Supporting Information

Ionic Nanocluster-Evolved Polymers for Low-Voltage Flexible Organic Nonvolatile Memory Transistors

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Experimental Section

Materials and Solutions: Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, weight-average molecular weight = 2,000 kDa, 15 wt% in H_2O) and aniline (AN, purity = ~99.5%) were purchased from Sigma-Aldrich (St Louis, Mo, USA). The molar ratio of AN to the repeating unit (one sulfonic acid group each) of PAMPSA was varied as 0, 0.2, 0.5, 0.8, 1.0, and 1.2 (PAMPSA:AN = 1:0, 1:0.2, 1:0.5, 1:0.8, 1:1, and 1:1.2) for the preparation of PAMPSA-AN solutions (solvent: deionized water). These solutions were subjected to stirring at room temperature for 3 days prior to wet-coating processes (spin-coating). P3HT (weight-average molecular weight = 70 kDa, polydispersity index (PDI) = 1.7, regioregularity = 97%) was supplied from Rieke Metals (Lincoln, NE, USA) and its solutions were prepared using toluene (12.5 mg/ml).

Film and Device Fabrication: Indium-tin oxide (ITO)-coated glass substrates (sheet resistance = ca. 10 ©/cm^2) were photolithographically patterned to make the ITO gate electrode lines (1 mm × 12 mm). After cleaning processes in acetone and isopropyl alcohol, the patterned ITO-glass substrates were treated with UV-ozone (28 mW/cm^2 for 20 min) using a UV-ozone cleaner (Ahtech, Korea). For the fabrication of OFETs, the PAMPSA-AN layers (thickness = 450 nm) were spin-coated on the patterned ITO-glass substrates by controlling coating conditions. The spin-coated PAMPSA-AN layers were subjected to thermal annealing processes by varying the temperature from 80 ºC to 150 ºC for 30 min. Note that the sheet resistance of ITO electrodes was almost similar (unchanged) before and after coating the PAMPSA-AN layers. Next, the P3HT channel layers (thickness = 60 nm) were spin-coated on top of the PAMPSA-AN layers at 1500 rpm for 30 s and soft-baked at 70 ºC for 15 min. After moving all samples to a vacuum chamber installed inside a nitrogen-filled glove box system, the 60 nm-thick silver (Ag) source/drain electrodes were deposited on the P3HT channel layers via thermal evaporation through a shadow mask at a base pressure of ca. 1×10^{-6} torr. The channel length (L) and width (W) of the OFETs fabricated were L = 70 μm and W = 2

mm, respectively. For the fabrication of flexible OFETs, the Ag gate electrodes (thickness = 60 nm) were deposited on the colorless polyimide (poly(hexafluoroisopropylidene diphthalic anhydride-co-2,2'-bis(trifluoromethyl)benzidine) (6FDA-TFDB)) films (thickness = 100 μm), followed by spin-coating of the PAMPSA-AN layers. Subsequent steps were the same as used for the processes using the ITO-glass substrates. All OFET devices were stored in the argon-filled glove box before measurement.

Measurements: The pH measurement of solutions was carried out using a pH meter (Model AB15, Fisher Scientific). The thickness of films and electrodes was measured using a surface profiler (Alpha Step 200, Tencor, USA). The optical absorption spectra of films were measured using a UV/VIS/NIR spectrometer (Lambda 750, PerkinElmer, Houston, TX, USA). The thermal decomposition of PAMPSA was measured using a thermogravimetric analyzer (TGA, Q600, TA Instruments). The XPS spectra of films were measured with an X-Ray photoelectron spectrometer (ESCALAB 250, Thermo Scientific, Inc.). The functional groups in the PAMPSA-AN films were measured using a Fourier transform-infrared spectrometer (FT-IR, 5700 Continum, Thermo Scientific, Inc.) in an attenuated total reflection (ATR) mode. The surface morphology of film samples was measured using an atomic force microscope (AFM; Nanoscope IVa, Digital Instruments, Tonawanda, NY, USA). The surface energy change in the PAMPSA-AN films was measured using a contact angle measurement system (model GSX, Surfacetech) that utilizes toluene drops as a probe. The crystal nanostructure of films was measured using a synchrotron radiation grazing incidence angle X-ray diffraction system (GIXD, wavelength = 1.212969 Å, 3C, SAXS I beamline, Pohang Accelerator Laboratory). The basic transistor and memory characteristics of OFETs were measured using a semiconductor parameter analyzer (4200 SCS, 2636 B, Keithley, USA). All OFET measurements were carried out under an inert condition by employing a sample holder that is charged with argon gas. The bending test of flexible OFETs was performed inside the same glove box filled with argon gas.

