Supporting Information

Ordering of Poly(3-hexylthiophene) in Solutions and Films: Effects of Fiber Length and Grain Boundaries on Anisotropy and Mobility

Nabil Kleinhenz[1], Nils Persson[2], Zongzhe Xue[2], Ping Hsun Chu[2], Gang Wang[2,3], Zhibo Yuan[1], Michael McBride[2], Dalsu Choi[2], Martha Grover[2] and Elsa Reichmanis[1,2,4]**

[1] School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA

[2] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, USA

[3] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China

[4] School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, GA, USA.

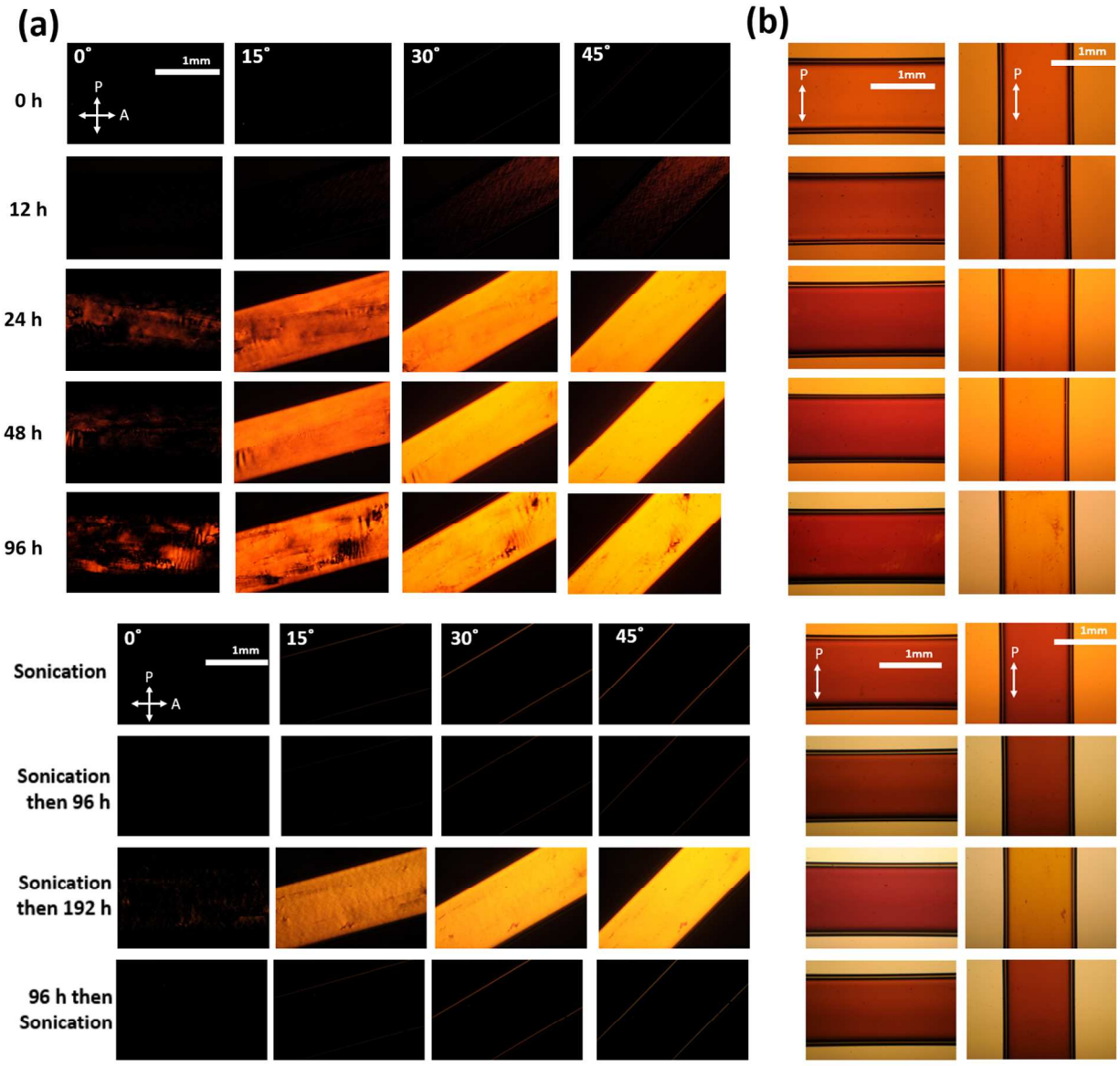


Figure S1: (A) Polarized Optical Microscopy (POM) images of capillaries filled with 5 mg/mL P3HT/Chloroform solutions processed as indicated, before filling. Angles refer to angle between long axis of capillary and analyzer. (B) Images taken with only one polarizer, showing linear dichroism as capillary is oriented parallel or perpendicular to polarizer. Suggests chains are perpendicular to capillary long-axis and fibers are parallel to capillary long-axis.[1]

