

**Electronic Supplementary Information**  
**Synthesis and Characterization of Polyisoprene-*b*-Polystyrene-*b*-  
Poly(3-Hexylthiophene) Triblock Copolymer**

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## Experimental

### Materials

All reactions were conducted under pre-purified nitrogen, using oven-dried glassware. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless otherwise noted. All solvents were freshly distilled prior to use. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Chloroform was distilled and collected over molecular sieves. Allyl-terminated poly(3-hexylthiophene) was synthesized according to previously published procedure.<sup>1</sup>

<sup>1</sup>H NMR spectra of the polymers were recorded on a Bruker Advance III 500 MHz spectrometer at 30 °C. <sup>1</sup>H NMR data are reported in parts per million as chemical shift relative to tetramethylsilane (TMS) as the internal standard. Spectra were recorded in CDCl<sub>3</sub>.

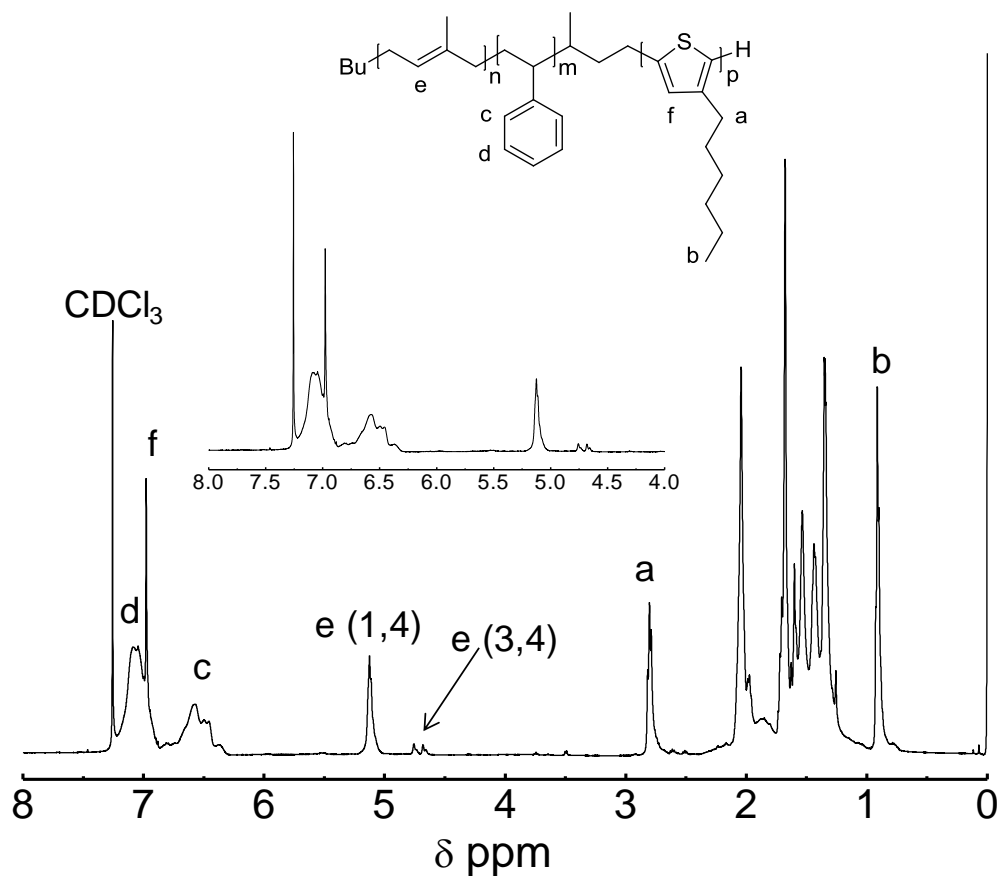
The polyisoprene-*b*-polystyrene segment was prepared by *living* anionic polymerization in moisture and oxygen free cyclohexane, according to the previously described method.<sup>2</sup>

