Supporting information for "A realistic description of the charge carrier wavefunction in microcrystalline polymer semiconductors" by David L. Cheung, David P. McMahon, and Alessandro Troisi

Force field details

As described in the text, the force field employed in this work was previously used in studies of tetrathiophene. It adopts a `first-generation' form, i.e. it uses harmonic potentials for the bond stretching and bond angle bending and a Lennard-Jones potential for the van der Waals interactions, with cross-terms being neglected. Explicitly the functional form for the force field is

$$E_{ff} = \sum_{bonds} \frac{1}{2} k_{bonds} \left(r - r_0 \right)^2 + \sum_{angles} \frac{1}{2} k_{angles} \left(\theta - \theta_0 \right)^2$$

$$+ \sum_{dihedrals} \sum_{m=1}^{4} \frac{1}{2} V_m (1 + \cos(m\phi + \delta_m))$$

$$\sum_{i<j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$

($\delta_m = 0$ for odd m and $\delta_m = 180°$ for even m).

The parameters for a given interaction depend on the atom types involved. The force field atoms types are defined in Figure S1. The force field used was based on that of Marcon and Raos[1,2], which has been comprehensively validated against substituted oligothiophenes and poly(3-butylthiophene)[3]. Bond stretching and bond angle bending parameters were taken from the MM3 force field[4]. The point charges were found from fitting to electrostatic potentials from density functional theory (B3LYP/6-311G*) calculations, with adjustments made to ensure electroneutrality, and the van der Waals parameters were taken (without modification) from the OPLS parameter set[5]. Van der Waals parameters for unlike atom types were determined using the usual geometric mixing rules ($\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$ and $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$). Van der Waals and electrostatic interactions between 1-4 bonded atoms are scaled by 0.5. The torsional force constants for the interring (S_{11}-C_1-C_1-S_{11}) dihedral were found from *ab initio* (MP2/aug-cc-pVTZ) calculations on 2-2'-bithiophene[6]. Other torsional force constants were taken from the OPLS parameter set, which has been specially optimized for reproducing condensed phase structures and thermodynamics of organic molecules.
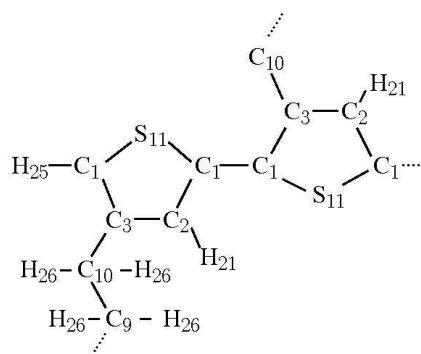
Figure S 1 Force field atom types

The force field parameters for bond stretching, bond angle bending, and torsional rotations are presented in Tables S1-S4

Table S1: Force field atom types (for definitions see Fig. S1).

Atom type	ε / kcal mol^{-1}	σ / Å	q / e
C_1	0.070	3.55	0.0748*
C_2	0.070	3.55	-0.1819
C_3	0.070	3.55	-0.1979
C_9	0.066	3.50	0
C_{10}	0.066	3.50	0.1984
S_{11}	0.250	3.55	-0.1496
H_{21}	0.030	2.42	0.1561
H_{25}	0.030	2.42	0.1919
H_{26}	0.030	2.50	0

* for terminal C_1 (bonded to H_{25}) q=-0.1171 e

Table S2: Bond stretching parameters. Force constants (k) given in kcal mol^{-1} Å^{-2} and equilibrium bond lengths given in Å.

i	j	k_{bond}	r_0
C_1	C_1	787.02	1.446
C_1	C_2	1026.15	1.386
C_1	C_3	1026.15	1.386
C_1	S_{11}	581.42	1.726
C_1	H_{25}	740.98	1.08
C_2	C_3	895.80	1.436
C_2	H_{21}	740.98	1.08
C_3	C_{10}	906.44	1.499
C_9	C_9	646.02	1.525
C_9	C_{10}	646.02	1.525
C_9	H_{26}	682.00	1.112
C_{10}	H_{26}	682.00	1.112

Table S3: Bond angle bending parameters. Force constants given in kcal mol^{-1} Å^{-1} rad^{-2} and equilibrium angles given in degrees.

