

Supporting Information

Improving Performance of Photonic Transistor Memory Devices using Conjugated Block Copolymers as a Floating Gate

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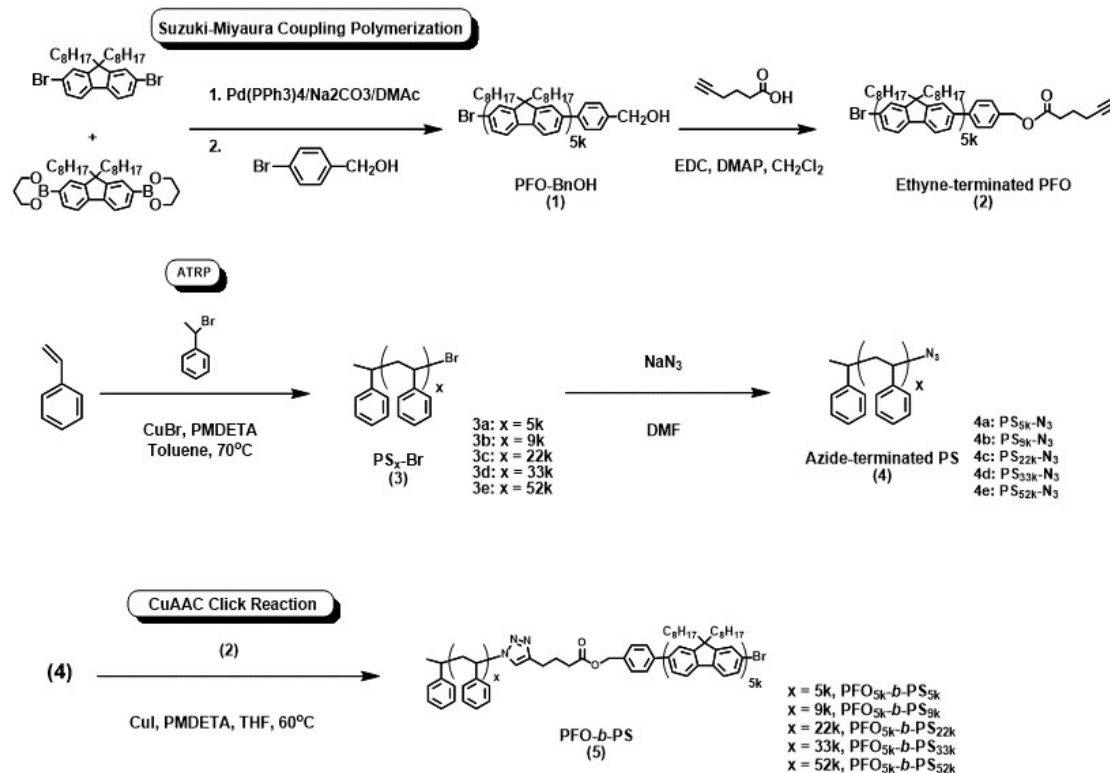
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Scheme S1. Synthetic route of studied polymers.

Synthesis of ethyne-terminated PFO_{5k}.

Poly[2,7-(9,9-dioctylfluorene)] with a benzyl alcohol group at the α -chain end (1000 mg, 0.2mmol), EDC (383.4 mg, 1mmol) and DMAP (243.3 mg, 1 mmol) were first dissolved in 20 mL of dry DCM. 5-Hexynoic acid (0.2177 ml) was later added in the flask and the reaction was conducted for 24 h at room temperature. After that, the solution underwent extraction concerning brine and DCM. The organic phase was collected and evaporated, and the residue was dissolved in THF and precipitated in a cold mixture of MeOH and acetone (9:1) to give a light-yellow powder of ethyne-terminated PFO_{5k} (860 mg, yield: 86%). $M_{n,NMR} = 5500 \text{ g mol}^{-1}$; $M_w/M_n = 1.27$.

Synthesis of 3a.

Styrene (9.09 g, 87 mmol), (1-bromoethyl)benzene (162 mg, 0.87 mmol) and PMDETA (45 mg, 0.26 mmol) were mixed. The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (38 mg, 0.26 mmol), the mixture was reacted at 80 °C under argon for 1 h. After quenching with air, the crude was precipitated in methanol to obtain a white solid (3.02 g). The monomer conversion and number-average molecular weight ($M_{n,NMR}$) determined by $^1\text{H-NMR}$ spectroscopy were 35% and $M_{n,NMR} = 5000 \text{ g mol}^{-1}$, respectively. Molecular weight evaluated by SEC: $M_{n(SEC)} = 4500 \text{ g mol}^{-1}$, $M_{w(SEC)} = 4900 \text{ g mol}^{-1}$, $M_w/M_n = 1.09$.

Synthesis of 3b.

Styrene (9.09 g, 87 mmol), (1-bromoethyl)benzene (162 mg, 0.87 mmol) and PMDETA (45 mg, 0.26 mmol) were mixed. The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (38 mg, 0.26 mmol), the mixture was reacted at 80 °C under argon for 6 h. After quenching with air, the crude was precipitated in methanol to obtain a white solid (5.07 g). The monomer conversion and number-average molecular weight ($M_{n,NMR}$) determined by $^1\text{H-NMR}$ spectroscopy were 65% and $M_{n,NMR} = 8,700 \text{ g mol}^{-1}$, respectively. Molecular weight evaluated by SEC: $M_{n(SEC)} = 7,200 \text{ g mol}^{-1}$, $M_{w(SEC)} = 7,600 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$.

Synthesis of 3c.

Styrene (9.09 g, 87 mmol), (1-bromoethyl)benzene (40 mg, 0.22 mmol) and PMDETA (19 mg, 0.11 mmol) were mixed. The mixture was degassed with three freeze-pump-thaw

cycles. After addition of CuBr (16 mg, 0.11 mmol), the mixture was reacted at 80 °C under argon for 10 h. After quenching with air, the crude was precipitated in methanol to obtain a white solid (3.04 g). The monomer conversion and number-average molecular weight ($M_{n,NMR}$) determined by $^1\text{H-NMR}$ spectroscopy were 41% and $M_{n,NMR} = 22,400 \text{ g mol}^{-1}$, respectively. Molecular weight evaluated by SEC: $M_{n(SEC)} = 15,600 \text{ g mol}^{-1}$, $M_{w(SEC)} = 16,400 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$.

Polymerization of 3d.

Styrene (9.09 g, 87 mmol), (1-bromoethyl)benzene (41 mg, 0.22 mmol) and PMDETA (100 mg, 0.58 mmol) were mixed. The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (85 mg, 0.58 mmol), the mixture was reacted at 100 °C under argon for 3 h. After quenching with air, the crude was precipitated in methanol to obtain a white solid (6.10 g). The ATRP conversion determined by $^1\text{H-NMR}$ spectroscopy with the crude product was 80% with $M_{n,NMR} = 33000$. Molecular weight evaluated by SEC: $M_n = 31000$, $M_w = 44000$, PDI = 1.42.

Polymerization of 3e.

Styrene (9.09 g, 87 mmol), (1-bromoethyl)benzene (27 mg, 0.15 mmol) and PMDETA (69 mg, 0.40 mmol) were mixed. The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (59 mg, 0.40 mmol), the mixture was reacted at 100 °C under argon for 3.5 h. After quenching with air, the crude was precipitated in methanol to obtain a white solid (7.11 g). The ATRP conversion determined by $^1\text{H-NMR}$ spectroscopy with the

crude product was 85% with $M_{n,NMR} = 52000$. Molecular weight evaluated by SEC: $M_n = 46000$, $M_w = 55000$, PDI = 1.20.

Azidation for 4a.

3a (2.50 g, 0.5 mmol) was mixed with NaN_3 (163 mg, 2.5 mmol) in 20 mL of DMF and kept stirred at 60 °C for 1 day. After that, the solvent was evaporated and the crude was dissolved in DCM and passed through a Al_2O_3 packed column to remove the catalyst residue. The organic phase is collected and the solvent is removed under reduced pressure. The polymer is precipitated in methanol to afford a white solid of 2.32 g (yield: 93%).

Azidation for 4b.

3b (2.50 g, 0.5 mmol) was mixed with NaN_3 (163 mg, 2.5 mmol) in 20 mL of DMF and kept stirred at 60 °C for 1 day. After that, the solvent was evaporated and the crude was dissolved in DCM and passed through a Al_2O_3 packed column to remove the catalyst residue. The organic phase is collected and the solvent is removed under reduced pressure. The polymer is precipitated in methanol to afford a white solid of 2.38 g (yield: 95%).

Azidation for 4c.

