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Electronic supplementary information

Push-pull architecture eliminates chain length effects on exciton dissociation

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1. Calculated overlap integrals

The overlap integral (J) describes the degree of spectral overlap between donor emission and acceptor absorbance.[1]

$$J = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \qquad (1)$$

$F_D(\lambda)$ is the corrected fluorescence emission of the donor with total area under the curve normalized to one and $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor. We calculate an overlap integral for energy transfer from P3HT to PPT6BT using absorbance and fluorescence spectra (Fig. S1) of $J = 5.9 \times 10^{13}$ M^{-1} cm^{-1} λ^4 and the overlap integral for energy transfer from PPT6BT to P3HT, $J = 5.9 \times 10^{11}$ M^{-1} cm^{-1} λ^4.

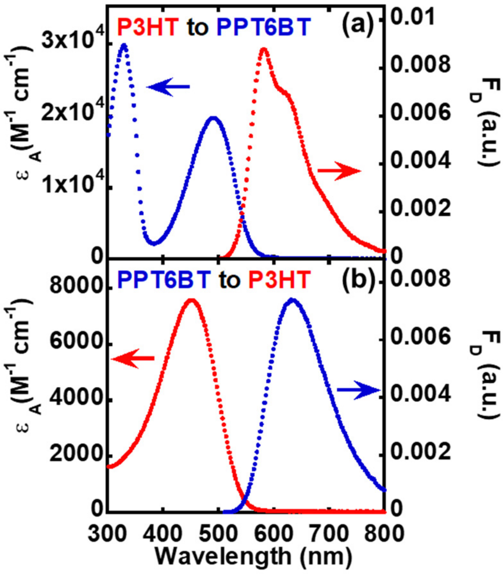


Fig. S1 Spectral overlap of donor emission and acceptor absorbance to qualitatively illustrate energy transfer from (a) P3HT to PPT6BT and (b) PPT6BT to P3HT.

2. Synthetic parameters used to modulate chain length

To adjust the molecular weight (chain length) of P3HT macroreagents (Table S1), the molar ratio of monomer to catalyst (mon:cat) was tuned (Table S2). To adjust the molecular weight (chain length) of the PPT6BT block during the chain extension reaction, an asymmetric molar ratio of the condensation monomers (T6BT:P) was used. Additionally, for P3HT(7), the acetone fraction was collected during Soxhlet purification to ensure a low molecular weight P3HT macroreagent.

Table S1. Synthesis conditions and molecular weight characterization of P3HT macroreagents

Polymer	Cat:mon	M_n (g mol^{-1})^b	$Đ^c$
P3HT(7)	0.05^a	1100	1.2
P3HT(23)	0.025	3900	1.1
P3HT(29)	0.02	4800	1.2
P3HT(31)	0.02	5100	1.2

[a] Acetone fraction collected during Soxhlet purification
[b] From ^{1}H NMR
[c] From GPC, PS-relative standards

Table S2. Synthesis conditions and molecular weight characterization of block copolymers

Block copolymer	P3HT M_n (g mol^{-1})^b	T6BT:P	PPT6BT M_n (g mol^{-1})^b
P3HT(7)-*b*-PPT6BT(8)	1100	0.75	5500
P3HT(7)-*b*-PPT6BT(10)	1100	0.90	7300
P3HT(23)-*b*-PPT6BT(5)	3900	0.75	3700
P3HT(29)-*b*-PPT6BT(2)	4800	0.45	1500
P3HT(29)-*b*-PPT6BT(10)	4800	0.90	7300
P3HT(31)-*b*-PPT6BT(6)	5100	0.90	4200

[a] Acetone fraction collected during Soxhlet purification
[b] From ^{1}H NMR

3. Particle size distributions for block copolymers in solution

Multiangle dynamic light scattering (DLS) was used to demonstrate that the block copolymers can be dissolved as isolated chains in dilute solutions. Assuming persistence lengths of ~ 3 and 4 nm for P3HT and PPT6BT, respectively, expected r_h values of ~3-5 nm are calculated using the freely-rotating worm-like chain model. Measured r_h values, in addition to unimodal particle size distributions, confirm isolated block copolymer chains with no aggregation in solution (Fig. S2).

