Supporting Information

Organic Memory Device and Synaptic Simulation Based on Indacenodithienothiophene (IDTT) Copolymers with Improved Planarity

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Materials and Methods

All commercially available solvents, reagents, and chemicals were used as received without further purification unless otherwise stated. ^{1}H spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of $CDCl_3$ or TMS as an internal reference and are given in ppm. Number-average (M_n) and weight average (M_w) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 85 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. UV-vis spectra were recorded on a UV-1601 Shimadzu Uv-vis spectrometer. Microwave experiments were performed in a Biotage initiator V 2.3. Thermogravimetric analysis (TGA) curves were collected on Mettler in nitrogen at 10 ^{0}C min^{-1} of heating rate from 30 °C to 650 °C. Cyclic voltammetry (CV) measurements of polymers films were performed under argon atmosphere using a CHI760E Voltammetry analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and the ferrocene/ferrocenium (Fc/Fc^+) was used as the internal reference for all measurements. The scanning rate was 100 mV/s. Polymer films were drop-casted from chloroform solutions on a Pt working electrode (2 mm in diameter). XRD analysis of the samples were carried out using a Rigaku Ultima IV multipurpose X-ray diffractometer, equipped with a Cu Ka X-ray tube operated at 40 KV and 30 mA, and a cross-beam optics. The XRD spectra were collected from 3 to 60° of 2θ angles with a step width of 0.02° and 1°/min. scan speed.

Device Fabrication

The OTFT devices were fabricated with a bottom-gate top-contact geometry. Si/SiO$_2$ substrate was procured from commercial sources and the thickness of the gate dielectric was 300 nm. The semiconductor layers were prepared by spin-coating 4 mg/ml copolymers P1-P3 solutions in chloroform on the gate dielectric layer. The rotation speed was kept at 2000 rpm for 40 s and then annealed at 120/150/200 °C for 30 min. 50 nm Au metal electrodes were evaporated on the semiconductor layer under vacuum using shadow masks. The channel width (W) and length (L) of the devices are 50 μm and 1000 μm, respectively. According to the saturation region of the transistor device, the field-effect mobility (μ) and the threshold voltage (V_{th}) can be determined as follow,

$$I_{DS} = \frac{W}{2L}\mu C_i (V_{GS} - V_{th})^2$$

where I_{DS} and V_{GS} are the source-drain current and the source-gate voltage, respectively. C_i is the capacitance of copolymer layer based dielectric which is measured per unit area.

The memory devices were fabricated with the same geometry as the OTFT devices. Si/SiO$_2$ substrate was also purchased from commercial sources while the thickness of the gate dielectric was 100 nm. The 6 nm Au NPs floating gate layer was deposited by thermal evaporator at a rate of 0.02 Å s^{-1} under 4×10^{-4} Pa and then 10 nm Al$_2$O$_3$ dielectric layer was fabricated by atomic layer deposition. After that, the copolymers P3 layers were prepared in the same condition for transistors. P3 was thermally annealed at 120°C for 30 min, and the Au electrodes were evaporated on it. Transistor and memory devices characterization were carried out using a Keysight B2902A Precision Source/Measure Unit. All of the mentioned processes were executed in the dark and inside the glove box under nitrogen condition.

Experimental Procedures

General Procedure for the Synthesis of IDTT-Copolymers P1-P3.
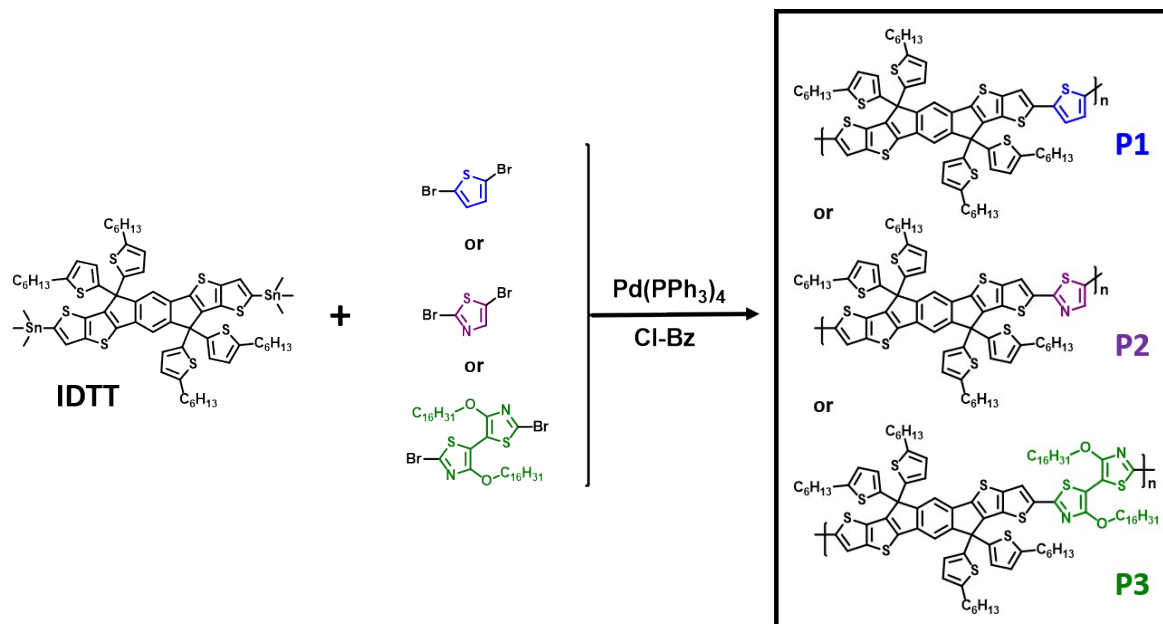
In a microwave vial equimolar amounts of 3,9-bis(trimethylstannane)-5,5',11,11'-tetrakis(5-hexylthiophen-2-yl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']-dithiopene (IDTT) (0.20 mmol) and 2,5-dibromothiophene (**P1**) or 2,5-dibromothiazole (**P2**) or 2,2'-dibromo-4,4'-dihexadecanoxy-5,5'-bithiazole (**P3**) were dissolved in anhydrous chlorobenzene (0.7 mL) followed by addition of tetrakis(triphenylphosphine)palladium(0) (2 mol%, 5.02 mg), the resultant mixture was degassed for 30 min with argon and securely sealed. The glass vial was placed into a microwave reactor and heated at 140 °C for 2 min, 160 °C for 2 min, and followed by 180 °C for 45 min. After being cooled to room temperature, the reaction mixture was precipitated into a mixture of methanol (200 mL) and concentrated HCl (2 mL) and stirred for 1 h at RT. The precipitate was filtered and extracted (Soxhlet) with methanol,