3c (2.50 g, 0.5 mmol) was mixed with NaN_3 (163 mg, 2.5 mmol) in 20 mL of DMF and kept stirred at 60 °C for 1 day. After that, the solvent was evaporated and the crude was dissolved in DCM and passed through a Al_2O_3 packed column to remove the catalyst residue.

The organic phase is collected and the solvent is removed under reduced pressure. The polymer is precipitated in methanol to afford a white solid of 2.45 g (yield: 98%).

Azidation for 4d.

3d (1.00 g, 0.03 mmol) was mixed with NaN₃ (10 mg, 0.15 mmol) in 15 mL of DMF and kept stirred at 60 °C for 1 day. After that, the crude solution was diluted with DCM and extracted with water and brine. The organic phase is collected and the solvent is removed under reduced pressure. The polymer is precipitated in methanol to afford a white solid of 0.87 g (yield: 87%).

Azidation for 4e.

3e (1.00 g, 0.02 mmol) was mixed with NaN₃ (7 mg, 0.10 mmol) in 15 mL of DMF and kept stirred at 60 °C for 1 day. After that, the crude solution was diluted with DCM and extracted with water and brine. The organic phase is collected and the solvent is removed under reduced pressure. The polymer is precipitated in methanol to afford a white solid of 0.82 g (yield: 82%).

Table S1. Material characterization of the studied polymers.

	$M_w(\text{SEC})$	M_w/M_n	T_g (°C)	λ_{Max}^{UV} (nm)	λ_{Max}^{PL} (nm)
PFO_{5k}-<i>b</i>-PS_{5k}	9100	1.29	70, 94	380, 427	437, 464, 493
PFO_{5k}-<i>b</i>-PS_{9k}	10700	1.12	69, 95	380, 426	437, 463, 494
PFO_{5k}-<i>b</i>-PS_{22k}	18900	1.11	70, 98	376, 427	436, 463, 491
PFO_{5k}-<i>b</i>-PS_{33k}	38000	1.54	51,97	378	433, 458, 490
PFO_{5k}-<i>b</i>-PS_{52k}	61000	1.24	48,97	379	431, 456, 488
PFO_{5k}	5000	1.27	71	380	432, 459
PS_{22k}	16400	1.05	96	--	--

Table S2. FET photonic memory device parameters of the studied polymers based on three batch of devices.

	State	μ_h (cm ² V ⁻¹ s ⁻¹)	V _{T,write} (V)	V _{T,erase} (V)	I _{on} /I _{off}
PFO_{5k}-b- PS_{5k}	As-cast	7.4×10 ⁻⁴ ± 4×10 ⁻⁵	3.2 ± 0.4	-18.1 ± 0.4	5.1×10 ¹ ± 4×10 ⁰
	Annealed	5.2×10 ⁻³ ± 2×10 ⁻⁴	3.1 ± 0.4	-22.0 ± 0.8	1.2×10 ² ± 1×10 ¹
PFO_{5k}-b- PS_{9k}	As-cast	4.3×10 ⁻⁴ ± 4×10 ⁻⁵	1.7 ± 0.2	-24.8 ± 1.7	1.0×10 ³ ± 2×10 ²
	Annealed	3.5×10 ⁻³ ± 3×10 ⁻⁴	3.0 ± 0.4	-21.3 ± 1.2	3.8×10 ³ ± 3×10 ²
PFO_{5k}-b- PS_{22k}	As-cast	7.1×10 ⁻³ ± 3×10 ⁻⁴	2.8 ± 0.2	-18.1 ± 0.4	1.2×10 ¹ ± 5×10 ⁰
	Annealed	7.4×10 ⁻³ ± 7×10 ⁻⁴	5.0 ± 0.3	-16.0 ± 0.8	1.0×10 ⁴ ± 1×10 ³
PFO_{5k}-b- PS_{33k}	Annealed	2.1×10 ⁻¹ ± 1×10 ⁻²	-6.3 ± 0.6	-17.8 ± 2.0	9.1×10 ² ± 1×10 ¹
PFO_{5k}-b- PS_{52k}	Annealed	1.3×10 ⁻¹ ± 1×10 ⁻²	-6.3 ± 0.5	-14.3 ± 0.7	8.5×10 ¹ ± 1×10 ⁰
PFO-blend- PS_{22k}	Annealed	7.6×10 ⁻³ ± 1×10 ⁻⁴	0.2 ± 0.04	-20 ± 1.2	1.0×10 ¹ ± 1×10 ⁰

Table S3. Dielectric properties, surface energy and FET device parameters of the thin films of the studied block copolymers.

	Thickness (nm) ^a	C_p (nF/cm ²) ^b	D_k ^c	θ_{water} (°) ^d	$\theta_{glycerol}$ (°) ^d	γ_D (mN/m) ^e	γ_P (mN/m) ^f	σ_s (mN/m) ^g
PFO_{5k}-<i>b</i>-PS_{5k}	24	100	2.7	97.3	75.8	45.9	0	45.9
PFO_{5k}-<i>b</i>-PS_{9k}	25	105	2.8	98.3	79.4	37.6	0.1	37.7
PFO_{5k}-<i>b</i>-PS_{22k}	23	118	3.2	101.9	84.5	32.0	0.1	32.1
PFO_{5k}-<i>b</i>-PS_{33k}	22	121	3.3	103.1	87.0	28.0	0.2	28.3
PFO_{5k}-<i>b</i>-PS_{52k}	27	129	3.5	103.5	88.0	26.2	0.3	26.5

^a Film thickness measured from a surface profilometer. ^b Capacitance derived from a metal-insulator-metal (MIM) structure. ^c Dielectric constant calculated from the capacitance. ^d Contact angle between the film and water or glycerol. ^e Distribution contribution of the surface energy. ^f Polar contribution of the surface energy. ^g Surface energy fitted by Owens and Wendt method.

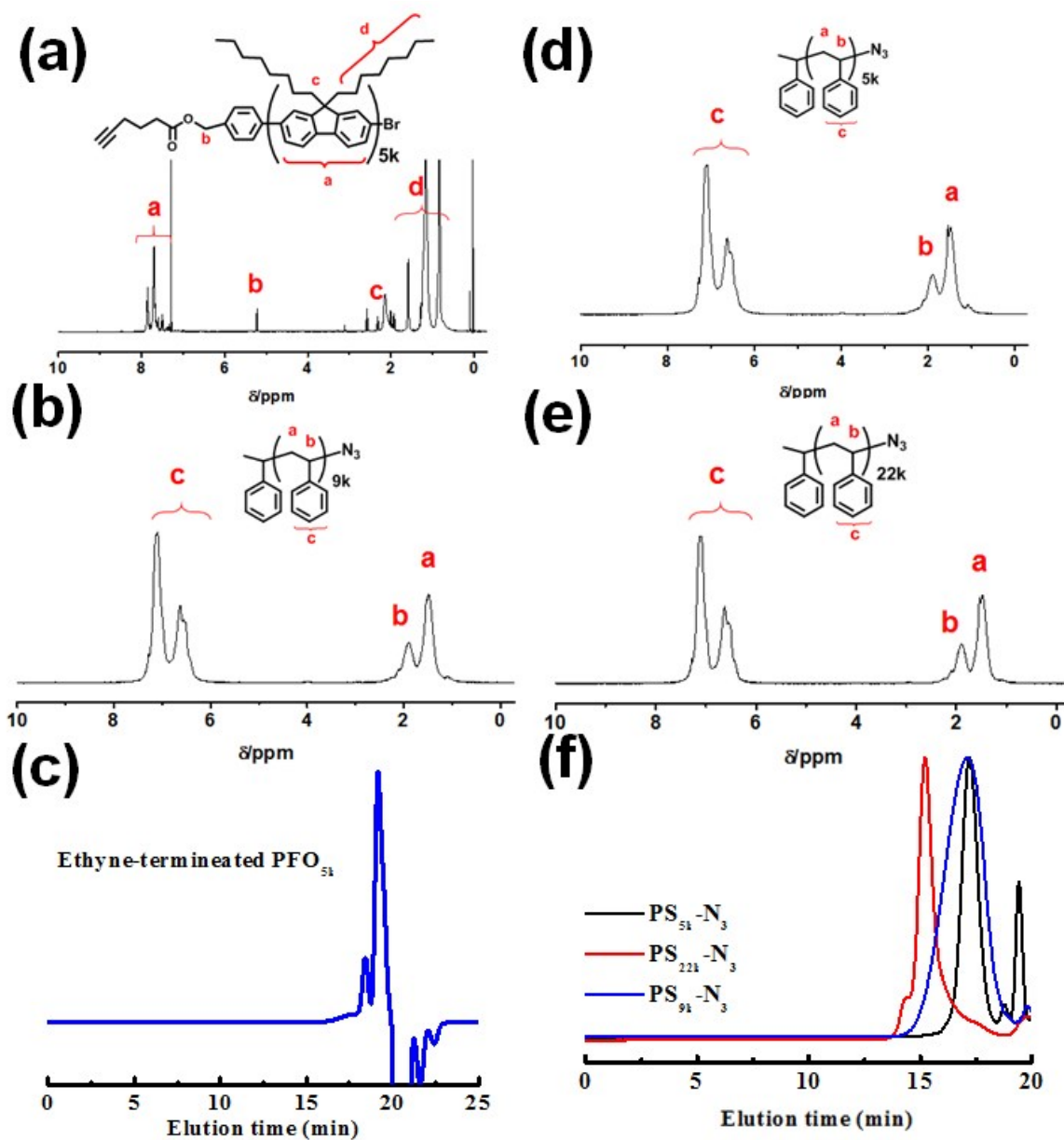


Fig. S1. $^1\text{H-NMR}$ spectrum for the synthesized (a) ethyne-terminated PFO_{5k} (b) azide-terminated PS_{5k} (c) azide-terminated PS_{9k} (d) azide-terminated PS_{22k}. SEC profiles of (e) ethyne-terminated PFO_{5k} (f) azide-terminated PS with various molecular weight in THF calibrated by PS.

