

Electronic Supplemental Information for:

Donor- π -Acceptor Double-Cable Polythiophenes Bearing Fullerene Pendant with Tunable Donor/Acceptor Ratio: A Facile Postpolymerization

*Minghua Li, Pan Xu, Jinguo Yang, Shangfeng Yang**

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials
for Energy Conversion & Department of Materials Science and Engineering, University of Science
and Technology of China (USTC), Hefei 230026, China

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in CDCl₃
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S1. ¹H NMR spectra of P3HT, Br-P3HT-1,2,3,4, 4-FPh-P3HT-1,2,3,4, and C₆₀-Ph-P3HT-1,2,3,4 in CDCl₃.

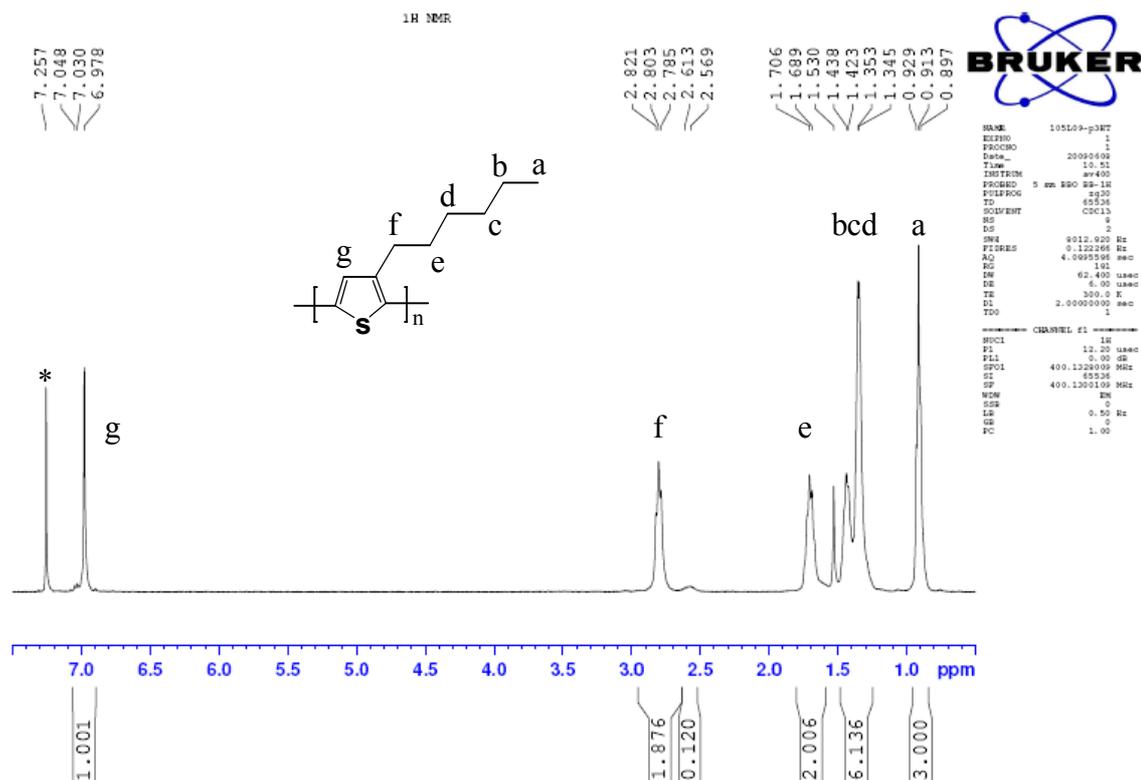


Figure S1. ¹H NMR spectra of P3HT in deuterated chloroform. The solvent line of CHCl₃ is marked with an asterisk.

