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Tuning the synthesis of fully conjugated block copolymers to minimize architectural heterogeneity

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1. NMR analysis of P3HT-b-PFTBT block copolymers

Compositions of P3HT-*b*-PFTBT block copolymers were determined by analysis of ^{1}H NMR data collected from deuterated chloroform solutions. The ratio of peak areas at 2.8 ppm (corresponding to α-CH_2 in P3HT) and at 2.0 ppm (corresponding to α-CH_2 of fluorine in PFTBT) were converted to mass fraction and are presented in Table 2 of the main text.

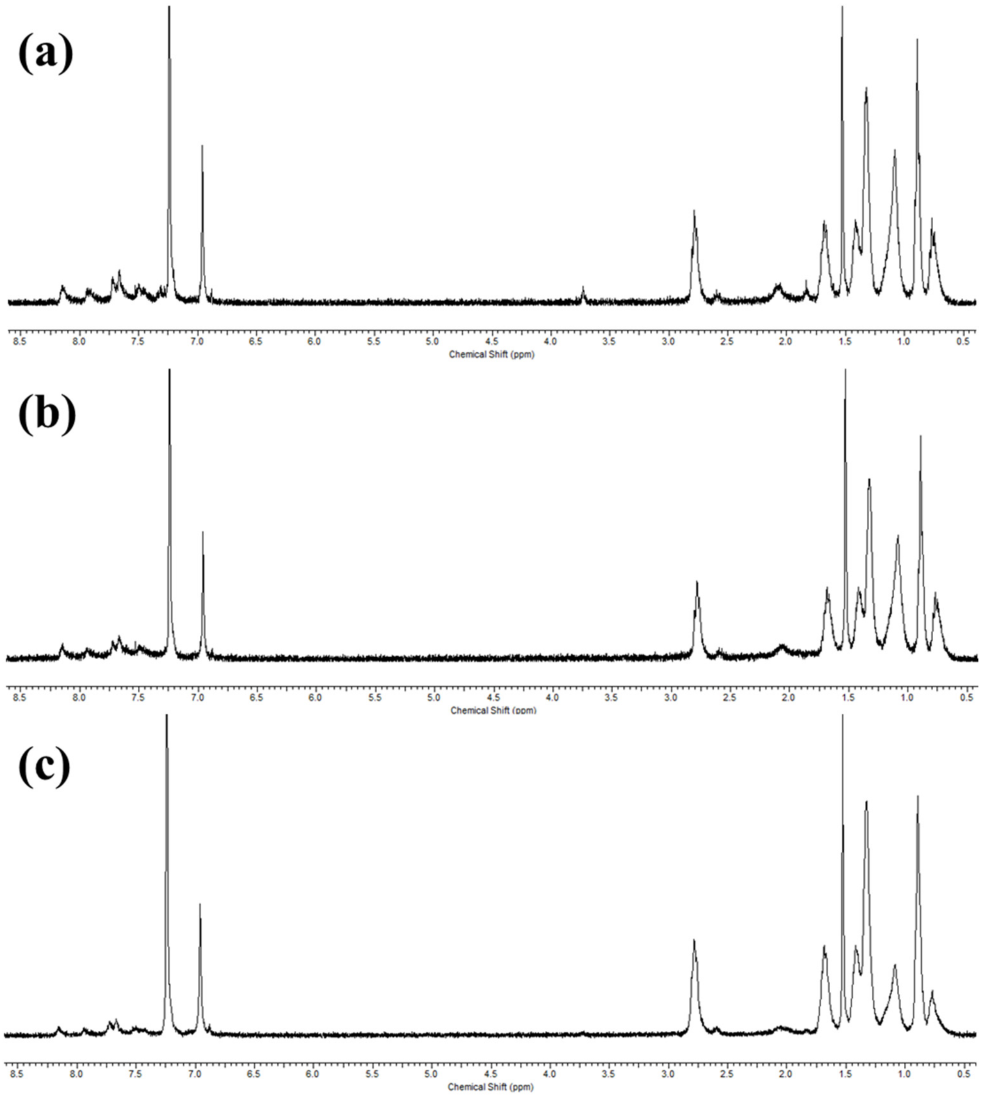

Figure S1. ^{1}H NMR spectra of P3HT-*b*-PFTBT block copolymers synthesized using different monomer feed ratios: (a) 0.91:1, (b) 1:1, and (c) 1:0.82 F:TBT (P3HT(1.0)-*b*-PFTBT(0.48), P3HT(1.0)-*b*-PFTBT(0.50), and P3HT(1.0)-*b*-PFTBT(0.55), respectively)