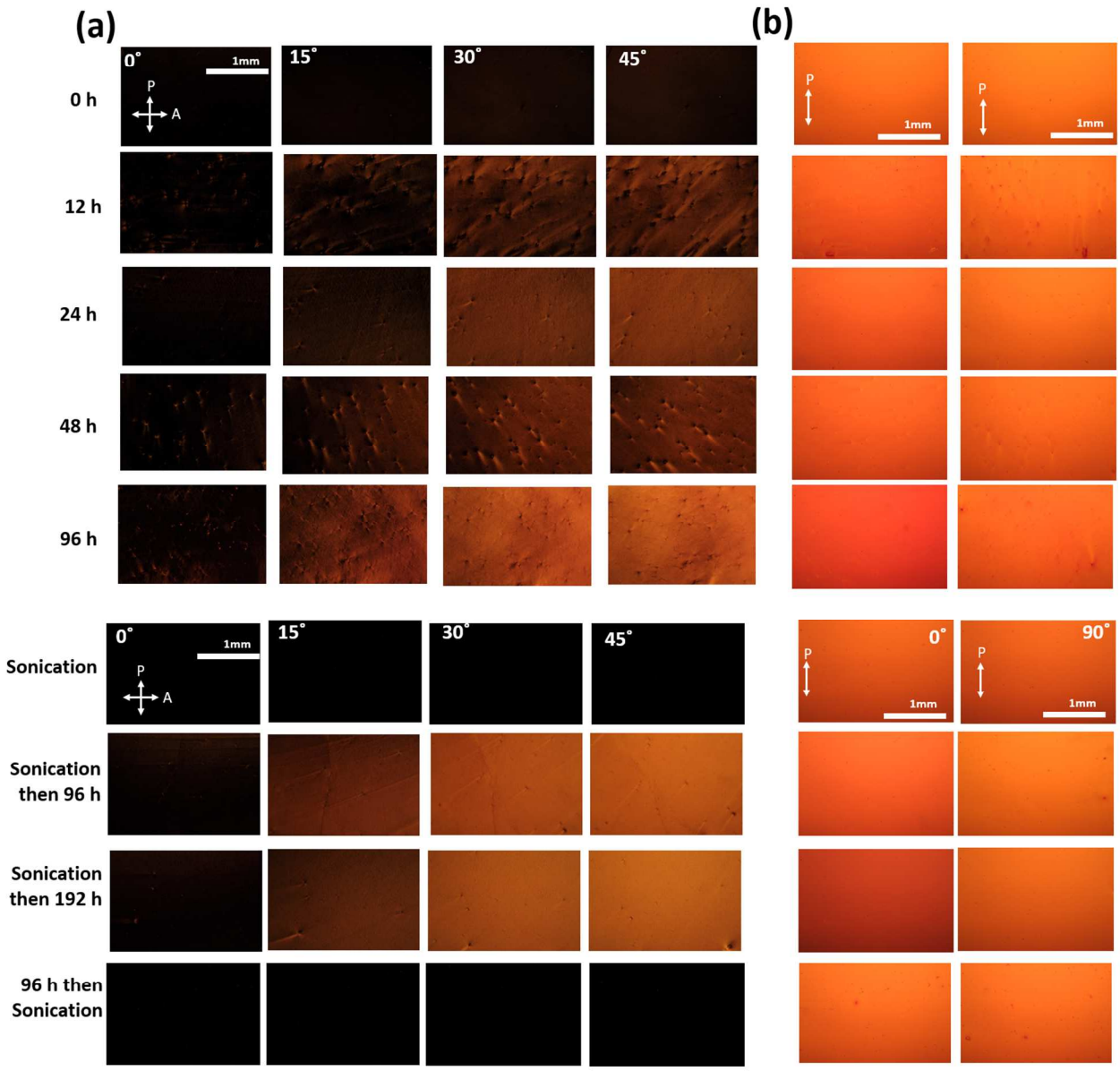


Figure S2: (A) Polarized Optical Microscopy (POM) images of capillaries filled with 5 mg/mL P3HT/Chloroform solutions processed as indicated, before filling. Angles refer to angle of stage as it rotates away from analyzer. (B) Images taken with only one polarizer, showing linear dichroism as film is rotated.