acetone, n-hexane, chloroform. The remaining polymer in chlorobenzene was precipitated into methanol, filtered and dried under vacuum to achieve the desired polymers as a dark solid. The ^{1}H NMR spectrum for all polymers exhibited broadening of the aromatic and alkyl sidechain protons. We attribute this to the aggregation effects.

P1: Yield 85% (103 mg), ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (2H), 7.39 (2H), 7.11 (2H), 6.79 (4H), 6.55 (4H), 2.66 (8H), 1.20-1.40 (32H), 0.83 (12H); GPC: M_n = 28,600 g/mol, Đ = 2.0; UV-Vis: λ_{max} = 545 nm (dilute chloroform solution).

P2: Yield 89% (112 mg), ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (1H), 7.72 (1H), 7.70 (2H), 7.41 (1H), 6.83 (4H), 6.58 (4H), 2.71 (8H), 1.62 (8H), 1.20-1.40 (24H), 0.85 (12H); GPC: M_n = 26,100 g/mol, Đ = 1.9; UV-Vis: λ_{max} = 548 nm (dilute chloroform solution).

P3: Yield (87%) 123 mg, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (4H), 6.84 (4H), 6.58 (4H), 4.51 (4H), 2.72 (8H), 1.88 (4H) 1.61 (8H), 1.20-1.40 (74H), 0.85 (18H); GPC: M_n = 35,400g/mol, Đ = 2.1; UV-Vis: λ_{max} = 610 nm (dilute chloroform solution).
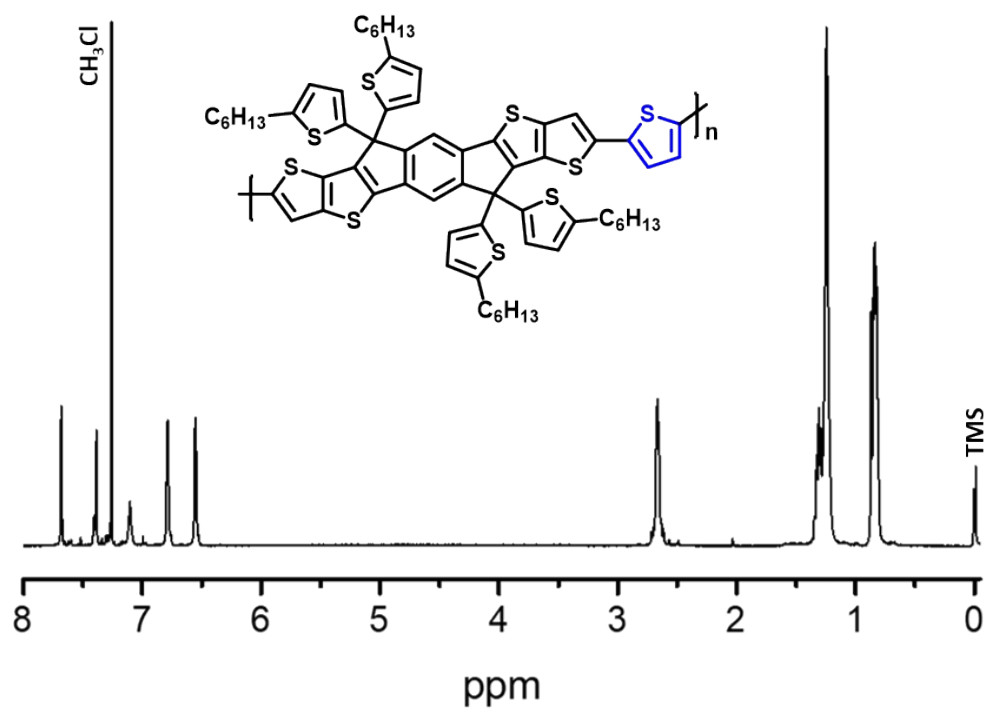
NMR characterization

