ELECTRONIC SUPPLEMENTARY INFORMATION

Optical Properties of Regioregular Poly(3-hexylthiophene) Aggregates From Fully Atomistic Investigations

*Linjun Wang**,[a] *and David Beljonne**,[b]

[a]Department of Chemistry, Zhejiang University, Hangzhou 310027, China

[b]Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, B-7000 Mons, Belgium

*Email: ljwang@zju.edu.cn; david.beljonne@umons.ac.be

Force field details for P3HT in Tinker format:

1. Atom type parameters:

```
atom    1    1    C    "opls_568 CS C3_thiophene_H       "    6    12.011    3
atom    2    2    C    "opls_637 CW C2_thiophene_body    "    6    12.011    3
atom    3    3    S    "opls_633 S  S_thiophene          "   16    32.060    2
atom    4    4    H    "opls_640 HA H3_thiophene         "    1     1.008    1
atom    5    5    C    "opls_135 CT CH3_alkane           "    6    12.011    4
atom    6    6    H    "opls_140 HC H_alkane             "    1     1.008    1
atom    7    5    C    "opls_136 CT CH2_alkane           "    6    12.011    4
atom    8    2    C    "opls_637 CW C2_thiophene_terminal"    6    12.011    3
atom    9    1    C    "opls_568 CS C3_thiophene_alkane  "    6    12.011    3
atom   10    4    H    "opls_640 HA H2_thiophene_terminal"    1     1.008    1
```

2. Van der Waals parameters:

```
vdw    1    3.55000    0.07600
vdw    2    3.55000    0.07000
vdw    3    3.55000    0.25000
vdw    4    2.42000    0.03000
vdw    5    3.50000    0.06600
vdw    6    2.50000    0.03000
```

3. Atomic charges:

```
charge    1   -0.094
charge    2   +0.011
charge    3   -0.052
charge    4   +0.109
charge    5   -0.180
charge    6   +0.060
charge    7   -0.120
charge    8   -0.175
charge    9   +0.015
charge   10   +0.186
```

4. Bond parameters:

```
bond    1    1    453    1.430
bond    1    2    513    1.392
bond    2    3    291    1.743
bond    1    4    370    1.080
bond    2    4    370    1.080
bond    2    2    394    1.460
bond    1    5    453    1.504
bond    5    6    341    1.112
bond    5    5    323    1.529
```

5. Angle parameters:

```
angle    2    1    4    35.25    123.0
angle    2    3    2    86.33     91.6
angle    1    1    2    39.57    110.3
angle    3    2    1    86.33    111.6
angle    3    2    4    28.78    123.0
angle    3    2    2    41.73    120.8
angle    1    2    4    35.25    125.1
angle    1    2    2    54.68    127.7
angle    1    1    4    35.25    124.4
angle    2    1    5    33.81    122.3
```

```
angle   1   1   5   33.81   122.3
angle   5   5   5   49.20   111.0
angle   5   5   6   42.45   109.3
angle   6   5   6   39.57   107.6
angle   1   5   5   38.85   110.6
angle   1   5   6   39.57   109.3
```

6. Improper torsion parameters:

```
imptors   4   1   1   2     1.100   180.0  2
imptors   5   1   1   2     1.100   180.0  2
imptors   4   1   2   3     1.100   180.0  2
imptors   2   1   2   3     1.100   180.0  2
```

7. General torsion parameters:

```
torsion   2   1   5   5   -0.714   0.0   1   0.000   180.0   2   0.000   0.0   3
torsion   2   1   5   6    0.000   0.0   1   0.000   180.0   2  -0.480   0.0   3
torsion   1   5   5   5    1.300   0.0   1  -0.050   180.0   2   0.200   0.0   3
torsion   5   5   5   5    1.300   0.0   1  -0.050   180.0   2   0.200   0.0   3
torsion   1   5   5   6    0.000   0.0   1   0.000   180.0   2   0.462   0.0   3
torsion   5   5   5   6    0.000   0.0   1   0.000   180.0   2   0.300   0.0   3
torsion   6   5   5   6    0.000   0.0   1   0.000   180.0   2   0.300   0.0   3
torsion   4   1   2   4    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   5   1   2   4    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   4   1   2   3    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   4   1   1   2    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   4   1   1   4    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   4   1   1   5    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   4   2   3   2    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   4   2   1   1    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   2   2   3   2    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   2   2   1   1    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   2   2   1   4    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   2   2   1   5    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   5   1   1   2    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   5   1   2   3    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   3   2   1   1    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   2   3   2   1    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   2   1   1   2    0.000   0.0   1   7.250   180.0   2   0.000   0.0   3
torsion   1   1   5   6    0.000   0.0   1   0.000   180.0   2   0.000   0.0   3
torsion   3   2   2   1    0.000   0.0   1   0.000     0.0   2   0.000   0.0   3
torsion   1   2   2   1    0.000   0.0   1   0.000     0.0   2   0.000   0.0   3
torsion   1   1   5   5   -0.652944 0.0   1   -0.43181    0.0   2   -0.221361 0.0   3
```