Allyl-terminated poly(3-hexylthiophene): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 2.80 (t, 2H), 3.49 (d, 2H), 5.11 (m, 2H), 5.98 (m, 1H) 6.95 (s, 1H), DP<sub>n</sub>=20; SEC: M<sub>n</sub>=4500 g/mol; PDI = 1.25.<sup>1</sup>

Polyisoprene-*b*-polystyrene: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 1.4 (t, *J* = 7 Hz, 3H), 1.53 (s, 3H), 1.61 (s, 3H), 1.67 (s, 3H), 2.0 (m, 2H) 4.7 (m, 1H), 5.1 (m, 1H), 6.5 (m, 2H) 7.1 (m, 3H), SEC: M<sub>n</sub>=3700 g/mol; PDI = 1.20.

### Synthesis of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT)

Polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer was synthesized by reacting the allyl-terminated poly(3-hexylthiophene) (M<sub>n</sub>=4500 g/mol; DP<sub>n</sub>(NMR)=20) as a solution in dry THF (5 mL) with the *living* polyisoprene-*b*-polystyryl lithium (M<sub>n</sub>(SEC)=3320 g/mol) in cyclohexane. The coupling reaction was allowed to proceed for 10 min at 40°C. The coupling reaction was performed in a glove box under nitrogen atmosphere. The copolymer was precipitated in methanol and washed with cold cyclohexane to remove the unreacted polyisoprene-*b*-polystyrene diblock copolymer. The composition of the block copolymer was estimated from <sup>1</sup>H NMR spectrum by integrating protons *a* vs protons *c* and *e* (Figure S1). The triblock copolymer contained 24.3 mol% regioregular poly(3-hexylthiophene), 31.5 mol% polyisoprene, and 44.2 mol% polystyrene. SEC: M<sub>n</sub>=7170 g/mol; PDI = 1.50.



**Figure S1.** <sup>1</sup>H NMR spectrum of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) ( $M_n=7170$  g/mol)

### Field-effect mobility measurements

Field-effect mobility measurements were performed on thin-film transistors with a common bottom-gate, bottom-contact configuration. Highly doped, n-type silicon wafers with a resistivity of 0.001-0.003  $\Omega$  cm were used as substrates. Silicon dioxide (SiO<sub>2</sub>) was thermally grown at 1000 °C on silicon substrate to obtain a 200 nm thickness. Chromium metal (5 nm) followed by 100 nm of gold were deposited by E-beam evaporation as source-drain contacts. The source-drain pads were formed by photo-lithographically patterning the metal layer. The SiO<sub>2</sub> on the back side of the wafer was etched with buffered oxide etchant (BOE from JT Baker) to generate

the common bottom-gate. The resulting transistors had a channel width of 475  $\mu\text{m}$  and channel lengths varying from 2 to 80  $\mu\text{m}$ . The measured capacitance density of the  $\text{SiO}_2$  dielectric was 17  $\text{nF}/\text{cm}^2$ . Prior to copolymer deposition, the substrates were cleaned by UV/ozone for 10 min. The devices were then cleaned in air with water, methanol, hexane, chloroform, and dried with nitrogen flow followed by vacuum for 30 minutes at 80  $^\circ\text{C}$ . The copolymer films were deposited in air by drop casting 10  $\mu\text{L}$  of a 1.0  $\text{mg}/\text{mL}$  solution in chloroform and allowed to dry in a Petri dish saturated with chloroform. The devices were then further annealed for 30 min at 120 $^\circ\text{C}$ . For the surface treated devices, the devices were cleaned in air with water, methanol, hexane, chloroform, and dried with nitrogen flow, followed by vacuum drying for 30 minutes at 80  $^\circ\text{C}$ . The devices were placed in a glass container in a solution of  $8 \times 10^{-3}$  M n-octyltrichlorosilane in dried toluene. The sealed container was placed in a glovebox at ambient temperature for 48 h. After 48 h, the devices were taken out of the glovebox and rinsed with freshly distilled toluene before baking them at 80  $^\circ\text{C}$  for 30 min in a vacuum oven. The devices were allowed to cool under vacuum. The polymer films were deposited in air by drop-casting 4–5 drops of 1  $\text{mg}/\text{mL}$  of polymer solution (in chloroform) filtered through a 0.2  $\mu\text{m}$  PTFE filter using a 25  $\mu\text{L}$  syringe. The devices were allowed to dry in a Petri dish saturated with chloroform. The devices were annealed under vacuum for 30 min at 120  $^\circ\text{C}$  prior to measurements. The devices were allowed to cool down to room temperature under vacuum after annealing. A Keithley 4200-SCS semiconductor characterization system was used to probe the devices. The probe station used for electrical characterization was a Cascade Microtech Model Summit Microchamber. When measuring current–voltage curves and transfer curves, VGS was scanned from +20 V to –100 V. All the measurements were performed at room temperature in air. A plot of  $I_{\text{DS}}^{1/2}$  vs.  $V_{\text{GS}}$  was obtained in the saturation regime and the field-effect mobilities were calculated using following equation:

