Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

for

# Semi-conductive micellar networks of all-conjugated diblock and triblock copolymer blends

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## Materials

Magnesium, *N*-bromosuccinimide (99%), 2-ethylhexyl bromide (95%), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) [Ni(dppp)$Cl_2$], and isopropyl magnesium chloride complex lithium complex solution (*i*PrMgCl·LiCl, 1.3M in THF) were purchased from Sigma Aldrich and used without further purification.

3-Bromothiophene (>97%), 3-hexylthiophene (>98%), and iodobenzene diacetate (>97%) were purchased from Tokyo Chemical Industry and used without purification.

Iodine was purchased from Alfa Aesar and used without purification.

Acetic acid (glacial, 99.7%), magnesium sulfate anhydrous (99.5%), sodium bicarbonate (99-100.5%), sodium sulfate anhydrous (99%), sodium thiosulfate anhydrous (95%), hydrochloric acid (35-37%), diethyl ether (99.5%), n-hexane (95%), acetone (99.5%), chloroform (99.5%), methyl alcohol (99.5%), tetrahydrofuran (99.5%), and dichloromethane (99.5%) were purchased from Samchun Chemicals.

Dichloromethane (DCM) and tetrahydrofuran (THF) were distilled over $CaH_2$ and sodium/benzophenone, respectively.

# Experimental Procedures

## *General Information*

$^1$H NMR spectra were recorded on Agilent 500-MR DD2 magnetic resonance system and Varian/Oxford As-500 using $CD_2Cl_2$ or $CDCl_3$ as solvents. Molecular weights of polymers were measured on Agilent 1260 infinity gel permeation chromatography (GPC) system equipped with a PL gel 5 $\mu$m mixed D column and differential refractive index detectors. THF was used as the GPC eluent with a flow rate of 1 mL min$^{-1}$ at 35 °C. A PS standard kit (Agilent Technologies) was used for calibration. Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Q10 from 0 °C to 300 °C with a scan rate of 10 °C min$^{-1}$ under an $N_2$ atmosphere. Calibration was performed by measuring the melting temperature of indium ($T_m$ = 429.75 K).

TEM was performed on a Hitachi 7600 operating at 100 kV. Specimens were prepared by placing a drop of the diluted polymer solution with anisole on a carbon-coated Cu grid (200 mesh, EM science). After 30 seconds, the remaining solution on the grid was removed with filter paper, and the grid was dried for more than 4 h. The atomic force microscopy (AFM) was performed on a Bruker NanoScope V Multimode 8 device at ambient temperature in tapping mode using non-contact mode silicon tips from Nanoworld (Pointprobe tip, NCHR type) with spring constant of 42 N m$^{-1}$ and tip radius of ≤ 8 nm. 7 $\mu$L of the diluted sample solution (0.1 mg/mL) was prepared and placed on a silicon wafer. Scanning electron microscopy (SEM) was performed on Hitachi S-4300 at an acceleration voltage of 15 kV. The sample was placed on a slide glass and then sputtered with Pt with a thickness of 3 nm by using Hitachi E-1030 ion sputter.

Doping of organogel from BCP blend of $P3HT_{120}$-*b*-$P3EHT_{100}$ and $P3HT_{54}$-*b*-$P3EHT_{62}$-*b*-$P3HT_{54}$ was performed by following procedures. The glass substrates were sequentially washed in detergent solution, acetone, and isopropyl alcohol using an ultrasonic cleaner. Prior to the deposition of the solution, the glass substrates were treated with ultraviolet (UV)-ozone plasma for 20 min to obtain a uniform P3HT thin film. The 9:1 BCP blend of $P3HT_{120}$-*b*-$P3EHT_{100}$ and $P3HT_{54}$-*b*-$P3EHT_{62}$-*b*-$P3HT_{54}$ in anisole (50 mg/mL) filtered by a 0.45 μm PTFE filter. The organogel was prepared by annealed of the BCP blend at 70 °C for 1 h before cooling and equilibration at room temperature. The organogel was doped by immersion in 1.0–10 mM $AuCl_3$/nitromethane solution for 1 h. The doped organogel was finally rinsed with methanol to remove excess dopants. Square-shaped gold electrodes with a thickness of 100 nm, separated by a distance of 15 mm, were thermally evaporated through a patterned shadow mask for ohmic contact between the organogel and the measurement probe.

X-ray powder diffraction (powder XRD) data were collected with Cu-Kα radiation ($\lambda$ = 1.5418 Å) on a Bruker D8 Advance powder diffractometer fitted with a 0.6 mm fixed divergence slit, knife-edge collimator and a LynxEye area detector. Data were collected between 5–30° ($2\theta$) with a step width of 0.02°. The samples were drop casted from chloroform solution onto silicon wafers prior to analysis.

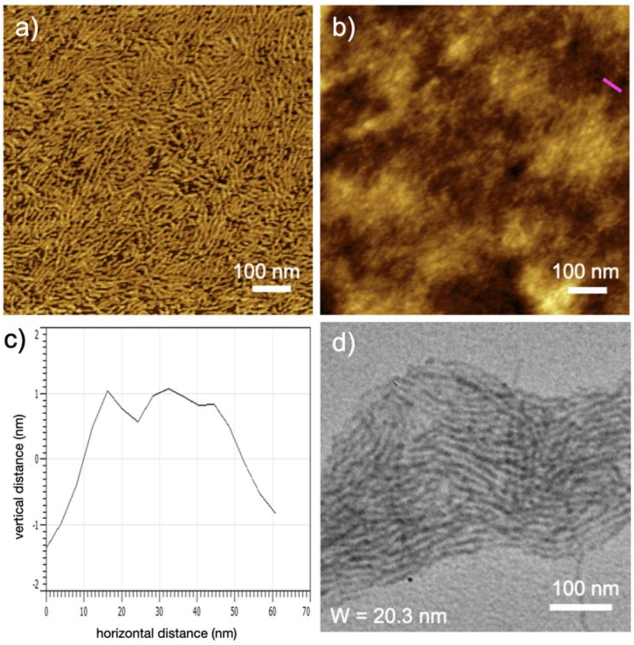


**Fig. S1** 1-D Nanowires obtained from the CDSA of P3HT$_{54}$-*b*-P3EHT$_{62}$ (1 mg/mL in anisole, 90 °C, slow cooling). (a) AFM phase image, (b) AFM height image, (c) AFM height profile and (d) TEM image.

