

Supporting Information

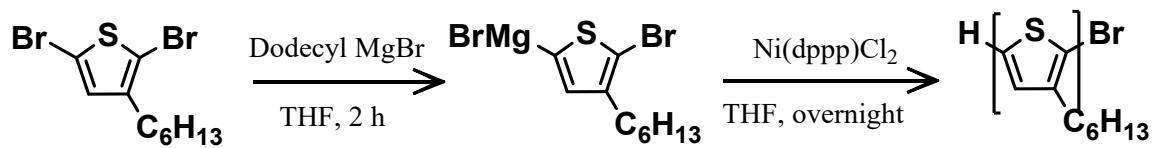
Precision Control of Molecular Weight Ratios in Fully Conjugated Block Copolymers Using Flow Synthesis

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Scheme S1. Synthetic route of monobrominated P3HT. (P3HT-Br)

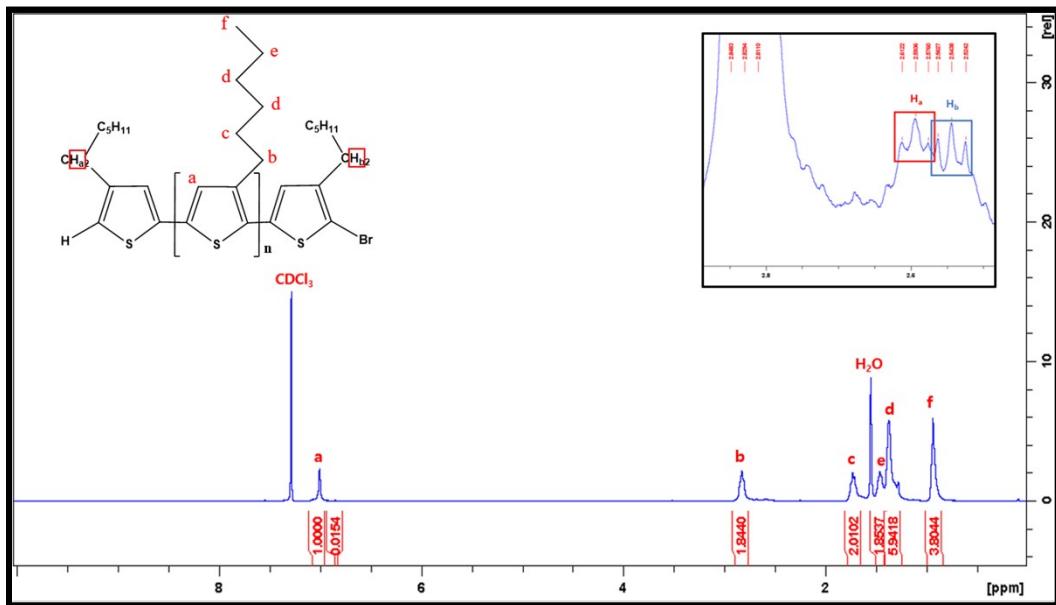


Fig. S1. ¹H NMR spectrum of P3HT-Br.