Table S1. Summary of transistor characteristics for the OFETs with the PAMPSA-AN layers (soft-baking at 80 ºC for 30 min) according to the AN ratio.

Parameters	AN (ratio)					
	0	0.2	0.5	0.8	1.0	1.2
V_{TH} (V)	-0.28	0.51	1.04	1.66	2.25	2.91
Mobility ($x10^{-3}$ cm^2/Vs)	11.0	17.0	30.0	8.0	5.0	1.0
$R_{ON/OFF}$ ($x10^3$)	0.078	0.171	1.020	0.092	0.019	0.003

Note) All data were extracted from the transfer curves at V_D = -5 V.

Table S2. Summary of transistor characteristics for the OFETs with the PAMPSA-AN layers (AN ratio = 0.5) according to the annealing temperature.

Parameters	Annealing Temperature (ºC)						
	80	110	140	145	150	155	160
V_{TH} (V)	1.04	0.91	0.74	0.68	0.62	0.75	0.82
Mobility ($x10^{-3}$ cm^2/Vs)	29.5	29.8	58.7	64.0	379.0	104.0	101.0
$R_{ON/OFF}$ ($x10^3$)	1.02	1.22	6.53	8.63	15.0	1.30	0.342
C_F ($x10^{-9}$ F/cm^2)	4.959	5.305	5.684	6.151	6.201	6.153	6.148

Note) All data were extracted from the transfer curves at V_D = -5 V. C_F denotes the capacitance of PAMPSA-AN films.

Table S3. Summary of transistor characteristics for the OFETs with the PAMPSA-AN layers (annealed at 150 ºC for 30 min) according to the AN ratio.

Parameters	AN (ratio)					
	0	0.2	0.5	0.8	1.0	1.2
V_{TH} (V)	0.78	0.68	0.62	0.66	-1.3	-1.2
Mobility ($x10^{-3}$ cm^2/Vs)	522.0	486.0	379.0	15.2	5.7	8.3
$R_{ON/OFF}$ ($x10^3$)	1160	33.5	15.0	0.433	0.005	0.004
C_F ($x10^{-9}$ F/cm^2)	8.202	6.593	6.201	5.249	4.824	4.499

Note) All data were extracted from the transfer curves at V_D = -5 V. C_F denotes the capacitance of PAMPSA-AN films.

Table S4. Calculated INC density as a function of AN ratio in the PAMPSA-AN films.

Parameter	AN (ratio)					
	0	0.2	0.5	0.8	1.0	1.2
Density (vol %)	0	1.24	5.41	9.31	10.88	12.26

Note) The volume density of INCs was calculated by considering the volume of single INC (0.904 nm^3) and PAMPSA-AN film (648 x 10^{-7} cm^3).

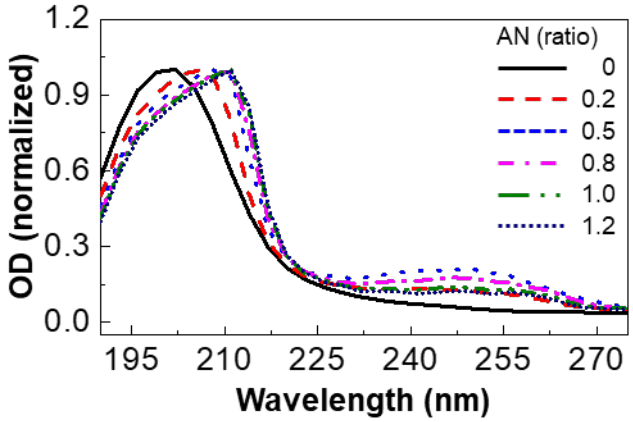

Fig. S1. Optical absorption spectra (normalized) of the PAMPSA-AN films coated on quartz substrates (soft-baking at 80 °C for 30 min) according to the AN molar ratio.