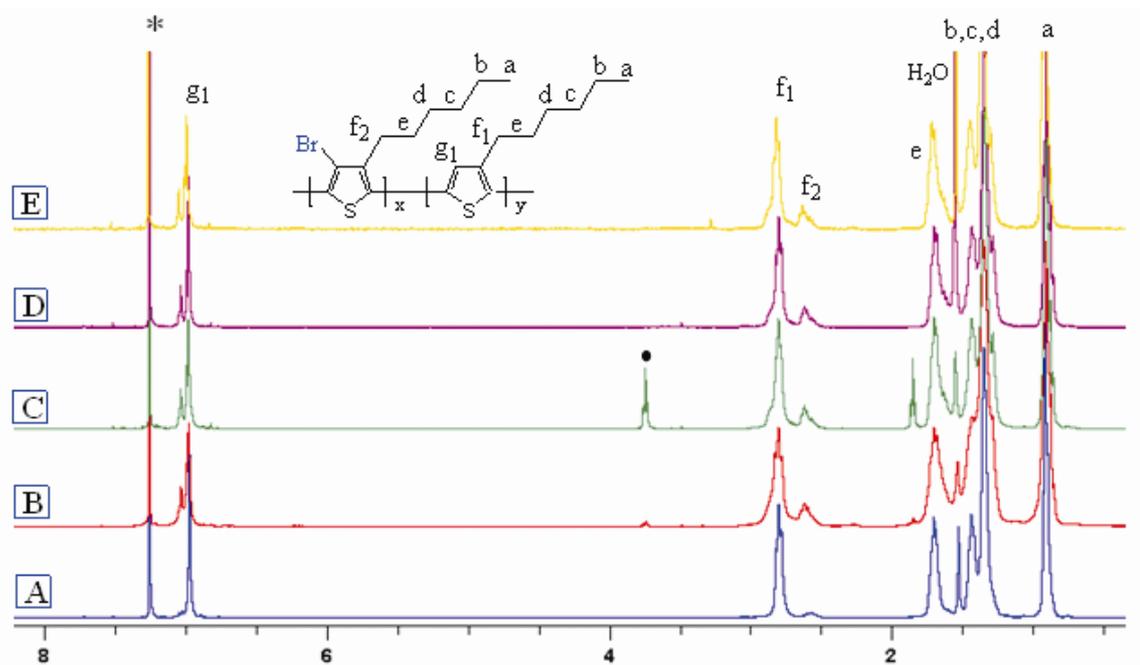


Figure S2. ^1H NMR spectra of **P3HT** (A), **Br-P3HT-1** (B), **Br-P3HT-2** (C), **Br-P3HT-3** (D), and **Br-P3HT-4** (E). All polymers were dissolved in deuterated chloroform, and spectra were recorded at room temperature. The solvent line of CHCl_3 is marked with an asterisk. The filled circle in curve C is due to an unknown impurity.

Br-P3HT-1: δ (ppm): 6.99 (g_1 , broad, 0.805H), 2.82 (f_1 , broad, 1.609H), 2.63 (f_2 , broad, 0.405H), 1.72 (e, broad, 2H), 1.37 (bcd, broad, 6H), 0.93 (a, broad, 3H).

Br-P3HT-2: δ (ppm): 7.00 (g_1 , broad, 0.825H), 2.81 (f_1 , broad, 1.630H), 2.63 (f_2 , broad, 0.365H), 1.68 (e, broad, 2H), 1.39 (bcd, broad, 6H), 0.91 (a, broad, 3H).

Br-P3HT-3: δ (ppm): 6.95 (g_1 , broad, 0.844H), 2.76 (f_1 , broad, 1.638H), 2.58 (f_2 , broad, 0.359H), 1.66 (e, broad, 2H), 1.30 (bcd, broad, 6H), 0.87 (a, broad, 3H).

Br-P3HT-4: δ (ppm): 6.98 (g_1 , broad, 0.883H), 2.80 (f_1 , broad, 1.689H), 2.61 (f_2 , broad, 0.283H), 1.68 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.90 (a, broad, 3H).