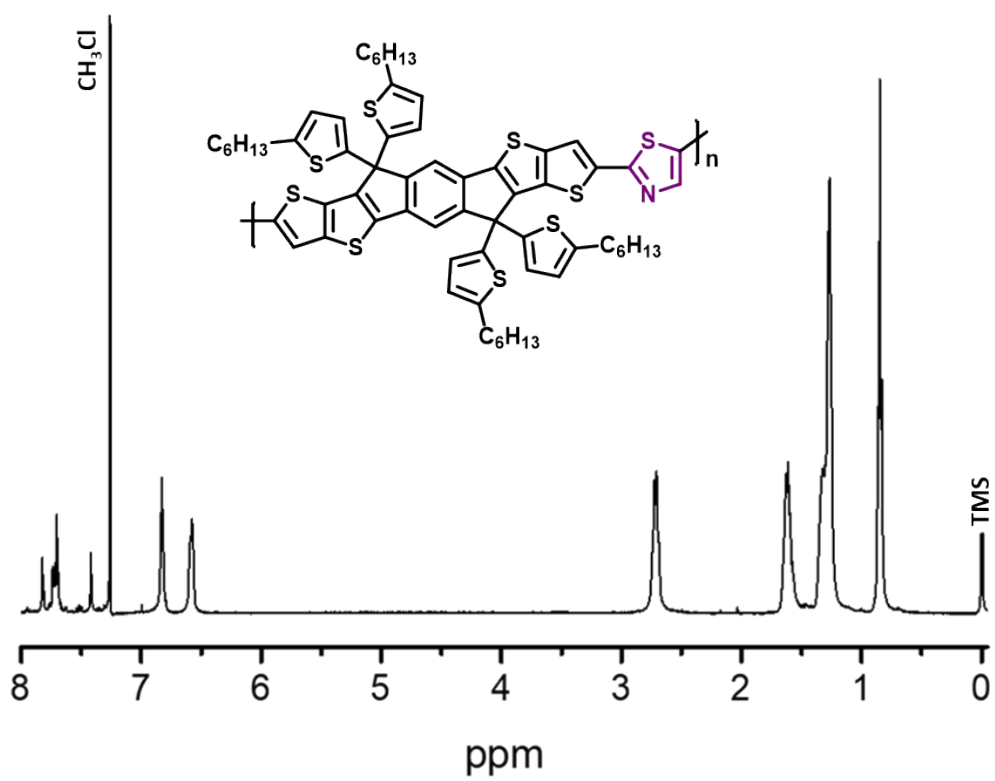**Figure S1.** ^{1}H NMR spectrum of **P1**.

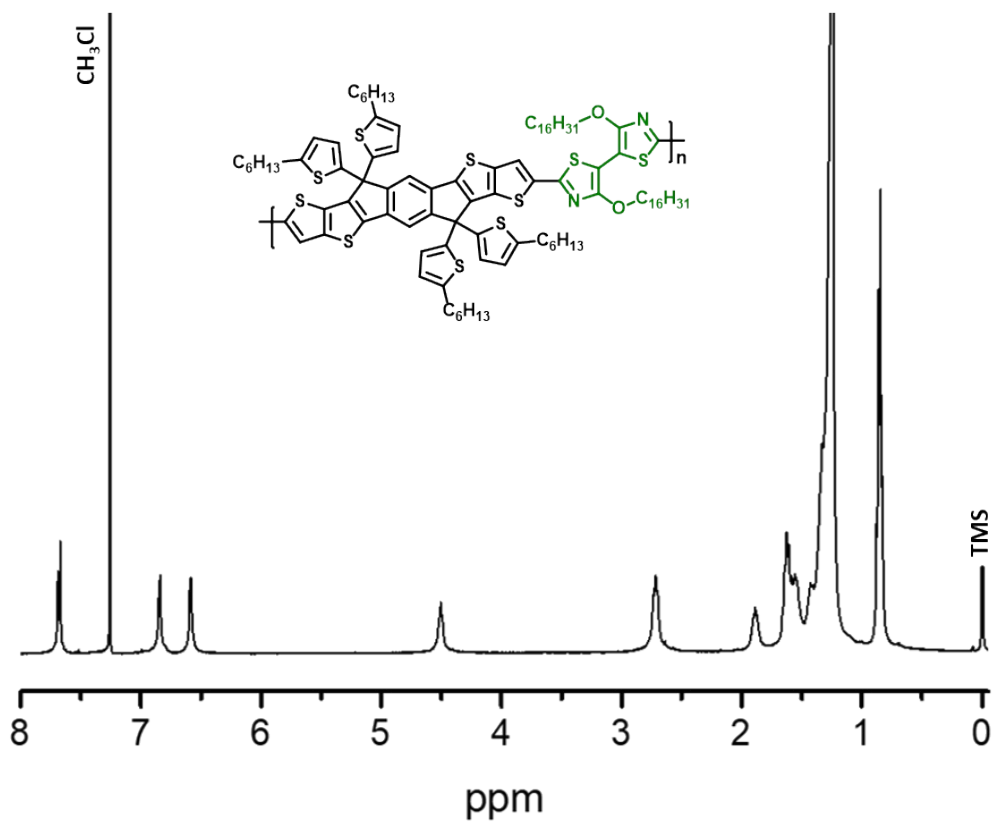**Figure S2.** ^{1}H NMR spectrum of **P2**.

Figure S3. ^{1}H NMR spectrum of **P3**.
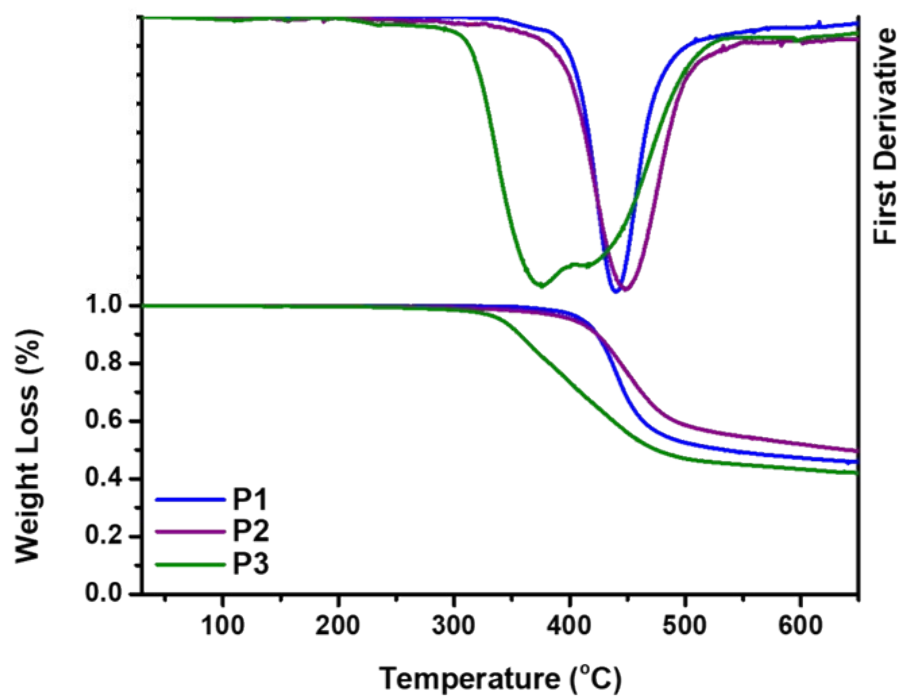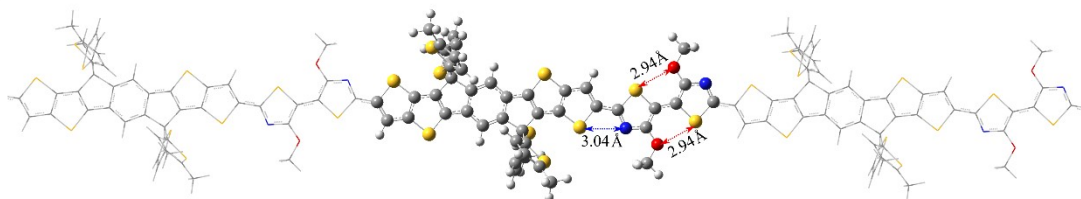
Thermal Properties

