Supporting Information

Ion Diffusion Coefficients in Poly(3-alkylthiophenes) for Energy Conversion and Biosensing: Role of Side-Chain Length and Microstructure

Jonathan K. Harris[a] and Erin L. Ratcliff[a,b,c]*

[a]Department of Chemical Engineering, University of Arizona, 1133 E. James E Rogers Way, Tucson Arizona 85721, United States

[b]Department of Materials Science and Engineering, University of Arizona, 1235 E. James E Rogers Way, Tucson Arizona 85721, United States

[c]Department of Chemistry and Biochemistry, University of Arizona, 1306 E. University Way, Tucson, AZ 85721, United States

* ratcliff@email.arizona.edu

1. **Electrochemical characterization of P3HT in acetonitrile and water**
2. **Additional GIWAXS data**
3. **Cyclic Voltammetry of P3BT, P3OT, and P3DT**
4. **Ordinary vs. Anomalous Fitting and Discussion**
5. **Nyquist Plots and EIS fitting parameters for P3AT films**
6. **Additional diffusion coefficient data**
7. **References**

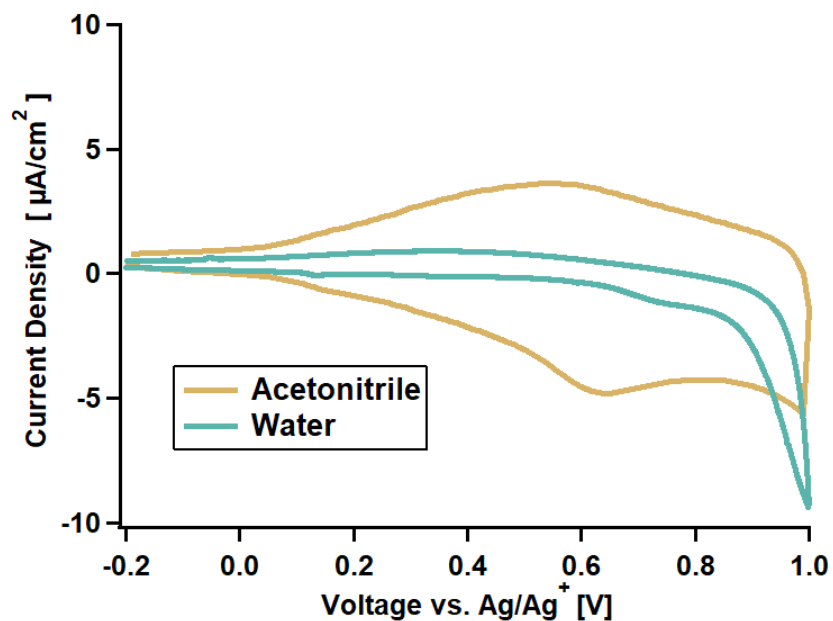# 1. Electrochemical characterization of P3HT in acetonitrile and water

Figure S1: Cyclic voltammetry of P3HT in acetonitrile vs water showing higher electroactivity in acetonitrile. Scan rate is 10 mV/s. Peak onset >0.8V is attributed to oxidation of water, with trace amounts in acetonitrile as well. Reference electrode for acetonitrile is Ag/Ag$^+$ in 0.01M AgNO$_3$, supporting electrolyte for cell is 0.1M TBAHFP. Reference electrode for water is Ag/AgCl in sat. KCl, supporting electrolyte for cell is 0.1M KCl. While there are small peaks visible in the cyclic voltammogram of water indicating some oxidation, acetonitrile provides greater access to the polymer's electronic states, which promotes the use of acetonitrile to accurately gauge the swelled polymer environment.
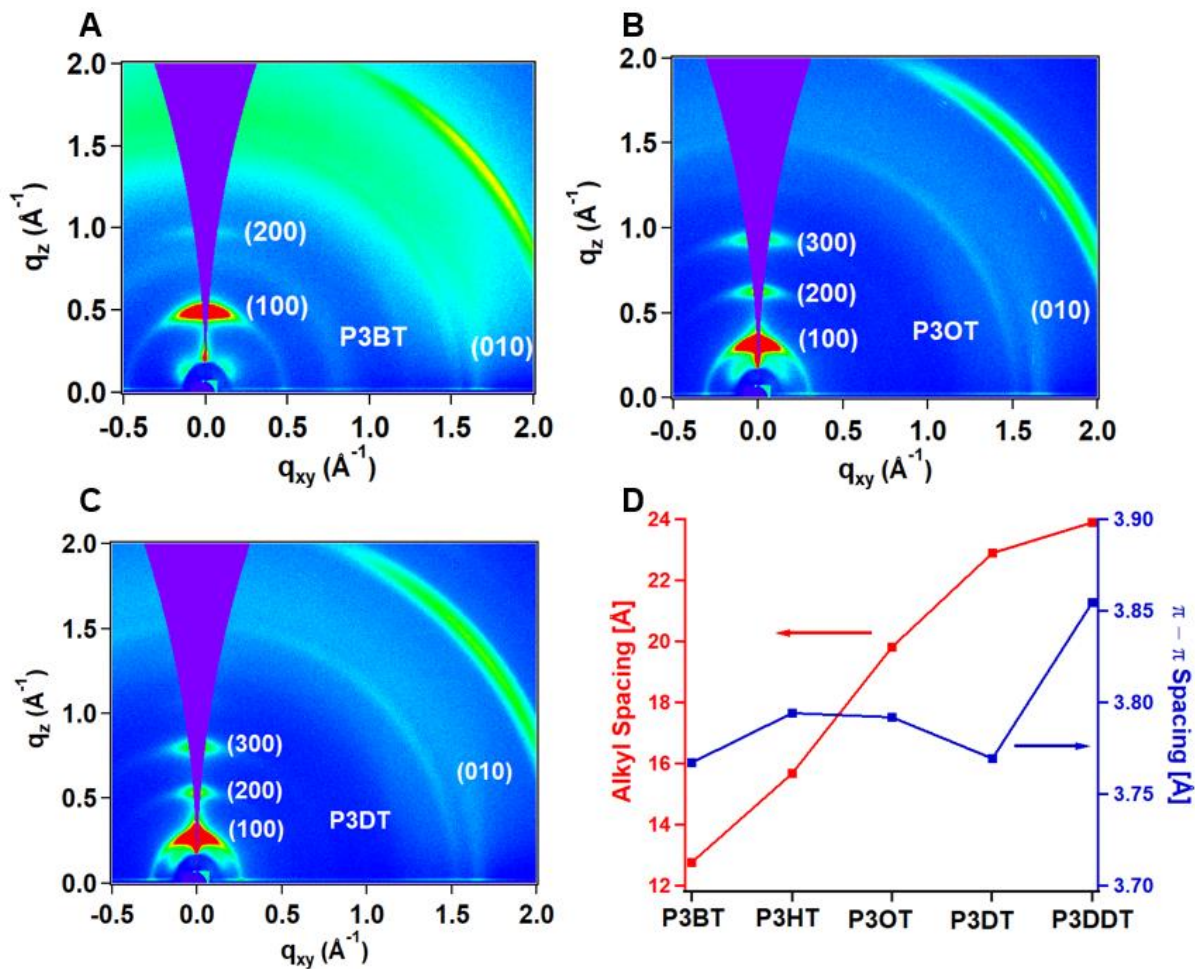
2. Additional GIWAXS data