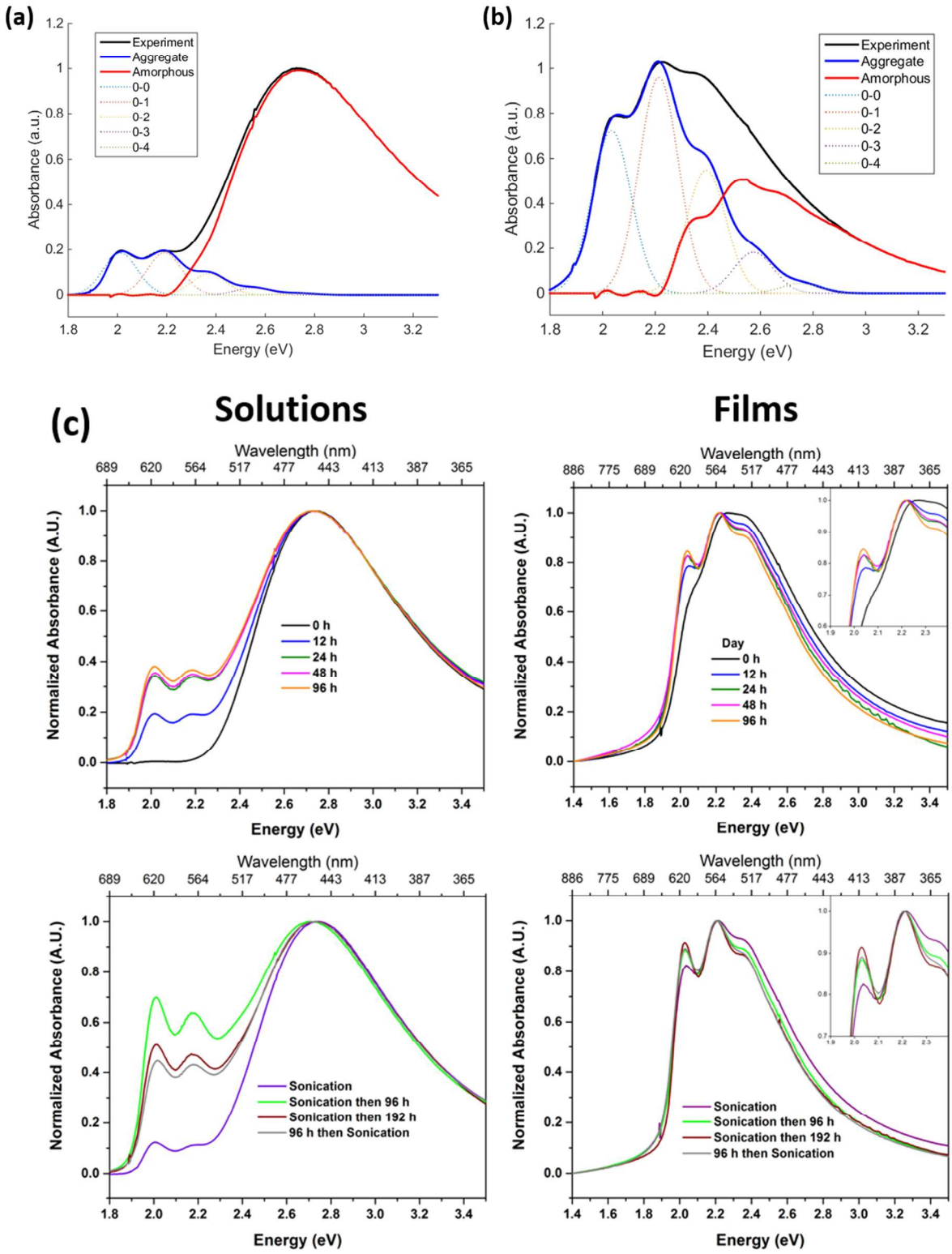


Figure S3: (A) Example of Franck-Condon fitting of normalized UV-Vis absorption spectra for obtaining percent aggregates in P3HT / Chloroform solution (a) and film (b) after 12 hours of aging, using methods described in literature:[2] (c) UV-vis curves for all samples.