Figure S4. (a) TGA thermograms of copolymers **P1-P3** under nitrogen flow at 10 °C min^{-1} of heating rate from 30 °C to 650 °C.

DFT Calculations

a)

b)

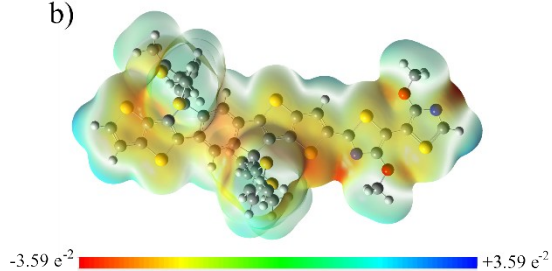-3.59 e^{-2} ▬▬▬▬▬▬▬▬▬▬▬▬▬▬ +3.59 e^{-2}

Figure S5. a) Intramolecular interactions in the optimized geometry of **P3** polymer structure. b) The electron density from total SCF density (isoval = 0.0004) was mapped with ESP for **P3** monomer unit.
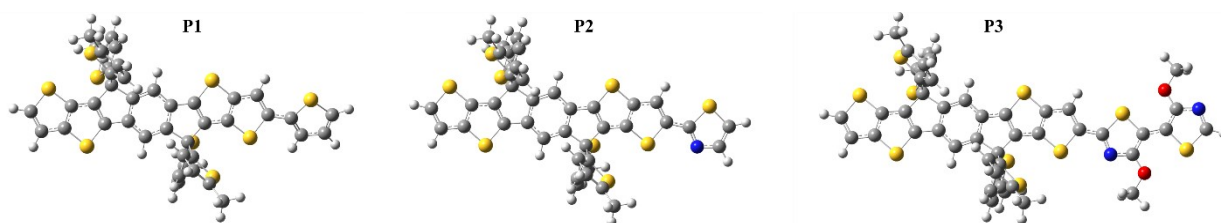

Figure S6. Three monomeric units based on which the reorganization energies were calculated.

Table S1. The calculated (B3LYP/6-31G**) internal reorganization energies, for both electron and hole carriers, for **P1-P3** monomers.

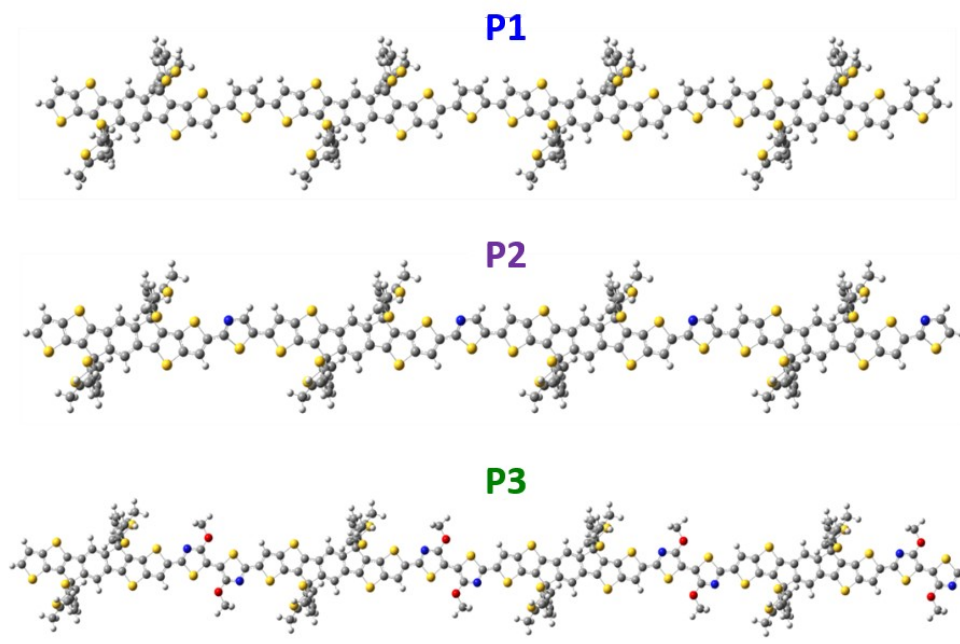|	λ_e (meV)	λ_h (meV)
P1	239	251
P2	237	225
P3	233	258

Figure S7. Three tetrameric structures optimized at B3LYP/6-31G** based on which the vertical transition energies were calculated.

Table S2. Vertical transition energies (E_{vert}/λ_{max} [eV/nm]), oscillator strengths (f), and electronic configurations of the lowest two excitations, as calculated by TD-DFT at CAM-B3LYP/6-31+G(d,p)/SMD($CHCl_3$) level.