2. Model reaction to demonstrate coupling to P3HT chain ends

As shown in Figure 3a, a model reaction was designed to demonstrate coupling to the Br chains ends of P3HT, where a single unit of fluorene was attached to the end of P3HT chains. P3HT (50 mg) was reacted with 9,9-dioctylfulorene-2-boronic acid pinacol ester (12 mg) in toluene (12 mL) at 90 °C for 20 hr. The same procedure as the synthesis of P3HT-*b*-PFTBT block copolymers was employed, $Pd(PPh_3)_4$ (6.7 mg) as catalyst, Aliquat 336 (1 drop), and tetramethylammonium hydroxide solution (20 wt% in water, 5.0 mL). Figure S2 shows the disappearance of peak at 2.55 ppm, which corresponds to the bromine end group of P3HT, after the reaction takes place. Comparing the integration areas of peaks at 2.55 ppm corresponding to α-CH_2 at bromine end groups in the starting materials and at 1.96 ppm corresponding to α-CH_2 of fluorene at the end of the product, a conversion of the model reaction was determined as 92% as shown in Table S1. Thus, coupling of fluorene to bromine end groups of P3HT readily occurs, suggesting chain extensions to form block copolymer products are possible.

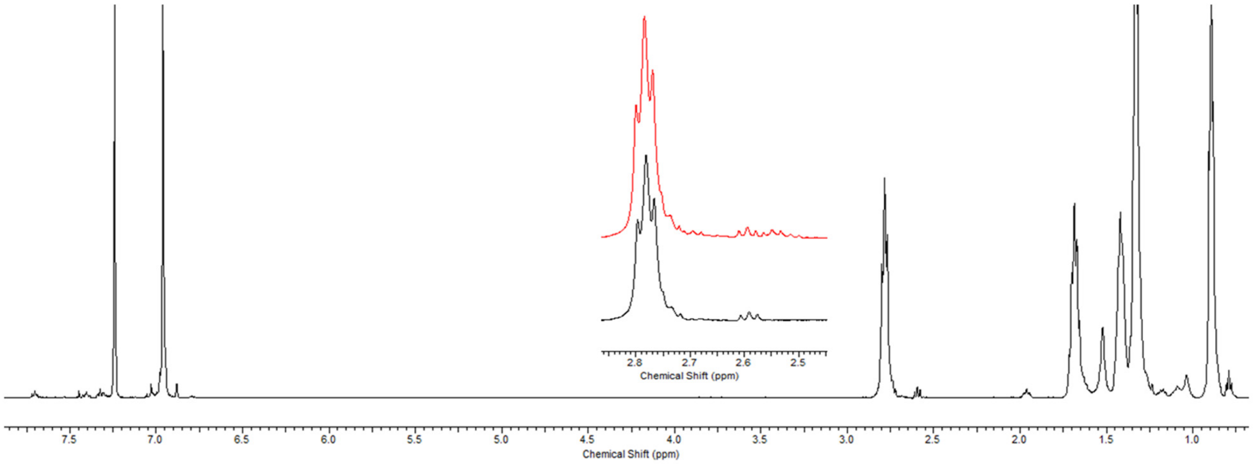

Figure S2. ^{1}H NMR spectrum of the product. Inset: comparison of ^{1}H NMR spectra of the starting material (red) and product (black). A peak at 2.55 ppm corresponding to α-CH_2 at bromine end groups in P3HT disappears over the model reaction.

Table S1. Analysis of model reaction

	Integration of peaks at (δ)			Conversion[d]
	2.60 ppm[a]	2.55 ppm[b]	1.96 ppm[c]	
Starting	1.00	0.91	N/A	92%
Product	1.00	N/A	1.68	

[a] 2H from αCH_2 at H-end. [b] 2H from αCH_2 at Br-end. [c] 4H from (αCH_2 x2) in fluorene. [d] Conversion was determined by comparison of integration areas of peaks normalized by the number of protons.