Figure S2: 2D GIWAXS plots for solid state films of A) P3BT, B) P3OT, C) P3DT, and D) summarized (from Table S1) calculated alkyl spacing and π - π spacings in Å. It is noted in Figure A that the (300) peak is pushed to larger values to not be visible above noise contributions from ITO substrate.
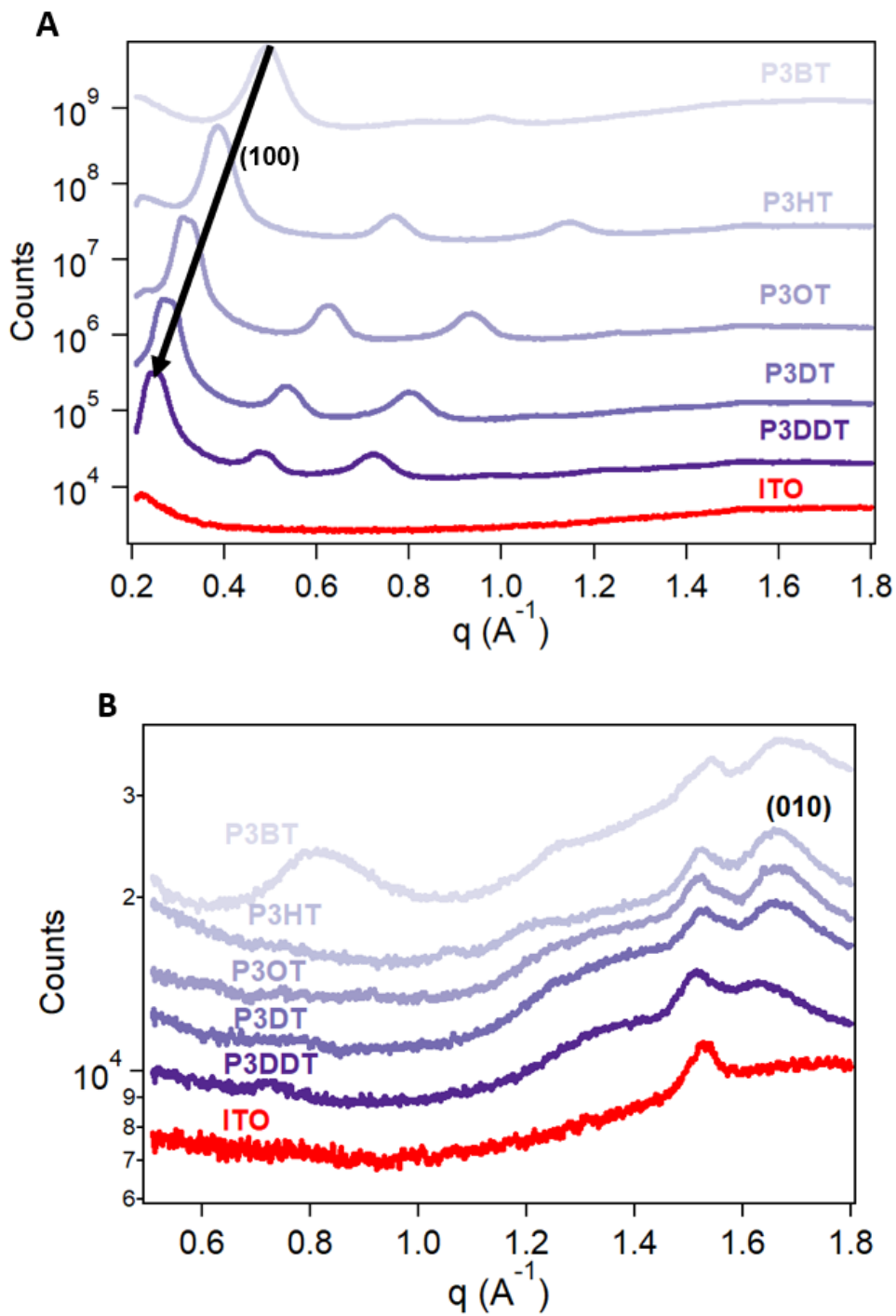
Figure S3: 1D plots from cakeslices of solid state films P3BT, P3HT, P3OT, P3DT, P3DDT, and underlying ITO for the A) q_z direction (0°-15°) and B) q_{xy} direction (75°-85°). The (h00) peaks are clearly visible for each polymer, while the ITO contributes no q_z signal, but does contribute a peak consistently around 1.52 Å^{-1} for the q_{xy} direction.