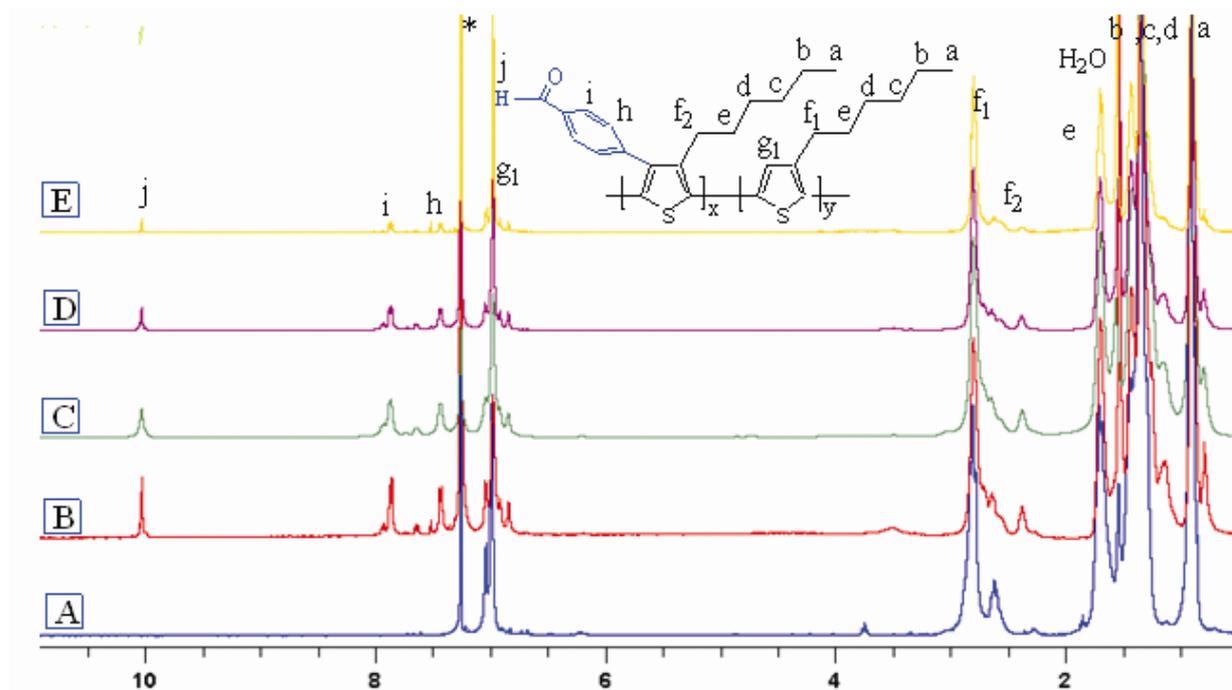


Figure S3. ^1H NMR spectra of **Br-P3HT-1** (A, copied from Figure S3B), **4-FPh-P3HT-1** (B), **4-FPh-P3HT-2** (C), **4-FPh-P3HT-3** (D), and **4-FPh-P3HT-4** (E). All polymers were dissolved in deuterated chloroform, and spectra were recorded at room temperature. The solvent line of CHCl_3 is marked with an asterisk.

4-FPh-P3HT-1: δ (ppm): 10.0 (j, single, 0.195H), 7.85 (i, double, 0.389H), 7.42 (h, d, 0.379H), 6.97 (g_1 , broad, 0.805H), 2.79 (f_1 , broad, 1.597H), 2.35 (f_2 , broad, 0.393H), 1.67 (e, broad, 2H), 1.33 (bcd, broad, 6H), 0.89 (a, broad, 3H).

4-FPh-P3HT-2: δ (ppm): 10.0 (j, single, 0.175H), 7.88 (i, double, 0.350H), 7.44 (h, d, 0.335H), 6.98 (g_1 , broad, 0.826H), 2.82 (f_1 , broad, 1.658H), 2.35 (f_2 , broad, 0.349H), 1.70 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.91 (a, broad, 3H).

4-FPh-P3HT-3: δ (ppm): 9.96 (j, single, 0.156H), 7.85 (i, double, 0.301H), 7.37 (h, d, 0.311H), 6.91 (g_1 , broad, 0.845H), 2.82 (f_1 , broad, 1.694H), 2.35 (f_2 , broad, 0.312H), 1.63 (e, broad, 2H), 1.36 (bcd, broad, 6H), 0.84 (a, broad, 3H). (letter a to j stands for chemical shift of different hydrogen)

4-FPh-P3HT-4: δ (ppm): 10.0 (j, single, 0.117H), 7.87 (i, double, 0.232H), 7.44 (h, d, 0.235H), 6.97 (g_1 , broad, 0.884H), 2.82 (f_1 , broad, 1.765H), 2.35 (f_2 , broad, 0.234H), 1.70 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.91 (a, broad, 3H).