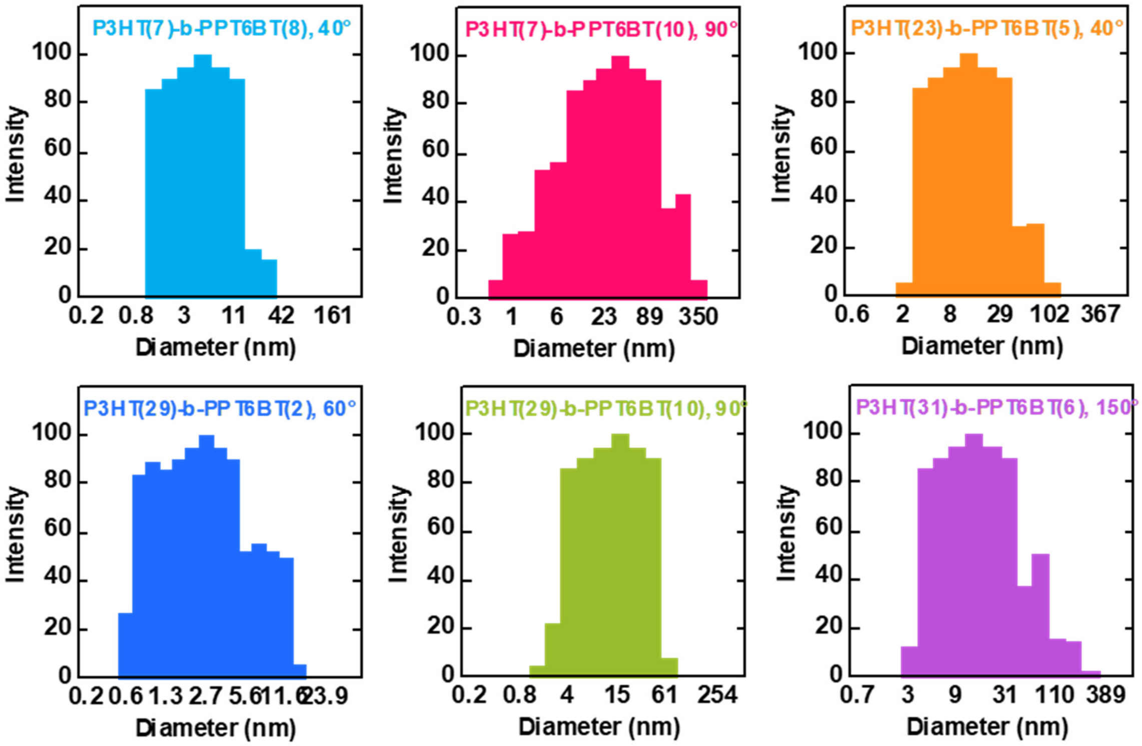


Fig. S2 Multiangle dynamic light scattering of block copolymers in chloroform solution. Representative unimodal particle size distributions.

4. Procedure used to quantify energy transfer from P3HT to PPT6BT and charge transfer from PPT6BT to P3HT

Steady state absorbance and photoluminescence spectra are recorded of isolated block copolymer chains in solution. Linear combinations of homopolymer absorbance and emission spectra nicely describe the block copolymer spectra as shown in the main text. For each sample, we deconvolute the block copolymer absorbance spectrum to determine the absorbance fraction of P3HT and the absorbance fraction of PPT6BT as a function of wavelength. We deconvolute the block copolymer emission spectrum to determine the contribution of each block individually to overall block copolymer emission. To determine the quantum yields (Φ) of P3HT homopolymer, PPT6BT homopolymer, and P3HT-*b*-PPT6BT block copolymers, we compare the absorbance and emission spectra to a dye of known quantum yield.

