Supporting information for:

Morphology and Charge Transport in Amorphous and Crystalline P3HT and PBTTT: Insights From Theory.

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Force field

The energy for the force field used corresponds to the CHARMM functional form:

$$U = \sum_{bonds} K_r \left(r - r_0\right)^2 + \sum_{angles} K_\theta \left(\theta - \theta_0\right)^2 + \sum_{dihedrals} \sum_{n=1}^{3} K_n \left(1 + \cos\left(n\Phi + \delta_n\right)\right)$$

$$+ \sum_{impropers} K_\psi \left(\psi - \psi_0\right)^2 + \sum_{nonbonded} \left\{ \epsilon_{ij} \left[\left(\frac{R_{min,i,j}}{r_{ij}}\right)^{12} - 2 \left(\frac{R_{min,i,j}}{r_{ij}}\right)^{6} \right] + \frac{q_i q_j e^2}{r_{ij}} \right\}. \quad (1)$$

were both ϵ_{ij} and $R_{min,i,j}$ were obtained through a geometric combination of the atomic $R_{min,i}$ and ϵ_i. All the parameters are reported in Table S1 (nonbonded), S2 (bonds), S3 (angles) and S4 (dihedrals). Parameters for P3HT and PBTTT were taken from Do et al.[S1,S2] and Marcon and Raos.[S3] Harmonic improper dihedral potentials $V_{improper} = K_\psi \left(\psi - \psi_0\right)^2$ were defined to maintain the planarity of the thiophene rings in P3HT and thienothiophenes in PBTTT with $K_\psi = 20 \; kcal/mol/rad^2$. The chemical structures of the polymers and solvents with the atom types used for the parameters, are depicted in Figure S1.

Table S1: Nonbonded parameters used in atomistic simulation. Atom types are defined in Figure S1.

Atom type i	$\epsilon_i(kcal/mole)$	$R_{min,i}/2$ (Å)	q_i (e)
S1	0.250000	1.9923701	-0.149600
C1	0.070000	1.9923701	0.074800
C2	0.070000	1.9923701	-0.181700
C3	0.070000	1.9923701	-0.141200
C4	0.066000	1.9643090	0.074800
C5	0.066000	1.9643090	-0.120000
C6	0.066000	1.9643090	-0.180000
H1	0.030000	1.3581791	0.181700
H2	0.030000	1.3581791	0.216000
H3	0.030000	1.4030776	0.060000

Table S2: Parameters used in harmonic bond length potential $U_{bond}(r) = K_r (r - r_0)^2$ in atomistic simulation. Atom types are defined in Figure S1.

Bond type	$K_r (kcal/mole/ \text{Å}^2)$	r_0 (Å)
S1 C1	291.25	1.732
C1 C2	514.27	1.364
C2 C2	453.10	1.428
C2 C3	514.27	1.364
C2 H1	370.63	1.080
C1 C1	392.29	1.430
C3 H2	370.63	1.080
C3 S1	291.25	1.732
C2 C4	317.00	1.510
C4 C5	268.00	1.529
C5 C5	268.00	1.529
C5 C6	268.00	1.529
C4 H3	340.00	1.090
C5 H3	340.00	1.090
C6 H3	340.00	1.090

Table S3: Parameters used in harmonic bond angle potential $U_{angle}(\theta) = K_\theta (\theta - \theta_0)^2$ in atomistic simulation. Atom types are defined in Figure S1.

