

A Quantitative Correlation between the Mobility and Crystallinity of Photocrosslinkable P3HT

*Claire H. Woo,^{1,2†} Claudia Piliego,^{2†} Thomas W. Holcombe³, Michael F. Toney,⁴ and Jean M. J. Fréchet^{*1,2,3}*

¹Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, ² Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, ³Department of Chemistry, University of California, Berkeley, CA 94720, ⁴Stanford Synchrotron Radiation Laboratory, Menlo Park, CA 94205.

Supporting Information.

Synthetic Details.

General. All chemicals were purchased from Aldrich and used without further purification unless stated otherwise. All reactions were performed under nitrogen in glassware that had been flame dried under vacuum. All compounds were characterized by ¹H NMR (400 MHz) and ¹³C NMR (75 MHz) on a Bruker AVB 400 or AVQ 400. High-resolution mass spectra and elemental analysis (CHNS) was performed at the University of California, Berkeley Department of chemistry analytical services. Polymer ¹H NMR (500 MHz) was obtained on Bruker DRX 500. For polymer molecular weight determination, polymer samples were dissolved in HPLC grade dichlorobenzene at a concentration of 1 mg/ml and stirred overnight at room temperature prior to filtering through a 0.2 µm PVDF filter and SEC was performed using HPLC

[†] These authors contributed equally to this work.

grade dichlorobenzene at a flow rate of 0.8 $\mu\text{L}/\text{min}$ on two 300 x 8 mm linear S SDV, 5 micron columns (Polymer Standards Services, USA Inc.) at 70 $^{\circ}\text{C}$ using a Waters (Milford, MA) 2690 separation module and a Waters 486 Tunable Absorption Detector monitored at 350 nm. The instrument was calibrated vs. polystyrene standards (1,050 – 135,000 g/mol) and data was analyzed using Millenium 3.2 software.

UV-Visible absorption spectra were obtained using a Cary 5000 Conc UV-Visible spectrophotometer. For thin film measurements polymers were spin coated onto cleaned quartz slides from chloroform solution (10 mg/ml). Polymer film thickness was measured by a Veeco Dektak profilometer. Photocrosslinking was carried out in a nitrogen-filled glove box by irradiating the polymer films with UV light ($\lambda = 254 \text{ nm}$) from a low-power hand-held lamp (2.1-2.4 mW cm^{-2}) with exposure time of 1 hour. To evaluate the extent of photocrosslinking, the irradiated polymer films were immersed into chloroform for 5 min, followed by rinsing with acetone for 3 minutes and then dried under a stream of nitrogen. UV-VIS absorption spectra and film thicknesses were then recorded on the polymer films after irradiation and solvent washing, and compared to the UV-vis absorption spectra and thicknesses of the same polymer films prior to irradiation.

FET device fabrication.

P3HT-Br10 OFETs were fabricated by spin coating the semiconductor solution on bottom-gate bottom-contact substrates. A doped p-type Si substrate served as the gate electrode with 300nm of thermally grown SiO_2 , used as the dielectric layer with a capacitance per unit area of 13 nF cm^{-2} . The source and drain electrodes consisted of 10 nm of Cr and 50 nm Au, patterned by conventional photolithography.

All the substrates were first cleaned in an ultrasonic bath using acetone and isopropanol for 10 min each and then rinsed with DI water. Next, the substrates were cleaned with a UV-ozone treatment to remove organic contaminants from the surface for 30 minutes. Prior to spin-coating of the solution, a surface treatment was performed by immersing the substrates in a 10 mM solution of octyltrichlorosilane in toluene for one hour. After rinsing them with toluene, the solutions of P3HT-Br10 (5-6 mg/mL) in chloroform were spin cast at 800 rpm to form a 70-100 nm thick layer. After the deposition the different treatments were applied: 1) crosslinking, by putting the samples under a UV lamp ($\lambda = 254$ nm) for 1 hour, 2) annealing on a hot plate at 150°C for one hour, 3) crosslinking (1hr) and then annealing (1hr) 4) crosslinking and annealing at the same time (1hr), by positioning the UV lamp on top of the hot plate.

The transistors were measured in vacuum using an Agilent 4155C semiconductor parameter analyzer. The carrier mobility (μ) was calculated from the drain-source current (I_{DS}) versus the gate voltage (V_{GS}) data in the saturation regime using the standard formula for field effect-transistors: $\mu = 2L/(WC_{ox})[d(I_{DS})^{1/2}/dV_{GS}]^2$, where L is the channel length (10-20 μ m), W is the channel width (200-800 μ m) and C_{ox} is the gate dielectric capacitance (13nFcm⁻²).