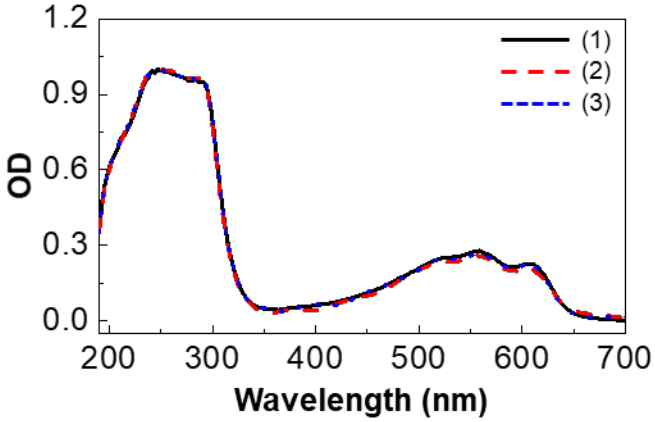

Fig. S2. Optical absorption spectra for P3HT/ITO-glass (1), P3HT/pristine PAMPSA/ITO-glass (2), and P3HT/PAMPSA-AN(0.5)/ITO-glass (3).

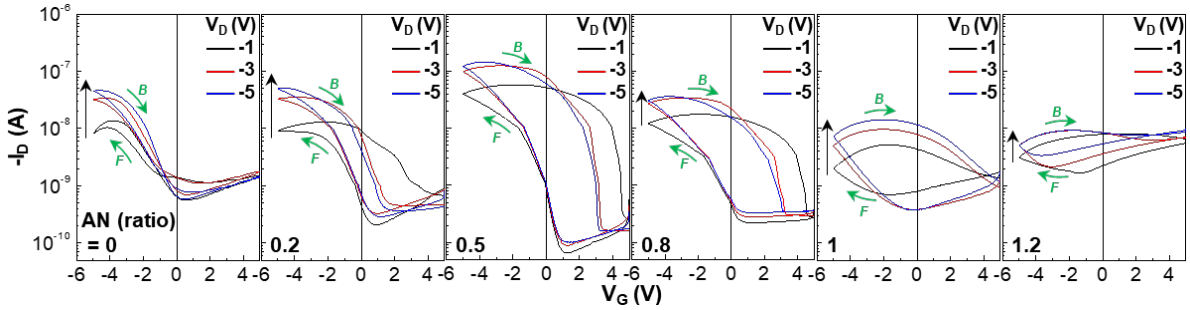

Fig. S3. Transfer characteristics (dark condition) for the OFETs with the PAMPSA-AN layers according to the AN molar ratio. The OFETs were soft-baked at 80 °C for 30 min. V_D is given on each graph (-1, -3, -5 V).

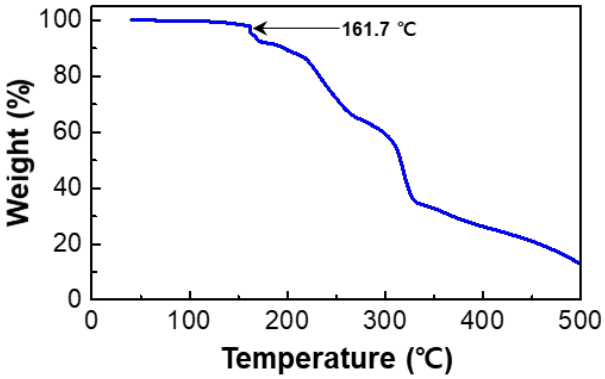

Fig. S4. TGA thermogram for the PAMPSA sample at a scan rate of 10 ^{o}C/min. The temperature for initial degradation was measured at 161.7 ^{o}C.