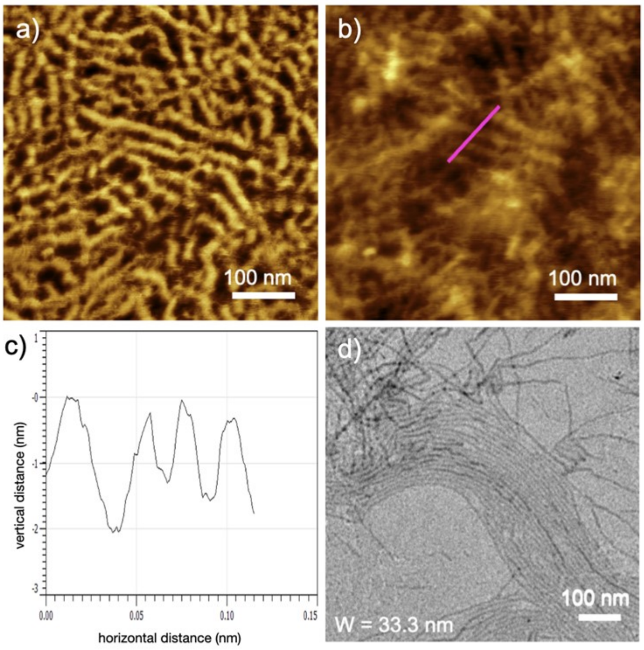


**Fig. S2** 1-D Nanowires obtained from the CDSA of P3HT$_{120}$-*b*-P3EHT$_{100}$ (1 mg/mL in anisole, 90 °C, slow cooling). (a) AFM phase image, (b) AFM height image, (c) AFM height profile and (d) TEM image.

| Temperature (°C) | 45 | 50 | 55 | 60 | 62 | 64 | 66 | 68 | 70 |
|---|---|---|---|---|---|---|---|---|---|
| $L_n$ (nm) | 35 | 113 | 243 | 544 | 780 | 1134 | 1826 | 2312 | 2970 |
| $\sigma$ (nm) | 5.4 | 19.3 | 37.2 | 136 | 260 | 366 | 495 | 734 | 1057 |
| $Đ$ | 1.07 | 1.06 | 1.08 | 1.09 | 1.08 | 1.12 | 1.13 | 1.18 | 1.21 |

**Table S1** Average length value ($L_n$), standard deviation ($\sigma$) and their dispersity values ($Đ$) of 1-D nanowires from the CDSA of P3HT$_{120}$-*b*-P3EHT$_{100}$ at different annealing temperatures.

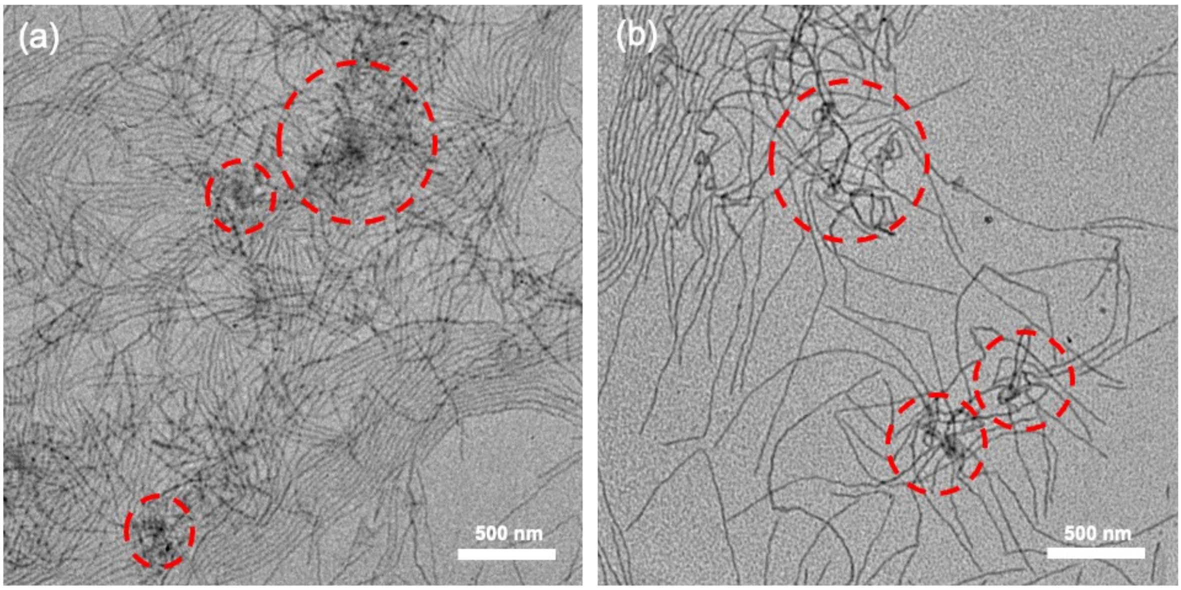


**Fig. S3** Self-assembled nanowires obtained from CDSA of P3HT$_{54}$-*b*-P3EHT$_{62}$ -*b*-P3HT$_{54}$ (1 mg/mL, 70 °C, slow cooling) (a) in anisole, (b) in cyclohexane. Red circle indicates the formation of islands of bundles of self-assembled nanowires.