Grazing-Incidence X-ray Scattering (GIXS).

GIXS experiments were conducted at the Stanford Synchrotron Radiation Laboratory on beamline 11-3. The sample is irradiated at a fixed incident angle on the order of a tenth of a degree and the GIXS patterns are recorded with a 2-D image detector (MAR345 image plate detector). GIXS patterns were recorded with an X-ray energy of 12.72 keV ($\lambda=0.975\text{\AA}$). To maximize the intensity from polymer sample, the incident angle (0.1° - 0.12°) was carefully chosen so that the X-ray beam penetrates the polymer sample completely but not the silicon substrate. Typical exposure times were 90-180 sec. To produce identical surface condition as

samples for FET device fabrication, the SiO₂/Si substrate was treated with OTS before spin coating the polymer. The GIXS samples were prepared by spin-coating the same solutions used for making FET devices onto silicon substrates at 800 rpm for 60s. The substrates were placed directly on top of a hot plate under Nitrogen for thermal annealing and they were placed under a hand-held UV lamp for photocrosslinking.

Atomic force microscopy (AFM).

AFM was performed to study the surface morphology of the P3HT-Br10 films. Topographical and phase images were obtained concurrently using a Veeco Multimode V AFM in tapping mode using RTESP tips.

Supporting Figures.

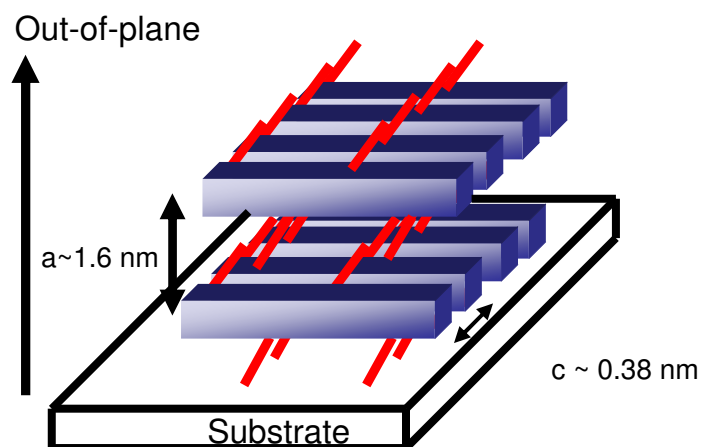


Figure S1. Schematic of the organization of P3HT-Br10 chains relative to the substrate and domain spacing.

