

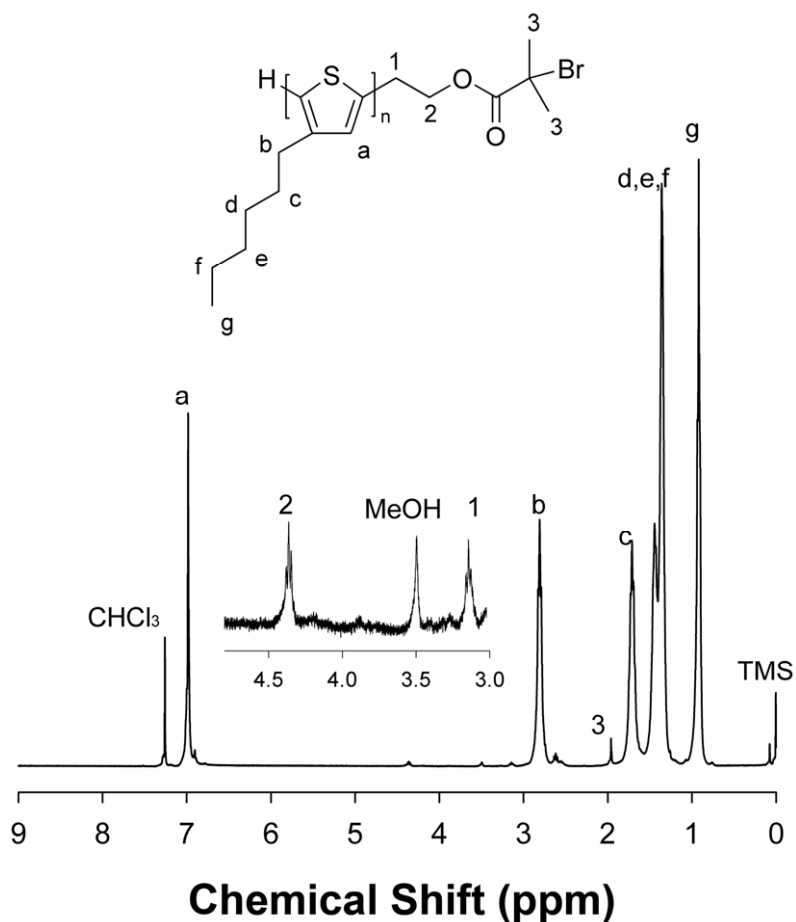
## Supplementary Information

### Synthesis and Photophysical Property of Well-Defined Donor-Acceptor Diblock Copolymer Based on Regioregular Poly(3-hexylthiophene) and Fullerene

