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Supplementary Materials for

Comparison of solution-mixed and sequentially processed P3HT:F4TCNQ films: effect of doping-induced aggregation on film morphology

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This PDF file includes: Supplementary Figures 1-3, Supplementary Tables 1 and 2, and discussion

Determination of doping level in sequentially doped films



Supplementary Figure 1: Linear fits to the IR absorption of mixed-solution films.

Doping level in sequentially doped films was estimated by fits to the IR absorbance of the doped films (0.5 - 0.6 eV), which is typically assigned to the P3HT polaron. Absorbance of all samples was normalized to 1 at the maximum of the P3HT absorption at 540 nm. Supplementary Figure 1 shows a plot of IR absorption vs. doping level for mixed-solution films, obtained from UV-vis-NIR spectra in Figure 1c. Two linear regions

Doping solution concentration (mg/ml)	Doping level from IR absorbance (mol%)
0.001	0.08 ± 0.29
0.003	0.10 ± 0.29
0.01	0.91 ± 0.29
0.03	2.50 ± 0.29
0.1	3.71 ± 0.29
0.3	4.34 ± 0.74
1.0	5.07 ± 0.84

Supplementary Table 1: Calculated doping levels for films sequentially doped from F4TCNQ: CH_3CN solutions

Supplementary Table 2: Calculated doping levels for films sequentially doped from 0.1 mg/ml F4TCNQ in CH₃CN, followed by F4TCNQ : CB solutions

CB doping solution concentration (mg/ml)	Doping level from IR absorbance (mol%)
0.3	6.20 ± 0.11
0.6	7.00 ± 0.11
1.0	8.25 ± 0.11

are visible, separated by a discontinuous region. This discontinuity occurs in the region where we expect F4TCNQ to begin intercalating into crystalline domains (Figure 2b).

For doping levels between 0-4% and 5.5-7%, the IR absorption of the sequentially doped films are used, along with coefficients of the linear fits, to solve for doping level. Error bars are calculated by the RMS error of the fits within these regions. In the discontinuous region, concentration is calculated by interpolation between the absorption of the 4% and 5.5% mixed-solution absorptions, as shown in Figure S1. Because we expect non-linear changes in absorption with respect to doping level in this region, the uncertainty of doping level estimates in this region is large. We estimate the uncertainty as the distance to the nearest data point plus the RMS errors of both the low and high doping regions, since interpolation between these regions is affected by the error in both the low and high doping fits. Thus, the error in this region is given by $|4.75 - x| + \delta_H + \delta_L$, where δ_H and δ_L are the RMS errors of the high and low doping level fits, respectively. Supplementary Tables 1 and 2 show the calculated doping levels of the sequentially doped films.

Roughness data from AFM images



Supplementary Figure 2: Root-mean-square roughness calculated from AFM images in Figure 3

Electron diffraction at 0.9 mol% doping



Supplementary Figure 3: Radially integrated electron diffraction patterns at ~ 0.9 mol% doping level. As in Figure 4, films (b-d) have similar doping levels, but different preparation methods. a) Undoped P3HT, b) P3HT:F4TCNQ sequentially doped from a 0.1 mg/ml acetonitrile solution, c) P3HT:F4TCNQ sequentially doped from a 0.1 mg/ml acetonitrile solution, wetted with 50μ L CB and allowed to dry (approx. 10 minutes) and d) P3HT:F4TCNQ doped at 0.9 mol% prepared by the mixed solution method. At this lower doping level, no shift in the $\pi - \pi$ stacking dimension is observed, yet the CB wetted film (c) remained insoluble. We can conclude from this observation that intercalation of F4TCNQ into P3HT crystallites is not required to render P3HT insoluble.