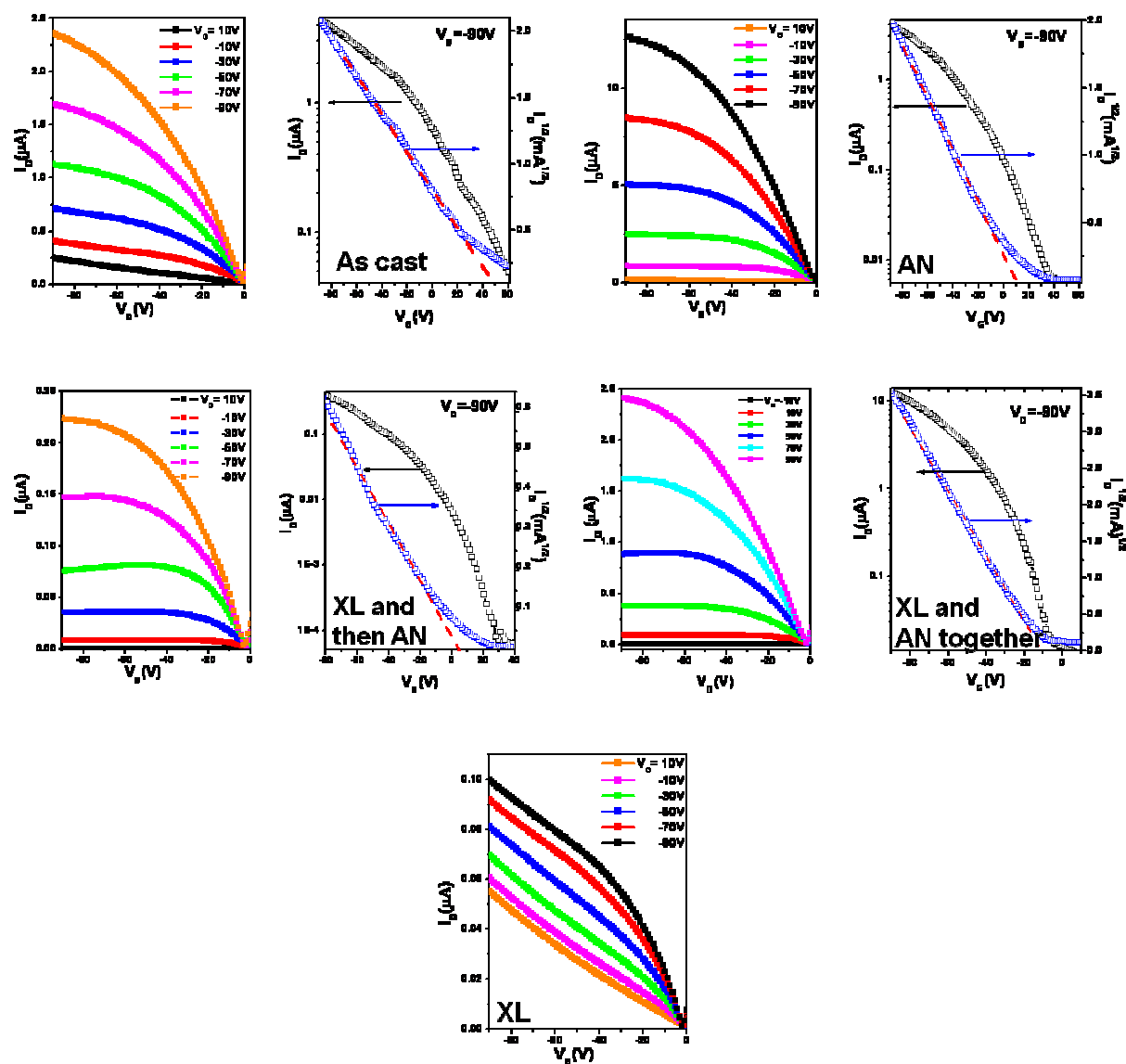


Figure S2. Output and transfer curves of P3HT-Br10 FET devices processed under 5 different conditions (XL = crosslinked, AN = annealed).

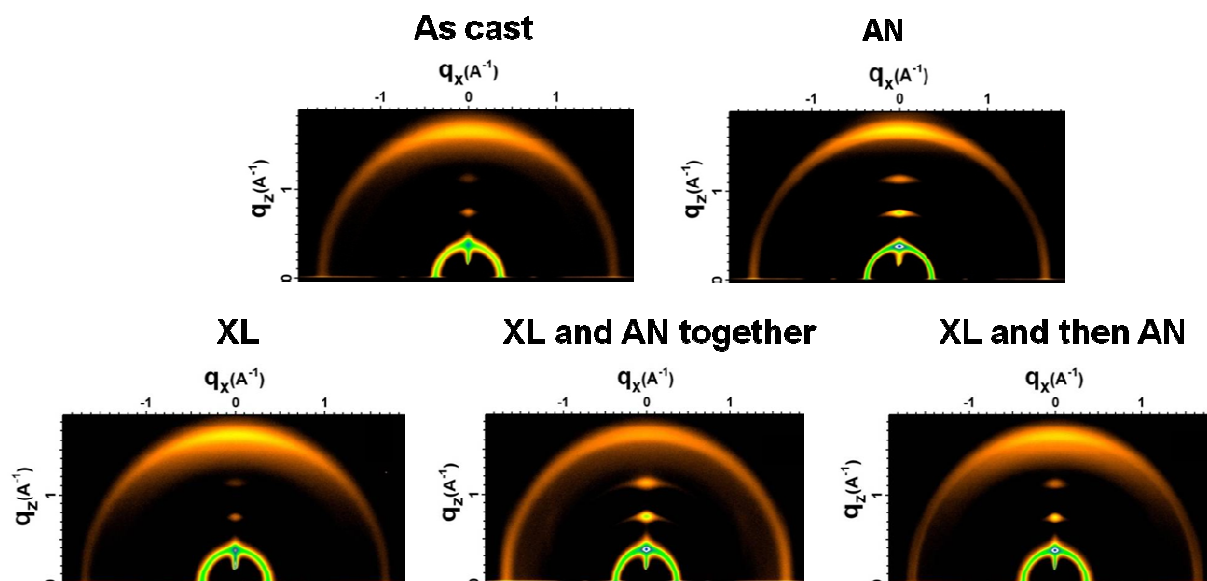


Figure S3. 2D GIXS patterns of P3HT-Br10 samples processed under 5 different conditions. (XL = crosslinked, and AN = annealed). All five samples showed a (100) lamellar stacking peak at $q \sim 0.38 \text{ \AA}^{-1}$ ($d \sim 17 \text{ \AA}$) and a (010) π - π stacking peak at $q = 1.65 \text{ \AA}^{-1}$ ($d = 3.8 \text{ \AA}$).