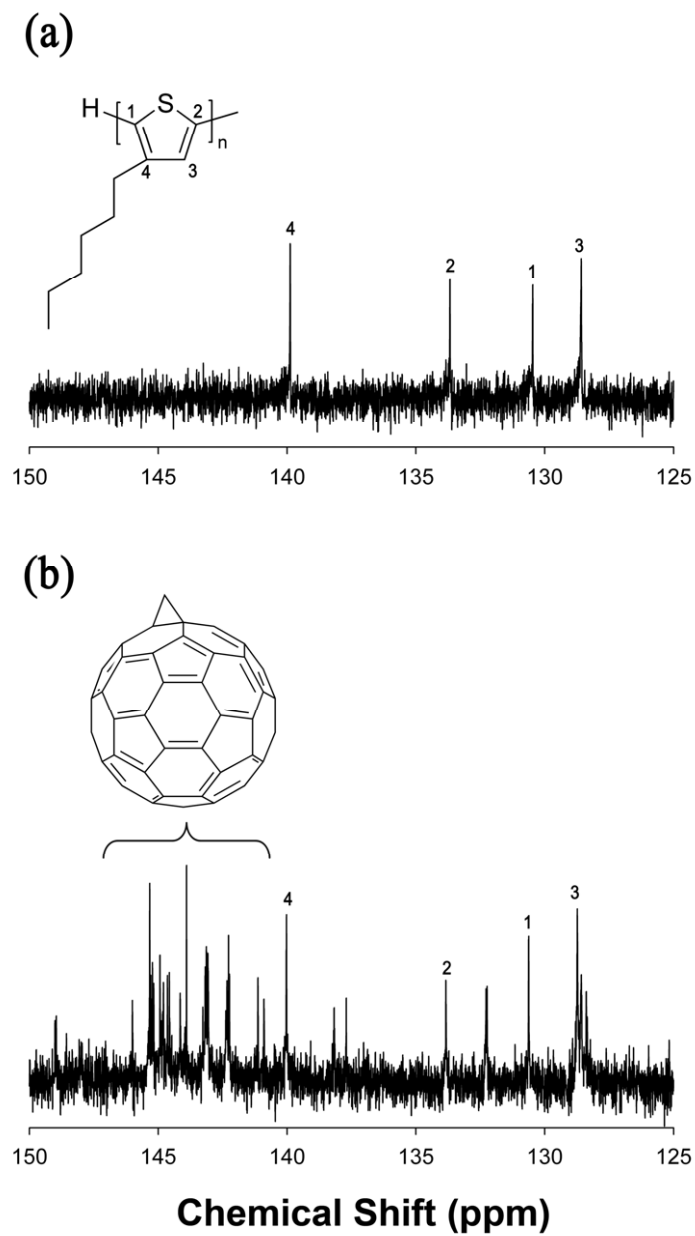
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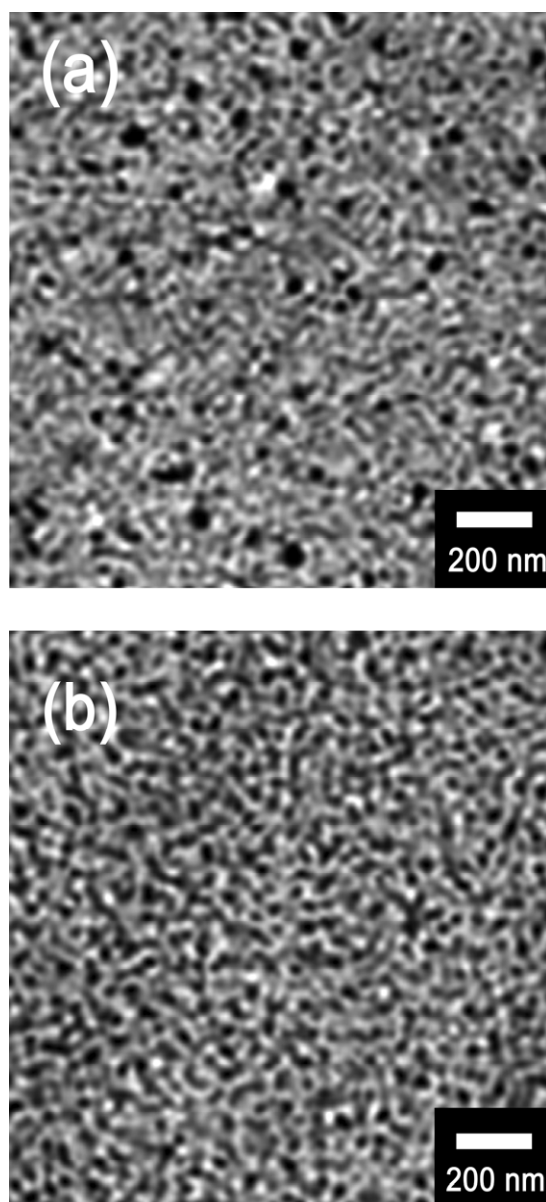
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USA.



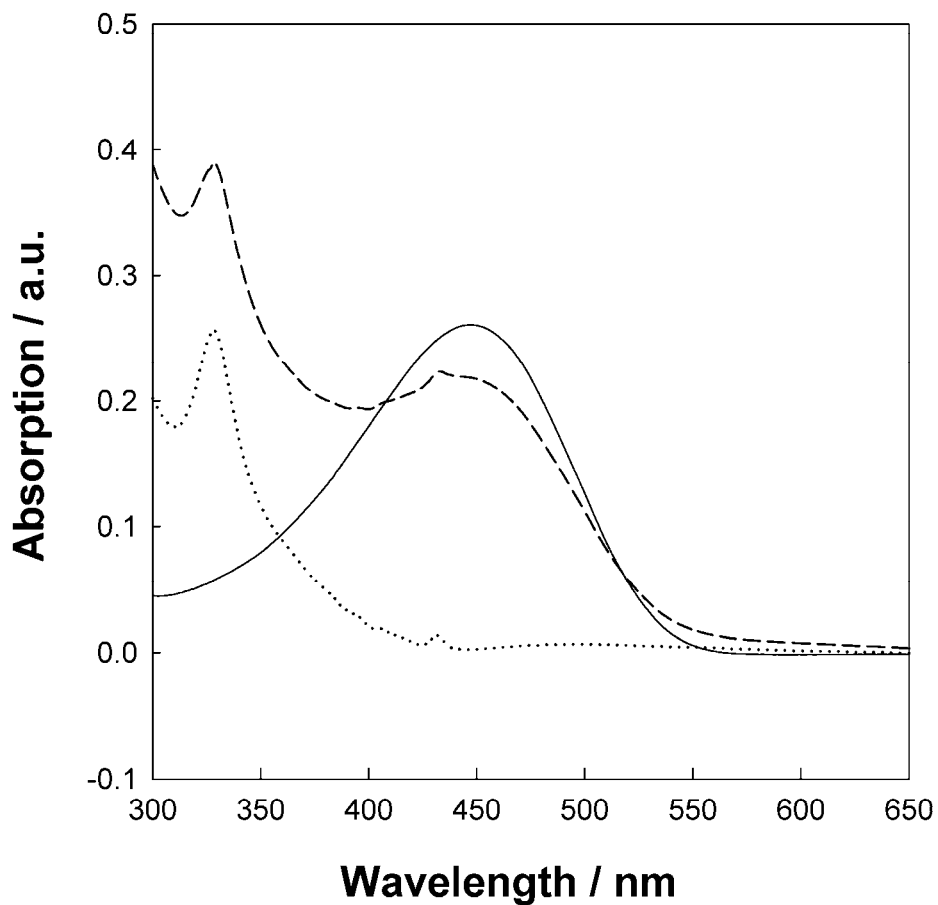
**Figure S1.** <sup>1</sup>H NMR spectrum of P3HT-macroinitiator in CDCl<sub>3</sub>.



