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Supporting Information

Synthesis of ABCBA-type Miktoarm H-shaped Copolymers with Poly(3hexylthiophene) Segments and Its Application to Intrinsically Stretchable Photonic Transistor Memory

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Materials.

Tetrahydrofuran (THF, Tokyo Chemical Industry Co.) was dried over sodium benzophenone and distilled before use under nitrogen (N₂). THF (deoxidized) for living anionic polymerization was purchased from Fujifilm Wako Chemical Co. and used as received inside glovebox (GB) under purified N₂ (O₂ < 10 ppm, H₂O < 10 ppm). Styrene (St) was washed with a sodium hydroxide (NaOH) aqueous solution, followed by drying over magnesium sulfate (MgSO₄). After filtration of MgSO₄, St was purified by distillation under reduced pressure over calcium hydride and immediately transferred into GB and stored under N₂. 1-(3-*tert*-Butyldimethylsilyloxy)methylphenyl-1-phenylethylene (DPE-TBSO) was kindly donated by DIC corporation (It can also be synthesized by the protocol previously reported¹). ω -Chain-endfunctionalized poly(3-hexylthiophene) (P3HT) with a 4-bromobutyl group (**P3HT-Br**, *M*_n(SEC) = 6,700, *D*_M (SEC) = 1.09, *M*_n(¹H NMR) = 5,300) was synthesized according the literature.² α , ω -Chain-end-functionalized poly(*n*butyl acrylate)s (PⁿBAs) with azide groups (**N₃-PⁿBA-N₃**, *M*_n (SEC)/*D*_M (SEC) = 11,000/1.11, 23,000/1.13, 94,000/1.15, *M*_n(¹H NMR) = 11,000, 30,000, 91,000) were synthesized according to the literature.³ Hex-5-ynoyl chloride was synthesized according to the literature.⁴ Other reagents were purchased from Tokyo Chemical Industry Co., Fujifilm Wako Chemical Co., Kanto Chemical Co., or Aldrich, Japan, and were used without further purification. Concerning the device fabrication, anhydrous chloroform (> 99.8%) and pentacene (99.0%) were purchased from Sigma-Aldrich and used without further purification.

Measurements.

¹H nuclear magnetic resonance (NMR) spectra were recorded with a JOEL JNM-ECX400 spectrometer at 25 °C using deuterated chloroform (CDCl₃) or on a JEOL JNM-ECX600 spectrometer at 25 °C using deuterated chloroform (CDCl₃). Number-average molecular weight (M_n) and molar-mass dispersity (D_M) were measured by size-exclusion chromatography (SEC) on a JASCO GULLIVER 1500 equipped with a pump (JASCO PU-1580 Intelligent HPLC Pump), an absorbance detector (JASCO UV-1575 Intelligent UV/VIS Detector, λ = 254 nm), and two polystyrene gel columns (Shodex GPC KF-804L, Shodex GPC KF-805L) with one guard column (Shodex Column GPC KF-G), based on a calibration curve using polystyrene standards. THF (40 °C) was used as a carrier solvent at the flow rate of 1.0 mL/min. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C/min for differential scanning calorimetry (DSC). The UV–Vis absorption spectra of polymer films were recorded on a Hitachi U-4100 spectrometer. A CHI 6273E electrochemistry station collected the cyclic voltammetry (CV) profile. The highest occupied molecular orbital (HOMO) level of the polymer film was defined by its oxidation potential in the CV profile under a three-electrode electrochemical system comprising a coated indium tin oxide (ITO) plate as a working electrode, Pt as an auxiliary electrode, and Ag/AgNO₃ as a reference electrode. The lowest unoccupied molecular orbital (LUMO) level of the polymer film was defined as LUMO = HOMO + E_{g} , where E_{g} is the optical bandgap derived from the UV–Vis absorption spectrum. The surface morphology of the polymer films was characterized using a Nanoscope 3D Controller atomic force microscopy (AFM, Digital Instruments) under the tapping mode at room temperature. GIWAXS and GISAXS measurements were conducted on beamline 23A1 in National Synchrotron Radiation Research Center (NSRRC), Taiwan. An X-ray wavelength of 0.124 nm and an incident angle at 0.15° were applied. Elastic moduli representing the surface mechanical properties of polymer films were measured by an AFM apparatus (Dimension Icon, Bruker) in the PeakForceTM tapping mode. The studied polymers were spin-coated on the bare wafer, followed by thermal annealing at 150 °C for 30 min. The spring constants of the cantilevers were 5 - 42 N/m with standard silicon tips (OTESPA). The applied force was in the range of 5 - 300 nN. The force set point was adjusted depending on each measurement for a reliable fit in the unload region (2 - 10 nm). The tip oscillated at 2 kHz below the cantilever resonant frequency (300 kHz). The elastic moduli of the studied polymers were fitted with the Derjaguin-Muller-Toporov (DMT) model, which is commonly used for samples with low adhesion and small tip radii.