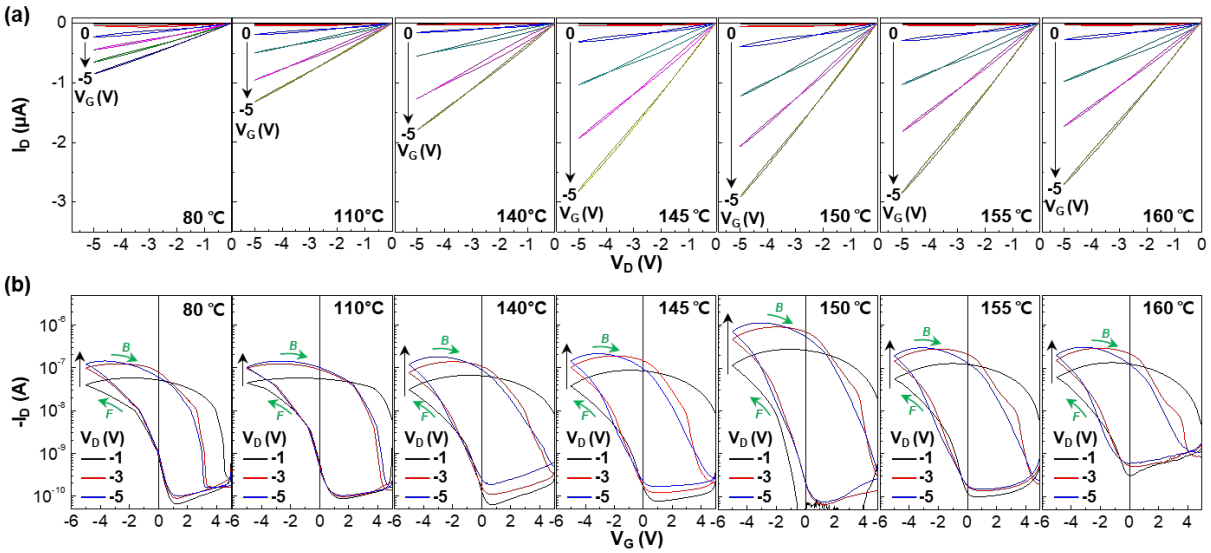

Fig. S5. Transfer characteristics (dark condition) for the OFETs with the PAMPSA-AN layers (AN ratio = 0.5) according to the thermal annealing temperature (80~160 ^{o}C for 30 min). V_D is given on each graph (-1, -3, -5 V).

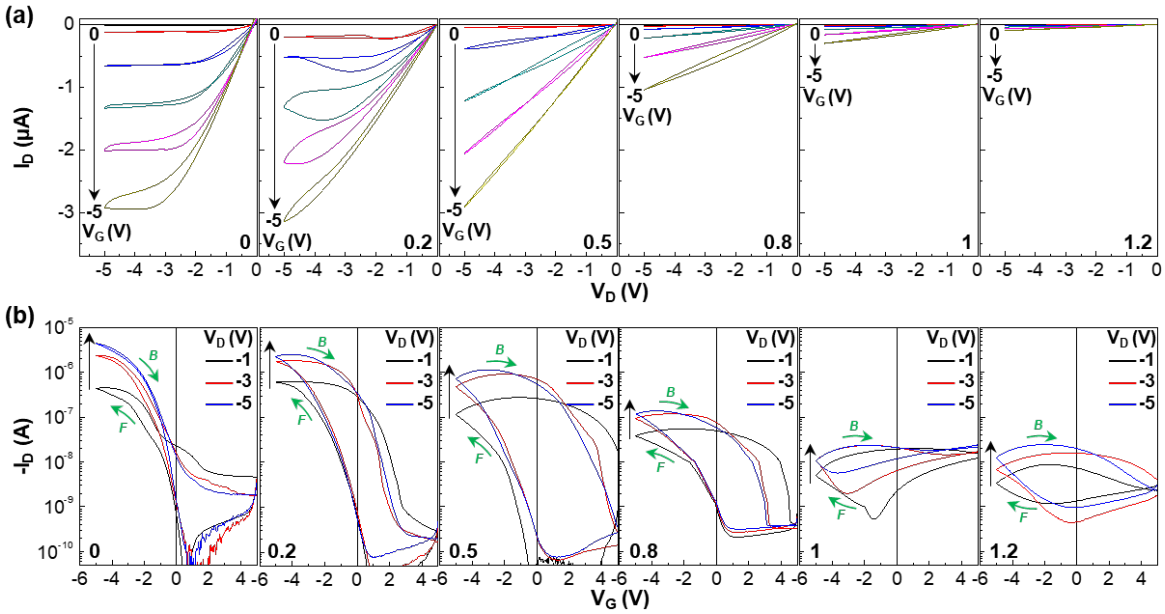

Fig. S6. Output (a) and transfer (b) characteristics (dark condition) for the OFETs with the PAMPSA-AN layers (thermal annealing at 150 °C for 30 min) according to the AN molar ratio. V_G (a) and V_D (b) are given on each graph.