Table S1: Calculated spacing values and literature values as calculated from simulation[1] for alkyl spacings and π - π spacings. Although simulation[1] predicts a steady increase in pi-pi spacing, compared experiment[2] behaves similarly to our results (relatively constant before increasing to P3DDT).

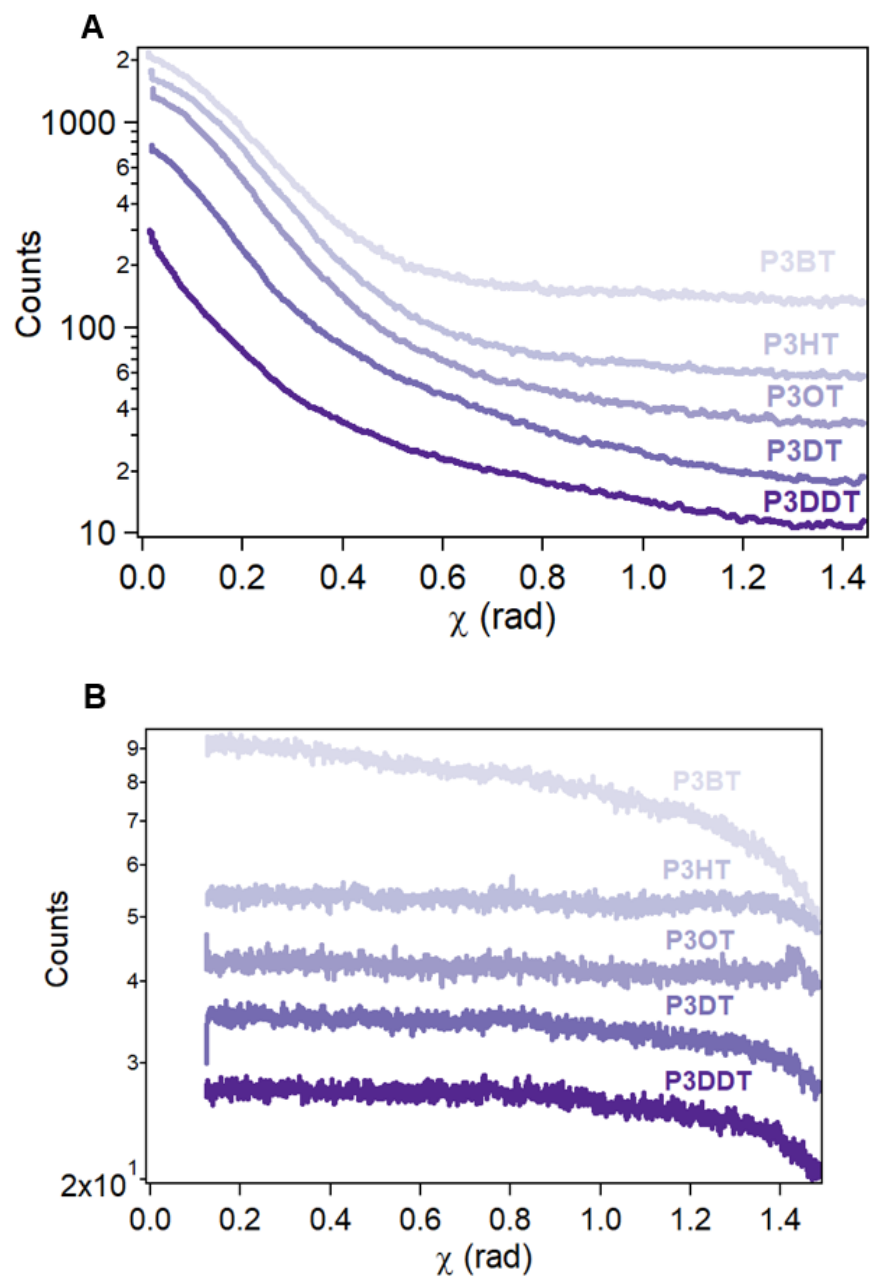| Polymer	Alkyl Spacing – Experiment [A]	π - π Spacing – Experiment [A]	Alkyl Spacing – Simulation[1] [A]	π - π Spacing – Simulation[1] [A]
P3BT	12.8	3.77	13.7	3.35
P3HT	15.7	3.79	15.6	3.4
P3OT	19.8	3.79	20.6	3.45
P3DT	22.9	3.77	25.5	3.45
P3DDT	23.9	3.85	25.4	4.1

Figure S4: Chi plots showcasing edge-on orientation for solid state films P3BT, P3HT, P3OT, P3DT, and P3DDT. Chi plots are generated integrating scattering intensity from 0° - 83° at a q range around the A) (100) peak and B) (010) peak for each polymer, such that all peaks are included but the origin is not included. Higher intensities in the low chi range, indicating that polymers stack primarily in the edge-on orientation, with alkyl spacing peaks in the q_z direction and π-π spacing in the q_{xy} direction. The resolution of the plots in (B) are hidden by the ITO signal (see cake slice in Figure S3).