Synthesis of PS-TBSO-P3HT.

The in-chain-functionalized polystyrene-*b*-P3HT (PS-*b*-P3HT) with a 3-(*tert*-butyldimethylsilyloxymethyl)phenyl group (**PS-TBSO-P3HT**) was synthesized by modifying the protocol previously reported.⁵ THF (20 mL) and St (1.2 g, 12 mmol) were placed in a flask and cooled to -80 °C in GB under N₂ (O₂ <10 ppm, H₂O < 10 ppm). Next, a cyclohexane/hexane solution of *sec*-butyllithium (1.2 M, 0.16 mL, 0.19 mmol) was added to the solution at -80 °C. After stirring for 10 min, DPE-TBSO (0.09 g, 0.29 mmol) was added. A small portion of the mixed solution was taken for the SEC measurement of the product ($M_n = 7,500$, $\mathcal{D}_M = 1.07$). After 5 min, a THF solution (7.0 mL) of **P3HT-Br**, which was purified by adding a THF solution of dibutylmagnesium (1.0 M, 0.2 mL, 0.2 mmol), was added to the mixed solution. The temperature was elevated to 50 °C until getting the orangish transparent solution, followed by standing for an additional 30 min. Finally, ethanol was added to the mixed solution for quenching. It was then poured into acetone to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **PS-TBSO-P3HT** as a dark purple solid. M_n (SEC)= 14,000, $\mathcal{D}_M = 1.15$, Yield: 0.55 g, 92%.

¹H NMR (400 MHz, CDCl₃) δ 7.21-6.98 (m), 6.84-6.29 (m), 4.65-4.60 (m), 2.96-2.61 (m), 2.50 (s), 2.01-1.77 (m), 1.72-1.61 (m), 1.54-1.14 (m), 1.00-0.82 (m), 0.07-0.02 (m).

Synthesis of PS-OH-P3HT.

PS-TBSO-P3HT (0.52 g, 37 µmol) was dissolved in THF (20 mL) in a flask, followed by the addition of tetra^{*n*} butylammonium fluoride (TBAF) in a THF solution (1.0 M, 0.7 mL, 0.7 mmol). The reaction mixture was stirred at room temperature overnight. It was poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded an in-chain-functionalized PS-*b*-P3HT with a 3- (hydroxymethyl)phenyl group (**PS-OH-P3HT**) as a dark purple solid. M_n (SEC) = 14,000, D_M =1.13, Yield: 0.50 g, 96%. ¹H NMR (400 MHz, CDCl₃) δ 7.21-6.88 (m), 6.77-6.30 (m), 4.56-4.43 (m), 2.87-2.67 (m), 2.50 (s), 1.96-1.79 (m), 1.75-1.59 (m), 1.51-1.26 (m), 0.96-0.82 (m).

Synthesis of PS-alkyne-P3HT.

PS-OH-P3HT (0.25 g, 17 µmol) and THF (30 mL) were placed in a flask, followed by the addition of hex-5-ynoyl chloride in a dichloromethane solution (1.0 M, 0.7 mL, 0.7 mmol). The reaction mixture was stirred at room

temperature for 30 min. It was poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded an in-chain-functionalized PS-*b*-P3HT with an ethynyl group (**PS-alkyne-P3HT**) as a dark purple solid. M_n (SEC) = 14,000, D_M =1.13, Yield: 0.23g, 92 %.

¹H NMR (400 MHz, CDCl₃) δ 7.09-6.91 (m), 6.83-6.28 (m), 5.06-4.92 (m), 2.96-2.62 (m), 2.50 (s), 1.98-1.78 (m), 1.74-1.64 (m), 1.58-1.14 (m), 0.93-0.82 (m).

Synthesis of ABCBA-type miktoarm H-shaped copolymers.

H-CP-39k: **PS-alkyne-P3HT** (0.16 g, 11 µmol based on M_n (SEC) = 14,000), **N₃-PⁿBA-N₃**, (65 mg, 5.9 µmol based on M_n (NMR)= 11,000), and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 15 mg, 0.18 mmol) were placed in a flask. Dry THF 15 mL was added to dissolve all the chemicals at an elevated temperature. The solution was degassed by three freeze–pump–thaw cycles. Next, CuBr (17 mg, 0.10 mmol) was added to the solution. After stirring at 60 °C for 3 h, the solution was directly passed through a short pad of an Al₂O₃ column to remove the copper catalyst. It was concentrated by reduced pressure and poured into methanol to precipitate the polymer. The polymer was then isolated by high-pressure liquid chromatography (HPLC) fractionation to afford an isolated ABCBA-type miktoarm Hshaped copolymer, **H-CP-39k**. It was poured into methanol to precipitate the polymer. After filtration of the polymer, freeze-drying from its benzene solution afforded **H-CP-39k** as a dark purple solid. M_n (SEC) = 39,000, \mathcal{D}_M = 1.06, Yield: 0.10 g, 47%.