Polymer	Excitation	E_{vert}/χ_{max}	f	Electronic configuration
P1	$S_0 \rightarrow S_1$	2.66 eV/466 nm	8.44	H $\rightarrow$ L (0.47) (44%); H-1 $\rightarrow$ L+1 (0.31) (20%)
	$S_0 \rightarrow S_2$	3.07 eV/404 nm	0.70	H $\rightarrow$ L+2 (0.33) (22%); H-1 $\rightarrow$ L+1 (0.27) (15%)
P2	$S_0 \rightarrow S_1$	2.56 eV/485 nm	8.65	H $\rightarrow$ L (0.48) (46%); H-1 $\rightarrow$ L+1 (0.30) (18%)
	$S_0 \rightarrow S_2$	2.90 eV/427 nm	0.60	H $\rightarrow$ L+2 (0.36) (26%); H-2 $\rightarrow$ L (0.33) (22%)
P3	$S_0 \rightarrow S_1$	2.21 eV/561 nm	9.88	H $\rightarrow$ L (0.46) (42%); H-1 $\rightarrow$ L+1 (0.30) (18%)

H and L represent HOMO and LUMO, respectively. Data in parentheses denote the contributions of the electronic configuration.

The calculated bandgaps of all copolymers agree well with the experimentally determined values, whereas HOMO/LUMO positions are shifted to the less negative potentials of approximately 0.7 eV (**Figure 2e**). The exchange of thiophene heterocycle with the electron-deficient thiazole units stabilizes both the HOMO and LUMO energy levels of **P2** compared to **P1**, with almost no effect on the bandgap. At variance, the insertion of additional thiazole unit in **P3** destabilizes the HOMO energy level (-4.30 eV) relative to **P1** (-4.58 eV) and **P2** (-4.61 eV), while LUMO is only slightly stabilized. This results in a reduced bandgap value that is in line with the experimental results (**Figure 2e**). The theoretically predicted bandgap of **P3** is 1.92 eV, which is overestimated by only 0.1 eV compared to the experimentally determined value (1.82 eV).

The relevant dihedral angles have been obtained upon the structure optimization using the periodic boundary conditions (PBC) calculations. We didn't use trimer structures for the dihedral angles' predictions, instead, we used infinite chains as PBC models. So, all consecutive dihedral angles are the same in every polymer, and average dihedral angles would coincide with the presented ones.
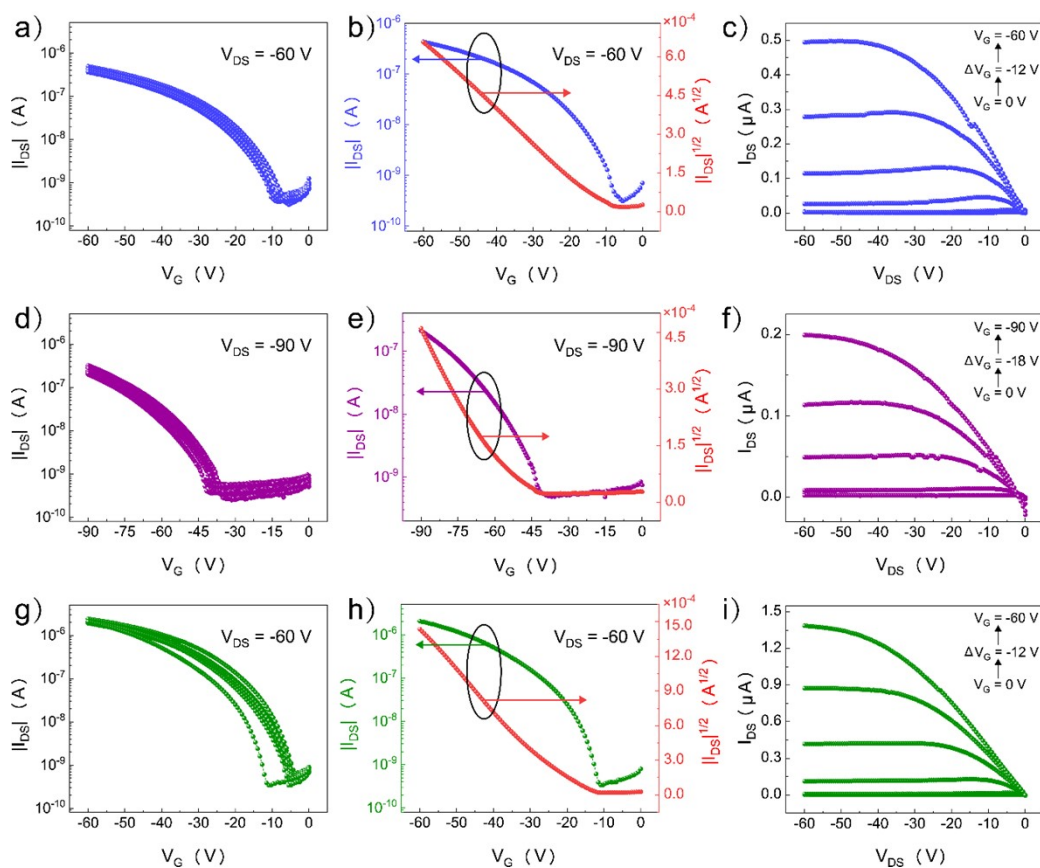
OFET Performance