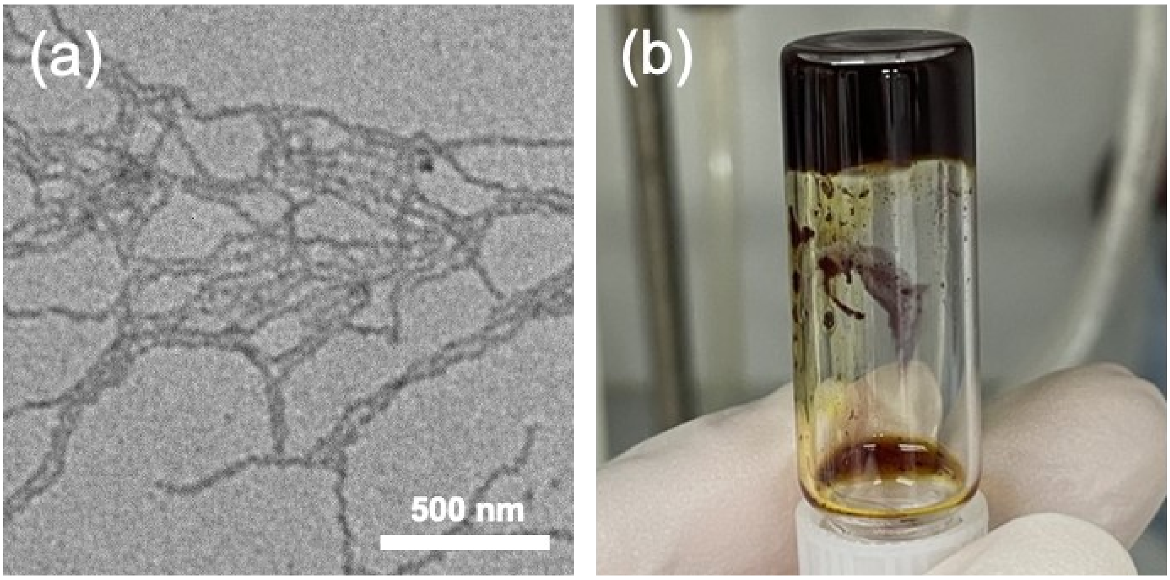


**Fig. S4** (a) TEM image and (b) photograph of the organogel obtained from CDSA of P3HT$_{54}$-*b*-P3EHT$_{62}$-*b*-P3HT$_{54}$ (100 mg/mL in anisole, 70 °C, slow cooling).

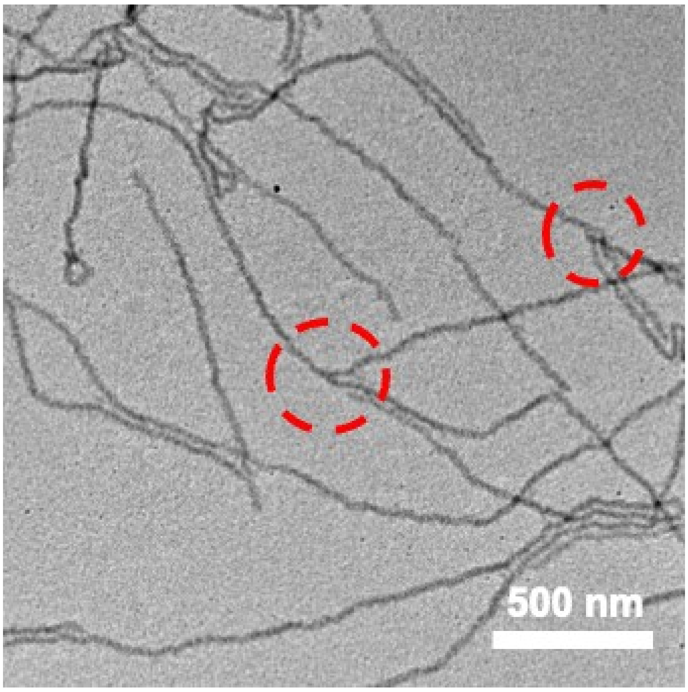
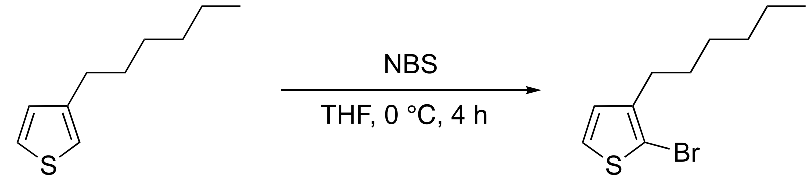
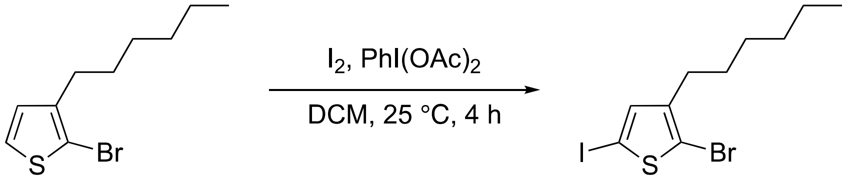


**Fig. S5** TEM image of Self-assembled nanowires obtained from the CDSA of the 9:1 (w/w) blend of P3HT$_{120}$-*b*-P3EHT$_{100}$ and P3HT$_{54}$-*b*-P3EHT$_{62}$ -*b*-P3HT$_{54}$ (20 mg/mL in anisole, 90 °C, slow cooling). Red circle indicates the formation of Y-junction and crosses of 1-D nanowires.

***Synthesis of 2-Bromo-3-hexyl-5-iodothiophene (1)***



**2-Bromo-3-hexylthiophene.** 3-Hexylthiophene (10.00 g, 59.4 mmol) was dissolved in a dry THF (100 mL). To this solution, *N*-bromosuccinimide (10.78 g, 59.4 mmol) was added to the mixture and stirred for 4 h at 0 °C. Upon completion, water was poured into the mixture to quench the residual *N*-bromosuccinimide and extracted with diethyl ether. The combined organic layers were then washed with 10% $Na_2S_2O_3$ (aq), 10% KOH (aq), and brine and dried over anhydrous $MgSO_4$. After filtration, residual solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane). The product was obtained as a yellow oil (12.4 g, 84.5%). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.23 (d, $J$ = 5.6 Hz, 1H), 6.84 (d, $J$ = 5.6 Hz, 1H), 2.62 – 2.52 (m, 2H), 1.58 (ddd, $J$ = 17.6, 12.7, 7.7 Hz, 2H), 1.40 – 1.26 (m, 6H), 0.90 (td, $J$ = 5.6, 2.2 Hz, 3H).

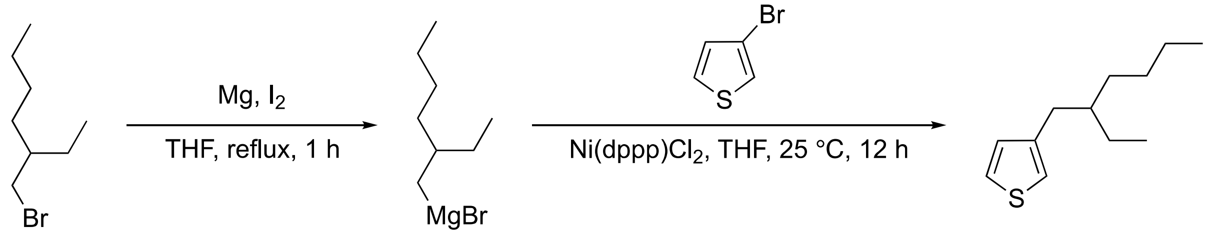


**1**

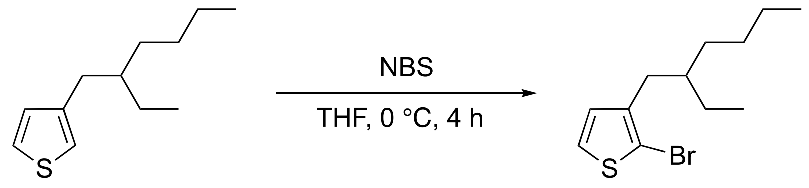
**2-Bromo-5-iodo-3-hexylthiophene.** 2-Bromo-3-hexylthiophene (12.4 g, 50.4 mmol) was dissolved in dry $CH_2Cl_2$ (50 mL) under $N_2$. Iodine (3.54 g, 27.9 mmol), and iodobenzene diacetate (9.72 g, 30.2 mmol) were added to the mixture and stirred at room temperature for 4