$$A(E) \propto \sum_{m=0} \left(\frac{S^m}{m!}\right)\left(1 - \frac{We^{-S}}{2E_p}\sum_{n\neq m}\frac{S^n}{n!\,n-m}\right)^2 \exp\left(\frac{\left(E - E_{0-0} - mE_p - \frac{1}{2}WS^m e^{-S}\right)^2}{2\sigma^2}\right)$$

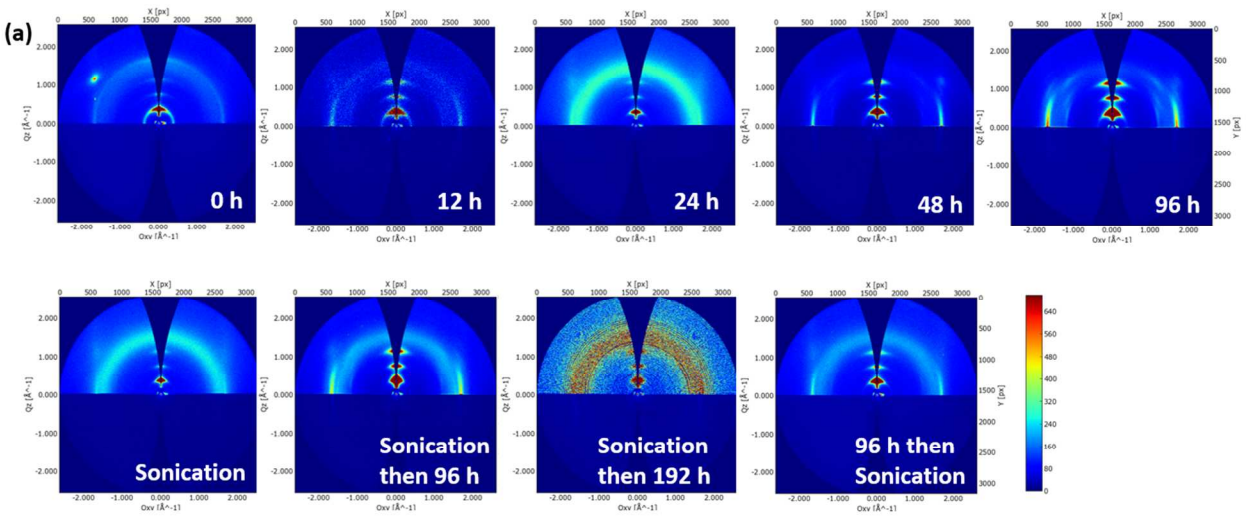
Parameters for the fit include:

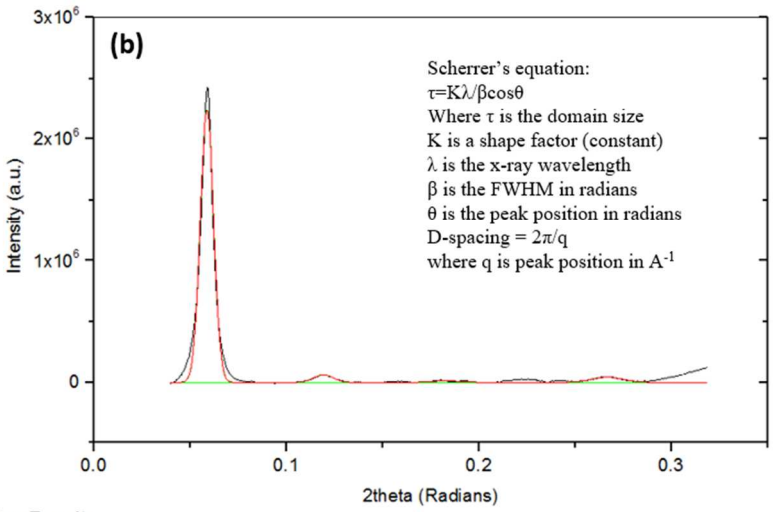
M=5

N=10

S=1

Ep=0.18





Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	19295.55304	0.00808	2.24232E6	0.05876	91.38982
2	Gaussian	754.45696	0.01167	60722.69696	0.11935	3.57335
3	Gaussian	228.65783	0.01755	12241.50051	0.18358	1.083
4	Gaussian	834.79176	0.01881	41686.87363	0.26662	3.95384

Figure S4: (A) All 2-D GIWAXS diffraction patterns. Note: Sonication then 192 h sample has lower signal to noise ratio, possibly due to an abnormally thin region of film that was exposed or an errant shorter beam time exposure. (B) Sample plot of 2-D images reduced to 1-D plots via integration of cake segments and analyzed using Origin Pro software for peak fitting.