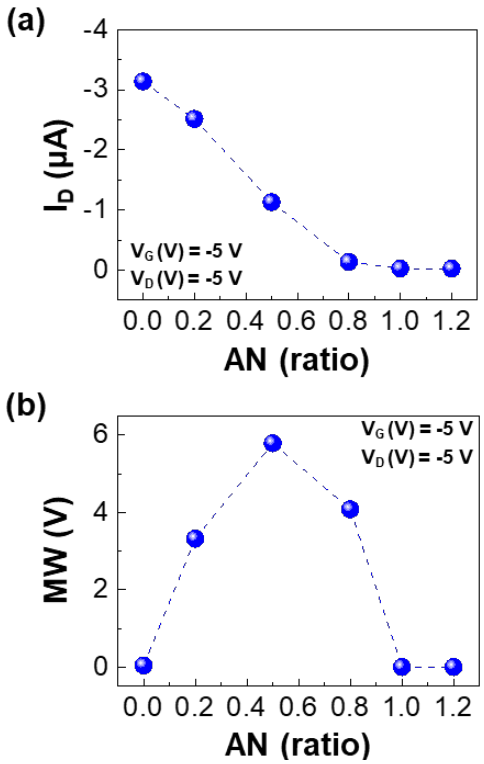

Fig. S7. Change of (a) drain current (I_D) and (b) memory window (i.e., threshold voltage difference between forward and backward sweeps) for the OFETs with the PAMPSA-AN layers (AN ratio = 0.5, annealing at 150 °C for 30 min). Data are taken from the transfer curves in Fig. S5b.

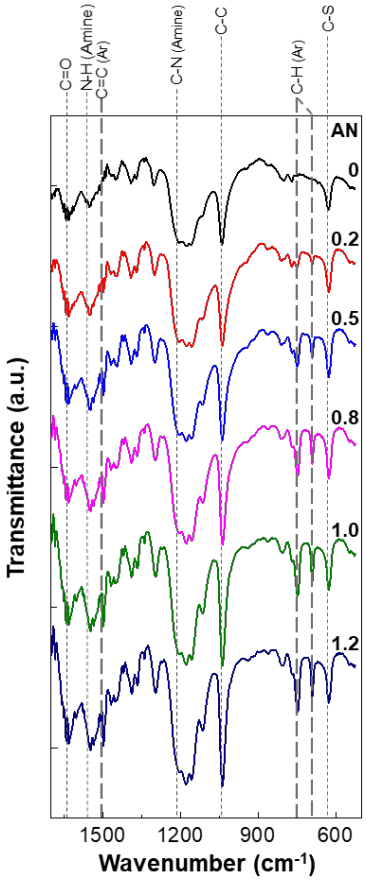

Fig. S8. FT-IR spectra (all AN ratios) for the PAMPSA-AN films annealed at 150 ^{o}C for 30 min.

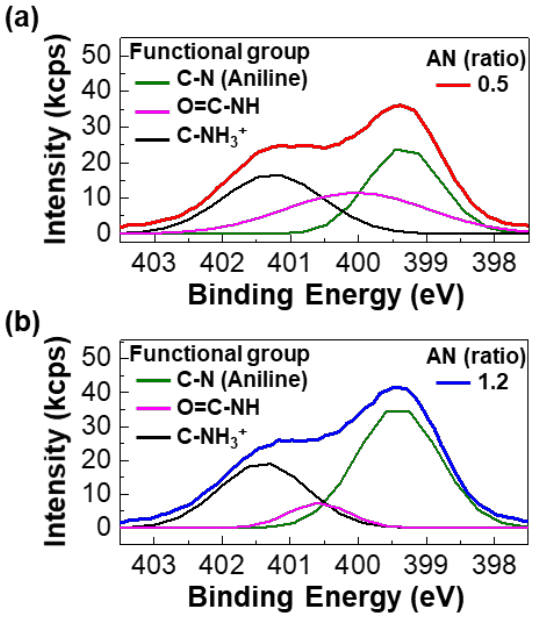

Fig. S9. Deconvolution results of N1s XPS spectra for the PAMPSA-AN films annealed at 150 ^{o}C for 30 min: (a) AN ratio = 0.5, (b) AN ratio = 1.2.