¹H NMR (400 MHz, CDCl₃) δ 7.20-6.87 (m), 6.80-6.36 (m), 5.02-4.92 (m), 4.13-3.91 (m), 2.87-2.75 (m), 2.50 (s), 2.37-2.20 (m), 1.99-1.84 (m), 1.76-1.66 (m), 1.61-1.56 (m), 1.43-1.36 (m), 0.95-0.84 (m).

Analogous polymers, H-CP-56k and H-CP-140k, were synthesized similarly to H-CP-39k.

H-CP-56k: *M*_n (SEC) = 56,000, *D*_M = 1.07, Yield: 79 mg, 34%.

¹H NMR (400 MHz, CDCl₃) δ 7.21-6.85 (m), 6.84-6.32 (m), 5.01-4.88 (m), 4.12-3.88 (m), 2.88-2.68 (m), 2.48 (s), 2.40-2.17 (m), 1.97-1.81 (m), 1.74-1.65 (m), 1.65-1.51(m), 1.48-1.28(m), 0.99-0.82 (m).

H-CP-140k: *M*_n (SEC) = 140,000, *D*_M = 1.16, Yield: 77 mg, 22%.

¹H NMR (400 MHz, CDCl₃) δ 7.18-6.89 (m), 6.78-6.35 (m), 4.13-3.83 (m), 2.84-2.75 (m), 2.47 (s), 2.44-2.18 (m), 1.98-1.81 (m), 1.69-1.50 (m), 1.44-1.33 (m), 0.99-0.84 (m).

Fabrication and Characterization of the Transistor Memory Device

A highly *n*-doped silicon wafer with a 300-nm-thick SiO₂ layer was used as the substrate of the transistor memory device with a bottom-gate/top-contact configuration. Note that the silicon wafer's surface was modified using an octadecyltrichlorosilane (ODTS) self-assembled monolayer. **H-CP** solution with a concentration of 6 mg/ml in chloroform was stirred overnight at room temperature to produce a homogeneous solution. The polymer solution was spin-coated onto the silicon wafer at a rotation speed of 1000 rpm for 30 s, and the film (50-nm-thick) was

annealed at 150 °C for 30 min in a nitrogen-filled glove box. Next, a 60-nm-thick pentacene layer was deposited onto the polymer film by using thermal evaporation. To define the source and drain electrodes, a 40-nm-thick gold layer was thermally deposited onto the pentacene film with a shadow mask (channel width/length = 1000 μ m/50 μ m). The transistor memory device was characterized using a Keithley 4200-SCS semiconductor parameter analyzer (Tektronix) in an N₂-filled glove box. The drain current in the transfer characteristics was collected at $V_d = -100$ V. Drain currents were measured after applying electric writing (OFF state, gate bias (V_g) = -100V; 2s) or photoerasing (ON state, 450 nm; 5 mW cm⁻²; 5 s) to the FET devices. The write-erase-read-erase (WRER) cycle was conducted by multiple electrical writing ($V_g = -100$ V; 2 s); reading ($V_d = -100$ V; $V_g = -50$ V); and photoerasing (450 nm; 5 mW cm⁻²; 5 s; $V_g = 20$ V). The memory device exhibited stable WRER operations along 12 consecutive cycles. To evaluate the stretchability of the polymer films, a film-transfer technique at 60 °C was applied according to the literature. The transferred polymer films were stretched to certain strain levels and printed back to a nontreated silicon wafer substrate with a 300-nm-thick SiO₂ layer.⁶



Figure S1. ¹H NMR spectra of P3HT-Br and PS-OTBS-P3HT.



Figure S2. ¹H NMR spectra of PS-OTBS-P3HT, PS-OH-P3HT, and PS-Alkyne-P3HT.







Figure S4. ¹H NMR spectra of (a) H-CP-56k and (b) H-CP-140k.



Figure S5. TGA curves of H-CP-39k, H-CP-56k and H-CP-140k.



Figure S6. DSC thermograms of (a) H-CP-39k, (b) H-CP-56k, and (c) H-CP-140k.



Figure S7. (a) 1D GIWAXS and (b) 1D GISAXS profiles along the out-of-plane direction or $q_z = 0.025$ Å⁻¹ of the regular polymer films.