3. GPC analysis of a mixture of P3HT and PFTBT homopolymers

GPC traces of a mixture of P3HT(1.0) and a representative PFTBT homopolymer were investigated and compared with the P3HT-*b*-PFTBT block copolymer. For consistency, the volume fractions of P3HT and PFTBT in the physical blend were prepared to match the block copolymer (P3HT:PFTBT ~ 68:32). The GPC trace of the P3HT/PFTBT blend retains features of both homopolymers; the RI trace does not distinguish between the two polymers given their similar retention times, but the UV-vis absorption becomes broader as expected. Thus, the GPC data is qualitatively different than the data from the P3HT(1.0)-*b*-PFTBT(0.55) block copolymer.

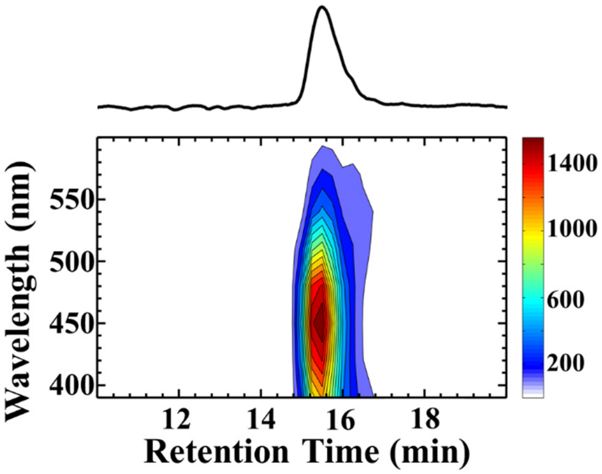

Figure S3. GPC traces of RI (top) and UV-Vis (bottom) detectors of a mixture of P3HT(1.0) and a representative PFTBT homopolymer. The volume fractions of P3HT and PFTBT were prepared according to those of P3HT(1.0)-*b*-PFTBT(0.55) (P3HT:PFTBT ~ 64:36 by mass).

4. RSoXS data from P3HT-b-PFTBT block copolymers

RSoXS data from P3HT-*b*-PFTBT block copolymers are shown in Figure S4 as intensity versus scattering vector q. The data corresponds to the Kratky plot ($I(q)q^2$ vs. q) shown in Figure 7 of the main text.

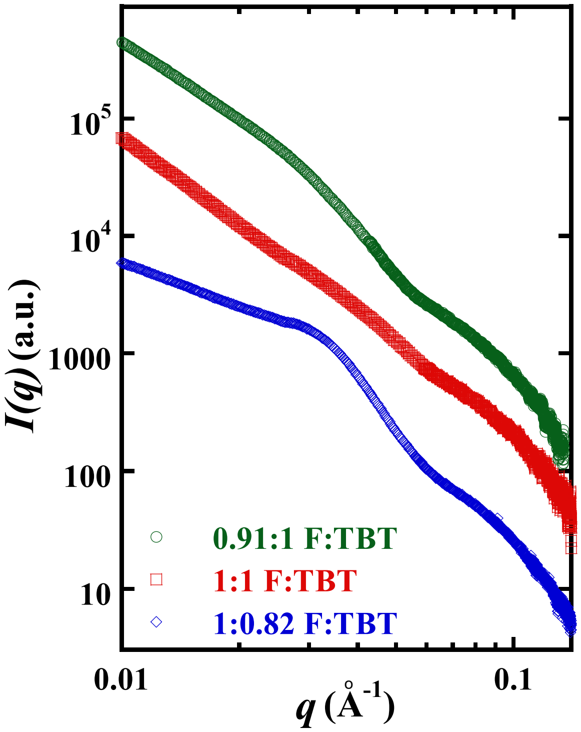

Figure S4. RSoXS data from P3HT-*b*-PFTBT block copolymers synthesized using different monomer feed ratios: 0.91:1, 1:1, and 1:0.82 F:TBT (P3HT(1.0)-*b*-PFTBT(0.48), P3HT(1.0)-*b*-PFTBT(0.50), and P3HT(1.0)-*b*-PFTBT(0.55), respectively). Intensities are vertically shifted for comparison. Less homopolymer impurities result in stronger microphase separation.