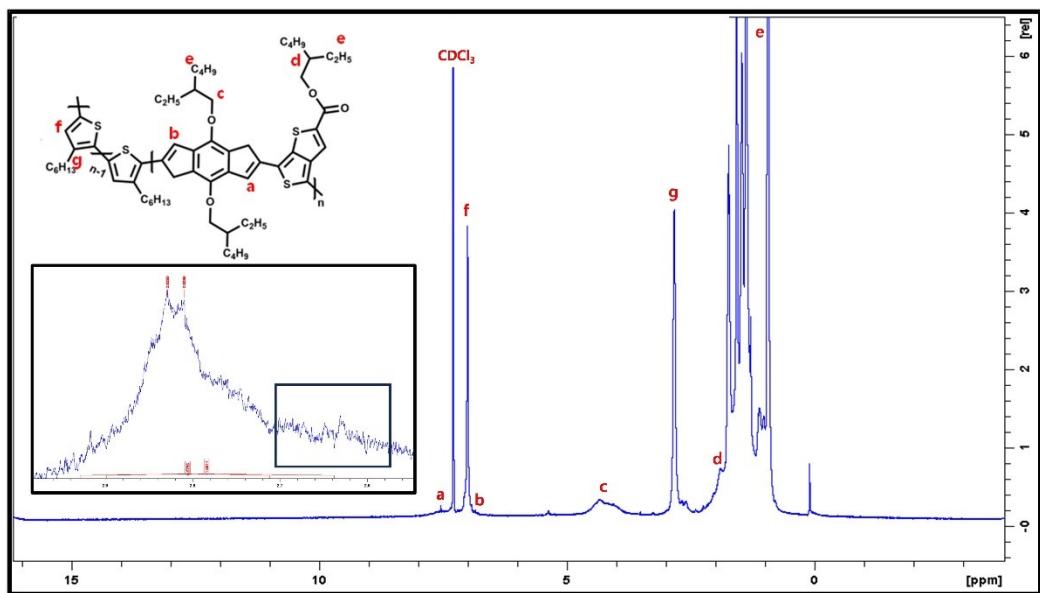


Fig. S2. ¹H NMR spectrum of P3HT-*b*-PTB7.

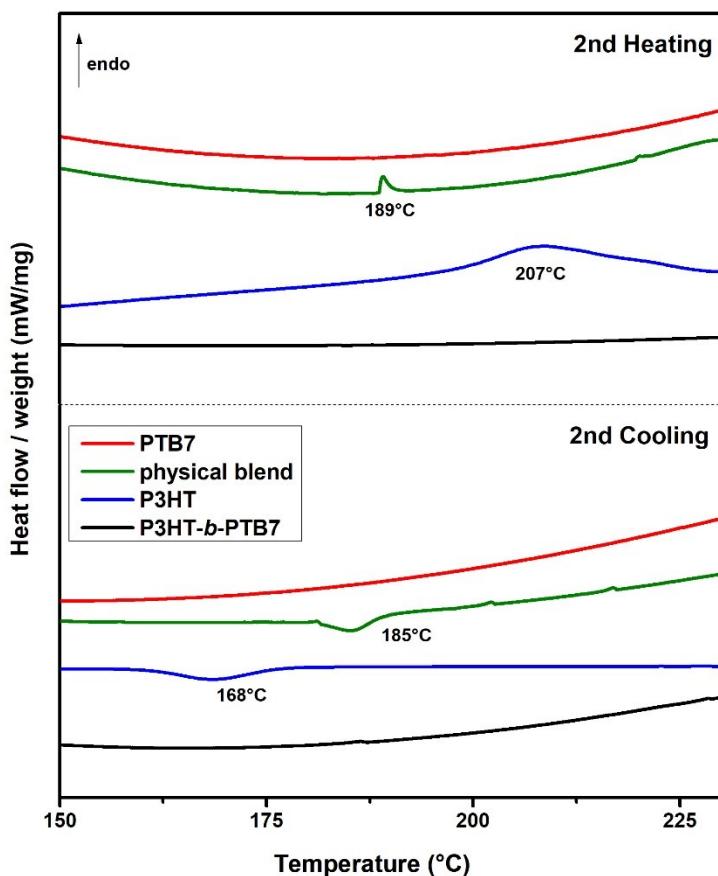


Fig. S3. The differential scanning calorimetry (DSC) graphs of P3HT, PTB7, P3HT-*b*-PTB7, and physical blend (P3HT:PTB7, 30:70) with heating/cooling rate of 10 °C min⁻¹ under nitrogen atmosphere.