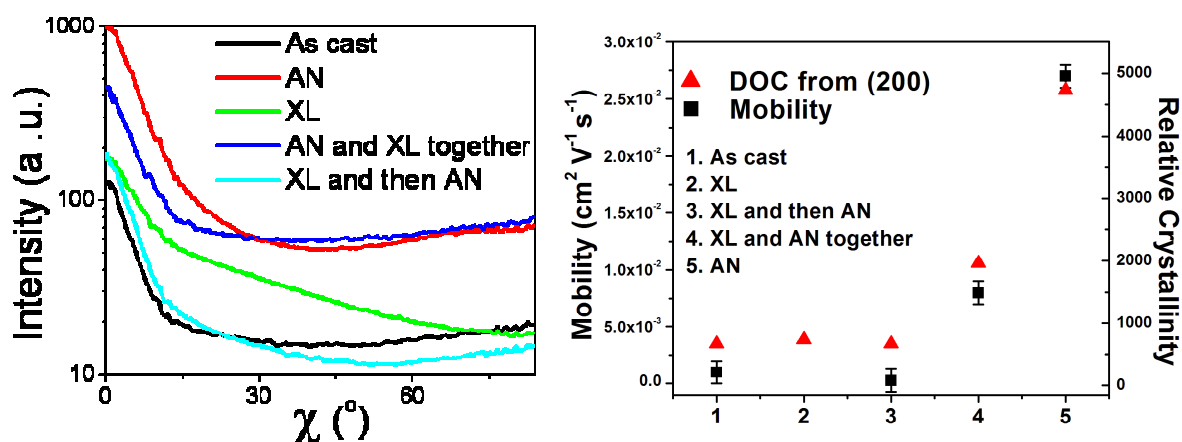


Figure S4. (left) Pole figures from the (100) Bragg reflection of P3HT-Br10 thin films processed under 5 different conditions ((XL = crosslinked, and AN = annealed). (right) Correlation of FET mobility and relative degree of crystallinity (DoC) estimated from integration of the pole figures on the left.