Angle type	$K_\theta(kcal/mole/rad^2)$	θ_0 (deg.)
C1 S1 C1	86.360	92.774
C1 S1 C3	86.360	92.774
S1 C1 C2	86.360	110.292
C1 C2 C2	39.582	113.322
C1 C2 C1	39.582	113.322
C2 C2 H1	35.263	123.700
C2 C2 C3	39.582	113.322
C2 C3 S1	86.360	110.292
C2 C1 C1	54.694	130.140
C2 C3 H2	35.263	125.100
C1 C2 H1	35.263	122.979
C3 C2 H1	35.263	122.979
S1 C1 C1	41.740	119.569
S1 C3 H1	28.787	124.609
C2 C2 C4	70.000	123.700
C1 C2 C4	70.000	122.979
C3 C2 C4	70.000	122.979
C2 C4 C5	63.000	114.000
C2 C4 H3	35.000	109.500
C4 C5 C5	58.350	112.700
C5 C5 C5	58.350	112.700
C5 C5 C6	58.350	112.700
C4 C5 H3	37.500	110.700
C5 C4 H3	37.500	110.700
C5 C5 H3	37.500	110.700
C5 C6 H3	37.500	110.700
C6 C5 H3	37.500	110.700
H3 C4 H3	33.000	107.800
H3 C5 H3	33.000	107.800
H3 C6 H3	33.000	107.800
H2 C3 S1	28.787	124.609

Table S4: Parameters used in dihedral potential $U_{dihedral}(\Phi) = K_n \left(1 + \cos\left(n\Phi + \delta_n\right)\right)$ in atomistic simulation. Atom types are defined in Figure S1.

Dihedral type	$K_n(kcal/mole)$	n	δ_n (deg.)
C2 C4 C5 C5	0.650	1	0.0
	-0.025	2	180.0
	0.100	3	0.0
C2 C4 C5 H3	0.231	3	0.0
C4 C5 C5 C5	0.650	1	0.0
	-0.025	2	180.0
	0.100	3	0.0
C5 C5 C5 C5	0.650	1	0.0
	-0.025	2	180.0
	0.100	3	0.0
C5 C5 C5 C6	0.650	1	0.0
	-0.025	2	180.0
	0.100	3	0.0
H3 C4 C5 C5	0.150	3	0.0
H3 C5 C5 C5	0.150	3	0.0
H3 C5 C6 H3	0.150	3	0.0
C4 C5 C5 H3	0.150	3	0.0
H3 C4 C5 H3	0.150	3	0.0
H3 C5 C5 H3	0.150	3	0.0
C5 C5 C6 H3	0.150	3	0.0
H3 C5 C5 C6	0.150	3	0.0
C2 C2 C4 H3	0.000	1	0.0
C2 C2 C4 C5	0.000	1	0.0
C1 C2 C4 H3	0.000	1	0.0
C3 C2 C4 H3	0.000	1	0.0
C1 C2 C4 C5	0.000	1	0.0
C3 C2 C4 C5	0.000	1	0.0
C2 C1 C1 S1	0.000	2	180.0
C2 C1 C1 C2	0.000	2	180.0
S1 C1 C1 S1	-0.0783	1	0.0
	2.7092	2	180.0
	0.0712	3	0.0
C3 S1 C1 C2	6.1465	2	180.0
C3 C2 C2 C1	-0.495	1	0.0
	1.579	2	180.0
C2 C2 C1 S1	9.2675	2	180.0
	3.000	3	0.0
C2 C3 S1 C1	6.608	2	180.0
C2 C2 C3 S1	10.413	2	180.0
	3.000	3	0.0
C1 C2 C2 C1	-0.495	1	0.0