I	j	K	k_{angle}	θ_0
C_1	C_1	C_2	109.35	126.67
C_1	C_1	C_3	109.35	127.67
C_1	C_1	S_{11}	83.45	120.76
C_2	C_1	S_{11}	172.66	111.64
C_3	C_1	S_{11}	172.66	111.64
H_{21}	C_1	S_{11}	57.55	123.00
H_{21}	C_1	S_{11}	70.50	125.10
H_{21}	C_1	C_2	70.50	125.10
C_1	C_2	C_3	79.13	110.28
H_{21}	C_2	C_3	70.50	124.40
C_1	C_3	C_2	79.13	110.28
C_1	C_3	C_{10}	67.72	122.30
C_2	C_3	C_{10}	67.72	122.30
C_9	C_9	C_9	96.40	111.00
C_9	C_9	C_{10}	96.40	111.00
C_9	C_9	H_{26}	84.89	109.31
C_{10}	C_9	H_{26}	84.89	109.31
H_{26}	C_9	H_{26}	79.13	107.60
C_3	C_{10}	C_9	77.70	110.60
C_3	C_{10}	H_{26}	79.13	109.31
C_9	C_{10}	H_{26}	84.89	109.31
H_{26}	C_{10}	H_{26}	79.13	107.60
C_1	S_{11}	C_1	172.66	91.63

Table S4: Torsional force constants in kcal mol^{-1}.

i	j	k	l	V_1	V_2	V_3	V_4
S_{11}	C_1	C_1	S_{11}	-0.38	-1.43	-0.02	0.92
C_2	C_1	C_1	S_{11}	0	0	0	0
C_2	C_1	C_1	C_3	0	0	0	0
C_3	C_1	C_1	S_{11}	0	0	0	0
C_1	C_3	C_{10}	C_9	0	0	0	0
C_3	C_{10}	C_9	C_9	0	0	0	0
C_3	C_{10}	C_9	H_{26}	0	0	0.462	0
C_{10}	C_9	C_9	C_9	1.74	-0.16	0.32	0
H_{26}	C_{10}	C_9	C_9	0	0	0.46	0
H_{26}	C_{10}	C_9	H_{26}	0	0	0.32	0
H_{26}	C_9	C_9	C_9	0	0	0.46	0
H_{26}	C_9	C_9	H_{26}	0	0	0.32	0
S_{11}	C_1	C_2	C_3	0	9.51	0	0
S_{11}	C_1	C_3	C_2	0	9.51	0	0
C_1	S_{11}	C_1	C_1	0	9.51	0	0
C_1	S_{11}	C_2	C_3	0	9.51	0	0
C_2	C_3	C_1	C_9	0	9.51	0	0
C_1	C_1	C_1	S_{11}	0	9.51	0	0

Force field validation

In order to test the accuracy of the force field, the interring torsional potential for 2-2'-bimethylthiophene has been calculated from the force field and from MP2/6-31G* calculations (note that the torsional potential was not parameterized against this molecule). This is shown in Fig. S2. As can be seen the force field potential reproduces the *ab initio* potential well, in particular it finds minima in the same angles as the MP2 potential. Only near 180° is there a major difference betweeen the two curves, with the force field overestimating the potential here.
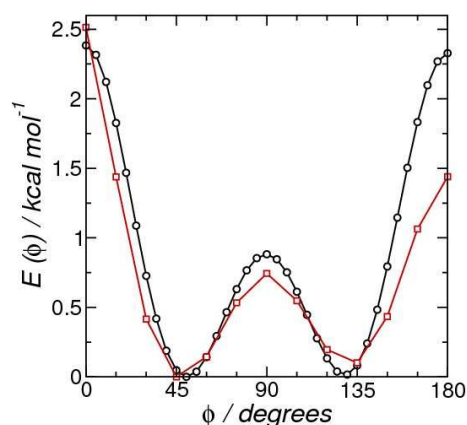
Figure S 2: 2-2'-bimethylthiophene torsional potentials calculated from the present force field (black, circles) and MP2/6-31G* (red, squares).

The accuracy of force field may also be assessed through the structure of the polymer crystal, which will be discussed extensively elsewhere. The main structural features may be seen in the ring-ring radial distribution function (Figure S3). The prominent peaks in this correspond to nearest and next-nearest neighbor rings on the same chain (~4 and ~7.6 A) and nearest and next-nearest neighbors on adjacent chains (~4.3 and 6 A). The locations of these peaks are in agreement with crystallographic data on this polymorph of P3HT[7].
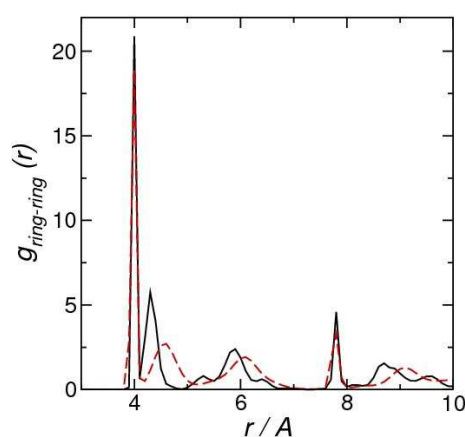

Figure S 3: Ring-ring radial distribution function at 100 K (black, solid line) and 300 K (red, dashed line).

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