$$\mu = \frac{2L}{WC_i} \frac{I_{\text{DS}}}{(V_{\text{GS}} - V_{\text{T}})^2}$$

where  $I_{\text{DS}}$  is the source-drain current, W is the channel width, L is the channel length,  $C_i$  is the capacitance of the dielectric,  $V_{\text{GS}}$  is the gate voltage, and  $V_{\text{T}}$  is the threshold voltage.

### **Tapping mode Atomic Force Microscopy (TMAFM)**

TMAFM investigation of thin film morphology was carried out using a Nanoscope IV-Multimode Veeco, equipped with an E-type vertical engage scanner. The AFM images were collected at room temperature in air using silicon cantilevers with nominal spring constant of 42 N/m and nominal resonance frequency of 320 kHz (standard silicon TESP Probes with aluminum coating on backside). A typical value of AFM detector signal corresponding to R.M.S. cantilever oscillation amplitude was equal to ~1 to 2 V and the images were acquired at 0.5 Hz scan frequency in 5x5  $\mu\text{m}$  scan areas. The samples were prepared by drop casting a solution of polymer in toluene (1mg/mL) on to mica substrates. The polymer thin films were annealed at 120°C prior to AFM measurements.

### **X-ray diffraction studies**

X-Ray diffraction patterns were obtained on a RIGAKU Ultima III diffractometer. Samples were subjected to Cu K $\alpha$  radiation ( $\lambda \sim 1.5406 \text{ \AA}$ ) and scanned from 1 to 40 degrees ( $2\theta$ ) at 0.04 degree intervals at a rate of 1 degree/min. A microscope cover glass was used as the sample substrate. The copolymer film obtained from chloroform was deposited in air by drop casting a 15.0 mg/mL polymer solution and allowed to dry in a Petri dish saturated with chloroform.