k

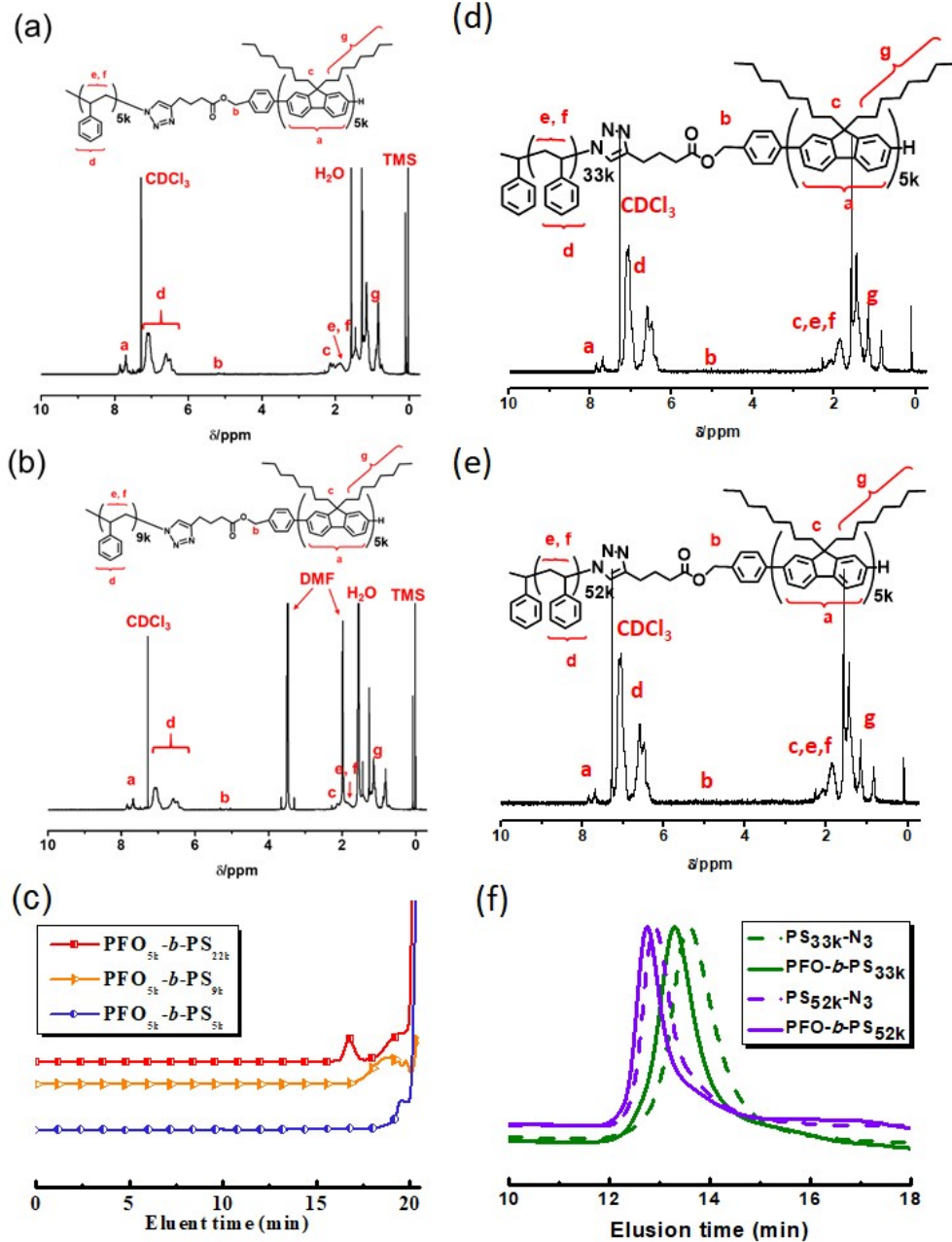


Fig. S2. $^1\text{H-NMR}$ spectrum for the synthesized (a) $\text{PFO}_{5\text{k}}\text{-}b\text{-PS}_{5\text{k}}$ and (b) $\text{PFO}_{5\text{k}}\text{-}b\text{-PS}_{9\text{k}}$. (c) SEC curves in THF calibrated by PS of the studied BCPs. $^1\text{H-NMR}$ spectrum for the synthesized (d) $\text{PFO}_{5\text{k}}\text{-}b\text{-PS}_{33\text{k}}$ and (e) $\text{PFO}_{5\text{k}}\text{-}b\text{-PS}_{52\text{k}}$. (f) SEC curves in THF calibrated by PS of $\text{PFO}_{5\text{k}}\text{-}b\text{-PS}_{33\text{k}}$ and $\text{PFO}_{5\text{k}}\text{-}b\text{-PS}_{52\text{k}}$.