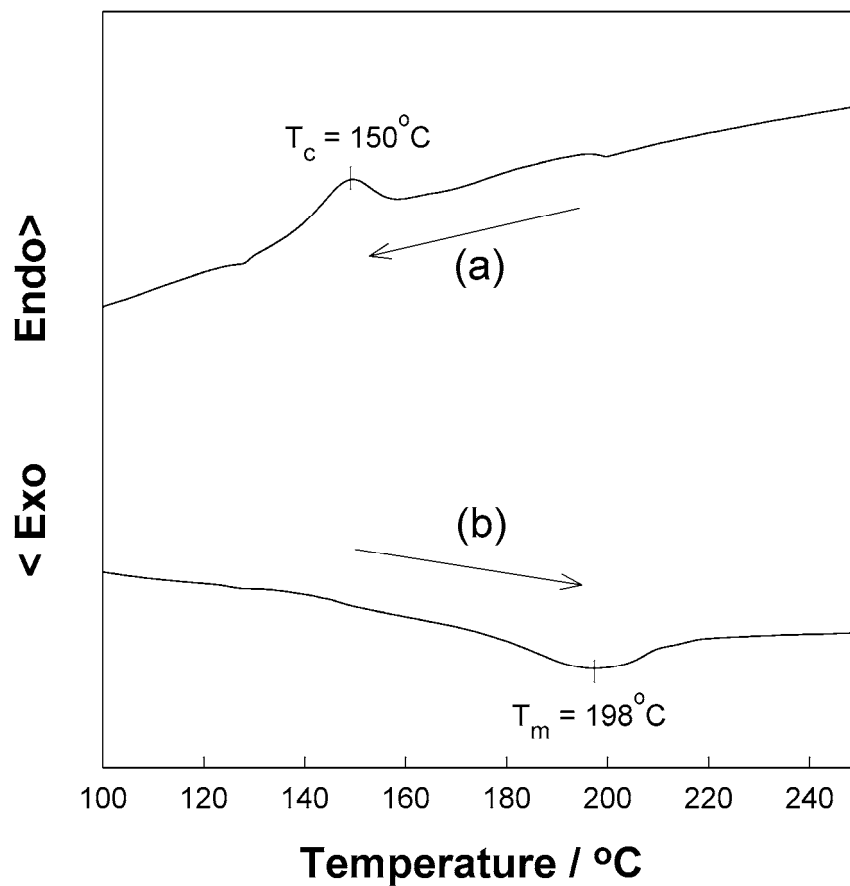
**Figure S2.** Aromatic region of  $^{13}\text{C}$  NMR spectra of (a) P3HT-*b*-P(MMA-*r*-HEMA) and (b) P3HT-*b*-C<sub>60</sub> diblock copolymer in CDCl<sub>3</sub>.



**Figure S3.** TEM images of the self-assembled structure of P3HT-*b*-C<sub>60</sub> diblock copolymer (a) before and (b) after thermal annealing. Thin films were prepared by spin-coating on silicon wafers with a native oxide surface layer from 1 wt% CHCl<sub>3</sub>/pyridine solution (95/5 v/v), and heated to 230 °C under vacuum for 5 h, and slowly cooled down to 150 °C and then annealed at 150 °C for 24 h.



**Figure S4.** UV-Visible spectra of P3HT-macroinitiator (solid line), PCBM (dotted line), and P3HT-*b*-C<sub>60</sub> diblock copolymer (dashed line) in chloroform solution.



**Figure S5.** DSC thermogram of the P3HT-*b*-C<sub>60</sub> diblock copolymer, measured at a cooling (a) and heating (b) rate of 10 °C/min.

**Table S1.** Elemental analysis of P3HT-macroinitiator, P3HT-*b*-P(MMA-*r*-HEMA), and P3HT-*b*-C<sub>60</sub> diblock copolymer.

Polymer	Carbon		Hydrogen		Sulfur	
	Calcd. <sup>a</sup>	Found	Calcd.	Found	Calcd.	Found
P3HT-macroinitiator	71.63	70.79	8.38	8.43	18.92	19.83
P3HT- <i>b</i> -P(MMA- <i>r</i> -HEMA)	67.63	66.21	8.23	8.40	13.19	15.63
P3HT- <i>b</i> -C <sub>60</sub>	77.13	69.91	5.81	5.99	8.62	9.86

<sup>a</sup> Calculated by integration of <sup>1</sup>H NMR signals where nine PCBAs are attached to each of the block copolymer.