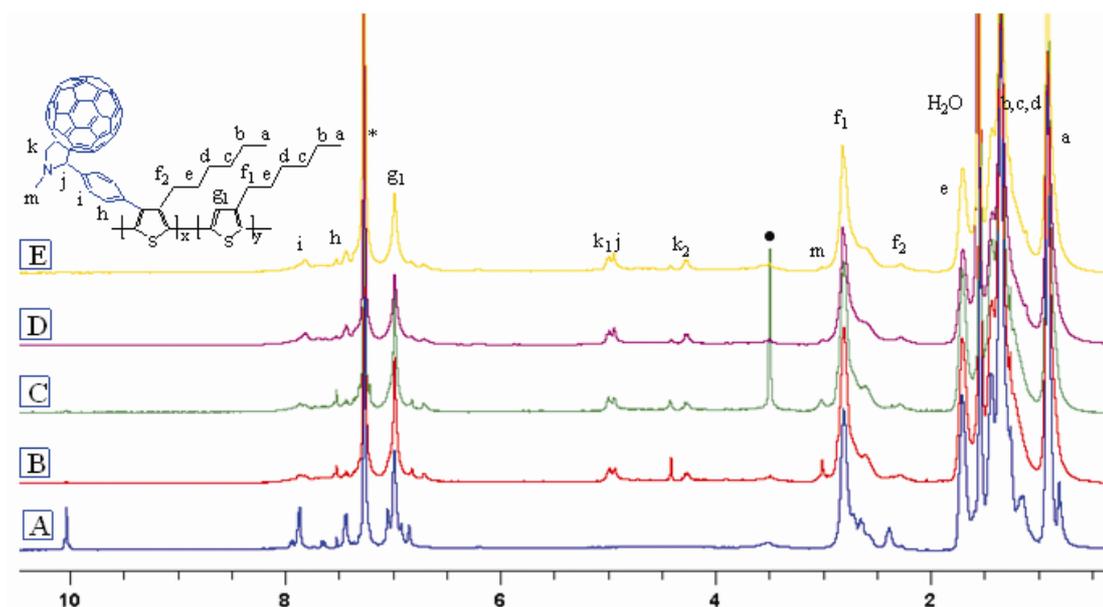


Figure S4. ^1H NMR spectra of **4-FPH-P3HT-1** (A, copied from Figure S4B), **C₆₀-Ph-P3HT-1** (B), **C₆₀-Ph-P3HT-2** (C), **C₆₀-Ph-P3HT-3** (D), and **C₆₀-Ph-P3HT-4** (E). All polymers were dissolved in deuterated chloroform, and spectra were recorded at room temperature. The solvent line of CHCl_3 is marked with an asterisk. The filled circle in curve C is due to the methanol impurity.

C₆₀-Ph-P3HT-1: δ (ppm): 7.80 (i, broad, 0.389H), 7.41 (h, broad, 0.379H), 6.97 (g_1 , broad, 0.805H), 4.98 (k_1 , double, $J = 10.4$ Hz, 0.193H), 4.93 (j, s, 0.206H), 4.25 (k_2 , double, $J = 10.4$ Hz, 0.195H), 3.0 (m, single, 0.554H), 2.81 (f_1 , broad, 1.704H), 2.35 (f_2 , broad, 0.394H), 1.69 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.89 (a, broad, 3H).

C₆₀-Ph-P3HT-2: δ (ppm): 7.80 (i, broad, 0.350H), 7.44 (h, broad, 0.335H), 6.98 (g_1 , broad, 0.826H), 5.00 (k_1 , double, $J = 10.4$ Hz, 0.175H), 4.93 (j, s, 0.173H), 4.25 (k_2 , double, $J = 10.4$ Hz, 0.176H), 3.0 (m, single, 0.533H), 2.81 (f_1 , broad, 1.784H), 2.35 (f_2 , broad, 0.349H), 1.70 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.91 (a, broad, 3H).