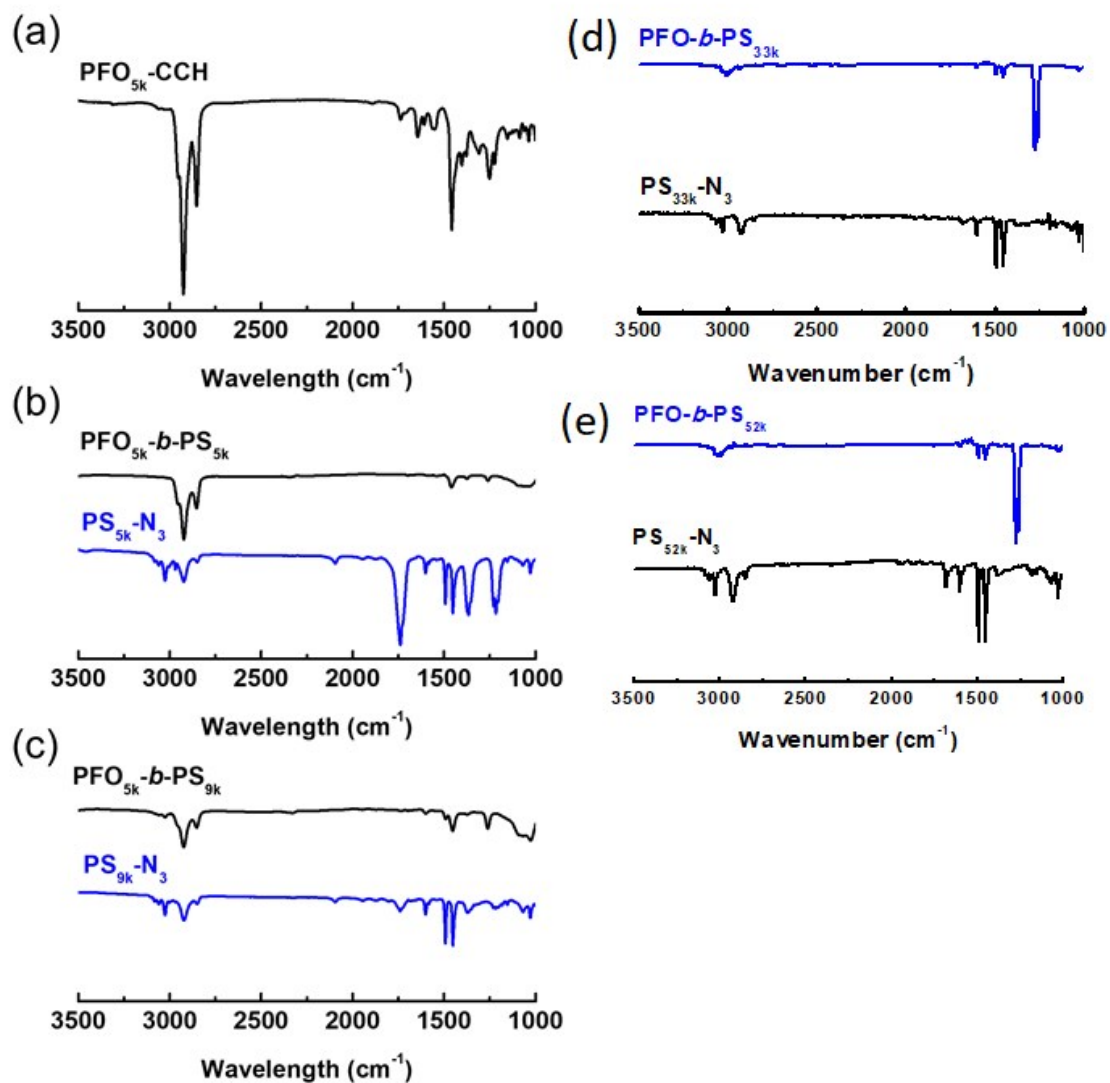


Fig. S3. FT-IR spectra for the studied polymers (a) ethyne-terminated PFO_{5k} homopolymer, (b) PFO_{5k}-*b*-PS_{5k} and PS_{5k}-N₃, (c) PFO_{5k}-*b*-PS_{9k} and PS_{9k}-N₃, (d) PFO_{5k}-*b*-PS_{33k} and PS_{33k}-N₃, and (e) PFO_{5k}-*b*-PS_{52k} and PS_{52k}-N₃.

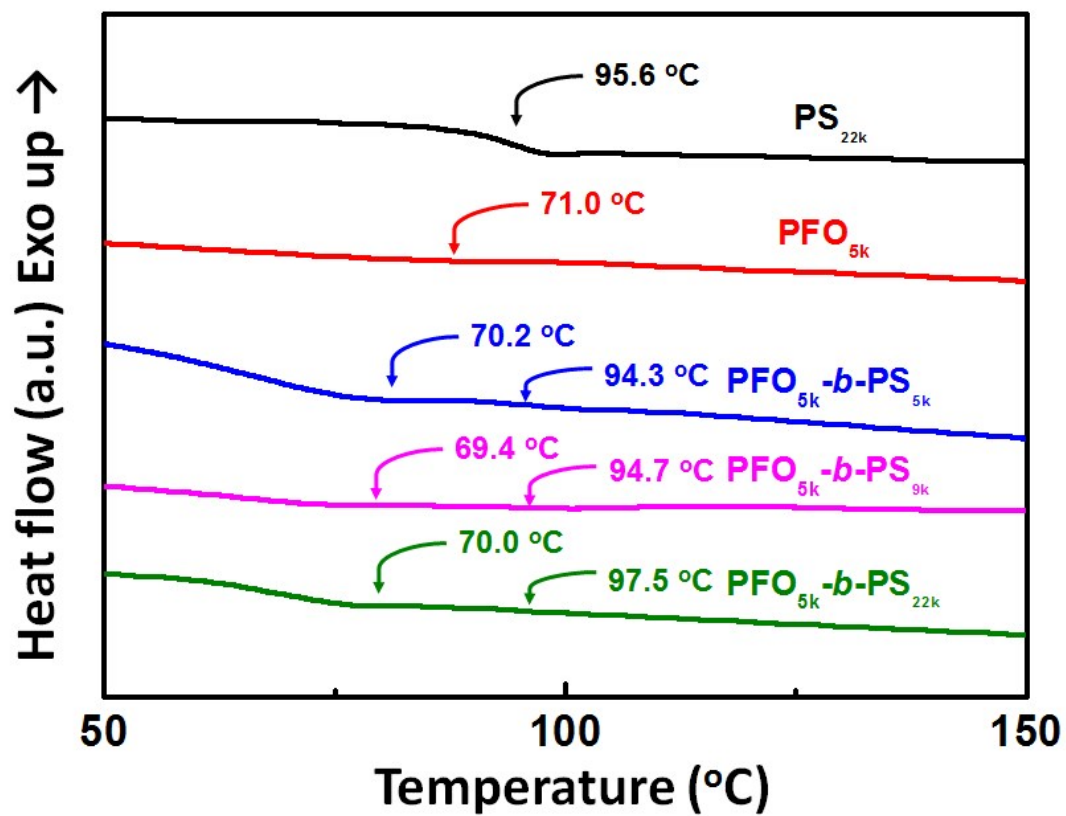


Fig. S4. DSC thermal histograms of the studied polymers.

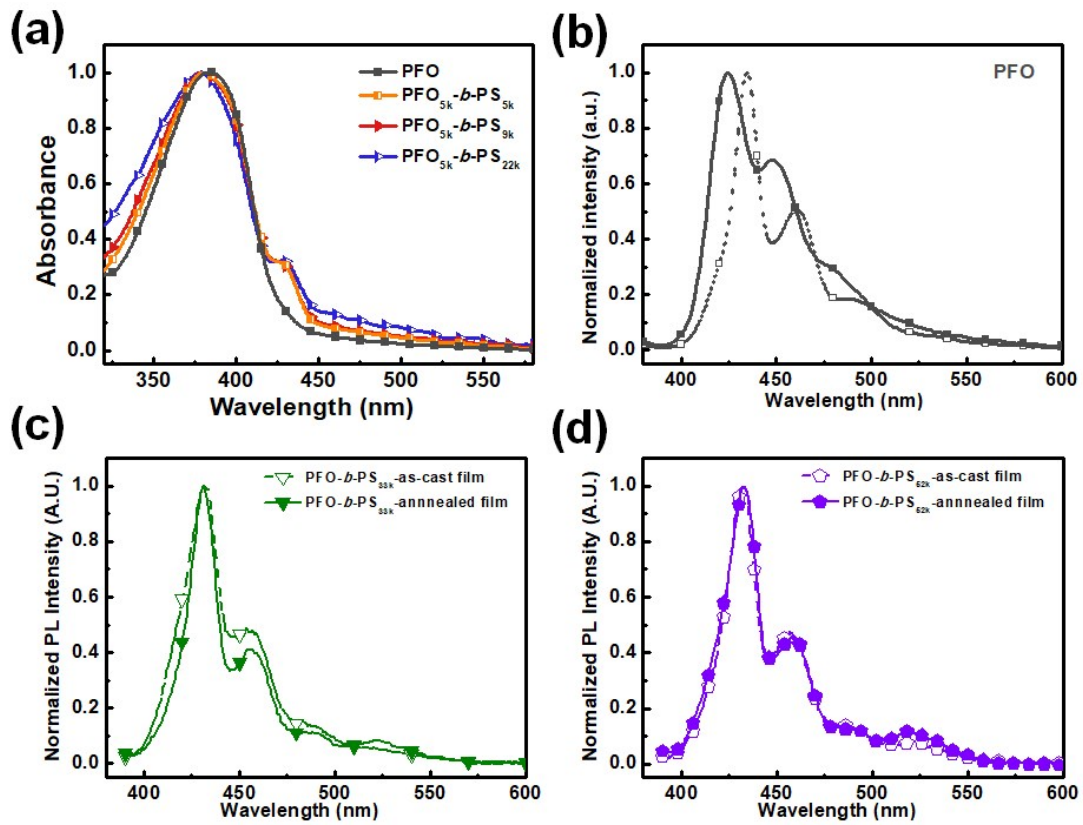


Fig. S5. (a) UV-Vis absorption spectra of the as-cast studied polymers films. PL emission spectra of the as-cast (dash line) and the annealed (solid line) for (b) PFO_{5k} (c) PFO_{5k}-*b*-PS_{33k} and (e) PFO_{5k}-*b*-PS_{52k} film.