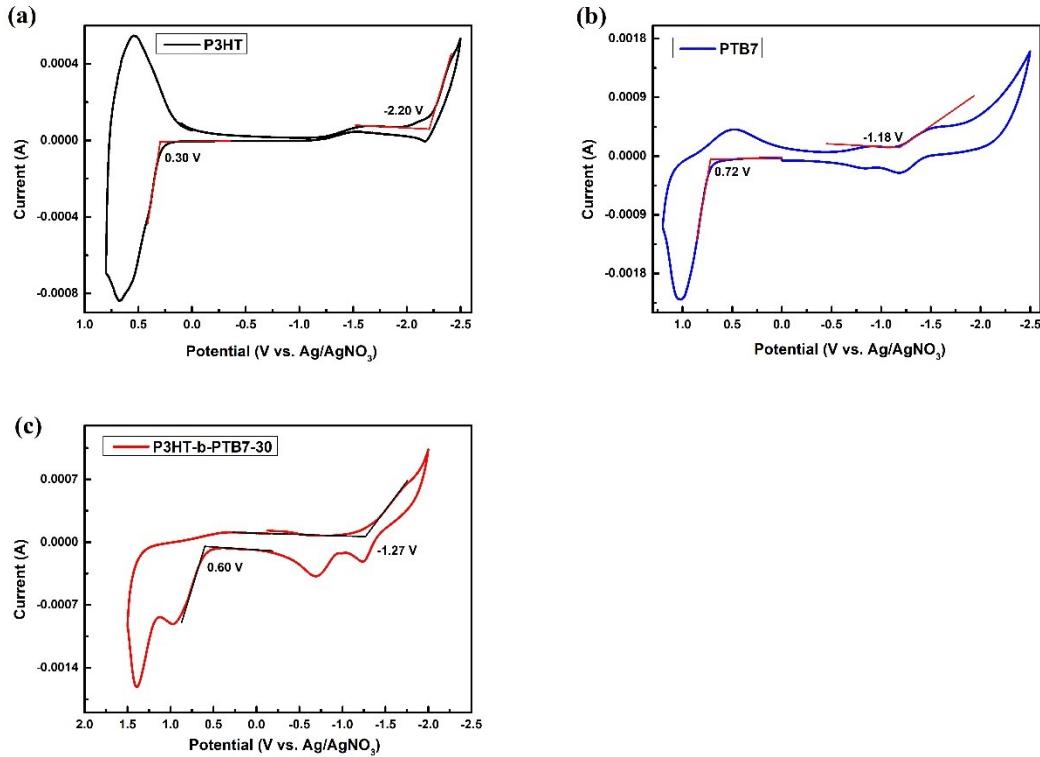


Fig. S4. Cyclic voltammogram of (a) P3HT, (b) PTB7, (c) P3HT-*b*-PTB7-30.

Table S1. Optical and electrochemical properties of P3HT, PTB7, and P3HT-*b*-PTB7-30.

| | E_{ox}^a (eV) | E_{red}^a (eV) | LUMO ^b (eV) | HOMO ^c (eV) |
|------------------------------|------------------------|-------------------------|------------------------|------------------------|
| P3HT | 0.30 | -2.20 | -2.49 | -4.99 |
| PTB7 | 0.72 | -1.18 | -3.51 | -5.41 |
| P3HT-<i>b</i>-PTB7-30 | 0.60 | -1.27 | -3.42 | -5.29 |

^a Obtained from onset potentials in the cyclic voltammogram. ^b LUMO = -4.8 - ($E_{\text{red}} - E_{1/2}^{\text{Fc/Fc}^+}$).

^c HOMO = -4.8 - ($E_{\text{ox}} - E_{1/2}^{\text{Fc/Fc}^+}$)

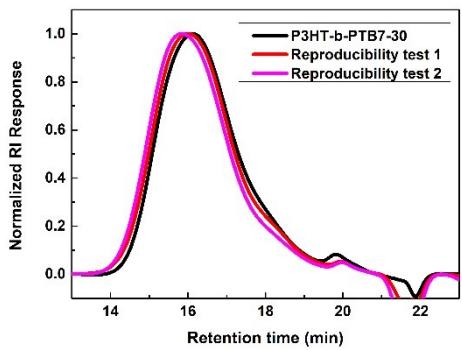


Fig. S5. Normalized GPC graph of three independent experiment for P3HT-*b*-PTB7-30.