h. The reaction was quenched by the addition of 10% $Na_2S_2O_3$ (aq). The mixture was extracted with diethyl ether. Combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After filtration, residual solvents were removed by evaporation under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane) to give a 2-bromo-5-iodo-3-hexylthiophene (**1**) as a pale-yellow oil (15 g, 80%). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 6.94 (d, *J* = 1.1 Hz, 1H), 2.54 – 2.46 (m, 2H), 1.58 – 1.46 (m, 2H), 1.35 – 1.22 (m, 6H), 0.91 – 0.83 (m, 3H). $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 144.94, 138.63, 111.93, 71.33, 54.27, 54.06, 53.84, 53.62, 53.41, 32.00, 31.97, 29.99, 29.51, 29.17, 23.07, 22.98, 14.30, 14.25. HRMS (ESI): calcd for $C_{10}H_{14}BrIS$ [$M^+$] = 372.9123 Da; found: 372.9074 Da.

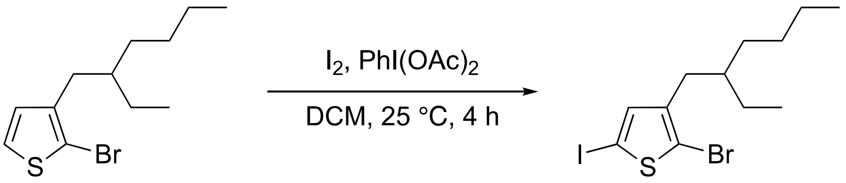
***Synthesis of 2-bromo-3-(2-ethylhexyl)-5-iodothiophene (2)***



**3-(2-Ethylhexyl)thiophene.** To a mixture of magnesium turnings (3.06 g, 126 mmol), dry THF (15 mL), and a catalytic amount of iodine in an oven-dried Schlenk flask (100 mL), a solution of 2-ethylhexylbromide (3.06 g, 126 mmol) in dry THF (30 mL) was added slowly at 0 °C under $N_2$. After refluxing for 1 h, the solution was added dropwise to a mixture of 3-bromothiophene (15 g, 93 mmol), $Ni(dppp)Cl_2$ (0.51 g, 0.9 mmol), and dry THF (50 mL) placed in an oven-dried Schlenk flask (250 mL) at 0 °C. After the mixture was stirred overnight at room temperature, the reaction was quenched by pouring 1 M HCl (aq) into the mixture. After extraction with $CHCl_3$, the organic layer was dried over anhydrous $Mg_2SO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane as an eluent to obtain a 3-(2-ethylhexyl)thiophene as a clear liquid. (16.2 g, 90%). $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$ 7.25 (dd, $J$ = 4.9, 3.0 Hz, 1H), 6.93 (td, $J$ = 4.5, 1.7 Hz, 2H), 2.58 (d, $J$ = 6.9 Hz, 2H), 1.61 – 1.54 (m, 1H), 1.36 – 1.20 (m, 8H), 0.89 (td, $J$ = 7.2, 3.3 Hz, 6H).



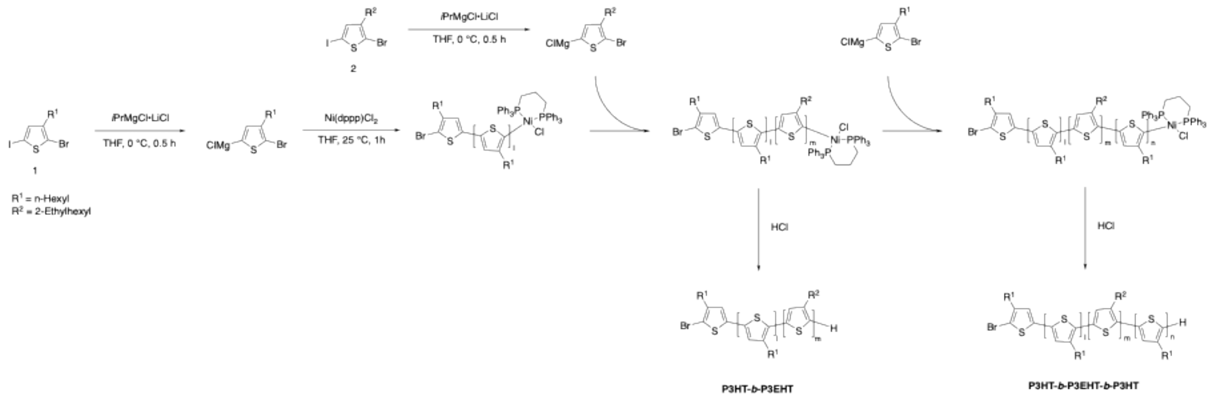
**2-Bromo-3-(2-ethylhexyl)thiophene.** Using 3-(2-ethylhexyl)thiophene (10.00 g, 50.9 mmol) and *N*-bromosuccinimide (9.24 g, 50.9 mmol), the reaction proceeded in the same manner as the synthesis of 2-bromo-3-hexylthiophene, which yield 2-bromo-3-(2-ethylhexyl)thiophene as a yellow oil (12.6 g, 86.1%). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.23 (d, *J* = 5.6 Hz, 1H), 6.81 (d, *J* = 5.6 Hz, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.67 – 1.58 (m, 1H), 1.37 – 1.21 (m, 8H), 0.93 – 0.84 (m, 6H).