First, we quantify energy transfer from P3HT to PPT6BT. By comparing the emission contribution of the P3HT block in each P3HT-*b*-PPT6BT sample to the quantum yield of P3HT homopolymer solution, we calculate the fraction of quenched P3HT excited states when P3HT is linked to PPT6BT in the block copolymer (f_Q). As discussed in the main text, we attribute any quenching of the P3HT block to excited state energy transfer from P3HT to PPT6BT. Next, we calculate the quantum yield of the PPT6BT acceptor block (Φ_A) by comparing the emission contribution of the PPT6BT block in the block copolymer to the quantum yield of PPT6BT homopolymer solution. A Φ_A greater than 1 indicates that the quantum yield of PPT6BT is enhanced when it is linked to P3HT in a block copolymer.

As discussed in the main text, we believe charge transfer occurs only by hole transfer from PPT6BT to P3HT. To quantify charge transfer, we calculate an expected block copolymer quantum yield by assuming all quenched P3HT excited states simply undergo energy transfer to PPT6BT followed by radiative decay in the PPT6BT block. We quantify overall emission quenching in the block copolymer by comparing the *expected* block copolymer quantum yield to the *measured* block copolymer quantum yield (data presented in Fig. 5). Any overall quenching is interpreted as charge transfer from PPT6BT to P3HT.

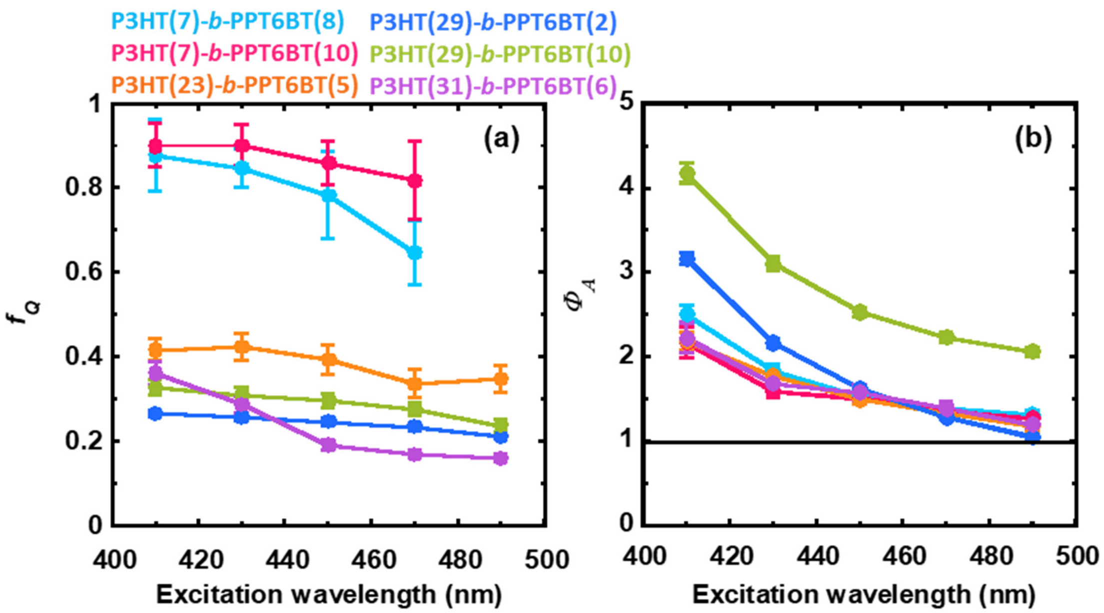


Fig. S3 Photoluminescence quenching analysis of P3HT-*b*-PPT6BT block copolymers. (a) Fraction of quenched P3HT excited states (f_Q) when P3HT is covalently linked to PPT6BT in a block copolymer. (b) Quantum yield of the PPT6BT acceptor (Φ_A) when PPT6BT is covalently linked to P3HT in a block copolymer.