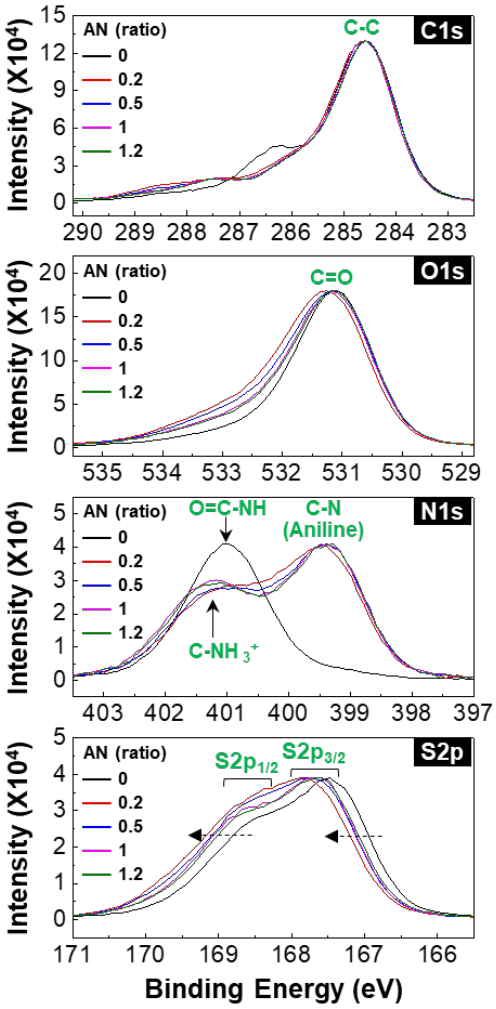

Fig. S10. XPS spectra (all AN ratios) for the PAMPSA-AN films annealed at 150 ºC for 30 min. The four atoms, carbon (C1s), oxygen (O1s), nitrogen (N1s), and sulfur (S2p), were investigated to examine the change of atom environments according to the AN ratio.

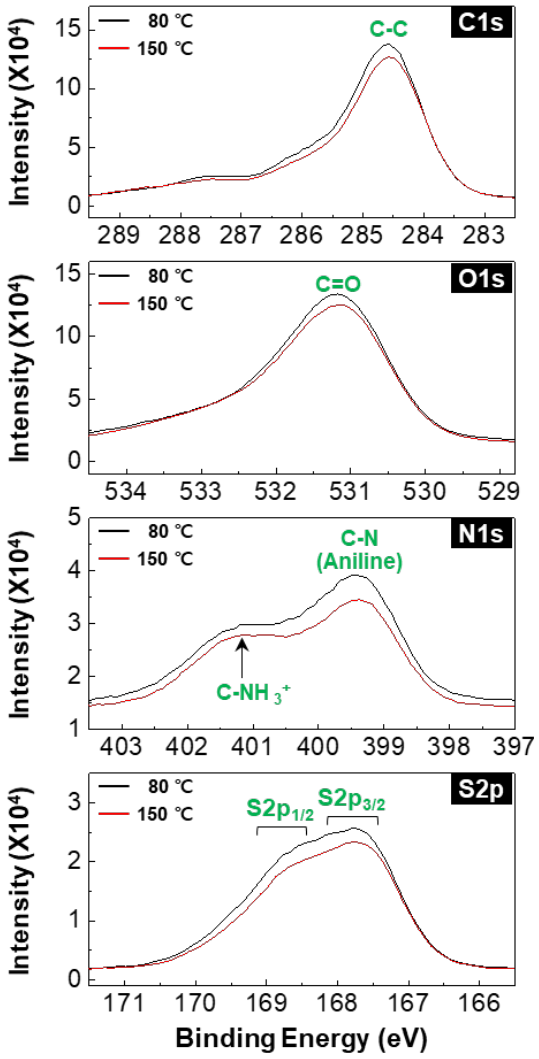

Fig. S11. Change of XPS spectra (C1s, O1s, N1s, S2p) between soft-baking at 80 ºC for 30 min and annealing at 150 ºC for 30 min for the PAMPSA-AN films (AN ratio = 0.5).