8. Torsion parameters for S_0:

```
torsion   3   2   2   3   -0.15451  0.0   1   -2.40627    0.0   2    0.801493 0.0   4
```

9. Torsion parameters for S_1:

```
torsion   3   2   2   3  -34.3824   0.0   2    6.37882    0.0   4   -2.2659   0.0   6
```

10. Cutoff parameters:

```
cutoff 15.0
vdw-cutoff 15.0
charge-cutoff 15.0
```

Figure S1. (a) Experimental[1] and (b) simulated X-ray diffraction pattern of P3HT crystal. The most obvious scattering peaks located at low angles, namely, (200), (400), and (600), are different order reflections arising from inter-lamella spacing of P3HT thin film. The broad "peak", (h20)'s, roughly corresponds to an intra-lamella chain-to-chain stacking distance. The three wide angle scattering broad peaks, (hkl)'s, (hk2)'s, and (hk3)'s, reflects the intra-chain repeat unit distance.

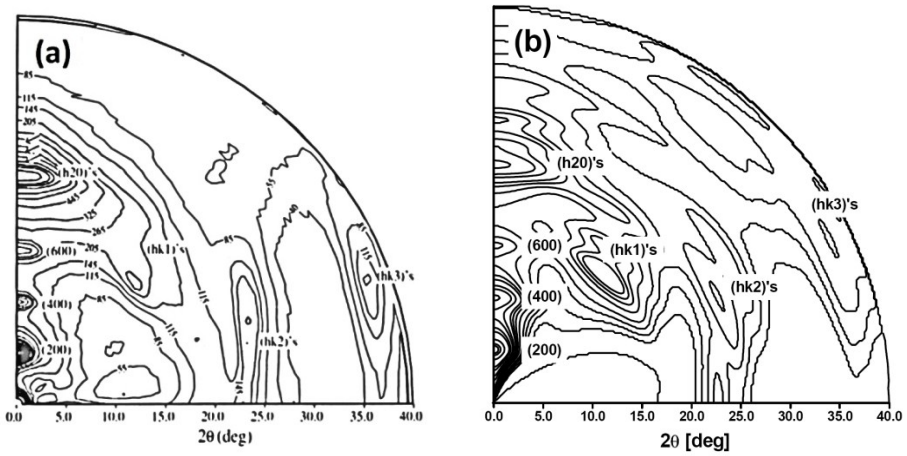

Figure S2. (a) Correlation between the lowest transition energies of two chains *m* and *n* in P3HT aggregate (20, 20). Only the results of the central 18 chains are shown. (b) Averaged correlation as a function of |*m*-*n*| using the central two chains as the reference. The dashed line is an exponential fit to get the correlation length l_0.

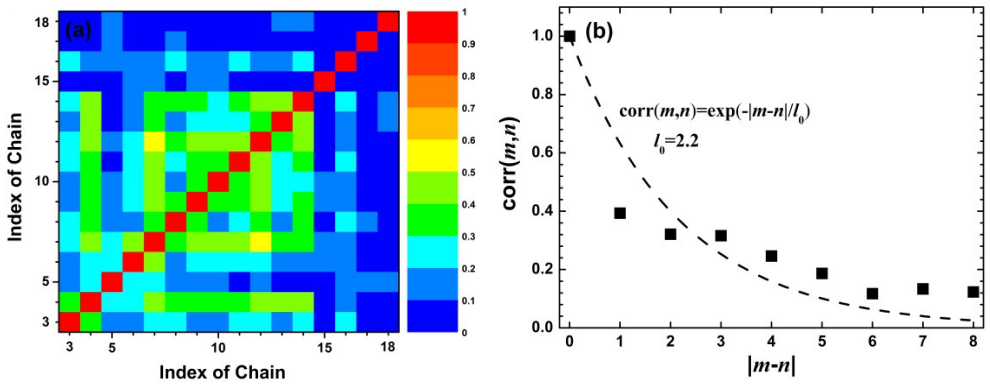

Table S1. The chain-length-dependent Huang-Rhys factor (S), exciton-phonon coupling constant (λ), mean first transition energy ($\langle E \rangle$), variance of the first transition energy (σ_E), mean exciton coupling between the nearest chains ($\langle J \rangle$), and variance of the exciton coupling (σ_J) for P3HT aggregates {(10, M), M = 10, 15, 20, 25, 30, 35, and 40}. The force fields used in the molecular dynamics are based on ground state (S_0) or first excited state (S_1) torsional potentials as given in parenthesis. All energies are in eV.