Figure S8. Consecutive transfer characteristics of the memory devices with (a) **H-CP-39k** and (b) **H-CP-140k** as an electret after applying electrical writing ($V_g = -100$ V; 2 s) or photoerasing (450 nm; 5 mW cm⁻²; 5 s). Note that the V_d was -100 V and the sweeping of V_g was from 10 to -100 V, and the numbers in the legend indicate the operational sequence of electrical writing (odd numbers)/photoerasing (even numbers). (c) Transfer characteristics of the memory device based on **H-CP-140k** with different types of photoerasing including the red light (650 nm; 5 mW cm⁻²; 5 s), green light (530 nm; 5 mW cm⁻²; 5 s), blue light (450 nm; 5 mW cm⁻²; 5 s), and UV light (254 nm; 2 mW cm⁻²; 10 s). (d) Transfer characteristics of the memory device based on **H-CP-140k** stored over 60 days under nitrogen atmosphere.



Figure S9. 2D GIWAXS patterns of the transferred/stretched BCP films at varied strain levels.



Figure S10. 2D GISAXS patterns of the transferred/stretched BCP films at varied strain levels.



Figure S11. Transfer characteristics of the memory devices with transferred/stretched HBCP films of (a) **H-CP-39k**, (b) **H-CP-56k**, and (c) **H-CP-140k** as an electret after applying electrical writing ($V_g = -100 \text{ V}$; 2 s) or photoerasing (450 nm; 5 mW cm⁻²; 5 s). Note that the V_d was -100 V and the sweeping of V_g was from 10 to -100 V, and the stretching direction is parallel to the channel direction.

Ref.	Architecture	Photoprogramming	Electrical programming	Reading	Memory ratio
[14]	Si/SiO ₂ /PFO- <i>b</i> -PS/	405 nm,	<i>V</i> _g = -40V;	<i>V_d</i> = -40 V;	10 ⁴ ;
	pentacene/Au ^a	30 mW cm ⁻² , 10 s	1s	<i>V</i> _g = -10 V	10 ⁴ s
[49]	Si/SiO ₂ /PBDTT- <i>b</i> -PNDIBT- <i>b</i> -		<i>V_g</i> = -100 V;	<i>V_d</i> = -50 V	~30;
	PBDTT/Au ^b		1s		150 s
[50]	Si/SiO ₂ /	405 nm; 10 mW	<i>V_g</i> = 150 V;	<i>V_d</i> = -100 V	10 ³ ;
	PII2T- <i>b</i> -PNDI2T/Au ^c	cm ⁻² , 5 s; V _g = -30V	2s		10 ⁴ s
[51]	Si/SiO ₂ /		<i>V_g</i> = 100V;	<i>V_d</i> = -100 V	10 ⁴ ;
	P3HT- <i>b</i> -Piso/Au ^d		1s		10 ⁴ s
[52]	Si/SiO ₂ /PF-b-	365 nm;	<i>V_g</i> = -40V;	<i>V_d</i> = -40 V	104;
	Piso/pentacene/Au ^e	0.92 mW cm ⁻² ; 20s	1s		10 ⁴ s
this	Si/SiO ₂ /H-CP/	450 nm;	$V_g = -100 \text{ V};$	<i>V_d</i> = -100 V;	10 ³ ;
work	pentacene/Au ^f	5 mW cm ⁻² ; 5 s	2 s	<i>V</i> _g = -50 V	10 ⁴ s

 Table S1. Summary of the device architectures, operating parameters, and device performances of the reported block copolymers-based phototransistors.

^aPFO-*b*-PS: polyfluorene-*block*-polystyrene. ^bPBDTT-*b*-PNDIBT-*b*-PBDTT: poly(benzodithiophene*alt*-thiophene)-*block*-poly(naphthalene diimide-*alt*-bithiophene)-*block*-poly(benzodithiophene*alt*-thiophene). ^cPII2T-*b*-PNDI2T: poly(isoindigo-*alt*-bithiophene)-*block*-poly(naphthalene diimide*alt*-bithiophene). ^dP3HT-*b*-Piso: poly(3-hexylthiophene)-*block*-poly(pendent isoindigo). ^ePF-*b*-Piso: polyfluorene-*block*-poly(pendent isoindigo). ^fH-CP: H-shaped block copolymer based on poly(3hexylthiophene), polystyrene, and poly(*n*-butyl acrylate).

H-CP-39k H-CP-56k H-CP-140k Strain ∆V_{th} **∆**V_{th} **∆**V_{th} $V_{\rm th, write}$ $V_{\rm th, erase}$ $V_{\rm th, write}$ $V_{\rm th,erase}$ V_{th,write} $V_{\rm th,erase}$ (%) (V) (V) (V) (V) (V) (V) (V) (V) (V) 0 60.5 60.0 -57.8 2.7 -58.3 1.7 -56.3 -1.9 54.4 50 6.7 52.1 15.0 47.6 -45.4 -32.6 -21.8 3.6 25.4 100 36.1 23.9 25.3 -19.5 16.6 -1.4 -29.6 4.6 34.2

Table S2. Memory device parameters of the transferred/stretched H-CP films at varied strain levels.

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