**2**

**2-Bromo-3-(2-ethylhexyl)-5-iodothiophene (2).** Using 2-bromo-3-(2-ethylhexyl)thiophene (12.6 g, 46mmol), iodine (3.23 g, 25.5 mmol), and iodobenzene diacetate (8.87 g, 27.6 mmol), the reaction proceeded in the same manner as the synthesis of 2-bromo-3-hexyl-5-iodothiophene, which yield 2-bromo-3-(2-ethylhexyl)-5-iodothiophene (**2**) as a pale yellow oil (14.8 g, 80.5%). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 6.93 (d, *J* = 1.2 Hz, 1H), 2.46 (d, *J* = 7.1 Hz, 2H), 1.59 – 1.50 (m, 1H), 1.34 – 1.19 (m, 8H), 0.92 – 0.83 (m, 6H). $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 144.19, 139.09, 112.60, 71.29, 54.27, 54.06, 53.84, 53.62, 53.41, 40.40, 33.74, 32.76, 29.16, 29.13, 25.96, 23.50, 23.41, 14.28, 11.21, 10.95 HRMS (ESI): calcd for $C_{12}H_{18}BrIS$ [$M^+$] = 399.9357 Da; found: 399.9360 Da.

### ***Synthesis of BCPs***



**Scheme S1** Synthetic scheme of P3HT-*b*-P3EHT and P3HT-*b*-P3EHT-*b*-P3HT.

**P3HT-*b*-P3EHT.** Schlenk flasks (100 mL) were flame-dried before use. **1** (0.3 mg, 0.8 mmol) was placed in one of the flasks under $N_2$. After adding dry THF (20mL), the solution was cooled to 0 °C. 1.3 M solution of *i*PrMgCl·LiCl in THF (0.62 mL, 0.8 mmol) was added via syringe and stirred for 30 min at 0 °C for activation. In the other flask, **2** (0.32 mg, 0.8 mmol) was activated with *i*PrMgCl·LiCl (0.62 mL, 0.8 mmol) in the same manner. Activated **1** was warmed up to room temperature, and Ni(dppp)$Cl_2$ catalyst (8 mg, 0.015 mmol) was added in one portion and stirred for 1 hour. The solution of activated **2** was added to the reaction mixture via syringe. After stirring for 1 hour, the polymerization was quenched by pouring 1 M HCl (aq). The crude polymer was washed by Soxhlet extraction using methanol and hexane and then extracted using $CHCl_3$. The extracted polymer was concentrated in vacuo, which yielded a purple solid of P3HT-*b*-P3EHT.

**P3HT-*b*-P3EHT-*b*-P3HT.** To synthesize P3HT-*b*-P3EHT-*b*-P3HT, Two batches of **1** and one batch of **2** were prepared in Schlenk flasks (100 mL). Polymerization proceeded in the same manner as the synthesis of P3HT-*b*-P3EHT. Before quenching the P3HT-*b*-P3EHT diblock copolymer, the second batch of activated **1** (0.8 mmol in 20 mL THF) was added via syringe. After 1 hour of stirring, the polymerization was quenched by pouring 1 M HCl (aq). The crude polymer was washed by Soxhlet extraction using methanol and hexane and then extracted using $CHCl_3$. The extracted polymer was concentrated in vacuo, which yielded a purple solid of P3HT-*b*-P3EHT-*b*-P3HT.

**Table S2** Polymerization results of BCPs

| Entry | [**1**] : [**2**] : [**1**] : [Ni] | Yield (%) | $M_n^{P1,b}$ [kDa] | $M_n^{P2,b}$ [kDa] | $M_n^{P3,b}$ [kDa] | $Đ^b$ |
|---|---|---|---|---|---|---|
| **1** | 60 : 0 : 0 : 1 | 77 | 11.2 | - | - | 1.08 |
| **2** | 0 : 50 : 0 : 1 | 68 | 9.9 | - | - | 1.12 |
| **3** | 60 : 50 : 0 : 1 | 75 | 9.1 | 21.4 | - | 1.15 |
| **4** | 120 : 100 : 0 : 1 | 81 | 20.5 | 41.2 | - | 1.18 |
| **5** | 60 : 100 : 0 : 1 | 73 | 8.2 | 19.8 | - | 1.19 |
| **6** | 50 : 70 : 50 : 1 | 66 | 10.1 | 21.5 | 28.8 | 1.32 |

[a]Isolated yield, [b]Number-average molecular weight ($M_n$) and dispersity ($Đ$) determined by GPC (THF) using PS standards. P1, P2, and P3 indicate the molecular weight of the first block, deblock copolymer and triblock copolymer, respectively.