Figure S8. Transfer characteristics of 10 devices and the best devices and output characteristics of the best devices in BG/TC OFET based on a-c) **P1**, d-f) **P2** and g-i) **P3** after thermal annealing at 120 °C.
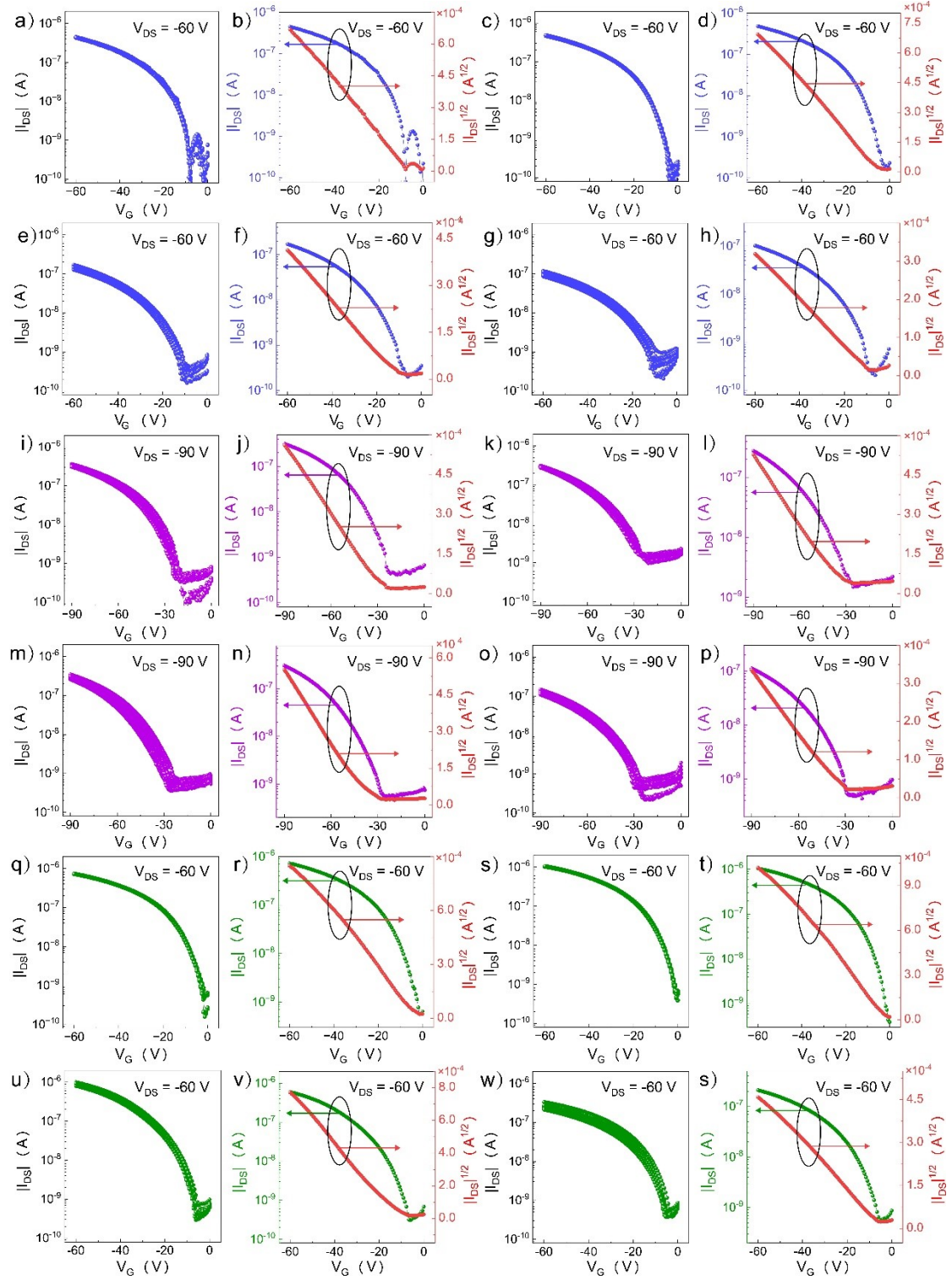
Figure S9. Transfer characteristics of 10 devices and the best devices after thermal annealing at 80°C based on a-b) **P1**, i-j) **P2** and q-r) **P3**, 100 °C based on c-d) **P1**, k-l) **P2** and s-t) **P3**, 150°C based on e-f) **P1**, m-n) **P2** and u-v) **P3** and at 200 °C based on g-h) **P1**, o-p) **P2** and w-s) **P3**.

Table S3. Summary of mobility, threshold voltage and on/off current ratio at different annealing temperature of copolymer **P1-P3**.

Polymer	Annealing Temperature	[a]μ_{max} (cm^2 V^{-1} s^{-1})	[b]μ_{ave} (cm^2 V^{-1} s^{-1})	[c]V_T (V)	[d]I_{on}/I_{off}
P1	80 °C	1.6×10^{-3}	$1.5 (\pm 0.1) \times 10^{-3}$	-6.13	10^3
	100 °C	1.7×10^{-3}	$1.6 (\pm 0.1) \times 10^{-3}$	-4.42	10^3
	120 °C	2.1×10^{-3}	$1.8 (\pm 0.2) \times 10^{-3}$	-10.56	10^3
	150 °C	7.8×10^{-4}	$6.6 (\pm 0.7) \times 10^{-4}$	-12.18	10^2
	200 °C	4.5×10^{-4}	$4.0 (\pm 0.3) \times 10^{-4}$	-7.65	10^2
P2	80 °C	8.1×10^{-4}	$7.6 (\pm 0.5) \times 10^{-4}$	-26.56	10^2
	100 °C	8.2×10^{-4}	$7.7 (\pm 0.5) \times 10^{-4}$	-31.73	10^2
	120 °C	2.0×10^{-3}	$1.5 (\pm 0.2) \times 10^{-3}$	-49.82	10^3
	150 °C	1.1×10^{-3}	$9.7 (\pm 0.5) \times 10^{-4}$	-35.91	10^2
	200 °C	3.7×10^{-4}	$3.2 (\pm 0.2) \times 10^{-4}$	-26.46	10^2
P3	80 °C	2.8×10^{-3}	$2.6 (\pm 0.2) \times 10^{-3}$	-2.48	10^3
	100 °C	4.3×10^{-3}	$4.1 (\pm 0.2) \times 10^{-3}$	-2.12	10^3
	120 °C	0.014	$1.0 (\pm 0.1) \times 10^{-2}$	-20.52	10^4
	150 °C	4.7×10^{-3}	$4.1 (\pm 0.5) \times 10^{-3}$	-10.38	10^3
	200 °C	1.2×10^{-3}	$9.2 (\pm 1.3) \times 10^{-4}$	-1	10^3