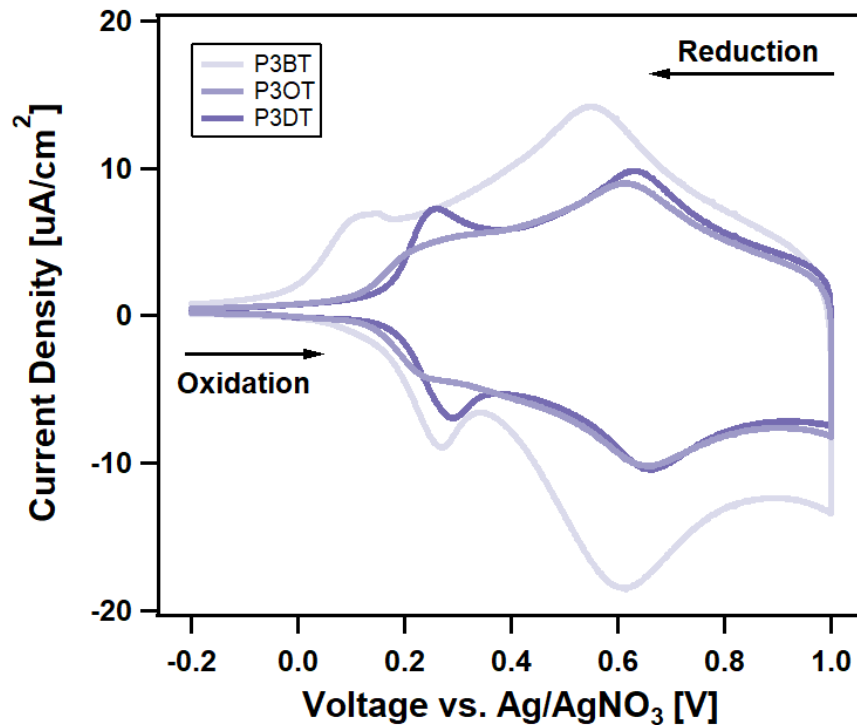## 3. Cyclic Voltammetry of P3BT, P3OT, and P3DT

Figure S5: Cyclic voltammograms of P3BT, P3OT, and P3DT films. Scan rate of 50 mV/s in 0.1M TBAHFP supporting electrolyte in acetonitrile. Reference electrode is Ag/Ag+ in 0.01M AgNO3 and 0.1M TBAHFP in acetonitrile.

4. Anomalous Diffusion (Generalized Finite Warburg) vs. Ordinary Diffusion (Finite-Length Warburg):
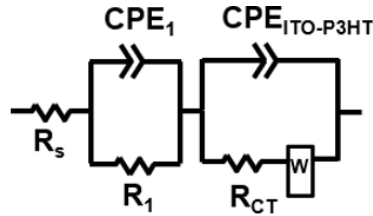

Figure S6: Circuit diagram used in fitting procedures.

Warburg diffusion is typically used to describe low-frequency diffusion processes. Each of these fits consider a finite diffusion boundary condition at the ITO-polymer contact, such that the ions can not diffuse into the metal contact and are blocked. The only difference is whether ordinary or anomalous diffusion is considered. As mentioned in the main text, this manifests itself as differences in the exponential continuity equation (Equation 3).

For simple scenarios, this can be viewed on a Nyquist plot as a 45° line in the low frequency regime before experiencing the blocking effect at the ITO-polymer contact as a close to 90° line. For a polymer system, the effects are a little more difficult to visualize on a Nyquist plot. Due to a distribution of trap states and electronic environment at the ITO-polymer contact, the Nyquist plots have low frequency lines that never fully reach 90° at low frequencies, let alone a 45° diffusive region before. This difference can be visualized in Figure 3 of the main text: when β is fixed as 0.5, the fit is not a well reproduction of the mid-low frequency area. Purely diffusive data found in Bisquert's work is also a good visualization of the differences.[3]

Final derivation of the impedance response leads to a slight alteration for estimating the ion diffusion coefficient in the polymer (Equation 4). For ordinary diffusion, $\omega_d = D/L^2$, and for anomalous diffusion, $\omega_d = (D/L^2)^{1/\beta}$. The thickness of the film, L, for this specific film is 20 x 10^{-7} cm. The ω_d as extracted from the ordinary fit is 1.5 Hz, leading to a diffusion coefficient of 2.6 x 10^{-9} cm^2/s. The ω_d and β extracted from the anomalous fit were 4.6 Hz and 0.44 respectively, leading to a diffusion coefficient of 4.8 x 10^{-10} cm^2/s.