***NMR spectra of monomers and BCPs***

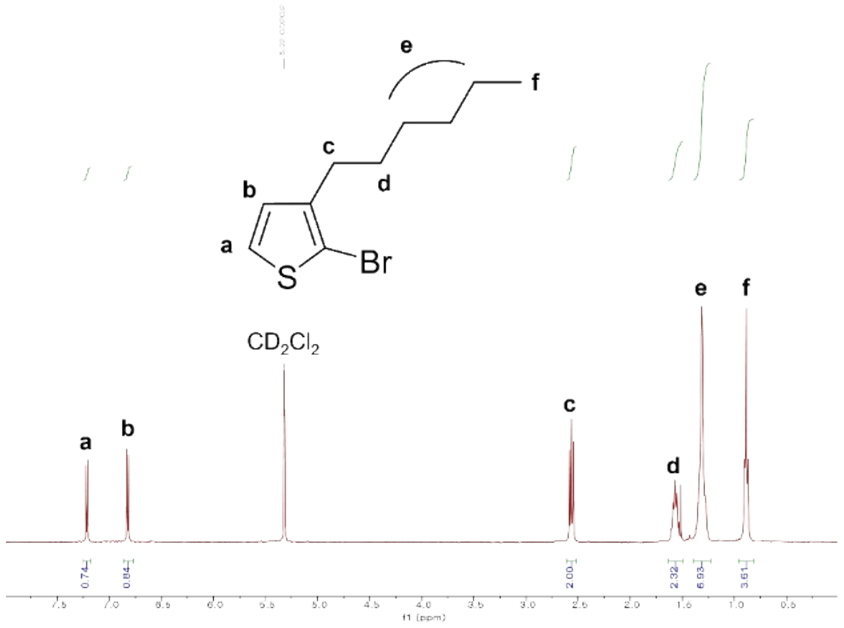


**Fig. S6** $^1$H NMR spectra of 2-Bromo-3-hexylthiophene.

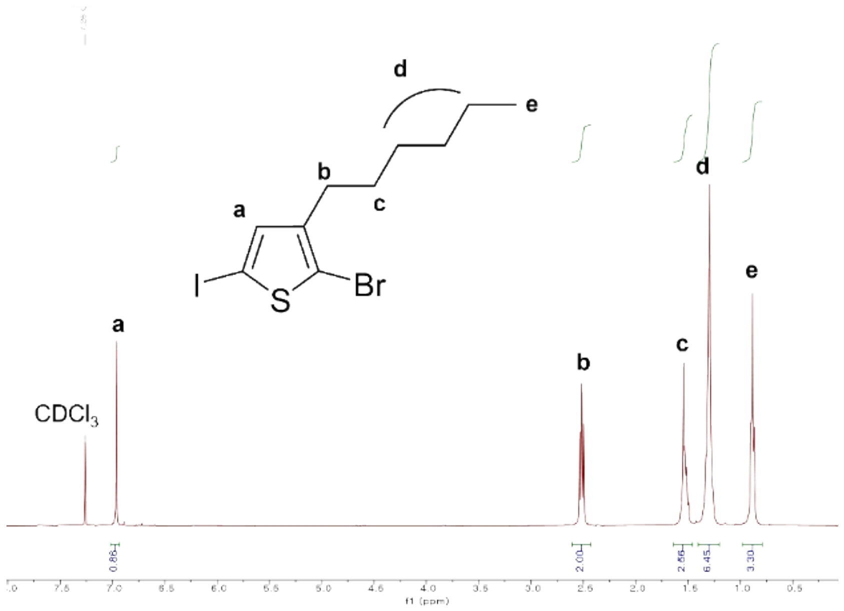


**Fig. S7** $^1$H NMR spectra of 2-Bromo-3-hexyl-5-iodothiophene.

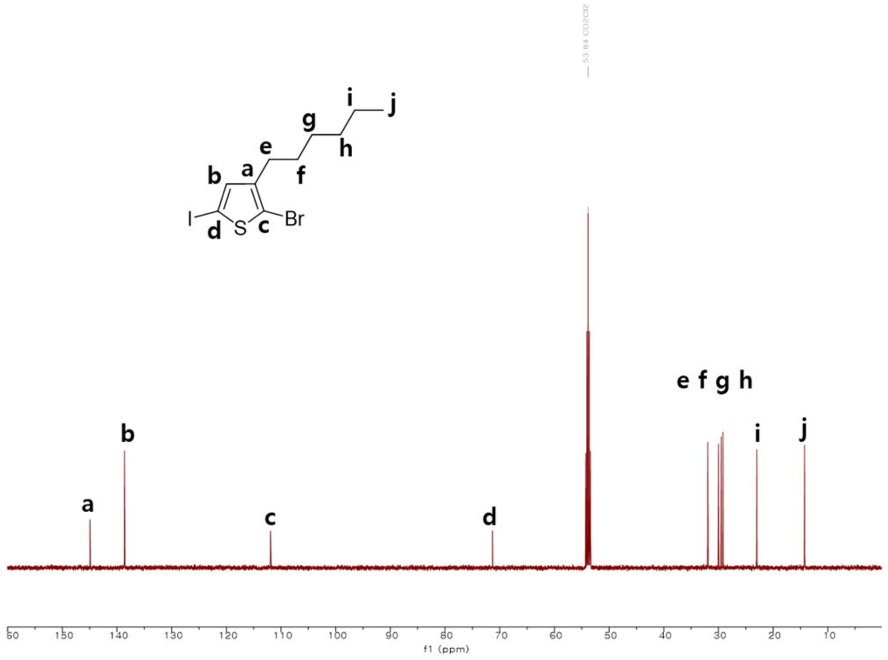


**Fig. S8** $^{13}$C NMR spectra of 2-Bromo-3-hexyl-5-iodothiophene.

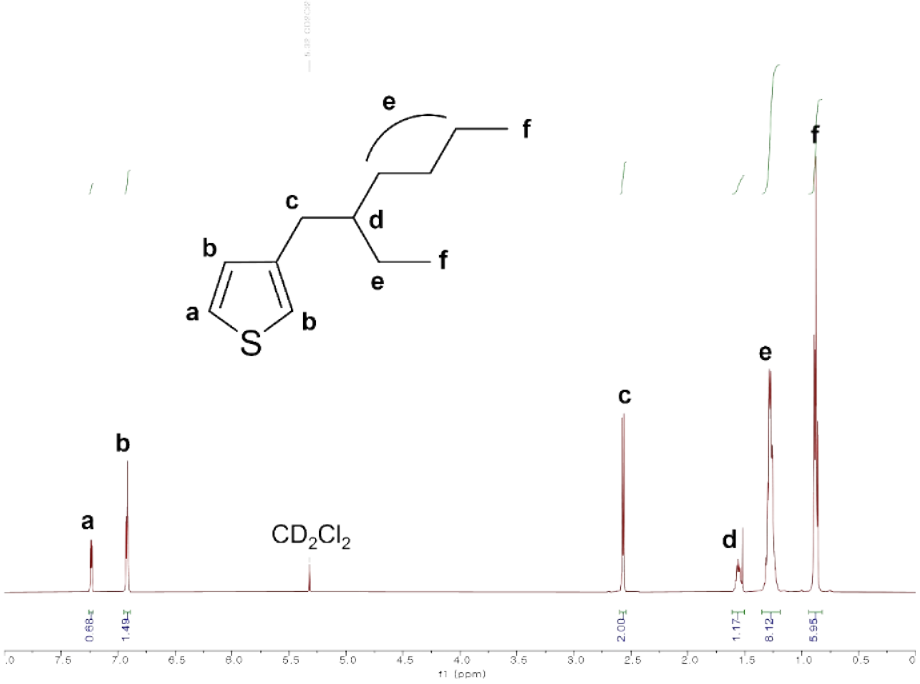


**Fig. S9** $^{1}$H NMR spectra of 3-(2-ethylhexyl)thiophene

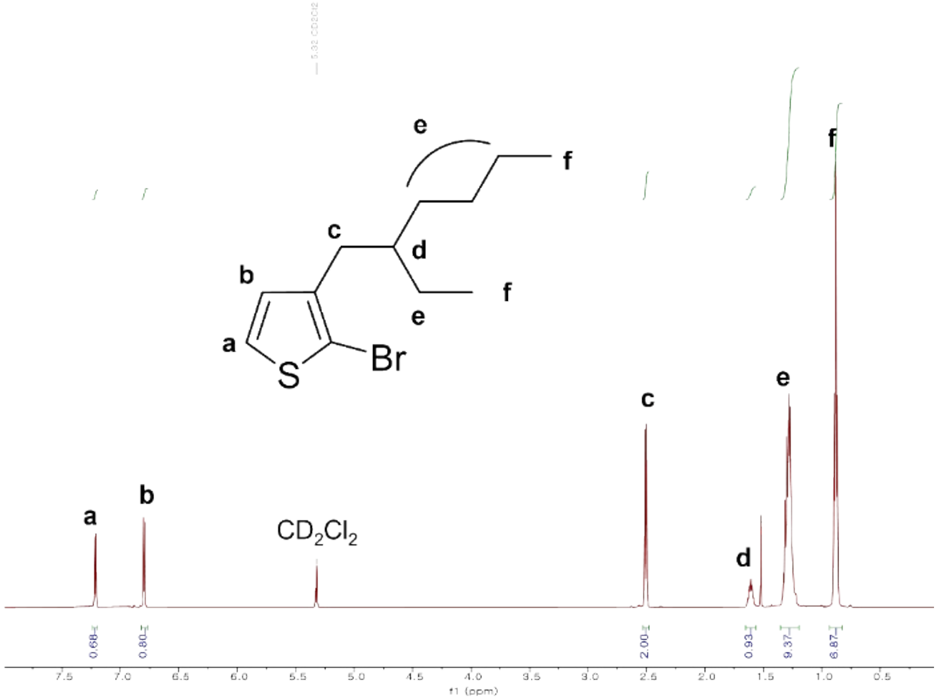