[a]Maximum value of the mobilities measured under the nitrogen atmosphere in the saturation regimes; [b]Average values of hole mobilities measured from 10 devices; [c]Threshold voltage; [d]On/off current ratio.
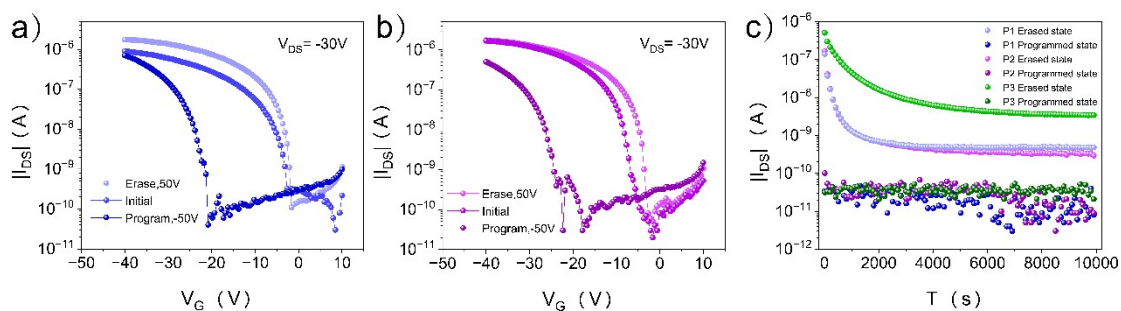
OFET Memory Performance

Figure S10. a-b) Transfer plots of **P1** and **P2** memory devices. c) Comparison of data retention capability of the **P1-P3** memory device.
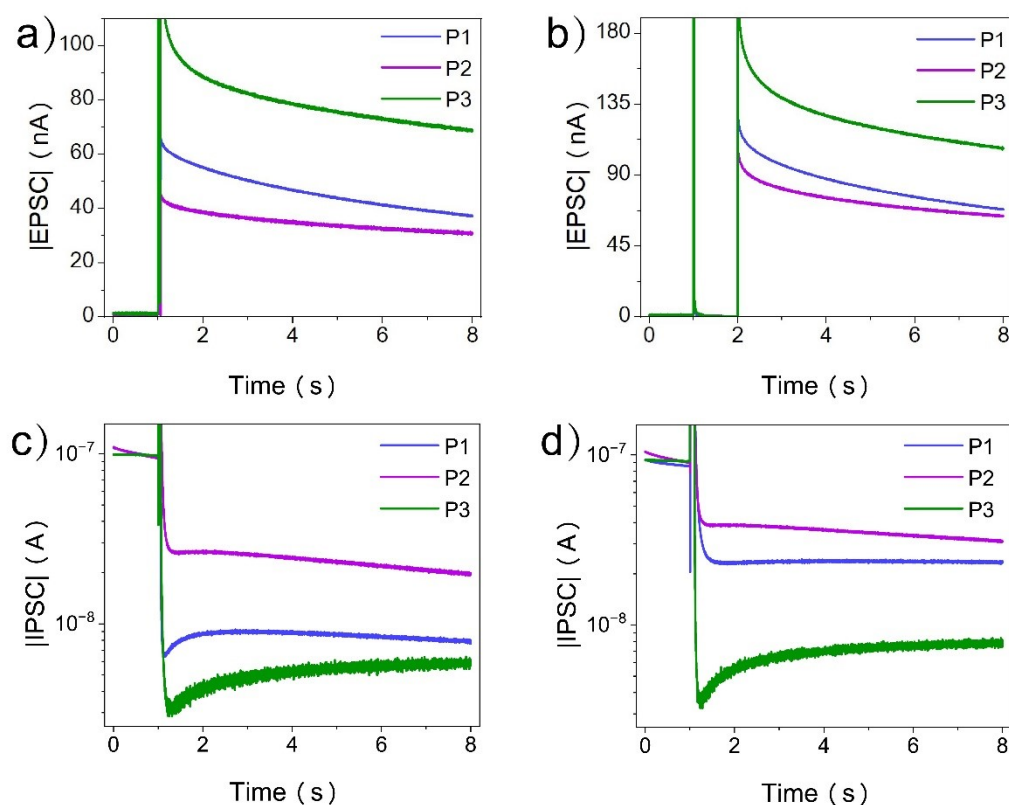
Synapse Simulation