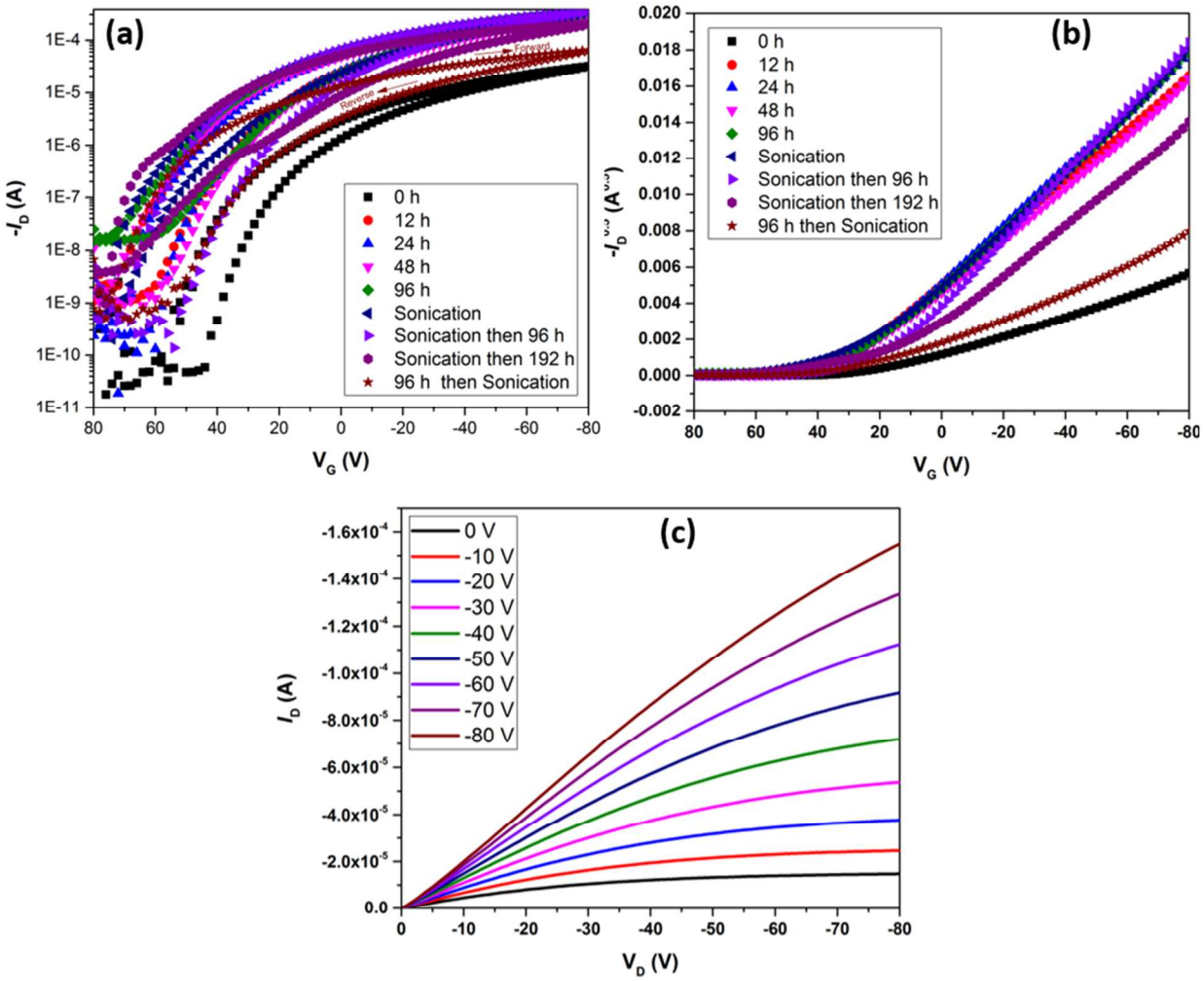


Figure S5: (a) Transfer characteristics of representative P3HT OFET devices (V_D = -80 V) swept in both forward (80 to -80 V) and backward (-80 to 80 V) directions. (b) Square root of drain current plotted vs V_G in backward direction, used to calculate slope for mobility. (c) Output characteristics of a Sonicated then 96 h aged sample.

Table S1: Threshold Voltages and On/Off Ratios

	V_T	V_T Standard Deviation	On/Off Ratio	On/Off Ratio Standard Deviation
0 h	2.20E+01	2.34E+00	6.67E+06	1.00E+07
12 h	3.16E+01	2.82E+00	2.10E+05	2.41E+05
24 h	2.75E+01	2.08E+00	6.78E+06	7.82E+06
48 h	3.13E+01	8.76E-01	1.04E+05	8.45E+04
96 h	3.33E+01	2.56E+00	3.99E+04	1.53E+04
Sonication	2.69E+01	1.83E+00	1.95E+05	1.43E+05
Sonication then 96 h	2.48E+01	2.97E+00	3.84E+06	3.74E+06
Sonication then 192 h	2.76E+01	8.47E-01	1.16E+05	1.01E+05
96 h then Sonication	2.29E+01	4.36E-03	2.86E+05	2.26E+05