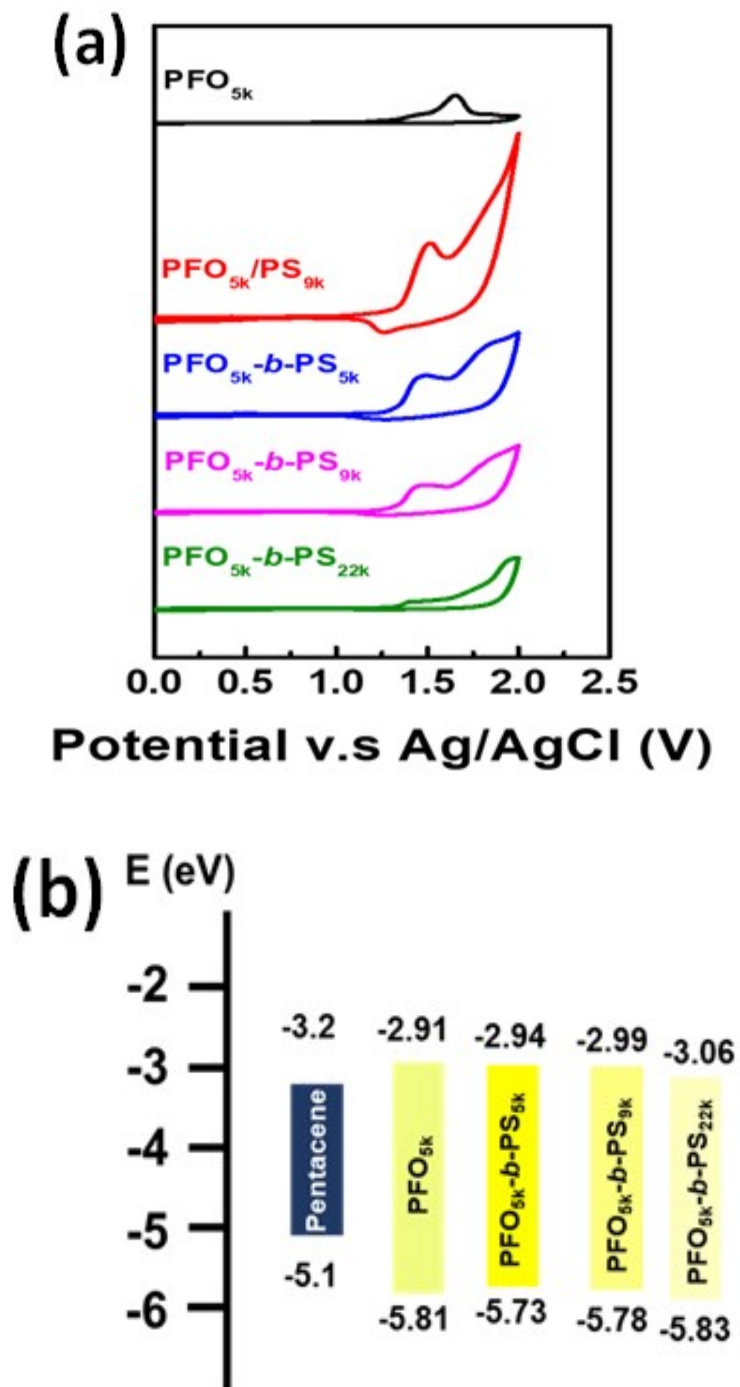


Fig. S6. (a) CV diagram for the studied polymers and the polymer blends of PFO/PS_{22k}. (b) Energy level diagram for pentacene and the studied polymers.

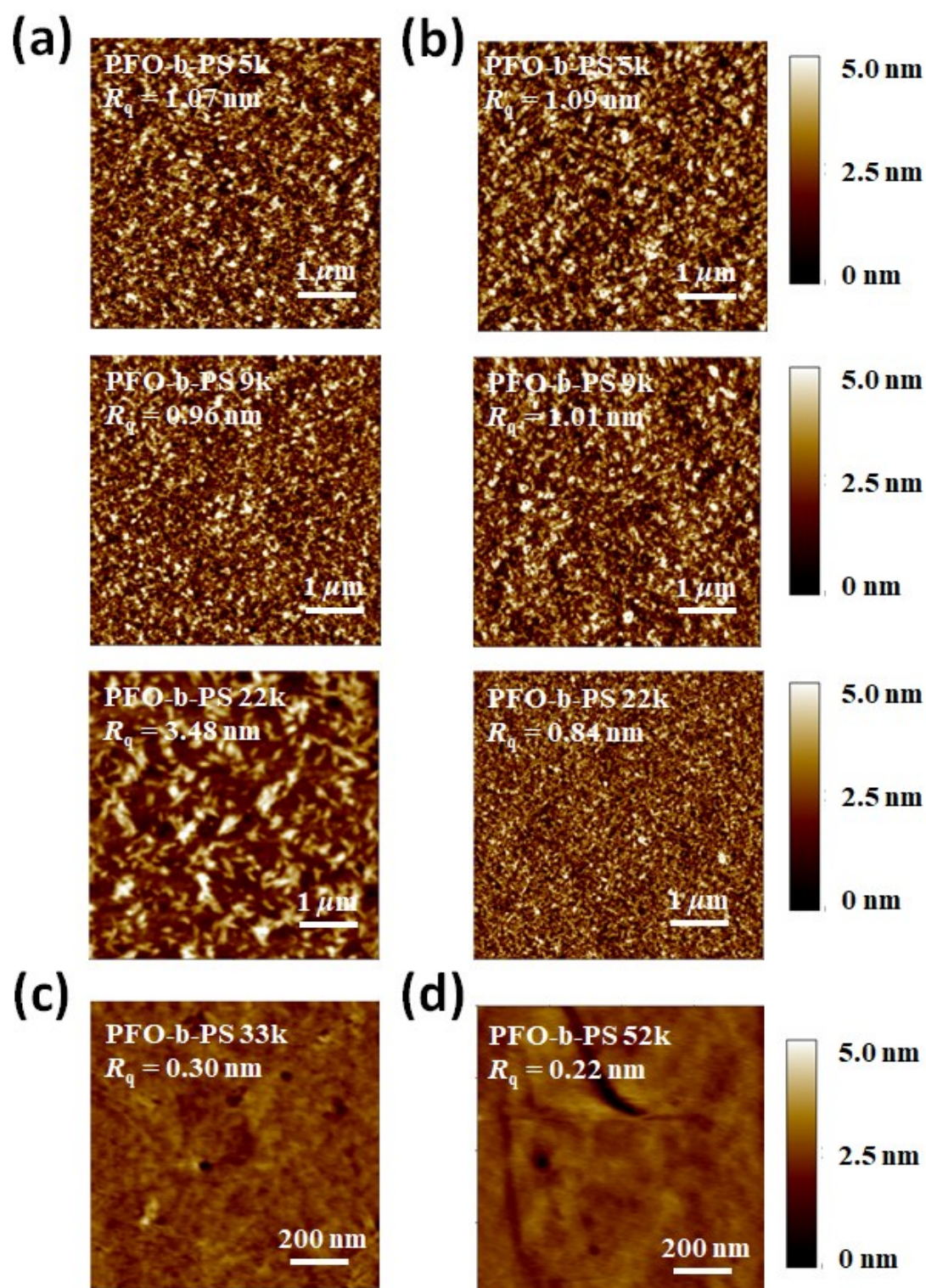


Fig. S7. AFM topographies of the (a) as-cast (b) annealed polymer films. (c) AFM topographies of the as-cast film for PFO_{5k}-b-PS_{33k}, and (d) PFO_{5k}-b-PS_{52k}.

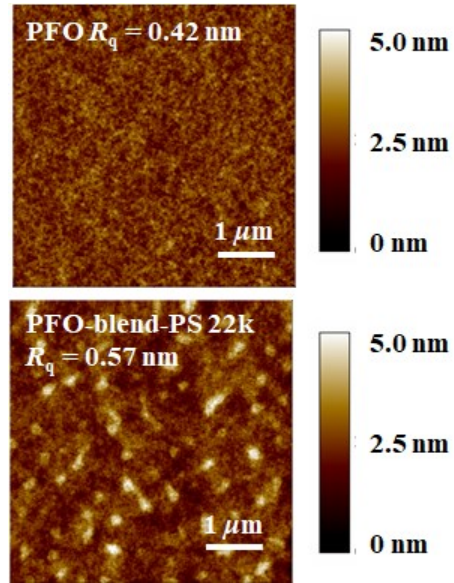


Fig. S8. AFM topographies of the PFO homopolymer and the polymer blends of PFO/PS_{22k}.

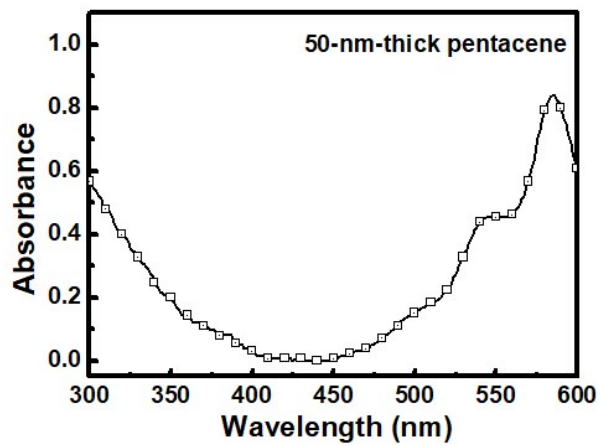


Fig. S9. UV-Vis absorption spectra of the thermally deposited 50-nm-thick pentacene.