C₆₀-Ph-P3HT-3: δ (ppm): 7.85 (i, broad, 0.302H), 7.42 (h, broad, 0.310H), 6.91 (g_1 , broad, 0.845H), 4.98 (k_1 , double, $J = 10.4$ Hz, 0.157H), 4.92 (j, s, 0.160H), 4.25 (k_2 , double, $J = 10.4$ Hz, 0.153H), 3.0 (m, single, 0.450H), 2.81 (f_1 , broad, 1.70H), 2.35 (f_2 , broad, 0.313H), 1.70 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.90 (a, broad, 3H).

C₆₀-Ph-P3HT-4: δ (ppm): 7.80 (i, broad, 0.234H), 7.42 (h, broad, 0.235H), 6.97 (g_1 , broad, 0.882H), 4.99 (k_1 , double, $J = 10.4$ Hz, 0.113H), 4.93 (j, s, 0.125H), 4.27 (k_2 , double, $J = 10.4$ Hz, 0.117H), 3.0 (m, single, 0.349H), 2.81 (f_1 , broad, 1.73H), 2.35 (f_2 , broad, 0.235H), 1.70 (e, broad, 2H), 1.34 (bcd, broad, 6H), 0.91 (a, broad, 3H).

S2. Estimation of the substitution ratio of Br-P3HT-1,2,3,4, 4-FPh-P3HT-1,2,3,4, and C₆₀-Ph-P3HT-1,2,3,4

Table S1. Estimated substitution ratio (x/n) and the number average molecular weight (M_n) of C₆₀-Ph-P3HT-1,2,3,4

| polymer | Integral of H(g ₁) | Integral of H(a)/3 | x/n (%) ^a | y/n (%) ^a | Estimated M _n ^b |
|---------------------------------|--------------------------------|--------------------|----------------------|----------------------|---------------------------------------|
| Br-P3HT-1 | 0.805 | 1 | 20 | 80 | - |
| Br-P3HT-2 | 0.825 | 1 | 18 | 82 | - |
| Br-P3HT-3 | 0.844 | 1 | 16 | 84 | - |
| Br-P3HT-4 | 0.883 | 1 | 12 | 88 | - |
| | Integral of H(j) | Integral of H(a)/3 | | | |
| 4-FPh-P3HT-1 | 0.195 | 1 | 20 | 80 | - |
| 4-FPh-P3HT-2 | 0.175 | 1 | 18 | 82 | - |
| 4-FPh-P3HT-3 | 0.156 | 1 | 16 | 84 | - |
| 4-FPh-P3HT-4 | 0.117 | 1 | 12 | 88 | - |
| | Integral of H(k ₂) | Integral of H(a)/3 | | | |
| C₆₀-Ph-P3HT-1 | 0.195 | 1 | 20 | 80 | 81744 |
| C₆₀-Ph-P3HT-2 | 0.176 | 1 | 18 | 82 | 77657 |
| C₆₀-Ph-P3HT-3 | 0.153 | 1 | 15 | 85 | 73570 |
| C₆₀-Ph-P3HT-4 | 0.117 | 1 | 12 | 88 | 65395 |

^a For **Br-P3HT**, $x/n = 1 - \text{Integral of H(g}_1\text{)} / (\text{Integral of H(a)/3})$; for **4-FPh-P3HT** and **C₆₀-Ph-P3HT**, $x/n = \text{Integral of H(j or k}_2\text{)} / (\text{Integral of H(a)/3})$; $y/n = 1 - x/n$; $n = x + y$;

^b Estimated from the molecular structure assuming that the degree of polymerization of **C₆₀-Ph-P3HT** (i.e., n, which is the sum of x and y) are same to that of **P3HT**.

S3. UV-Vis absorption spectra of P3HT, Br-P3HT-1,2,3,4, 4-FPh-P3HT-1,2,3,4, and C₆₀-Ph-P3HT-1,2,3,4 in CDCl₃.