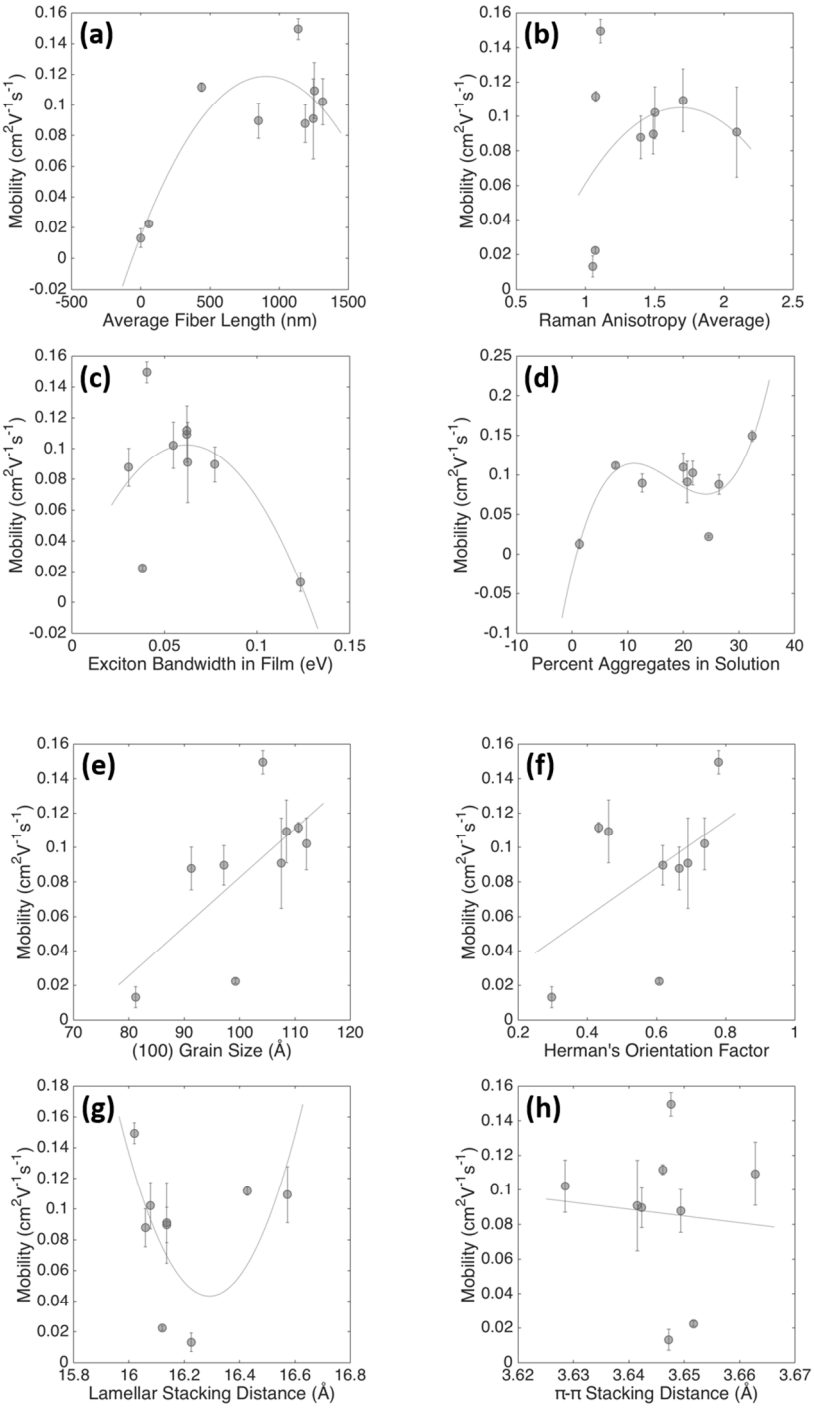


Figure S6. Mobility as a function of (a) average fiber length, (b) Raman anisotropy, (c) film exciton bandwidth, (d) percent aggregates in solution, (e) (100) grain size, (f) Herman's Orientation Factor, (g) lamellar stacking distance, and (h) π-π stacking distance.

Sample	Persistence Length (nm)
12 h	2469
24 h	2428
48 h	3580
96 h	1231
Sonication	4259
Sonicated then 96 h	1313
Sonication then 192h	816
96 h then Sonication	286

Figure S7: Persistence lengths were calculated from AFM images using a fit of the mean square end-to-end distance function in FiberApp, and were taken at the processing length which yielded the fit with the lowest error. Sample aged for 0 h gave no visible fiber to measure.

Persistence lengths were mostly greater than 800 nm, in alignment with the fibers' low degree of curvature. The π-π-stacking interactions responsible for holding fibers together must be somewhat compliant to shear forces during deposition, however, since a finite persistence length (some curvature) is observed. It is unlikely, however, that these shear forces are capable of breaking π-π-stacking interactions, given that fiber length increases with aging time in the post-deposition solid state.