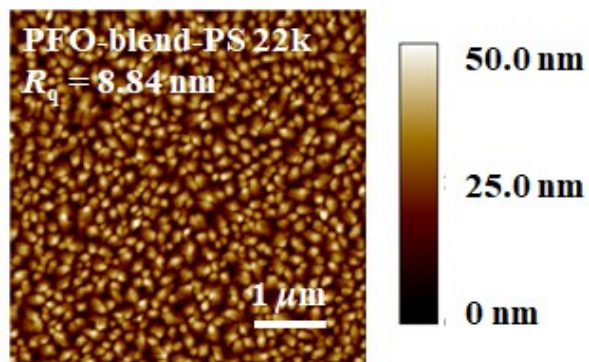


Fig. S10. AFM topographies of the pentacene film deposited on the PFO.

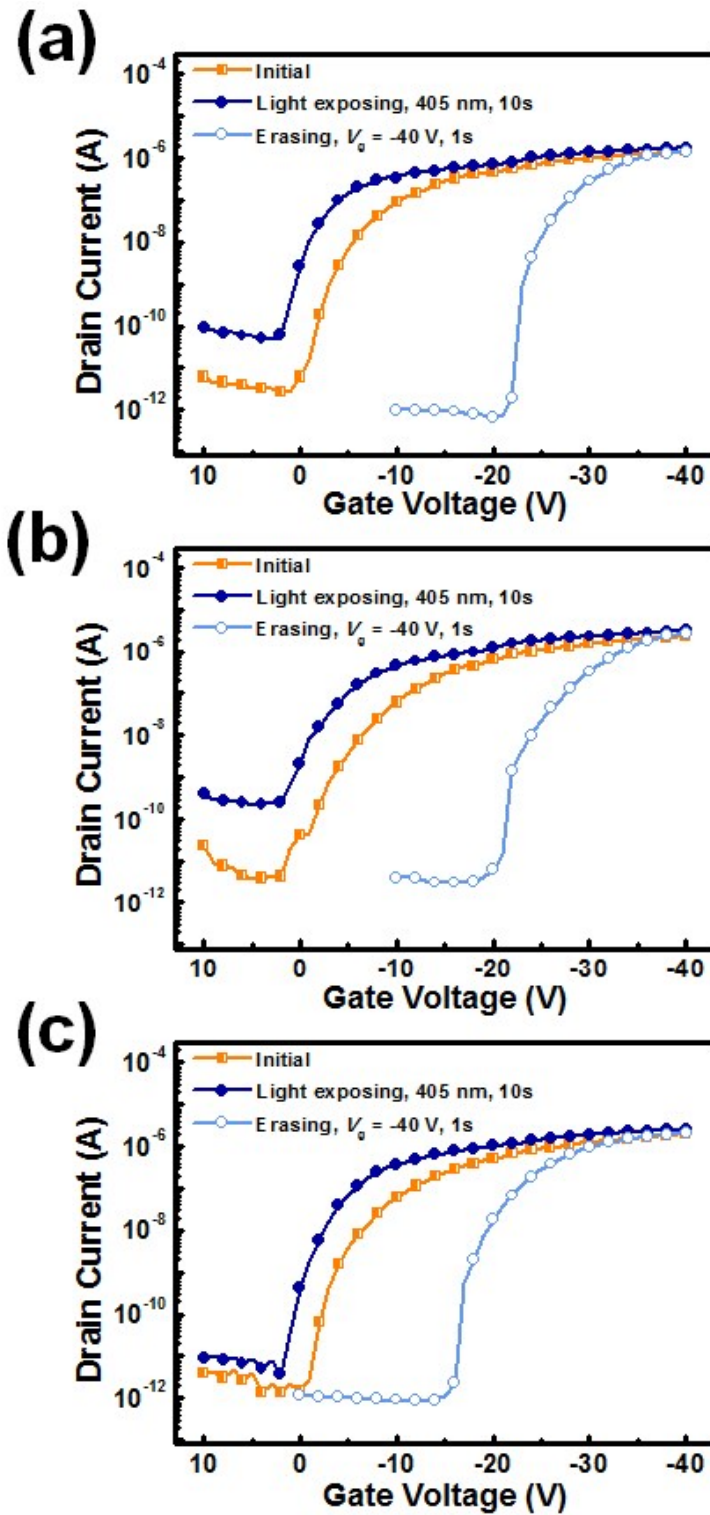


Fig. S11. Transfer characteristics of the FET photonic memory device with the as-cast polymer film (a) PFO_{5k}-*b*-PS_{5k}, (b) PFO_{5k}-*b*-PS_{9k}, and (c) PFO_{5k}-*b*-PS_{22k} as the electrets. (d) Transfer curves of the FET photonic memory device with the annealed film of the polymer blends, PFO_{5k}/PS_{22k} as the electrets.

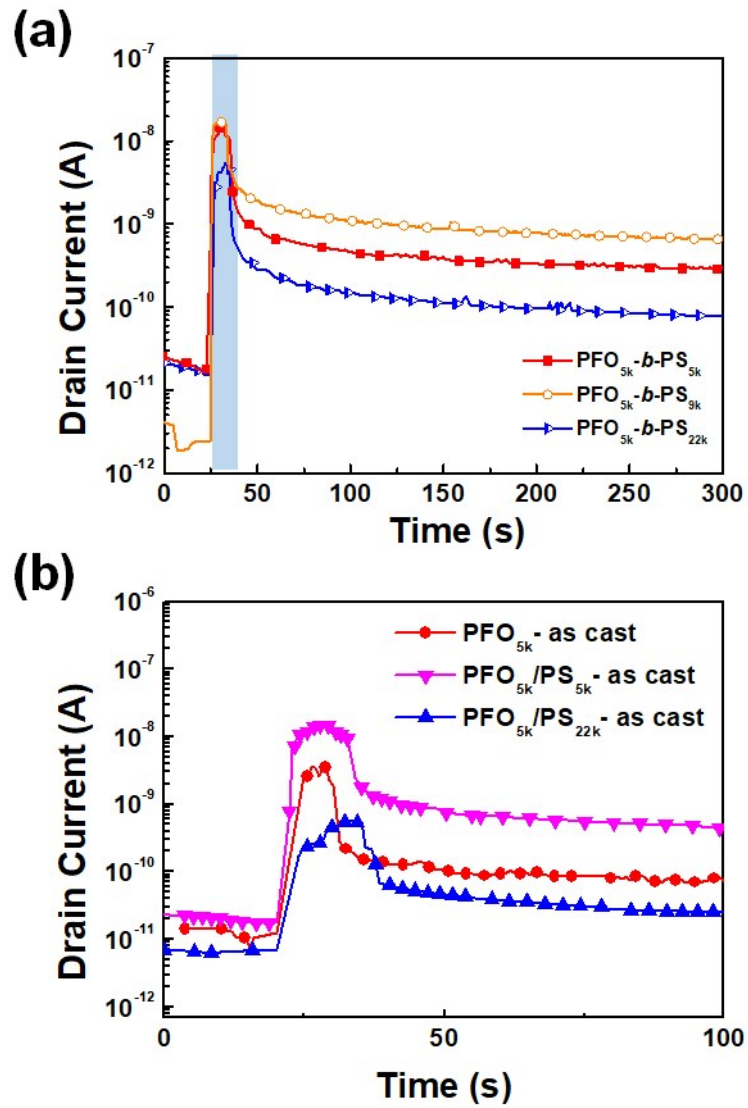


Fig. S12. Transient characteristics of the photonic FET memory devices of (a) the as-cast BCPs and (b) PFO homopolymer or the relevant polymer blends as the electret.