Table S2. Molecular weight and dispersity of P3HT-*b*-PTB7-30 and products of reproducibility tests.

| polymer | M_n (kDa) | M_w (kDa) | \mathcal{D} |
|-------------------------|-------------|-------------|---------------|
| P3HT- <i>b</i> -PTB7-30 | 27.9 | 64.0 | 2.30 |
| Reproducibility test 1 | 28.0 | 74.7 | 2.67 |
| Reproducibility test 2 | 29.2 | 79.7 | 2.73 |

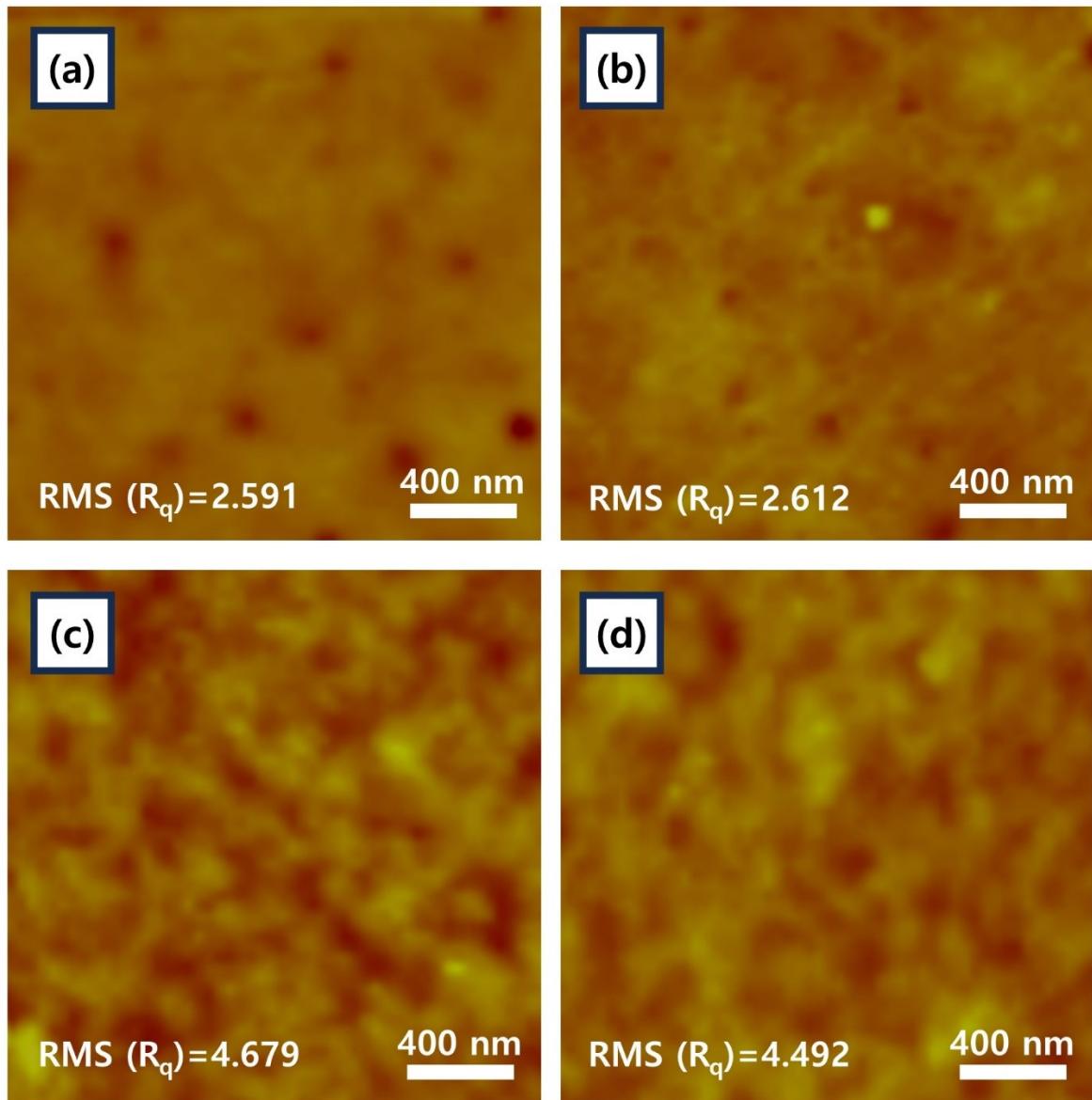


Fig. S6. AFM topography images ($2 \mu\text{m} \times 2 \mu\text{m}$) and calculated route mean square roughness (R_q) of fabricated OSC devices. (a) P1:PC₇₁BM, (b) P2:PC₇₁BM, (c) P3HT/PTB7:PC₇₁BM and (d) PTB7:PC₇₁BM