	1.6515	2	180.0
C1 S1 C1 C2	6.6935	2	180.0
C1 C2 C1 S1	3.625	2	180.0
C1 C2 C1 C1	-0.495	1	0.0
	1.6515	2	180.0
C1 S1 C1 C1	6.6935	2	180.0
S1 C1 C1 S1	3.625	2	180.0
S1 C1 C1 C2	9.2675	2	180.0
S1 C1 C1 C2	3.000	3	0.0
C2 C1 C1 C2	3.625	2	180.0
C1 C2 C2 H1	0.125	1	0.0
	1.906	2	180.0
	-0.275	3	0.0
C3 C2 C2 H1	0.125	1	0.0
	1.8215	2	180.0
	-0.275	3	0.0
S1 C3 C2 H1	-2.121	1	0.0
	3.261	2	180.0
H2 C3 C2 H1	5.068	2	180.0
C1 S1 C3 H2	0.466	2	180.0
H2 C3 C2 C2	0.125	1	0.0
	3.966	2	180.0
	-0.275	3	0.0
S1 C1 C2 H1	-2.121	1	0.0
	2.9020	2	180.0
C1 C1 C2 H1	0.125	1	0.0
	1.906	2	180.0
	-0.275	3	0.0
C1 C1 S1 C1	0.382	2	180.0
	0.200	3	0.0
C2 C2 C1 C1	-0.335	1	0.0
	3.922	2	180.0
C3 S1 C1 C1	0.383	2	180.0
	0.200	3	0.0
C1 C1 C2 H1	0.125	1	0.0
	3.5295	2	180.0
	-0.275	3	0.0
C1 C1 C2 C1	-0.335	1	0.0
	3.922	2	180.0
C1 C1 C2 C4	0.125	1	0.0
	3.5295	2	180.0
	-0.275	3	0.0
C3 C2 C2 C4	0.125	1	0.0
	1.8215	2	180.0
	-0.275	3	0.0

S6

S1 C1 C2 C4	-2.121	1	0.0
	2.9020	2	180.0
H1 C2 C2 C4	2.435	2	180.0
C1 C2 C2 C4	0.125	1	0.0
	1.906	2	180.0
	-0.275	3	0.0
S1 C3 C2 C4	-2.121	1	0.0
	3.261	2	180.0
H2 C3 C2 C4	5.068	2	180.0

References

(S1) Do, K.; Huang, D. M.; Faller, R.; Moule, A. J. A comparative MD study of the local structure of polymer semiconductors P3HT and PBTTT. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14735–14739.

(S2) Huang, D. M.; Faller, R.; Do, K.; Moule, A. J. Coarse-Grained Computer Simulations of Polymer/Fullerene Bulk Heterojunctions for Organic Photovoltaic Applications. *J. Chem. Theory Comput.* **2010**, *6*, 526–537.