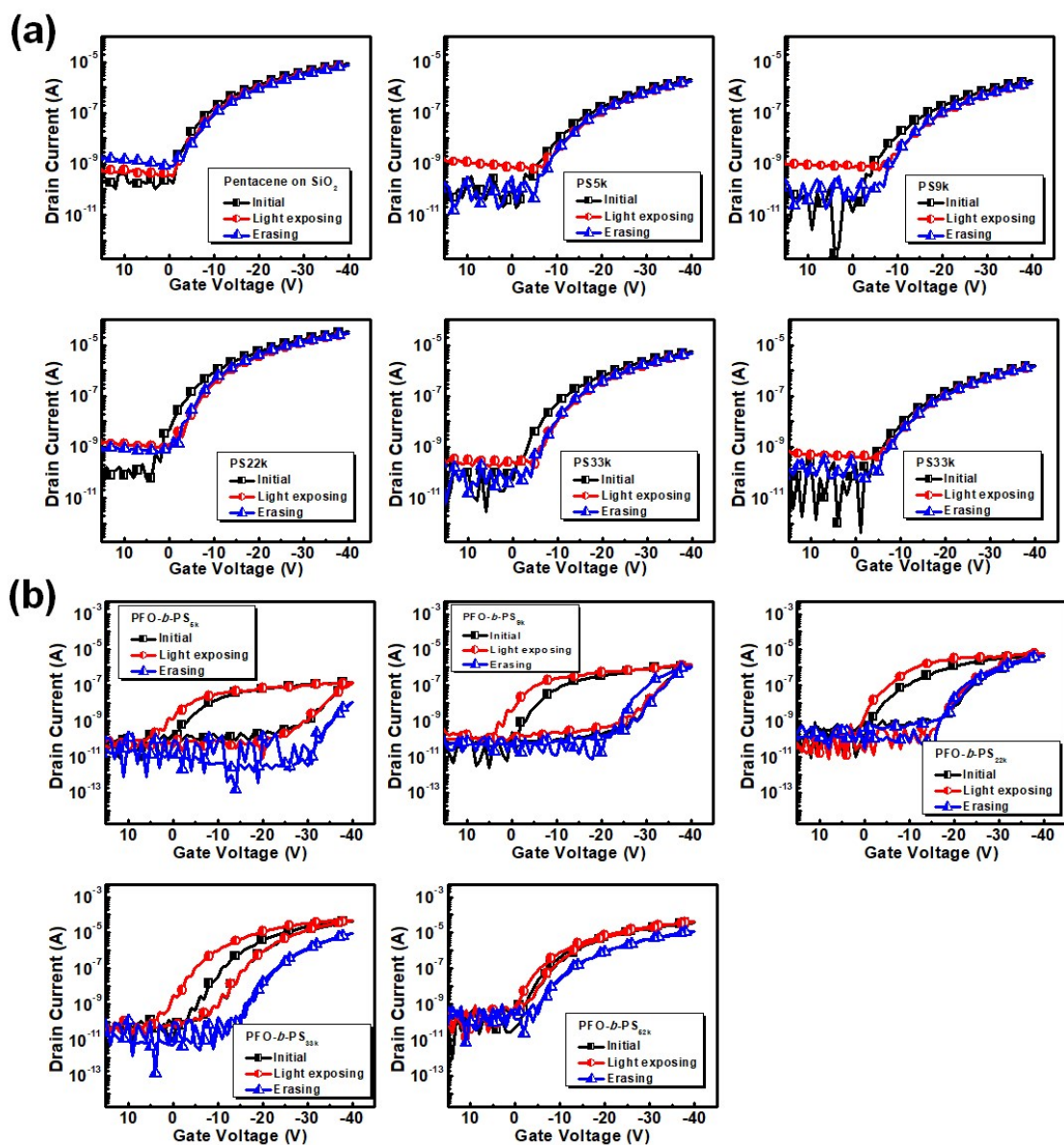


Fig. S13. (a) FET transfer characteristics of the devices with 100-nm-thick SiO₂ and bi-layered structure of PS/SiO₂ as the dielectrics. (b) Dual-sweep transfer characteristics of the FET photonic memory devices with the studied BCPs as the electrets.

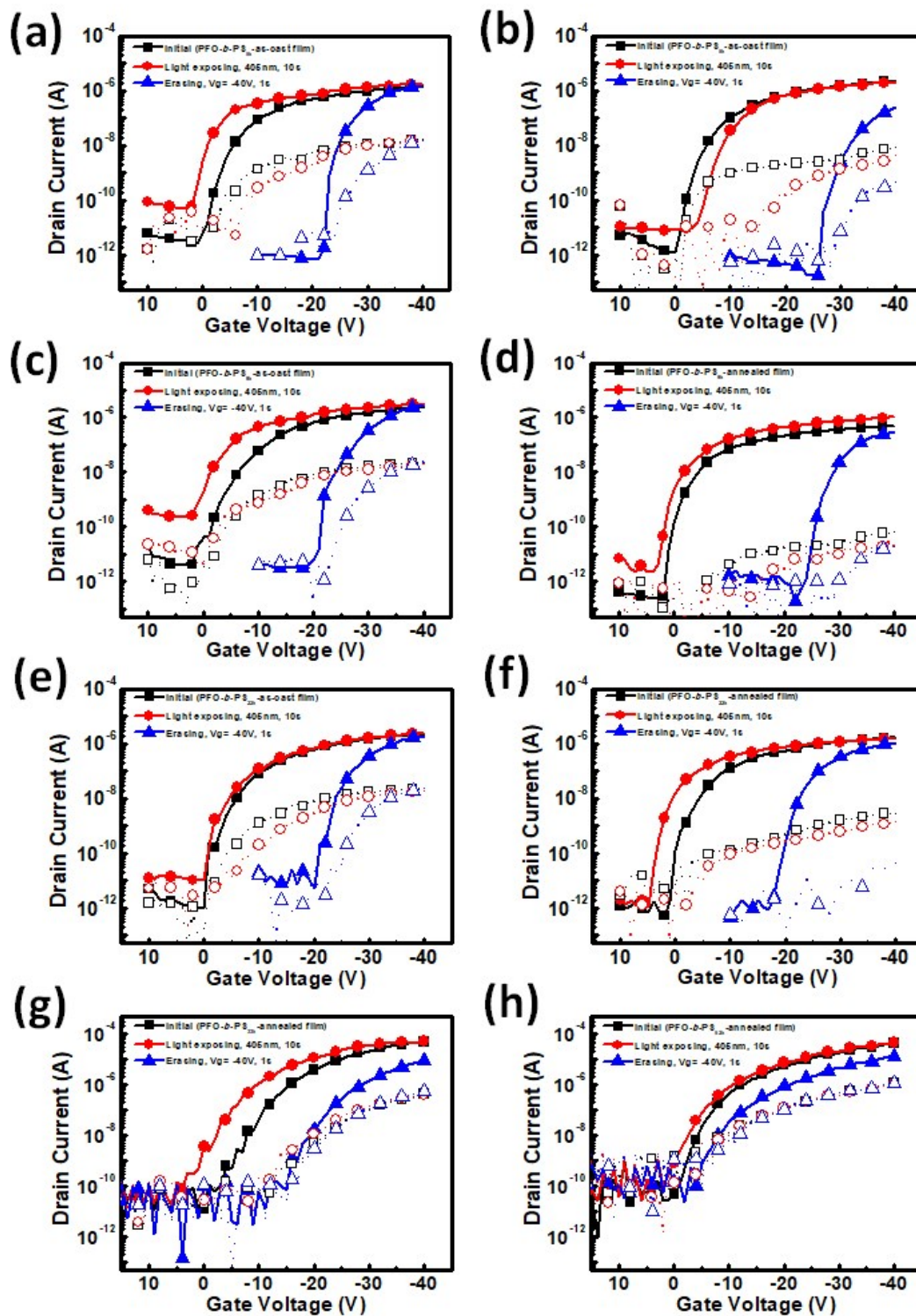
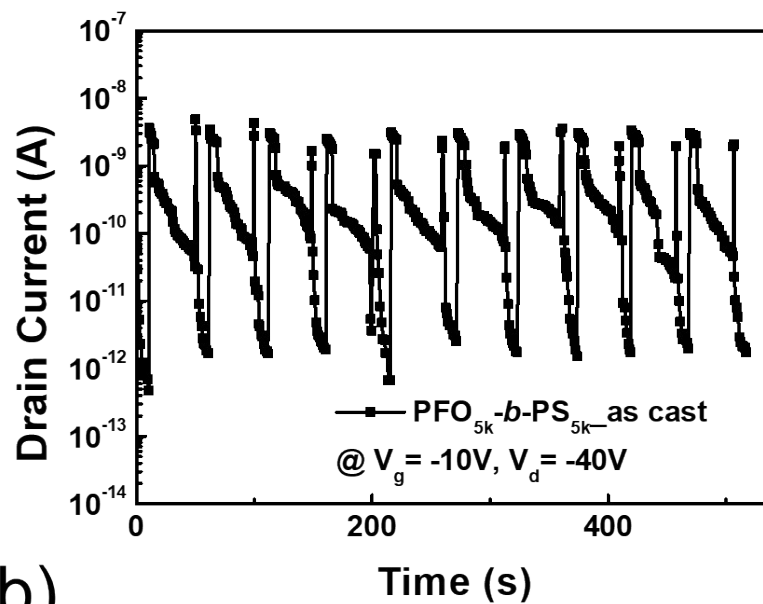


Fig. S14. The drain current and gate current obtained from the FET transfer characteristics of the devices with the studied BCPs of (a) as-cast PFO_{5k}-b-PS_{5k} (b) annealed PFO_{5k}-b-PS_{5k} (c) as-cast PFO_{5k}-b-PS_{9k} (d) annealed PFO_{5k}-b-PS_{9k} (e) as-cast PFO_{5k}-b-PS_{22k} (f) annealed PFO_{5k}-b-PS_{22k} (g) annealed PFO_{5k}-b-PS_{33k} (h) annealed PFO_{5k}-b-PS_{52k} film as the electrets.

