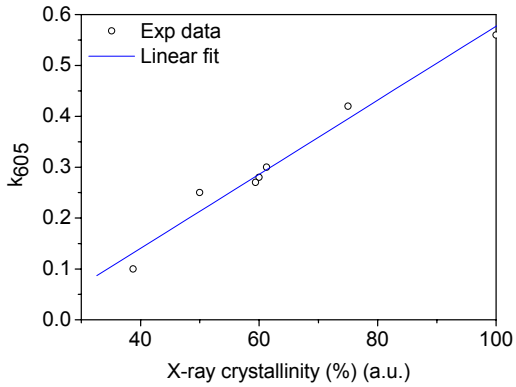

Figure S7 Relation between extinction coefficient (k) in P3HT and the crystallinity calculated from the [100] pattern.