5. Nyquist Plots With Fits for Each Polymer In Study

Each Nyquist fit was done between frequencies of 68 kHz to 2.1 Hz. The electrochemical cell is acetonitrile with 0.1M TBAHFP supporting electrolyte. The reference electrode for each is Ag/Ag⁺ with 0.01M AgNO₃ and 0.1M TBAHFP in acetonitrile.
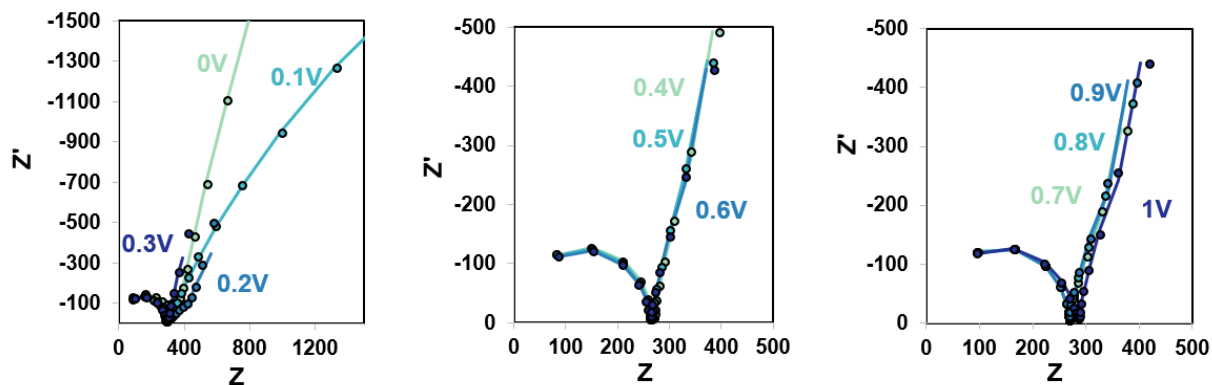
Figure S7: Nyquist plots of impedance (circles) with fits (solid lines) for regioregular P3HT
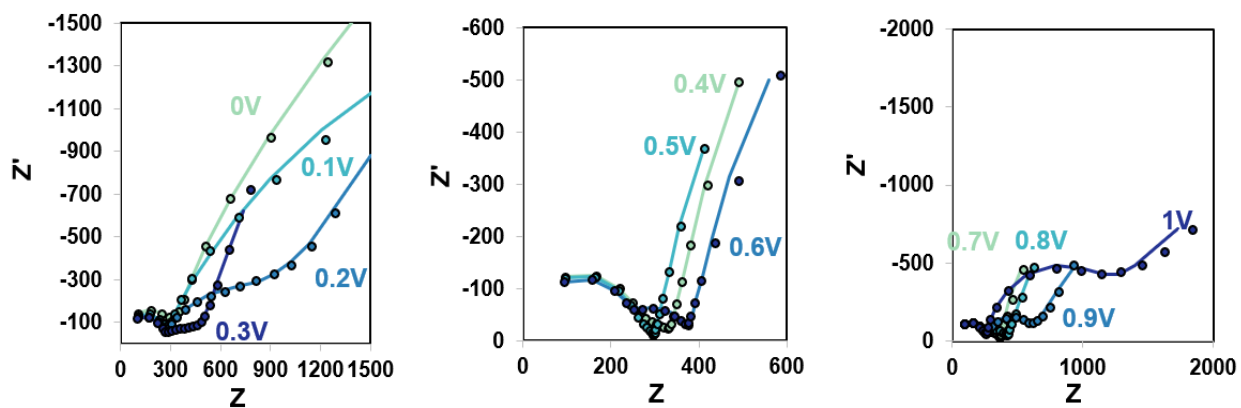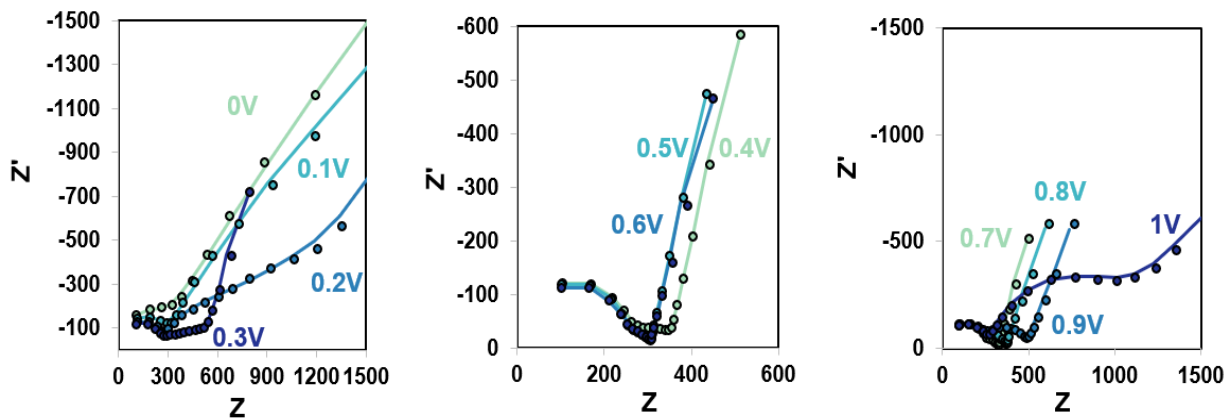
Figure S8: Nyquist plots of impedance (circles) with fits (solid lines) for regioregular P3BT

Figure S9: Nyquist plots of impedance (circles) with fits (solid lines) for regioregular P3OT
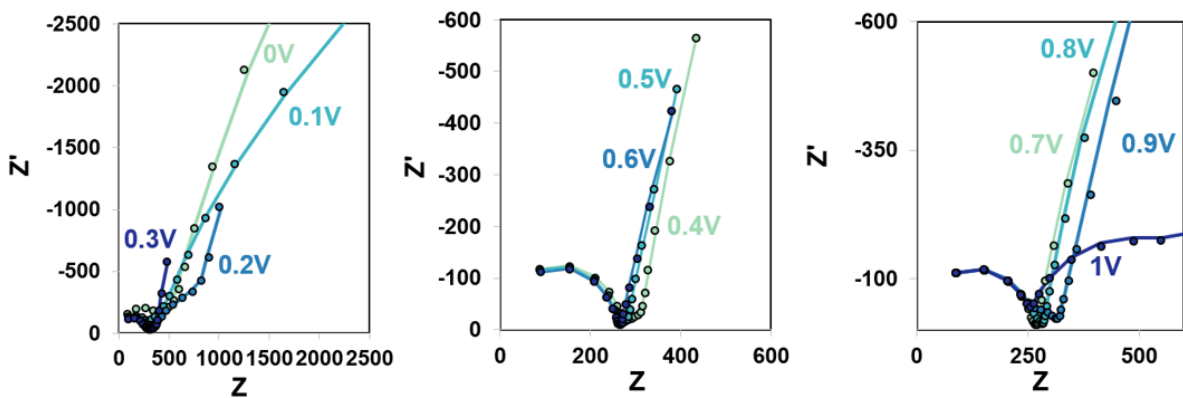

Figure S10: Nyquist plots of impedance (circles) with fits (solid lines) for regioregular P3DT
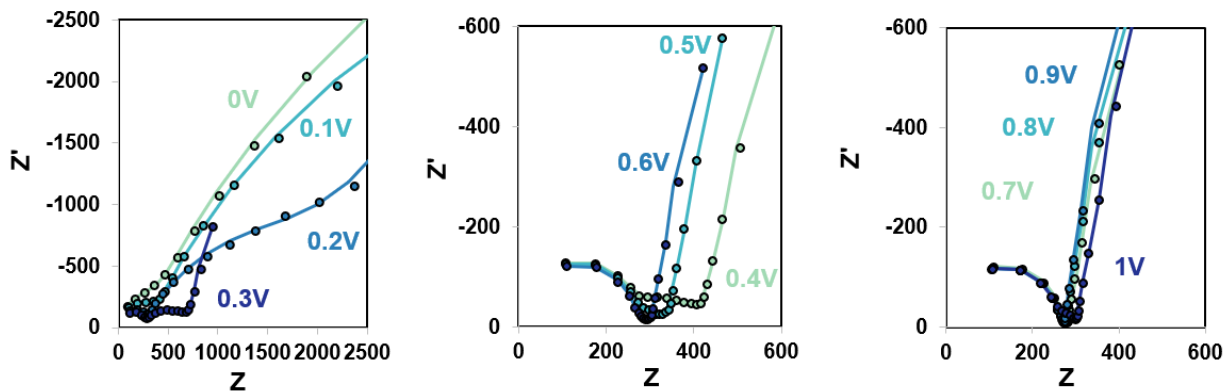