5. Model to calculate exciton diffusion length along P3HT chains in chloroform solution

The exciton density profile along the P3HT chains was modeled using an equation for one dimensional diffusion.[2-4] We assume energy transfer to PPT6BT is the only source of P3HT exciton quenching in the block copolymer not present in the P3HT homopolymer. The exciton density profile along the P3HT homopolymer is modeled as:

$$D\frac{d^2y(x)}{dx^2}-\frac{y(x)}{\tau}+k_{gen}c=0 \tag{2}$$

Where D is the diffusion coefficient, $y(x)$ is the exciton density as a function of distance along the chain, τ is the exciton lifetime in the absence of the quencher (assumed to be ~ 600 ps for P3HT[5, 6]), and $k_{gen}c$ is the rate of exciton formation. This differential equation can be solved analytically assuming a constant density profile along the chain and using boundary conditions:

$$\frac{dy(0)}{dx}=\frac{dy(L)}{dx}=0 \tag{3}$$

Where the contour length of the chain extends from 0 to L and the PPT6BT block is linked at L.

The exciton density profile along the P3HT block of P3HT-b-PPT6BT is modeled as:

$$D\frac{d^2y(x)}{dx^2}-\frac{y(x)}{\tau}+k_{gen}c-k_{FRET}(x)y(x)=0 \tag{4}$$

Where k_{FRET} is the quenching rate due to Förster resonance energy transfer (FRET).[1] The equation for calculating the rate of energy transfer is:

$$k_{FRET}=\frac{1}{\tau}\left(\frac{R_0}{L-x}\right) \tag{5}$$

Where R_0 is the Förster distance, defined as the donor-acceptor distance at which FRET efficiency drops to 50%.[1] The PPT6BT block is linked at L and therefore $L-x$ is the distance from the P3HT-PPT6BT donor-acceptor interface. R_0 is calculated using Equation 6.

$${R_0}^6=\frac{9(ln10)\kappa^2\Phi_{P3HT}}{128\pi^5Nn^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4d\lambda \tag{6}$$

κ^2 describes the relative orientation of the transition dipoles of the donor and acceptor, assumed to be 2/3, Φ_{P3HT} is the quantum yield of P3HT (~ 0.25), N is Avogadro's number, and n is the refractive index of the solvent ($n_{chloroform}$ = 1.45). We calculate an R_0 value of approximately 2.4 nm. The exciton density profile along the block copolymer must be solved numerically using boundary conditions:

$$\frac{dy(0)}{dx}=0;\ y(L-c)=0 \tag{7}$$

Mathematically, assuming the exciton density goes to 0 at L would result in a singularity; the donor and acceptor are directly linked. Therefore, we assume that the distance (c) from L at which the FRET rate constant becomes approximately 2 orders of magnitude greater than radiative emission ($k_{rad}=\Phi_{P3HT}/\tau \sim 4 \times 10^8$ s^{-1}), the exciton density is effectively 0. At a c value of 1.5 nm away from the donor-acceptor interface k_{FRET} is ~ 3×10^{10} s^{-1} and thus, the exciton density is assumed to go to 0 at this point.

f_Q is modeled by comparing the integrated exciton density along the length of the P3HT homopolymer and block copolymer. The data was fit using a diffusion coefficient, D = 1.0 nm^2 s^{-1}. Solving $L_D=\sqrt{D\tau}$ for the exciton diffusion length, L_D, we obtain L_D = 2.5 nm.

6. Estimated number of monofunctional P3HT-PT6BT chains in each sample

Due to the statistical nature of polymers and the step-growth mechanism used to synthesize the PPT6BT block, we expect there to be a relatively broad distribution of chain lengths in all synthesized samples of P3HT-*b*-PPT6BT. We can calculate the expected fraction of *i*-mers (*i* being the number of repeat units) based on the dispersity (*Đ*) and number averge molecular weight (M_n) using the Shulz-Zimm distribution.[7]

$$P(M_i) = \frac{Z^{z+1}}{\Gamma(z+1)} \frac{{M_i}^{z-1}}{{M_n}^{z}} exp\left(-\frac{zM_i}{M_n}\right) \tag{8}$$