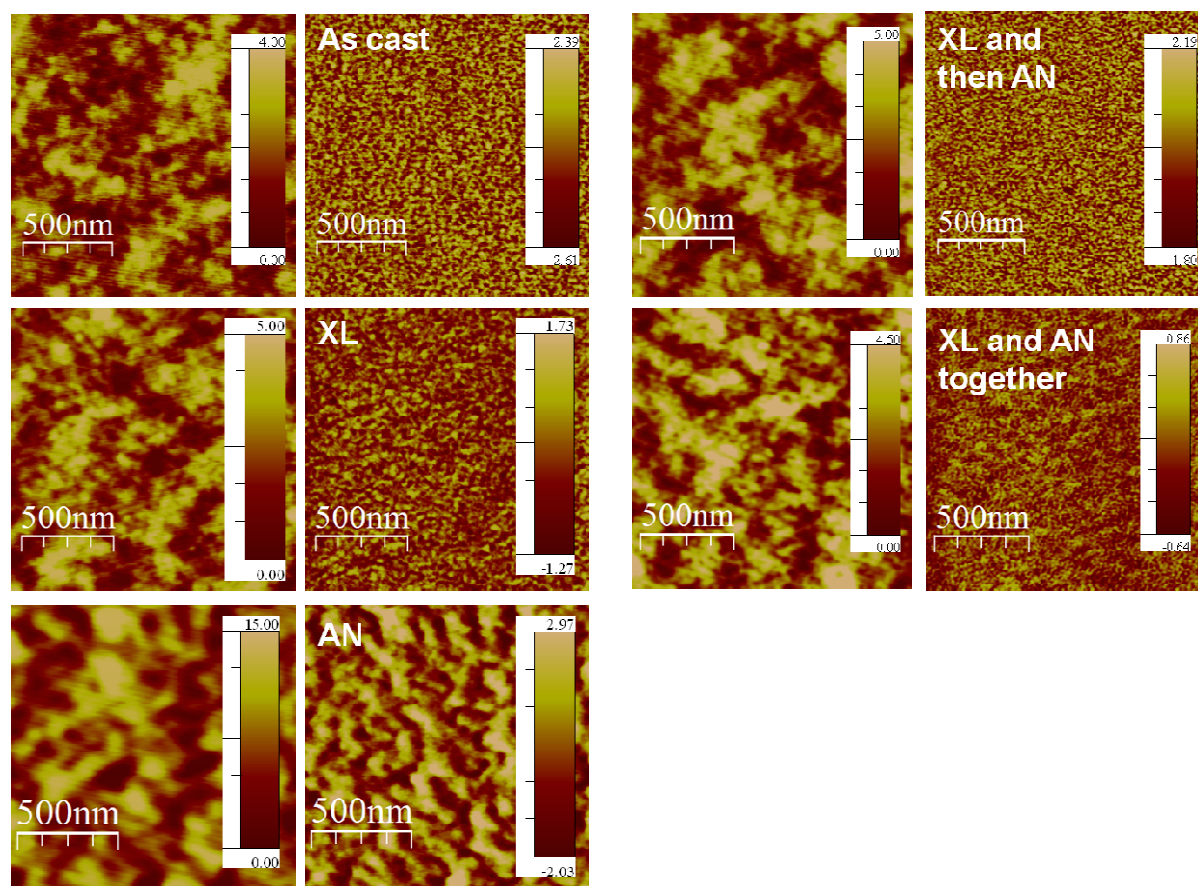


Figure S5. AFM images of P3HT-Br10 thin films processed under the five different conditions. (XL = crosslinked, and AN = annealed)

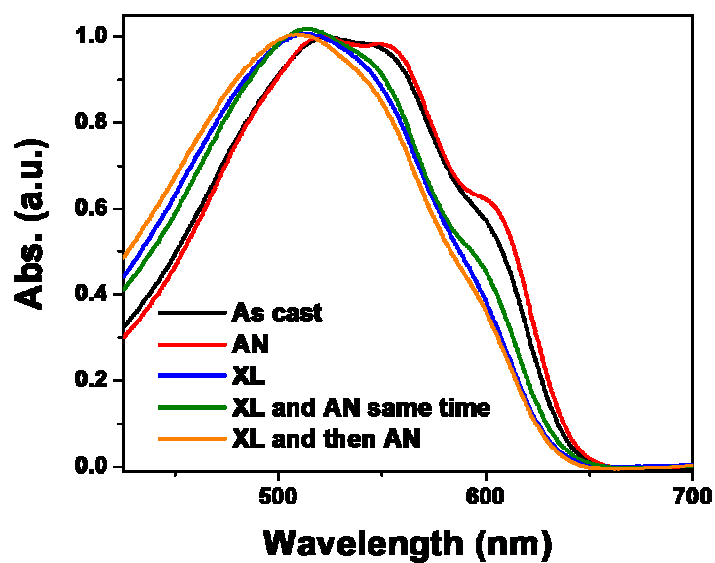


Figure S6. UV-Vis absorption spectra (normalized to 1) of P3HT-Br10 thin films processed under five different conditions. (XL = crosslinked, and AN = annealed)