Figure S11: Nyquist plots of impedance (circles) with fits (solid lines) for regioregular P3DDT
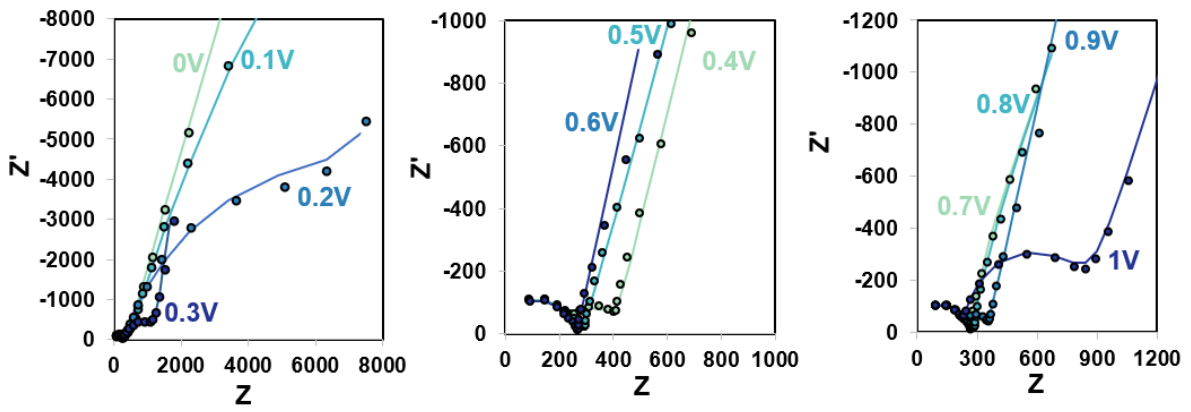
Figure S12: Nyquist plots of impedance (circles) with fits (solid lines) for electrochemically deposited P3HT
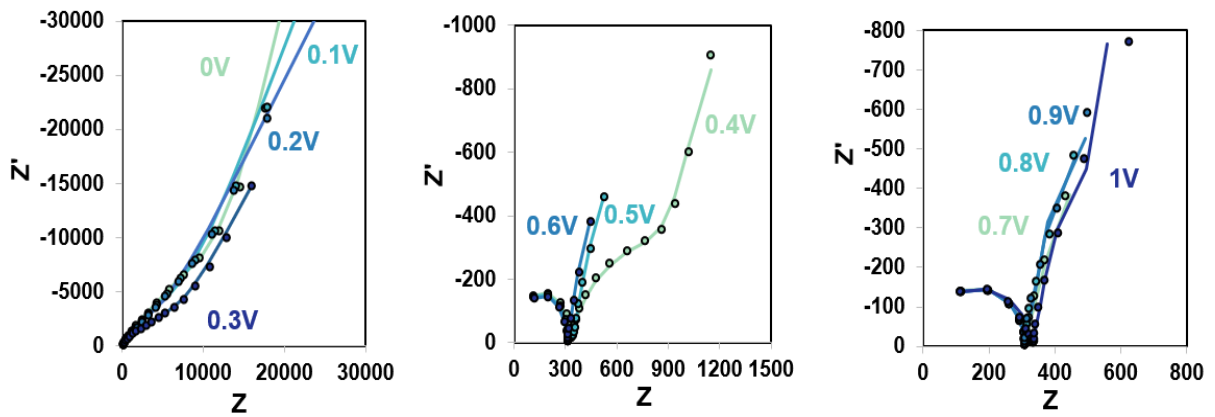

Figure S13: Nyquist plots of impedance (circles) with fits (solid lines) for regiorandom P3HT

Full tabulated data for all films can also be found in the SI as a .xls file.
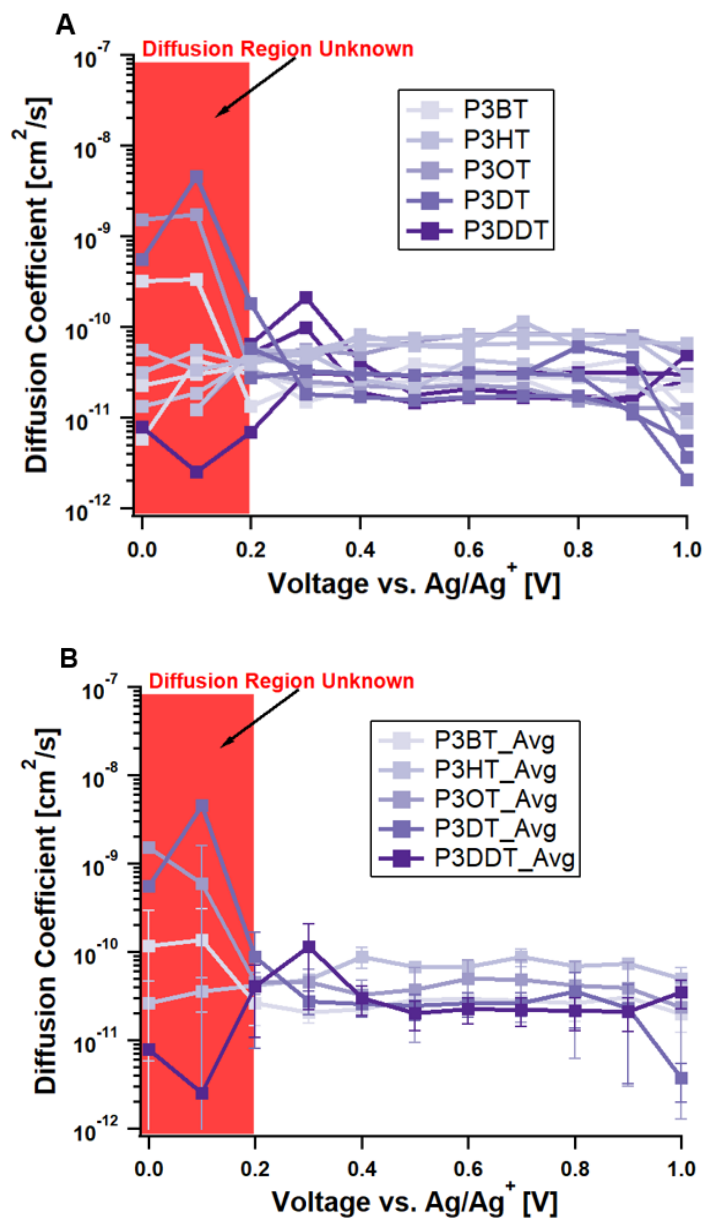
6. Additional Diffusion Coefficient Data