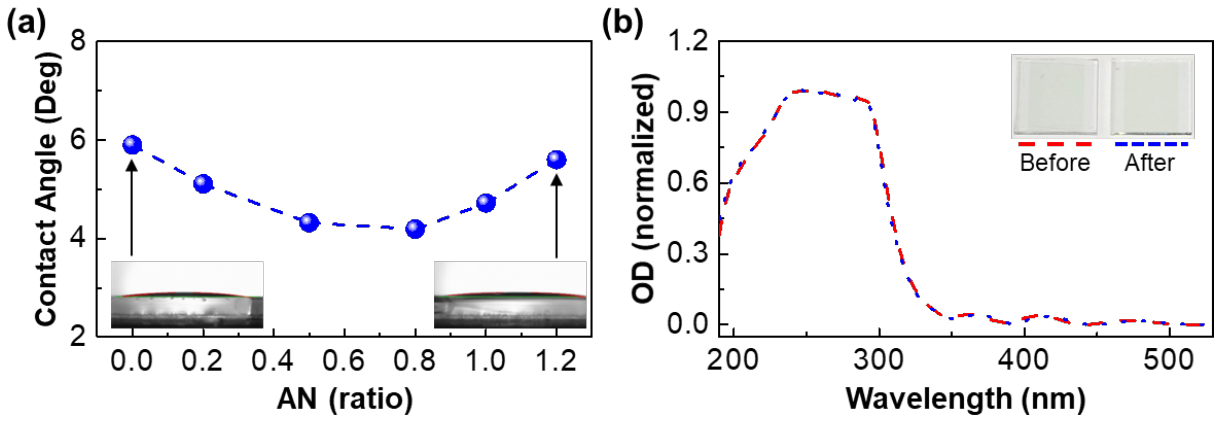

Fig. S12. (a) Contact angle of the PAMPSA-AN films coated on ITO-glass substrates (annealed at 150 ºC for 30 min) according to the AN molar ratio (inset: photographs for the toluene drop on the surface of the PAMPS-AN films). (b) Optical absorption spectra for the PAMPSA-AN(0.5)/ITO-glass sample before and after toluene drop test.

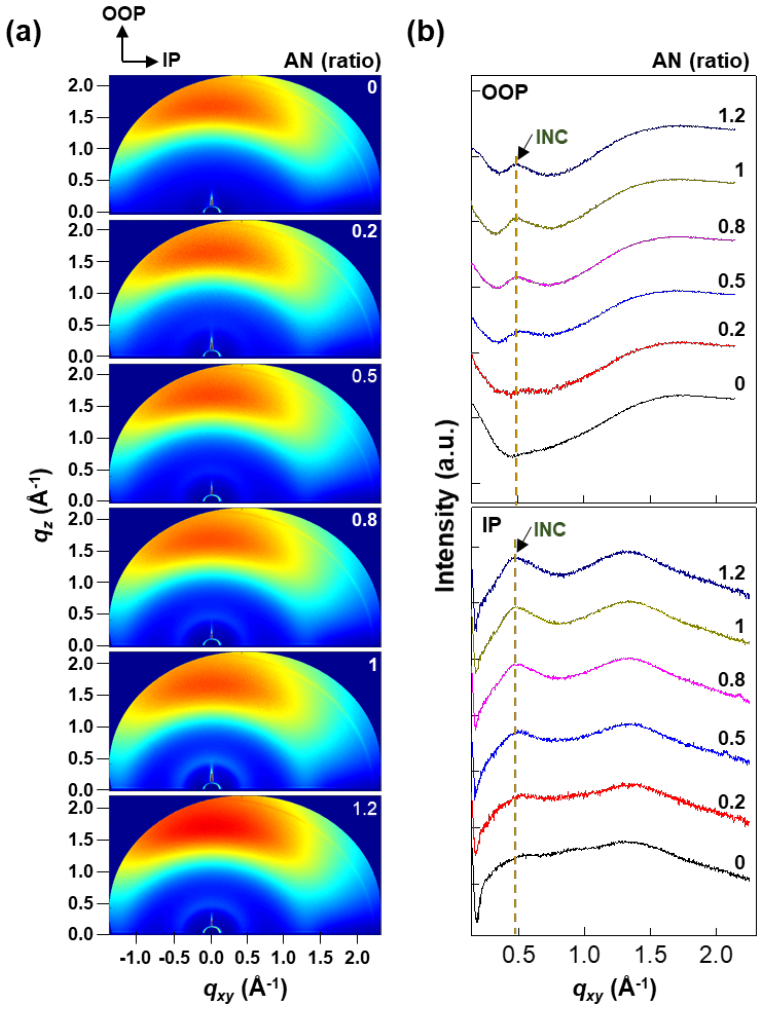

Fig. S13. (a) 2D GIXD images and (b) 1D GIXD profiles for the PAMPSA-AN films annealed at 150 ºC for 30 min. The "INC" points out the diffraction peaks from the ionic nanoclusters in the films. Note that the out-of-plane (OOP) and in-plane (IP) 1D profiles are shown on the top and bottom graphs, respectively.