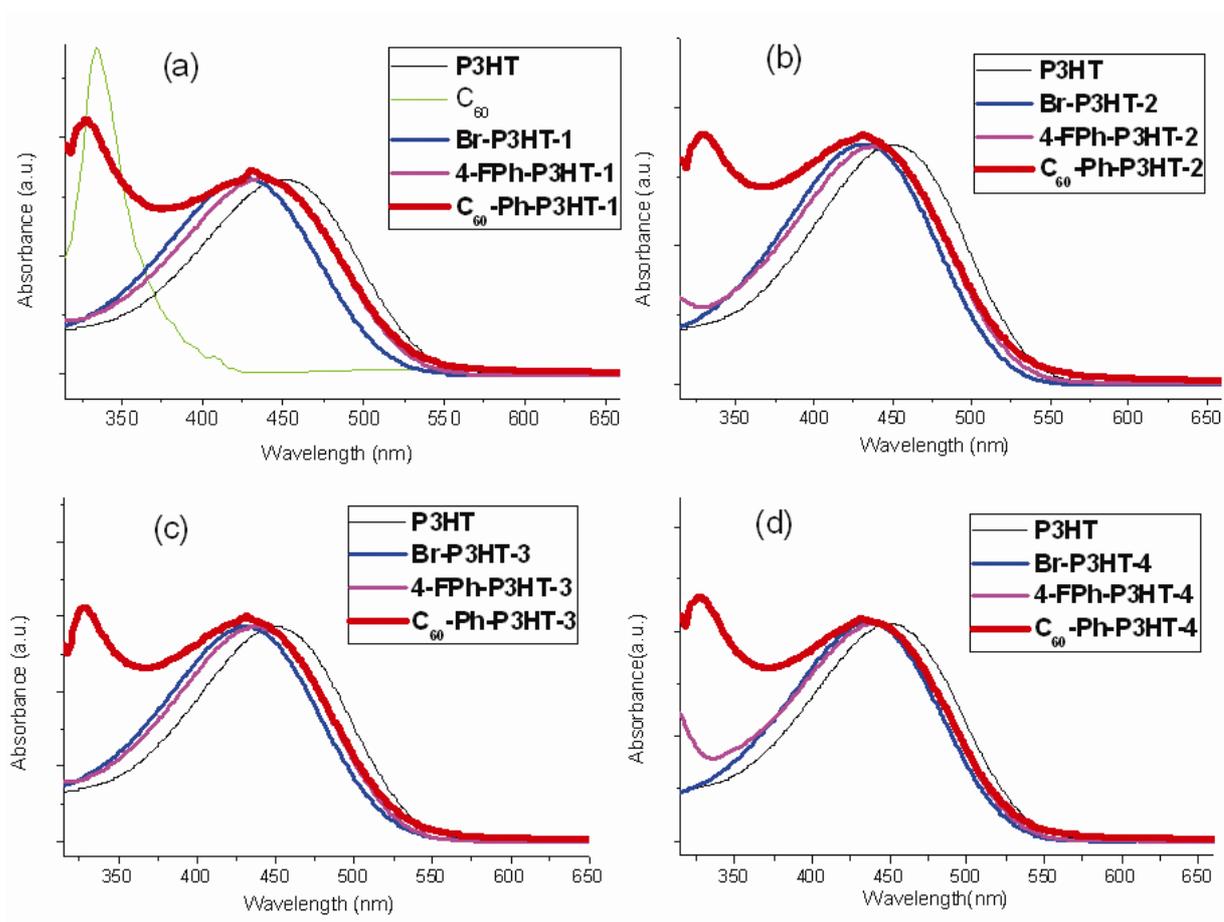


Figure S5. UV-Vis absorption spectra of P3HT, C₆₀, Br-P3HT, 4-FPh-P3HT and C₆₀-Ph-P3HT in CHCl₃. Substitution ratio: 1 - 20% (a); 2 - 18% (b); 3 - 15% (c); 4 - 12% (d).