Figure S14: Diffusion coefficients as a function of potential for (A) three films of each poly(3-alkylthiophene) considered in the text. Cell is in acetonitrile in 0.1M TBAHFP with Ag/Ag+ reference in 0.01M AgNO₃. Red box indicates voltage below which diffusion is through a region that is a mix of mass transport from concentration gradient in solution and through polymer, such that it is ambiguous and can't be attributed solely to diffusion through the polymer environment. (B) is the average of each films with associated standard deviations. Error bars at higher standard deviations are skewed by the log scale. Diffusion of ion without polymer was found to be 2 x 10⁻⁷ cm²/s.
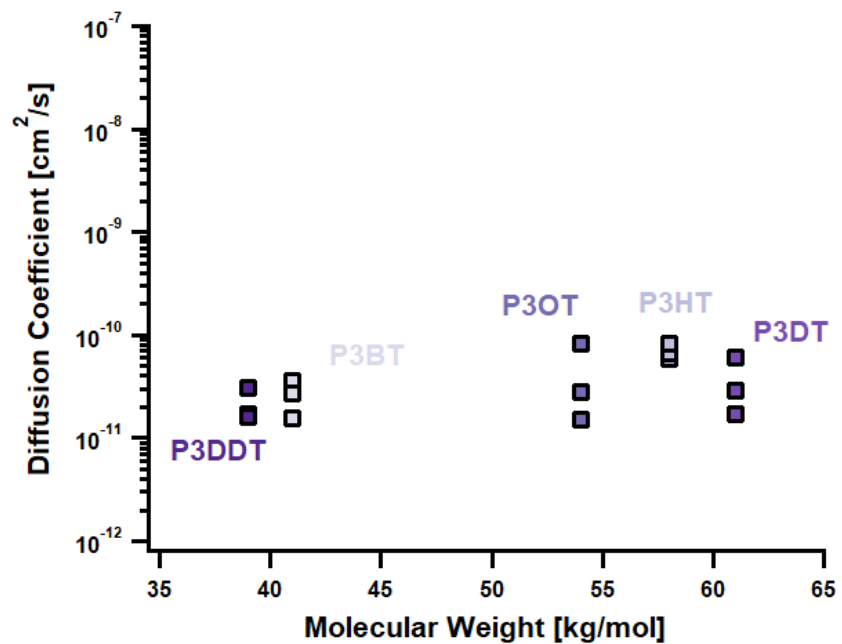
Figure S15: Diffusion coefficient at 0.8V vs. Ag/Ag$^+$ in 0.01M AgNO$_3$ in acetonitrile, as a function of molecular weight for three films of each five different polymers considered in main text.
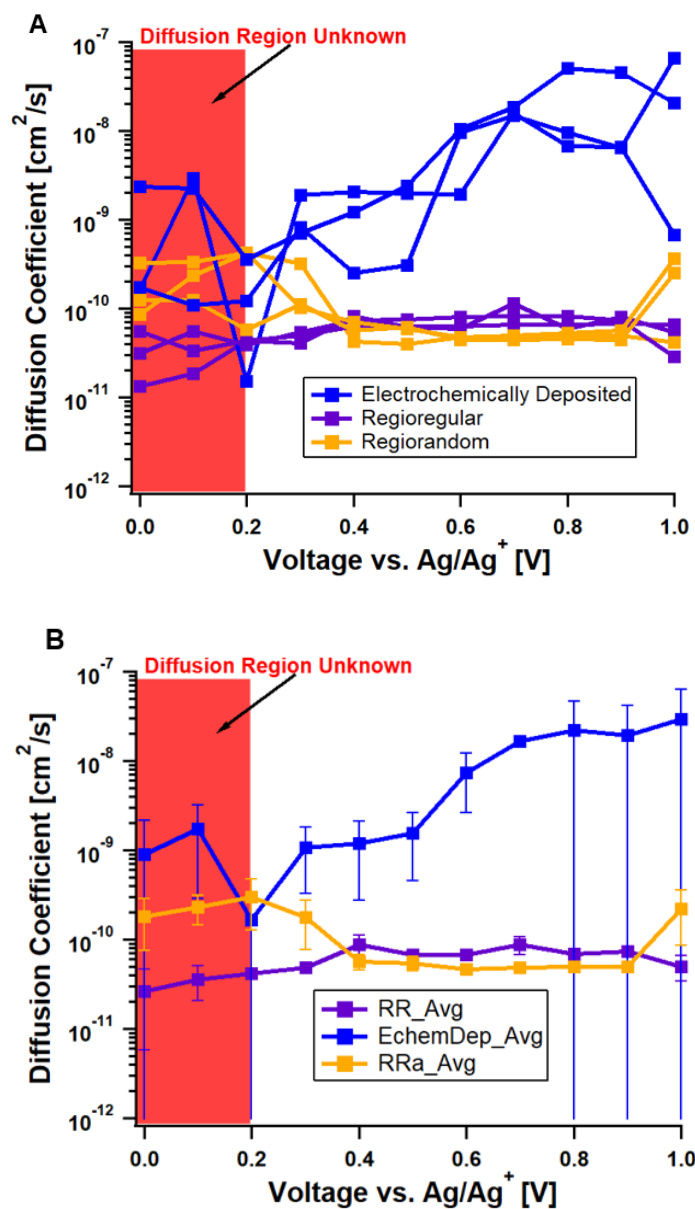
Figure S16: Diffusion coefficients as a function of potential for (A) three films of each microstructure, in acetonitrile with 0.1M TBAHFP as supporting electrolyte, and reference Ag/Ag$^+$ in 0.01M AgNO$_3$ in acetonitrile. Red box indicates voltage below which diffusion is through a region that