$$z = \frac{1}{Đ - 1} \tag{9}$$

$P(M_i)$ is the probability of a polymer chain with i repeat units, z describes the dispersity according to Equation 9, and Γ is the gamma function. For relatively broad molecular weight distributions, *Đ* ~ 2, the mol fraction of *i*-mers decreases monotonically with *i*. Therefore, chains functionalized with a single PPT6BT repeat unit, referred to as P3HT-PT6BT, have the highest probability of forming relative to any other *i*-mer. We estimate a *Đ* of 2 in the PPT6BT block of P3HT(29)-*b*-PPT6BT(2), consistent with expectations for a step-growth polymerization mechanism.[7] Using Equation 8, we calculate that ~ 40% of P3HT chains within the P3HT(29)-b-PPT6BT(2) sample are likely to be functionalized with only one PT6BT repeat unit (P3HT-PT6BT). Furthermore, assuming these P3HT-PT6BT chains do not effectively generate CT states, we calculate an expected CT state yield for the different X_n values of PPT6BT present in all the block copolymers examined. Thus, if there were not efficient exciton dissociation from P3HT-PT6BT chains, we expect the CT state yield for P3HT(29)-*b*-PPT6BT(2) would be only ~ 12% (Table S2). Nevertheless, we measure a CT state yield of ~ 23%, demonstrating efficient exciton dissociation despite a single push-pull functionality.

Table S2 Fraction of P3HT-PT6BT chains and expected CT state yield

	***Đ* = 2**	
PPT6BT X_n	x_1[a)]	Expected CT[b)]
2	0.39	12%
5	0.18	18%
6	0.15	18%
10	0.09	19%

[a)] fraction of mono-funtionalized P3HT chains; [b)] expected CT state yield if no CT observed from PPT6BT X_n = 1

It is surprising that no chain length effects are observed in PPT6BT, particularly when the molecular weight is low (average chain length is short). We demonstrate that low molecular weight PPT6BT maintains the same optical properties as the high molecular weight polymer by measuring the absorption coefficient per monomer of PPT6BT (at 490 nm) as a function of PPT6BT block M_n. Because the absorption coefficient is based on moles of PT6BT present, it is necessary to normalize by weight fraction and X_n of the PPT6BT block. A constant absorption coefficient that is independent of molecular weight is strong evidence that optical properties of PPT6BT with $X_n = 2$ are representative of a high molecular weight polymer (Fig. S3).