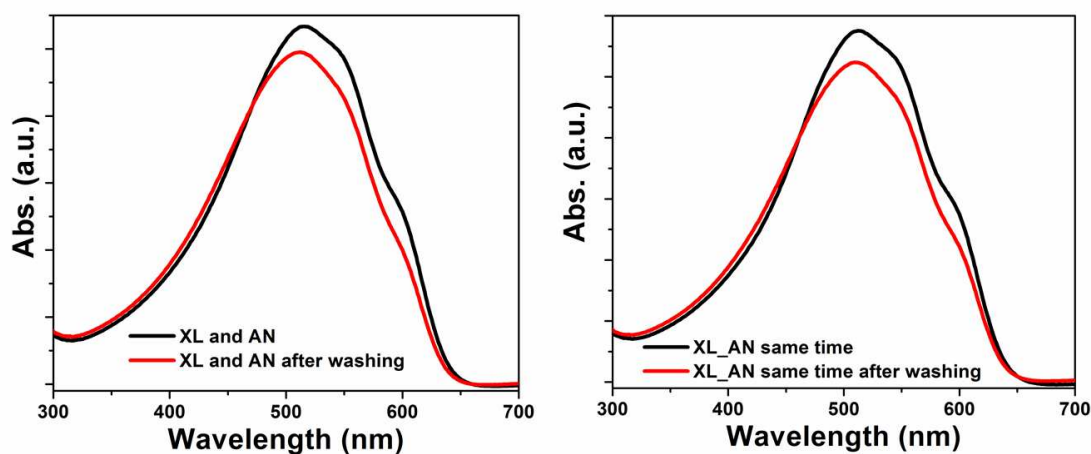
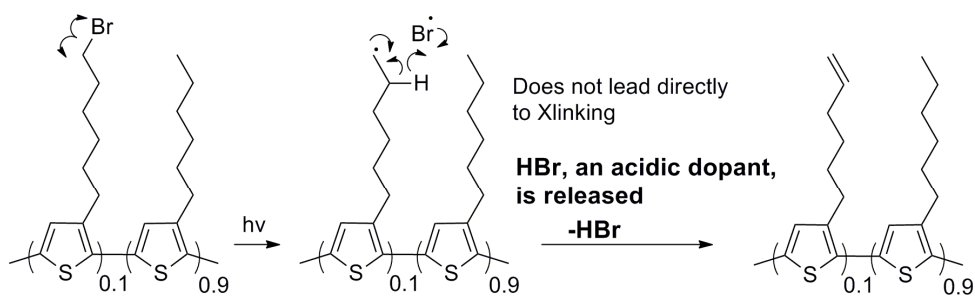
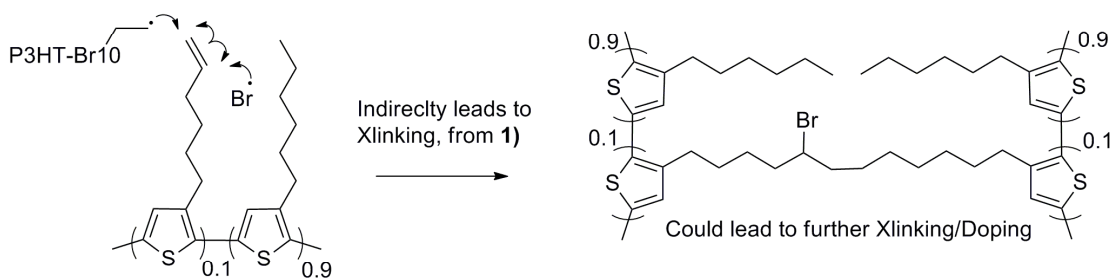


Figure S7. Absolute UV-Vis absorption spectra of P3HT-Br10 thin films before crosslinking and after the “crosslinking + washing” procedure. The ratio between the integrated area under the two curves is: $[\text{XL and AN after washing}]/[\text{XL and AN}]=0.95$ and $[\text{XL and AN same time after washing}]/[\text{XL and AN same time}]=0.94$.

1)



2)



3)

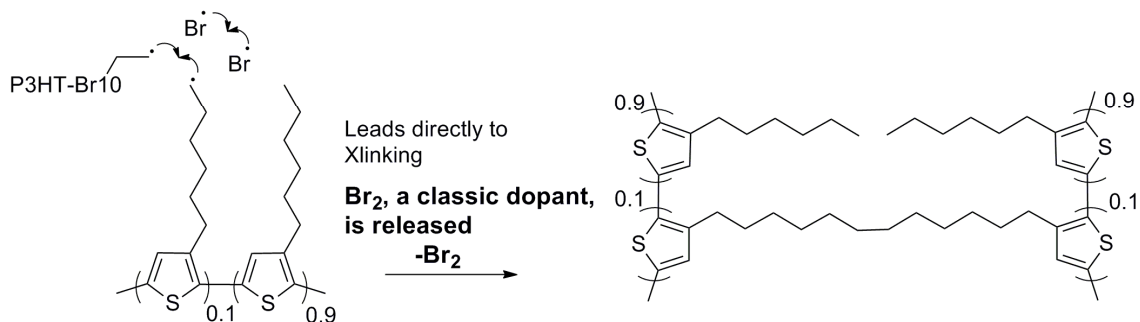


Figure S8. Three possible crosslinking mechanisms, two of which elucidate two possible doping situations: one based upon acidic HBr doping and the other based on elemental Bromine.