## Molecular Model

For atomistic simulations, we use the all-atom (AA) force field potential developed by Cheung, et. al.[1] (based off of the OPLS-AA forcefield[2]) to simulate the thiophene rings. Due to the similarity to the OPLS-AA model, the OPLS-UA forcefield[2] is used to model the side chains to decrease computational load. A depiction of our model is given in Figure SX1. The non-bonded interactions are defined by a combination of Lennard-Jones (LJ) and Coulombic interactions truncated at a cut-off of 10Å. The parameters for homonuclear non-bonded interactions is given in table SX1. Mixing rules for heteronuclear non-bonded interactions and scaling of non-bonded interaction for bonded atoms follows the OPLS-AA forcefield. Parameters for the bond, and angle potentials are given in table SX2, and SX3, respectively. For dihedrals, the Cheung model uses the standard OPLS potential and dihedrals using this potential are parameterized in table SX4. Work by Poelking, and Andrienko used density functional theory to accurately re-parameterize the ring-ring, and ring-side chain dihedrals using a different potential form which is given in SX5. To account for the change in partial charges due to the change in chemistry, the charges of thiophene atoms along with the first atom bonded to the ring are altered to maintain charge neutrality and respect the relative values of muliken charges calculated using BLYP 6-31G*. The remaining atoms in the side chains are assigned charges according to the OPLS-UA forcefield. The charges are given in Fig. SX1.

Fig. SX1. Depiction of the end, and inner monomers of P3EGT and P3MEGT. Charges of the atoms are given.

Table SX1 Non-boned parameters used in the AA model. The atom types are defined in Fig SX.

| Atom type | $\varepsilon$ / (Kcal/mol) | $\sigma$ / Å |
|---|---|---|
| $C_1$[a] | 0.07 | 3.55 |
| $C_2$[a] | 0.07 | 3.55 |
| $C_3$[b] | 0.118 | 3.8 |
| $C_4$[b] | 0.17 | 3.8 |
| H[a] | 0.03 | 2.5 |
| O[b] | 0.17 | 3.0 |
| S[a] | 0.25 | 3.55 |

[a]Adapted from Ref. [1]
[b]Adapted from Ref [2]

Table SX2 Harmonic bond parameters, where the potential is defined by harmonic

potential; $U_{bond} = k_b(r - r_0)^2$

| Type | $k_b$ / (Kcal / (mol·Å$^2$)) | $r_0$ / Å |
|---|---|---|
| C$_1$-C$_2$[a] | 514.27 | 1.364 |
| C$_2$-C$_2$[a] | 453.1 | 1.428 |
| C$_1$-C$_1$[a] | 392.29 | 1.43 |
| S-C$_1$[a] | 291.25 | 1.732 |
| C$_1$-H[a] | 370.63 | 1.08 |
| C$_2$-H[a] | 370.63 | 1.08 |
| C$_2$-C$_3$[b] | 317. | 1.51 |
| C$_2$-O[b] | 450.0 | 1.364 |
| C$_3$-C$_3$[b] | 260.0 | 1.526 |
| C$_3$-O[b] | 320.0 | 1.425 |
| O-C$_4$[b] | 320.0 | 1.425 |

[a]Adapted from Ref. [1]
[b]Adapted from Ref [2]

Table SX3 Harmonic angle parameters, where the potential is defined by harmonic

potential; $U_{angle} = k_\theta (\theta - \theta_0)^2$

| Type | $k_\theta$ / (Kcal / (mol·radian$^2$)) | $\theta_0$ / degree |
|---|---|---|
| C$_1$-S-C$_1$ | 86.36 | 92.774 |
| S-C$_1$-C$_2$ | 86.36 | 110.292 |
| C$_1$-C$_2$-C$_2$ | 39.582 | 113.322 |
| S-C$_1$-C$_1$ | 41.74 | 119.569 |
| C$_1$-C$_1$-C$_2$ | 35.263 | 130.14 |
| S-C$_1$-H | 28.787 | 124.609 |

| | | |
|---|---|---|
| $C_2$-$C_1$-H | 35.263 | 125.1 |
| $C_1$-$C_2$-H | 35.263 | 122.979 |
| $C_2$-$C_2$-H | 35.263 | 123.7 |
| $C_2$-$C_2$-$C_3$ | 70.0 | 123.7 |
| $C_1$-$C_2$-$C_3$ | 70.0 | 122.98 |
| $C_2$-$C_2$-O | 70.0 | 123.7 |
| $C_1$-$C_2$-O | 70.0 | 122.979 |
| $C_2$-$C_3$-O | 50.0 | 109.5 |
| $C_2$-O-$C_3$ | 75.0 | 111.0 |
| $C_3$-O-$C_3$ | 100.0 | 111.8 |
| O-$C_3$-$C_3$ | 80.0 | 109.5 |
| $C_3$-O-$C_4$ | 100.0 | 111.8 |

[a]Adapted from Ref. [1]
[b]Adapted from Ref [2]