S4. 3D AFM images of P3HT and C₆₀-Ph-P3HT-1,2,3,4

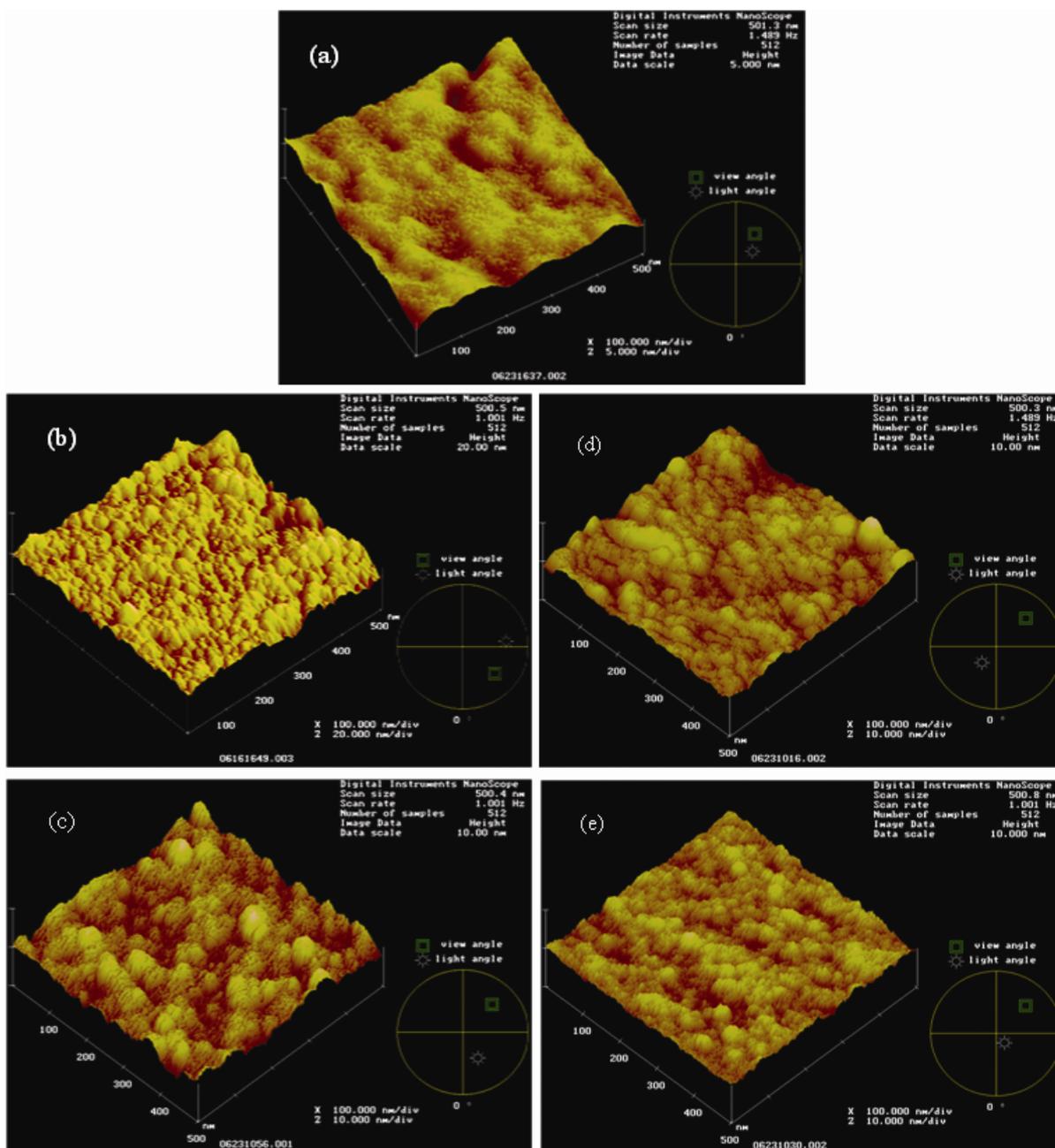


Figure S6. 3D AFM images of P3HT (a) and C₆₀-Ph-P3HT-1 (b), 2 (c), 3 (d), 4 (e).