(S3) Marcon, V.; Raos, G. Free Energies of Molecular Crystal Surfaces by Computer Simulation: Application to Tetrathiophene. *J. Am. Chem. Soc.* **2006**, *128*, 1408–1409.
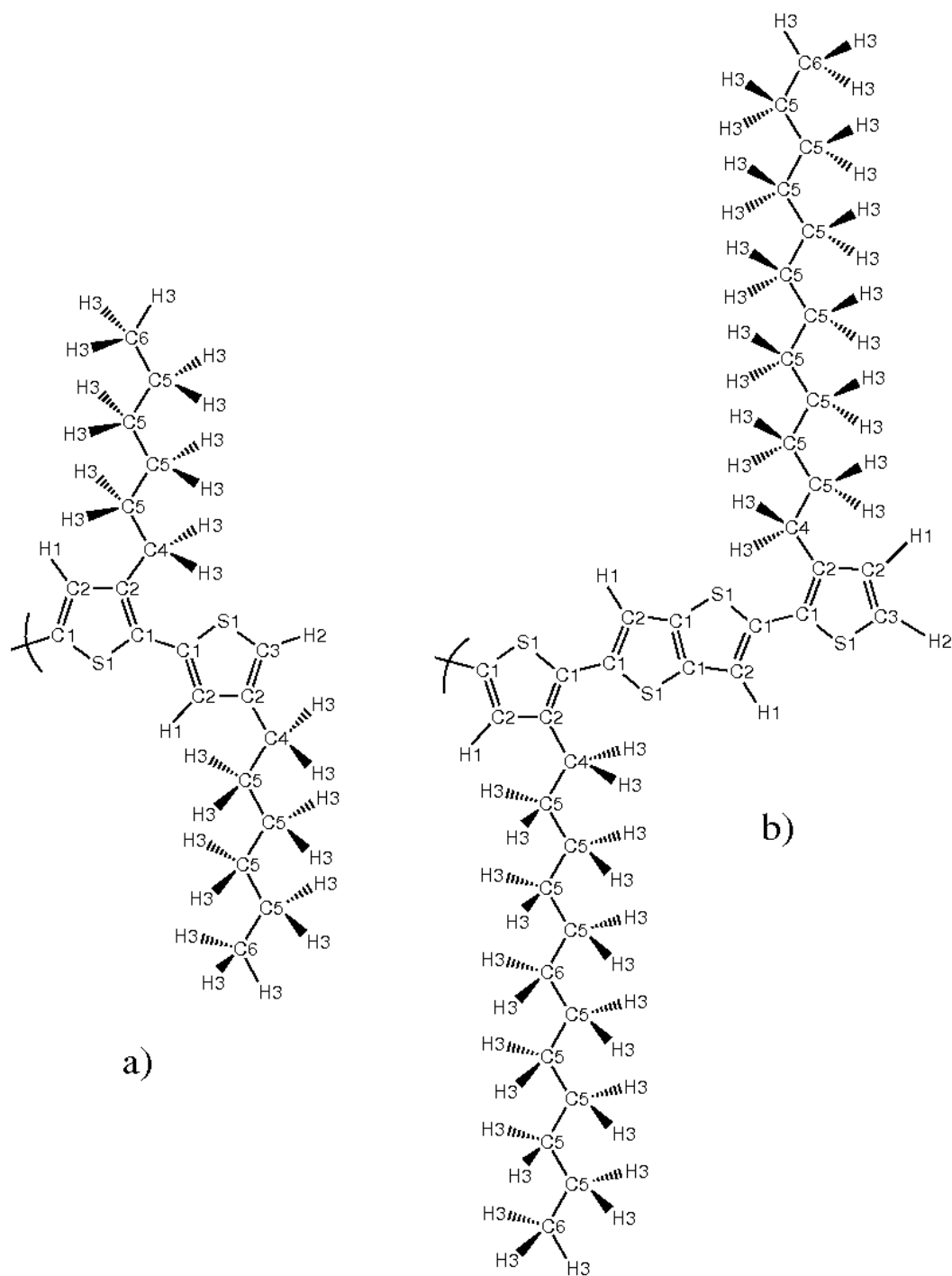
Figure S1: Chemical structure and atom types used in the force field definition of: a) the last two monomers of a poly(3-hexylthiophene) (P3HT) chain; b) the end monomer of a poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) chain.
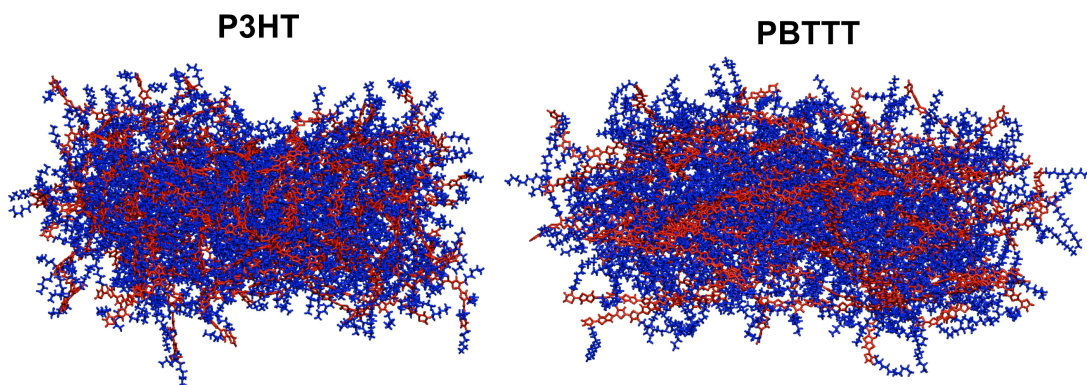
P3HT   **PBTTT**

Figure S2: Representative snapshots of the simulated periodic boxes of P3HT and PBTTT in amorphous phase. The backbones of the polymers are depicted in red and the side chains in blue.