(a)



(b)

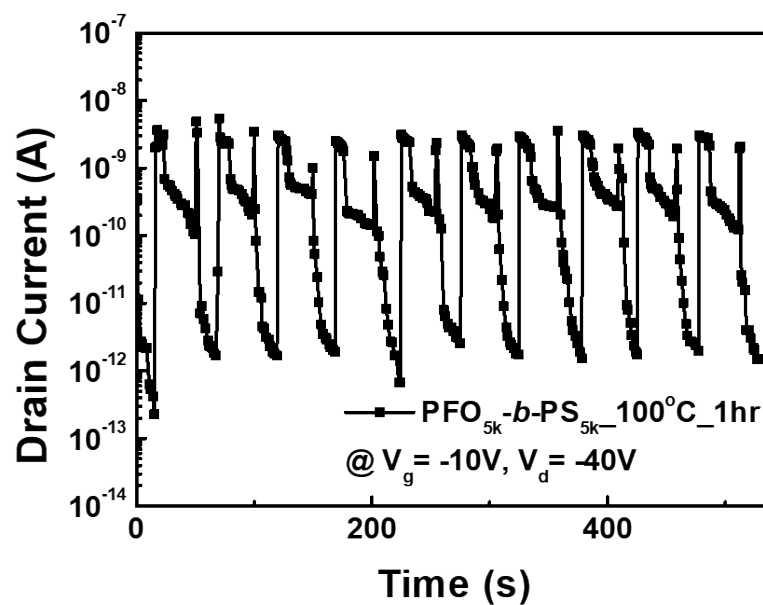
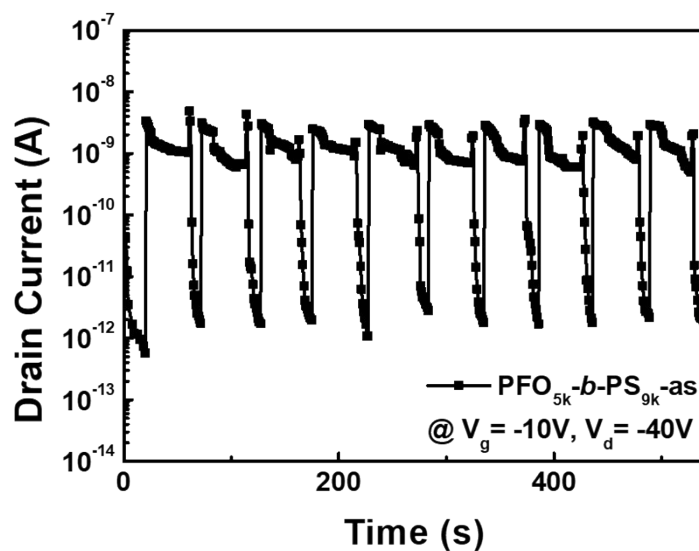


Fig. S15. The photo-writing (405 nm; 30 mW/cm² for 10 s), electrical erasing (-40 V; 1s) cycle of the photonic FET memory devices based on the (a) as-cast and (b) thermal-annealed PFO_{5k}-*b*-PS_{5k} film as the electrets.

(a)



(b)

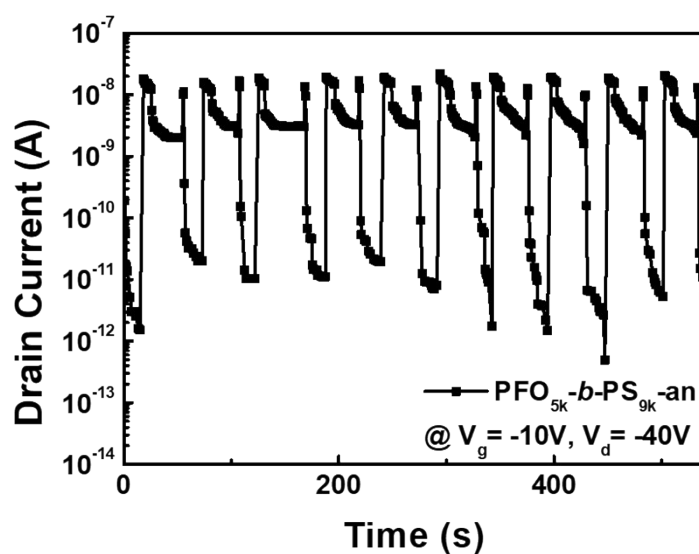


Fig. S16. The photo-writing (405 nm; 30 mW/cm² for 10 s), electrical erasing (-40 V; 1s) cycle of the photonic FET memory devices based on the (a) as-cast and (b) thermal-annealed PFO_{5k}-*b*-PS_{9k} film as the electrets.

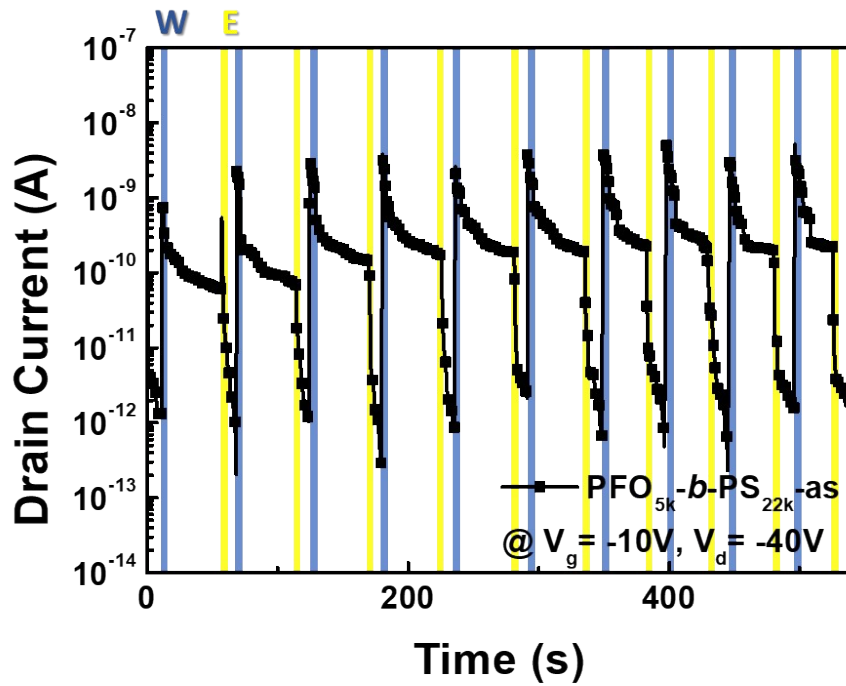


Fig S17. The photo-writing (405 nm; 30 mW/cm² for 10 s), electrical erasing (-40 V; 1s) cycle of the photonic FET memory devices based on the as-cast PFO_{5k}-*b*-PS_{22k} film as the electrets.

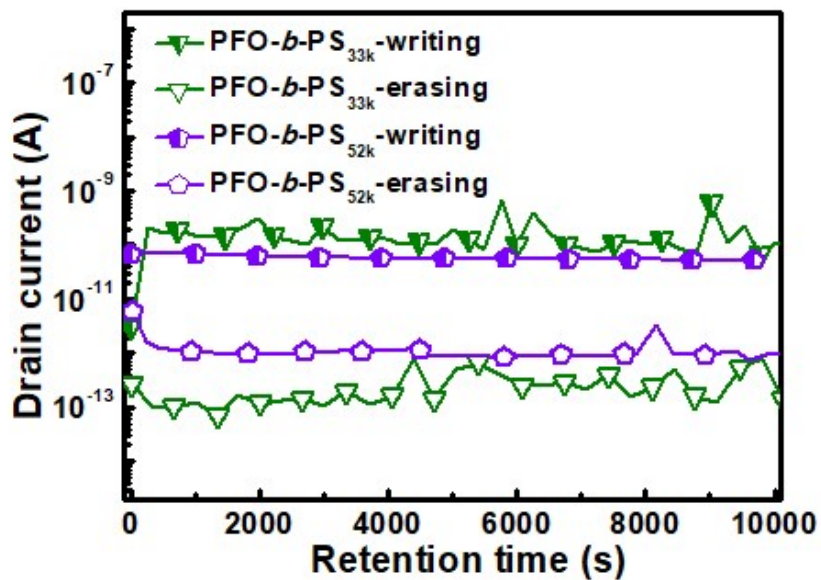


Fig. S18. Long-term stability of the photonic FET memory device based on thermal-annealed PFO_{5k}-*b*-PS_{33k} and PFO_{5k}-*b*-PS_{52k} film as the electret at $V_d = -40$ V and $V_g = -10$ V by photowriting (405 nm; 30 mW/cm² for 10 s).