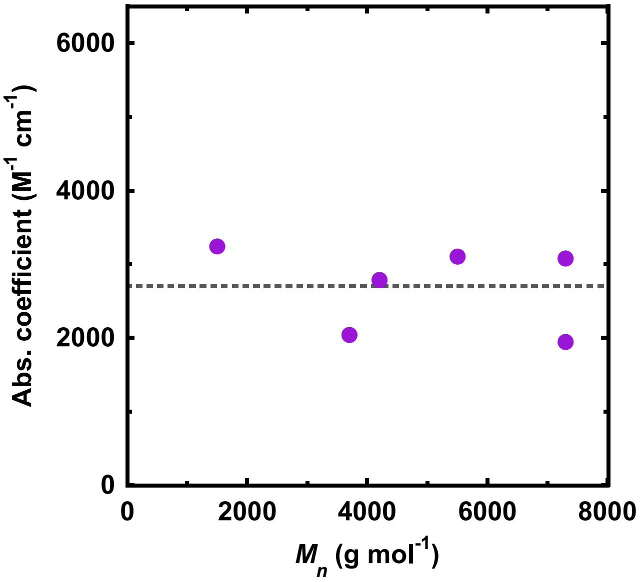
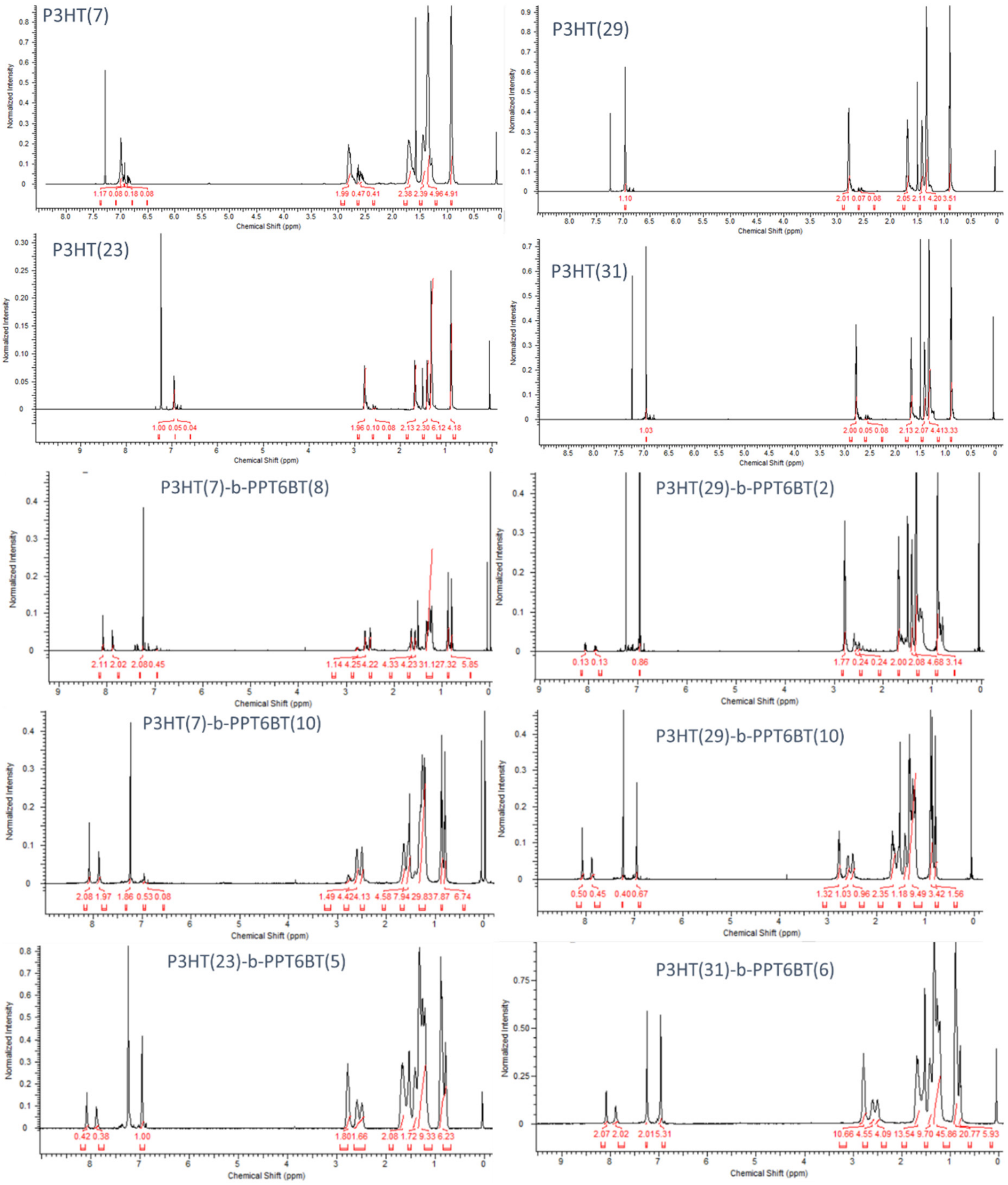


Fig. S4 Absorbance per PT6BT monomer of each block copolymer sample as a function of PPT6BT block molecular weight.

7. NMR spectra


P3HT(7)

P3HT(29)

P3HT(23)

P3HT(31)

P3HT(7)-b-PPT6BT(8)

P3HT(29)-b-PPT6BT(2)

P3HT(7)-b-PPT6BT(10)

P3HT(29)-b-PPT6BT(10)

P3HT(23)-b-PPT6BT(5)

P3HT(31)-b-PPT6BT(6)

Fig. S5 NMR spectra of P3HT macroreagents and block copolymers measured in deuterated chloroform on a Bruker 850 MHz instrument (360 or 500 MHz).

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