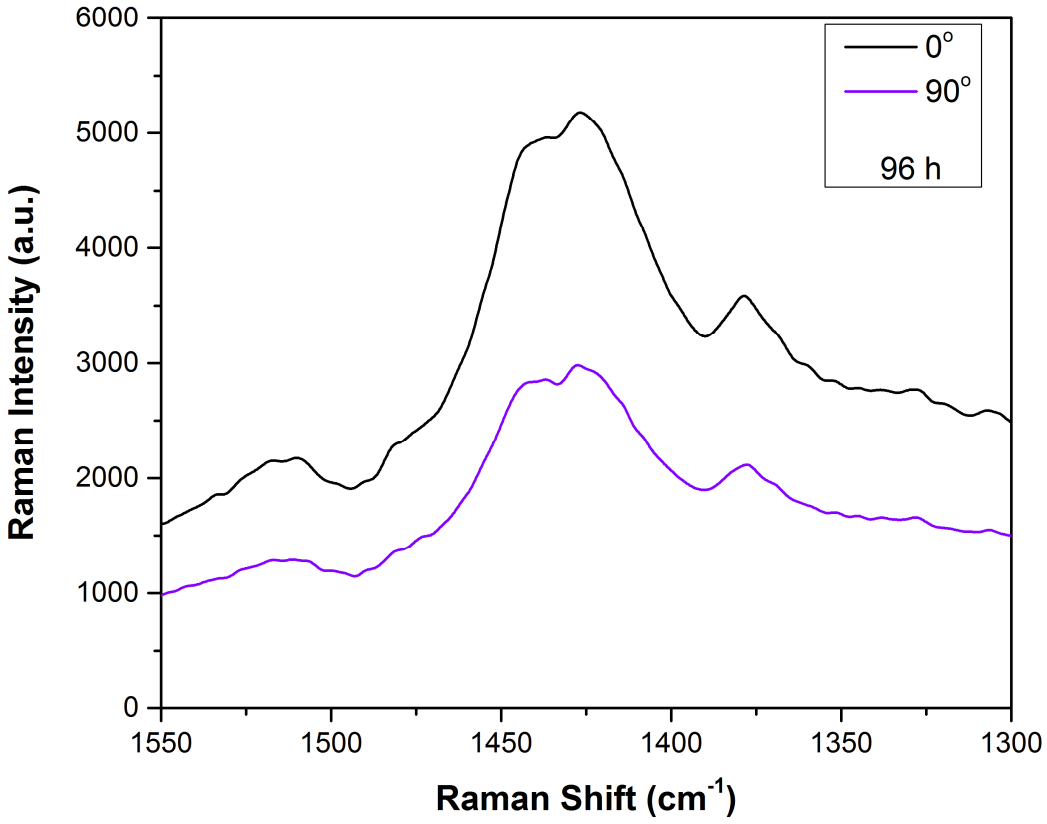


Figure S8: Example of Raman spectra obtained from P3HT film spin coated from solution aged 96 h. Region of interest is C=C double bond stretch: peaks fit from 1495 to 1390 cm^{-1} with Lorentzian curves to obtain peak height and compare for highest peak vs when sample was rotated by a further 90˚.

References:

(1) Kleinhenz, N.; Rosu, C.; Chatterjee, S.; Chang, M.; Nayani, K.; Xue, Z.; Kim, E.; Middlebrooks, J.; Russo, P. S.; Park, J. O.; Srinivasarao, M.; Reichmanis, E. Liquid Crystalline Poly(3-Hexylthiophene) Solutions Revisited: Role of Time-Dependent Self-Assembly. *Chem. Mater.* **2015**, *27*, 2687–2694.

(2) Turner, S. T.; Pingel, P.; Steyrleuthner, R.; Crossland, E. J. W.; Ludwigs, S.; Neher, D. Quantitative Analysis of Bulk Heterojunction Films Using Linear Absorption Spectroscopy and Solar Cell Performance. *Adv. Funct. Mater.* **2011**, *21*, 4640–4652.