M	S	λ	$\langle E \rangle$ (S_0)	σ_E (S_0)	$\langle J \rangle$ (S_0)	σ_J (S_0)	$\langle E \rangle$ (S_1)	σ_E (S_1)	$\langle J \rangle$ (S_1)	σ_J (S_1)
10	1.02	1.01	2.270	0.045	0.067	0.0037	2.172	0.014	0.070	0.0013
15	0.77	0.88	2.162	0.038	0.042	0.0031	2.081	0.013	0.044	0.0008
20	0.73	0.85	2.102	0.030	0.031	0.0030	2.045	0.010	0.030	0.0006
25	0.64	0.80	2.085	0.026	0.023	0.0032	2.025	0.009	0.021	0.0006
30	0.62	0.79	2.075	0.018	0.015	0.0028	2.012	0.008	0.017	0.0006
35	0.61	0.78	2.052	0.015	0.011	0.0029	2.007	0.008	0.013	0.0005
40	0.59	0.77	2.057	0.014	0.009	0.0046	2.003	0.007	0.010	0.0006

Table S2. Chain-length-dependent energies for the first absorption peak (E_{A1}) and the first emission peak ($E_{0\text{-}0}$), the calculated Stokes shift (SS), the intensity ratios between the first and second absorption peaks (I_{A1}/I_{A2}), the intensity ratios between the first and second emission peaks ($I_{0\text{-}0}/I_{0\text{-}1}$), and the intensity ratios between the third and the second emission peaks ($I_{0\text{-}2}/I_{0\text{-}1}$) for P3HT aggregates. The force fields used in the molecular dynamics are based on either purely ground state (S_0) torsional potential or a combination of first excited state potential for the central chain and ground state potential for other chains (S_{01}) as shown in parenthesis. Calculations using S_0 force filed are based on aggregates {(10, M)}, while that adopting S_{01} force field are based on aggregates {(9, M)}, with M = 10, 15, 20, 25, 30, 35, and 40. The experimental room-temperature results of nanofiber (NF)[2] and thin film (TF)[3] are also given. All energies are in eV.

M	E_{A1} (S_0)	$E_{0\text{-}0}$ (S_0)	$E_{0\text{-}0}$ (S_{01})	SS (S_0)	SS (S_{01})	I_{A1}/I_{A2} (S_0)	$I_{0\text{-}0}/I_{0\text{-}1}$ (S_0)	$I_{0\text{-}0}/I_{0\text{-}1}$ (S_{01})	$I_{0\text{-}2}/I_{0\text{-}1}$ (S_0)	$I_{0\text{-}2}/I_{0\text{-}1}$ (S_{01})
10	2.30	2.20	2.14	0.10	0.16	0.364	0.370	0.716	0.482	0.448
15	2.22	2.13	2.06	0.09	0.16	0.428	0.404	1.050	0.369	0.329
20	2.15	2.09	2.03	0.06	0.12	0.535	0.508	1.084	0.332	0.302
25	2.12	2.08	2.02	0.04	0.10	0.717	0.593	0.953	0.289	0.271
30	2.11	2.08	2.00	0.03	0.11	0.929	0.843	1.185	0.271	0.257
35	2.07	2.06	2.01	0.01	0.06	1.014	0.927	1.236	0.261	0.249
40	2.08	2.06	2.00	0.02	0.08	1.161	1.143	1.458	0.249	0.237
NF	2.01	1.94		0.07		1.015	1.485		~0.285	
TF	~2.07	~1.85		~0.22		~0.602	~0.548		0.452	

References

1.T. J. Prosa, M. J. Winokur, J. Moulton, P. Smith and A. J. Heeger, *Macromol.*, 1992, **25**, 4364-4372.

2.E. T. Niles, J. D. Roehling, H. Yamagata, A. J. Wise, F. C. Spano, A. J. Moulé and J. K. Grey, *J. Phys. Chem. Lett.*, 2012, **3**, 259-263.

3.J. Clark, C. Silva, R. H. Friend and F. C. Spano, *Phys. Rev. Lett.*, 2007, **98**, 206406.