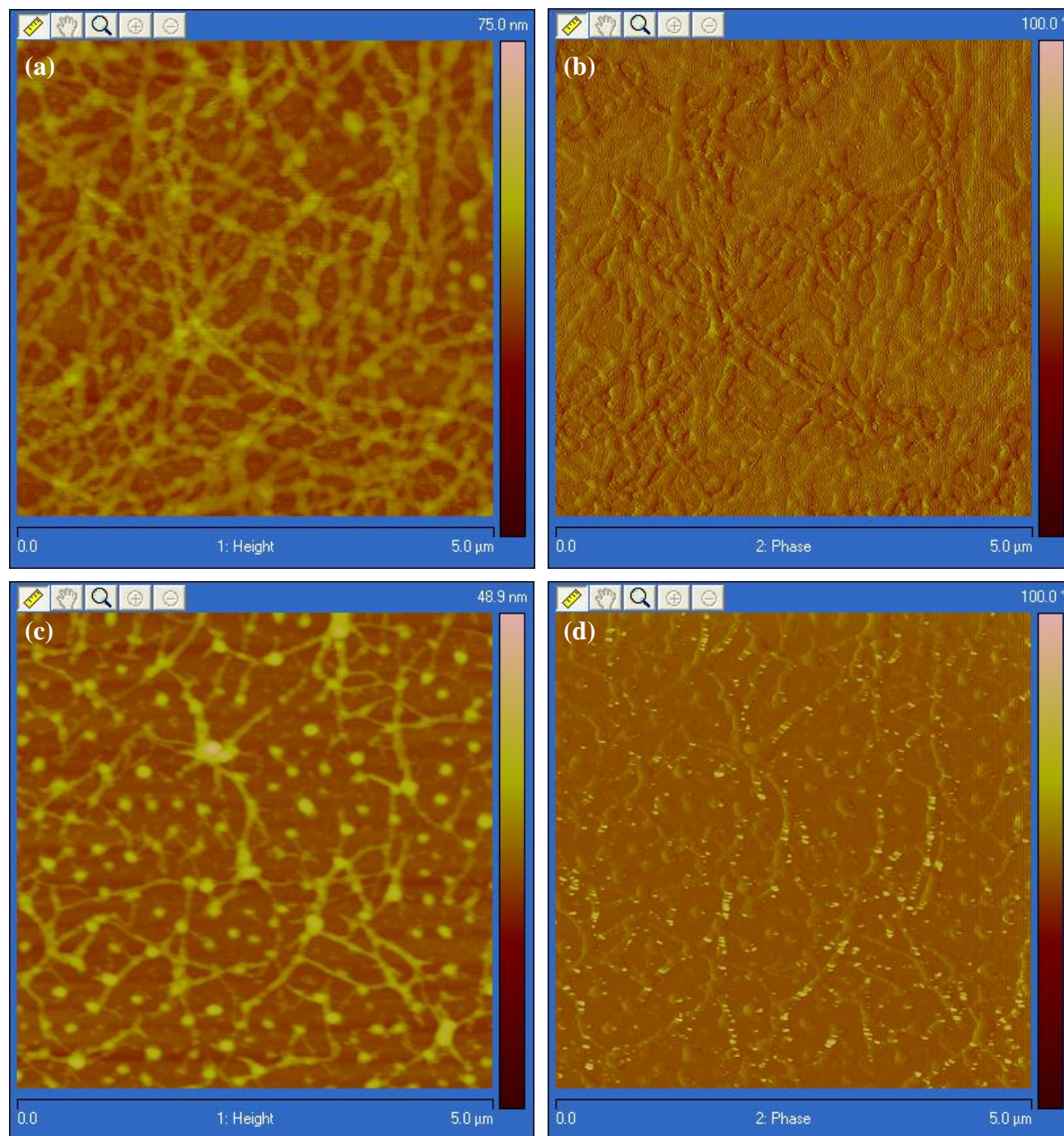
### **Electrical conductivity measurements**

Conductivity of triblock copolymer was measured on thin polymer film by the standard four-point probe method at ambient conditions. The polymer solution in anhydrous chloroform was drop casted onto a clean cover glass slips. The solvent was evaporated in an open atmosphere. The film was oxidized by exposure to iodine vapors for 12 hrs. A minimum of five readings were taken for the selected uniform film area. The film thickness was measured using an Ambios Technology XP-1 Stylus Profiler.