Table SX4 OPLS torsional parameters, where the potential is defined as; $U_{dihedral} = \sum_{n=1}^{4} \frac{1}{2} V_n [1 + (-1)^{n+1} \cos n\phi]$

| Type | $V_1 \left( \frac{1 Kcal}{mol} \right)$ | $V_2 \left( \frac{Kcal}{mol} \right)$ | $V_3 \left( \frac{Kcal}{mol} \right)$ | $V_4 \left( \frac{Kcal}{mol} \right)$ |
|---|---|---|---|---|
| $C_1$-S-$C_1$-$C_2$[a] | 0 | 9.51 | 0 | 0 |
| S-$C_1$-$C_2$-$C_2$[a] | 0 | 9.51 | 0 | 0 |
| $C_1$-$C_2$-$C_2$-$C_1$[a] | 0 | 9.51 | 0 | 0 |
| $C_2$-$C_3$-O-$C_3$[b] | 0.65 | -0.25 | 0.67 | 0 |
| $C_3$-O-$C_3$-$C_3$[b] | 0.65 | -0.25 | 0.67 | 0 |

| | | | | |
|---|---|---|---|---|
| O-C$_3$-C$_3$-O[b] | -.55 | 0 | 0 | 0 |
| C$_3$-C$_3$-O-C$_4$[b] | 0.65 | -.25 | 0.67 | 0 |
| C$_2$-O-C$_3$-C$_3$[b] | 0.65 | -.25 | 0.67 | 0 |

[a]Adapted from Ref. [1]
[b]Adapted from Ref [2]

Table SX5 Multi-Harmonic torsional parameters, where the potential is defined by harmonic
potential; $U_{dihedral} = \sum_{n=1}^{6} V_n \cos^{n-1}\phi$

| Type | $V_1 \left(\frac{Kcal}{mol}\right)$ | $V_2 \left(\frac{Kcal}{mol}\right)$ | $V_3 \left(\frac{Kcal}{mol}\right)$ | $V_4 \left(\frac{Kcal}{mol}\right)$ | $V_5 \left(\frac{Kcal}{mol}\right)$ | $V_6 \left(\frac{Kcal}{mol}\right)$ |
|---|---|---|---|---|---|---|
| S-C$_1$-C$_1$-S[c] | 5.2132 | -0.0502 | -3.4139 | 0.1124 | -1.5909 | 0.1268 |
| C$_1$-C$_2$-C$_3$-O[c] | 0.1866 | -0.9069 | 0.0550 | 1.2440 | -0.0359 | 0.2321 |
| C$_1$-C$_2$-O-C$_3$[c] | 0.1866 | -0.9069 | 0.0550 | 1.2440 | -0.0359 | 0.2321 |

[c]Adapted from Ref [3]

Calculating Ionic mobility

Conventionally the ion mobility in simulations is from the diffusion constant based on the

Einstein mobility relation, $\mu = Dq/kT$. Here, μ is the charge mobility, q is the charge, k is the

Boltzmann constant, T is the temperature, and D is the diffusion constant calculated through

the mean-square displacement (MSD) using

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{\delta}{\delta t} \langle X_0^2(t) \rangle$$

However, this relationship is not valid in presence of external electric field. This is because on

application of an electric field, the ion starts to drift. Hence, the total displacement is given by

$$\langle X_E^2(t) - X_0^2(t) \rangle = (vt)^2$$

The ionic mobility can be calculated using this drift velocity using:

$$\mu = \frac{vt}{E}$$

where E is the applied electric field. We hence used the above equation as the basis for our mobility calculations. The calculated self-diffusion of Li$^+$ ions in the system with no applied field, is ~$10^{-8}$cm$^2$/s which is insignificant compared to the calculated drift velocities so then the expression for calculating the drift velocity becomes:

$$\langle X_E^2(t) \rangle = (vt)^2$$

which simplifies the calculation process. Fig SX2 shows how the MSD of each ion is fit to eq X. Ions showing a good fit to the expression are considered "mobile", i.e. moving in a way that can be described as under the influence of an electric field. For each mobile ion the fit is used to extract $v$ and the mobility is calculated from that.
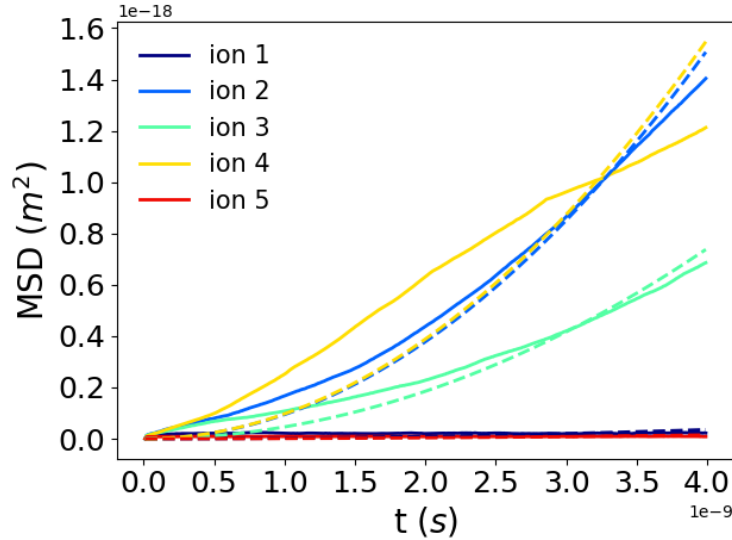


Fig. SX2. MSD plots of ions (solid lines) with the best fit to eq X for each ion plotted in the same color as a dashed line.

**REFERENCES**

1. Huang, David M., et al. "Coarse-grained computer simulations of polymer/fullerene bulk heterojunctions for organic photovoltaic applications." *Journal of Chemical Theory and Computation* 6.2 (2009): 526-537.
2. Jorgensen, William L., David S. Maxwell, and Julian Tirado-Rives. "Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids." *Journal of the American Chemical Society* 118.45 (1996): 11225-11236.
3. Poelking, Carl, and Denis Andrienko. "Effect of polymorphism, regioregularity and paracrystallinity on charge transport in poly (3-hexylthiophene)[P3HT] nanofibers." *Macromolecules* 46.22 (2013): 8941-8956.