**Fig. S10** $^1$H NMR spectra of 2-Bromo-3-(2-ethylhexyl)thiophene.

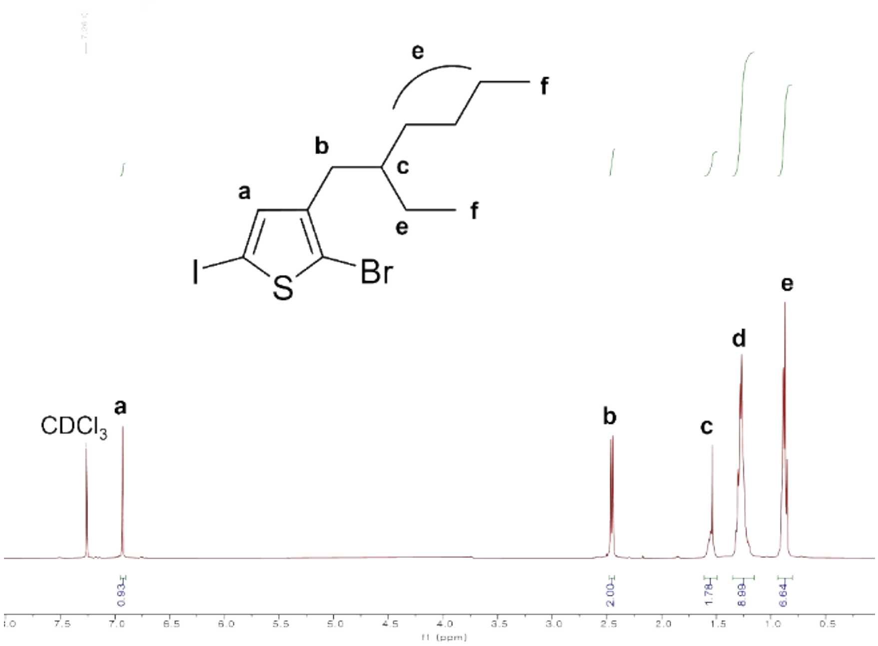


**Fig. S11** $^1$H NMR spectra of 2-Bromo-3-(2-ethylhexyl)-5-iodothiophene.

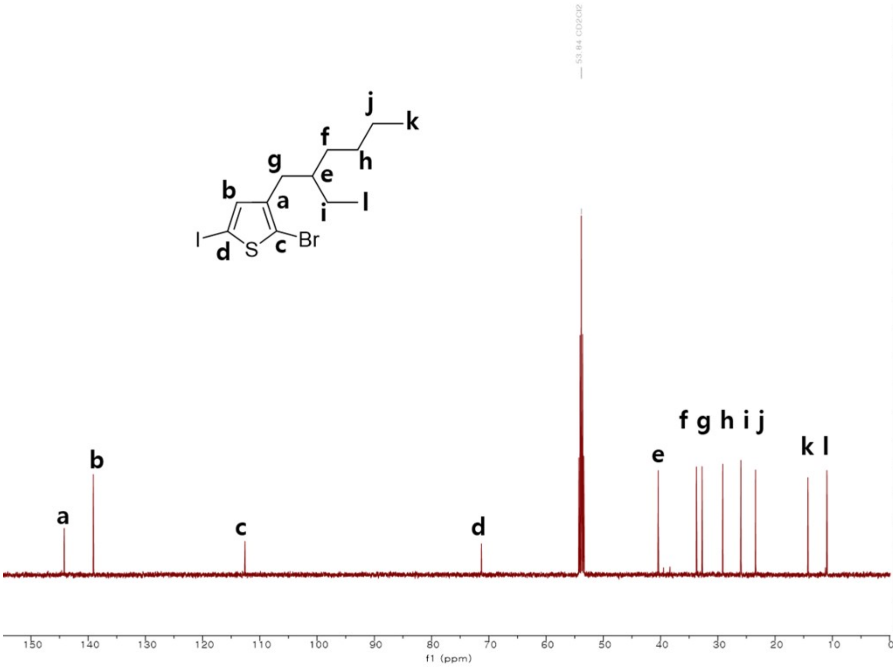


**Fig. S12** $^{13}$C NMR spectra of 2-Bromo-3-(2-ethylhexyl)-5-iodothiophene.

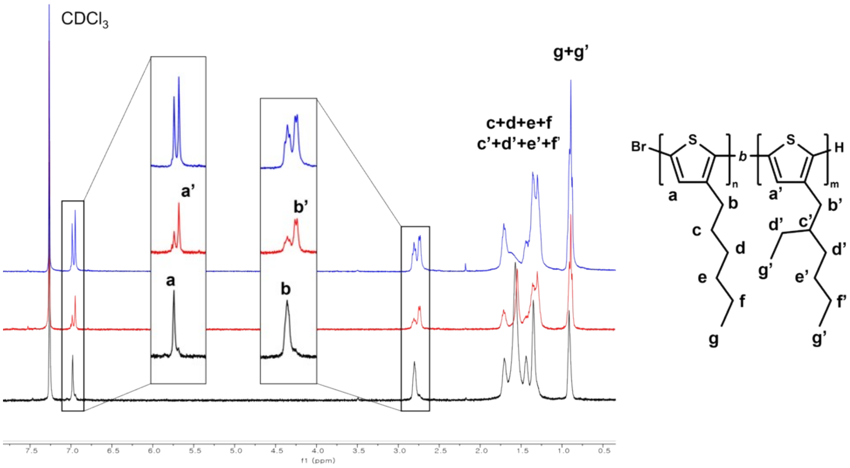


**Fig. S13** Stacked $^{1}$H NMR spectra of P3HT (black), P3HT$_{120}$-*b*-P3EHT$_{100}$ (red), and P3HT$_{54}$-*b*-P3EHT$_{62}$-*b*-P3HT$_{54}$ (blue).