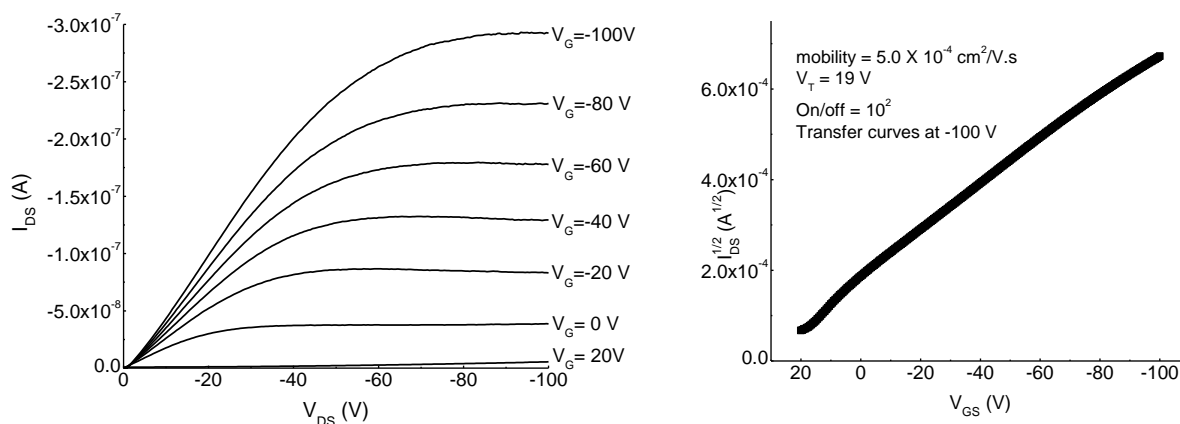
The conductivity  $\sigma$  [ $\text{S cm}^{-1}$ ] was calculated according to the following equation:

$$\sigma = 1 \div (4.53 * R * l)$$

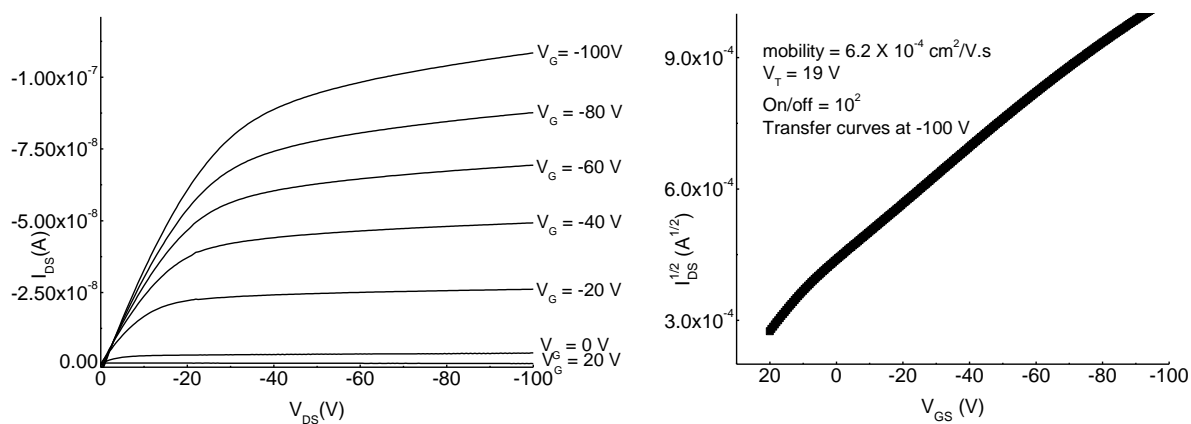
where R is the resistance ( $R=V/I$ ) [ $\Omega$ ] and l is the film thickness [cm].



**Figure S2.** Height and phase TMAFM (a, b) of PI-PS-P3HT (non-annealed); height and phase TMAFM (c,d) of PI-PS-P3HT (annealed)



**Figure S3.** Current-voltage characteristics of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) on untreated OFET device; left: output curves at different gate voltages; right: transfer curves at  $V_{DS} = -100$  V ( $\mu = 5.0 \times 10^{-4}$  cm<sup>2</sup>/V s,  $V_T = 19.0$  V, on/off ratio =  $10^2$ ,  $W = 475$   $\mu$ m,  $L = 20$   $\mu$ m)



**Figure S4.** Current-voltage characteristics of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) on OFET device treated with octyl trichlorosilane (OTS); left: output curves at different gate voltages; right: transfer curves at  $V_{DS} = -100$  V ( $\mu = 6.2 \times 10^{-4}$  cm<sup>2</sup>/V s,  $V_T = 19.0$  V, on/off ratio =  $10^2$ ,  $W = 475$   $\mu$ m,  $L = 20$   $\mu$ m)

#### References:

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