Figure S11. a,b) |EPSC| generated by erasing operation (a: amplitude: 50V, width: 0.05s; b: amplitude: 40V, width: 1s) with base voltage as -10V and V_{DS} as -10V of **P1-P3** device. c,d) |IPSC| generated by programming operation (c: amplitude: -45V, width: 0.05s; d: amplitude: -40V, width: 0.1s) with base voltage as -10V and V_{DS} as -10V of **P1-P3** device.
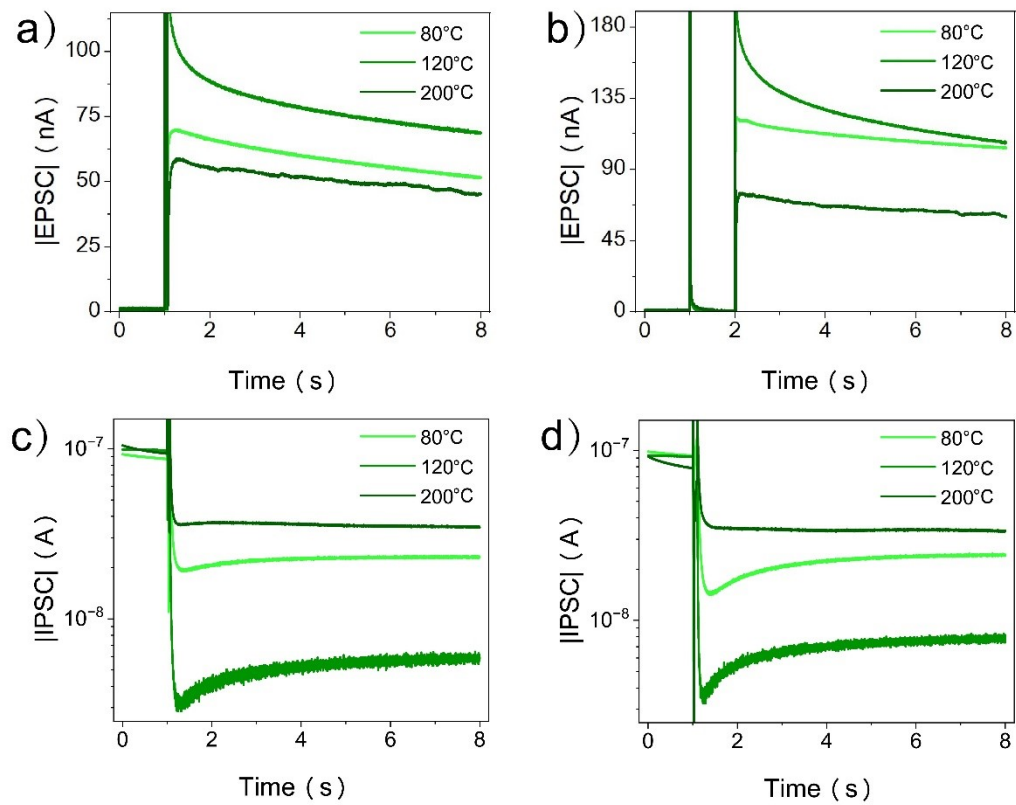
Figure S12. a,b) |EPSC| generated by erasing operation (a: amplitude: 50V, width: 0.05s; b: amplitude: 40V, width: 1s) with base voltage as -10V and V_{DS} as -10V of **P3** device annealed at 80°C, 120°C and 200°C. c,d) |IPSC| generated by programming operation (c: amplitude: -45V, width: 0.05s; d: amplitude: -40V, width: 0.1s) with base voltage as -10V and V_{DS} as -10V of **P3** device annealed at 80°C, 120°C and 200°C
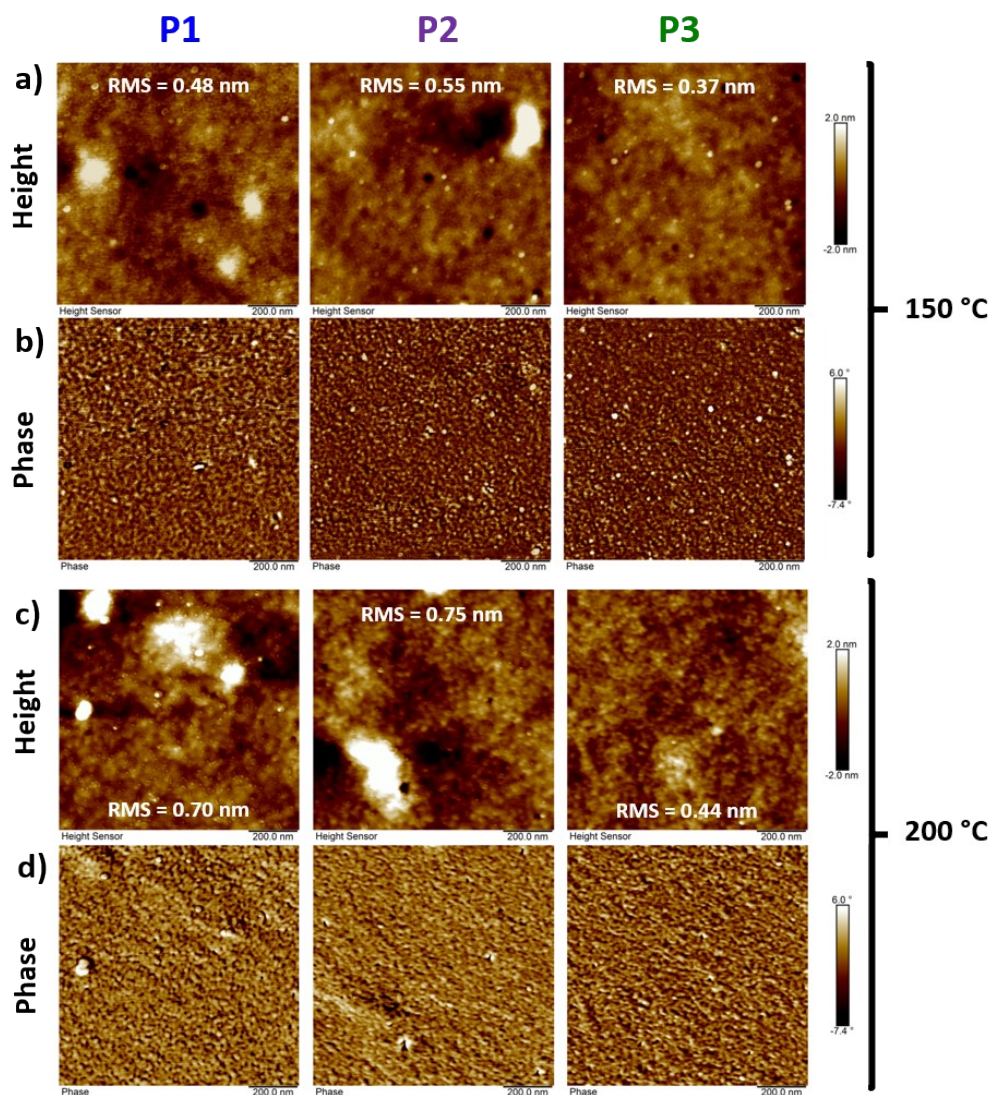
Morphological Properties

Figure S13. Tapping-mode AFM images of (a-c) height, (b-d) phase in 1 μm × 1 μm scan size of copolymers **P1-P3** annealed at 150 °C (a-b) and 200 °C for 15 min.