is a mix of mass transport from concentration gradient in solution and through polymer, such that it is ambiguous and can't be attributed solely to diffusion through the polymer environment. (B) is the average of each films with associated standard deviations. Error bars at higher standard deviations are skewed by the log scale. Diffusion of ion without polymer was found to be 2 x 10^{-7} cm^2/s.
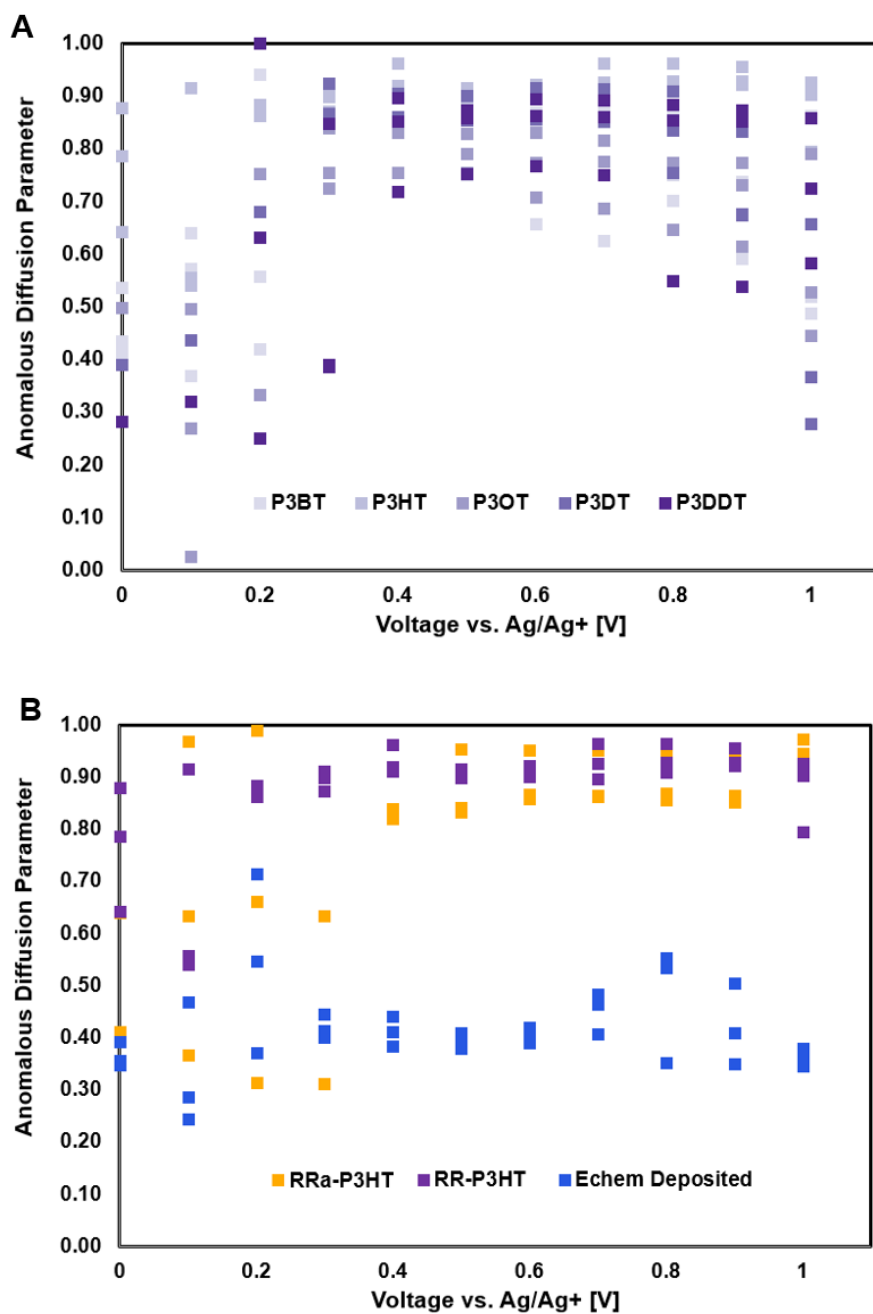
Figure S17: Anomalous diffusion parameter for (A) all side chains and (B) electrochemically deposited P3HT and spin coated RR-P3HT and RRa-P3HT for comparison. $\beta = 0.5$ for normal Warburg diffusion. The electrochemically deposited P3HT approaches normal diffusion behavior, while the regioregular is highly anomalous. The other spin coated polymers roughly follow this same trend and further shows the differences between the electrochemically deposited fabrication method and spin-coating.

7. References

[1] J. Corish, D. A. Morton-Blake, F. Bénière and M. Lantoine, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 671–677.

[2] K. Tashiro, M. Kobayashi, T. Kawai and K. Yoshino, *Polymer*, 1997, **38**, 2867–2879.

[3] J. Bisquert, G. Garcia-Belmonte and Á. Pitarch, *ChemPhysChem*, 2003, **4**, 287–292.