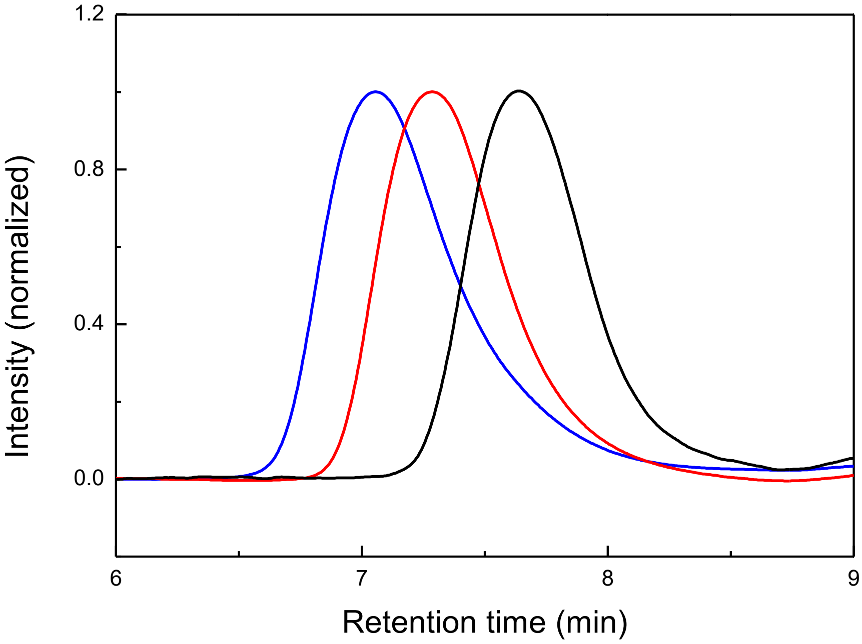


**Fig. S14** GPC chromatogram of P3HT$_{54}$ (black), P3HT$_{54}$-*b*-P3EHT$_{62}$ (red), and P3HT$_{54}$-*b*-P3EHT$_{62}$-*b*-P3HT$_{54}$ (blue).

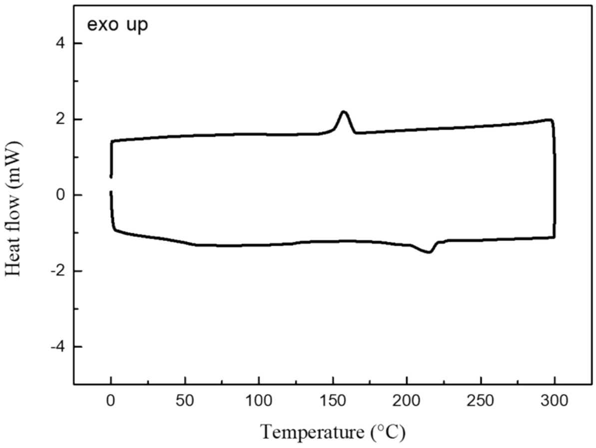


**Fig. S15** DSC thermogram of P3HT$_{120}$-*b*-P3EHT$_{100}$, $T_m = 169.2$ °C

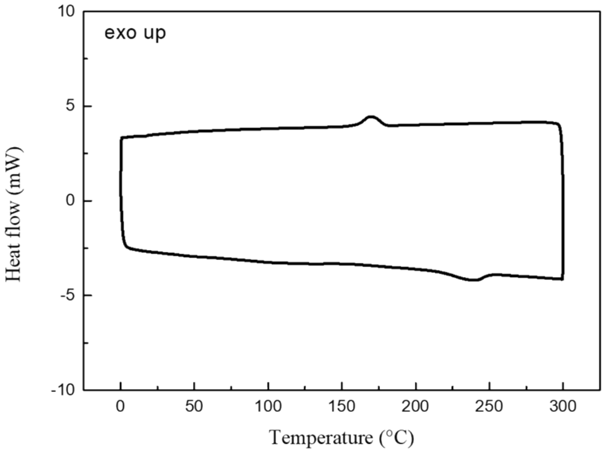


**Fig. S16** DSC thermogram of P3HT$_{54}$-*b*-P3EHT$_{62}$-*b*-P3HT$_{54}$, T$_m$ = 144.3 °C

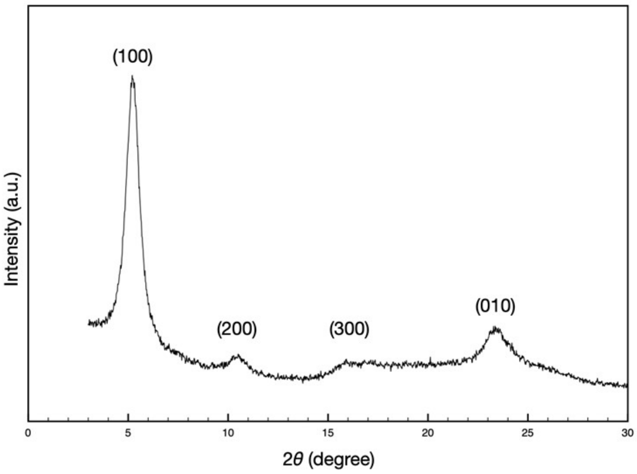


**Fig. S17** PXRD intensities as a function of the scattering angle 2$\theta$ for P3HT$_{54}$-*b*-P3EHT$_{62}$.

**Additional comments on PXRD data.** X-ray diffraction pattern of P3HT$_{54}$-*b*-P3EHT$_{62}$ showed peaks at 2 $\theta$ = 5.20°, 10.50°, 15.92°, and 23.36°. The (100), (200), and (300) reflection peaks at 2 $\theta$ = 5.20°, 10.50°, and 15.92° correspond to a lamellar ordering with *d*-spacings of 17.0 Å, 8.42 Å, and 5.56 Å, respectively, as reported in previous studies.[1–4] The (010) reflection peak at 2 $\theta$ = 23.26° corresponds to a $\pi$-$\pi$ stacking with a *d*-spacing of 3.80 Å.

# References

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