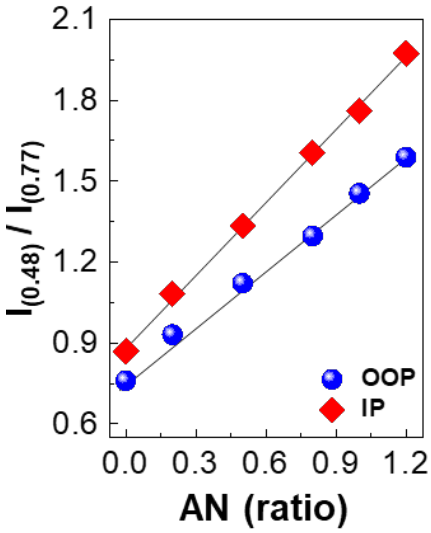

Fig. S14. The GIXD intensity ratio ($I_{0.48}/I_{0.77}$) as a function of the AN ratio. "$I_{0.48}$" and "$I_{0.77}$" denote the GIXD intensities at q_{xy} = 0.48 and q_{xy} = 0.77, respectively. Note that the intensity ratio is linearly increased with the AN ratio for both OOP and IP directions.

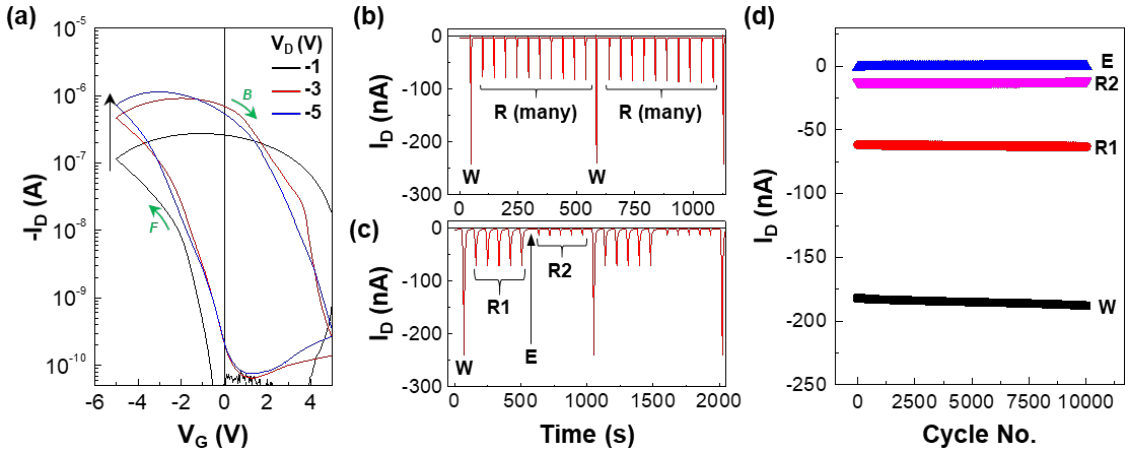

Fig. S15. Memory operation results for the OFETs with the PAMPSA-AN layers (AN ratio = 0.5, annealing at 150 °C for 30 min, glass substrates): (a) Transfer curves by scanning from V_G = +5 V to V_G = -5 V at three different drain voltage conditions, (b) writing-once-reading-many (WORM) operation results (W: V_G = -5 V and V_D = -5 V; R: V_G = -1 V and V_D = -5 V), (c) writing-reading-erasing-reading (WRER) operation results (W: V_G = -5 V and V_D = -5 V; R1, R2: V_G = -1 V and V_D = -5 V; E: V_G = +5 V and V_D = -5 V), (d) retention characteristics during 10,000 WRER cycles with the same operation conditions as used for (c).

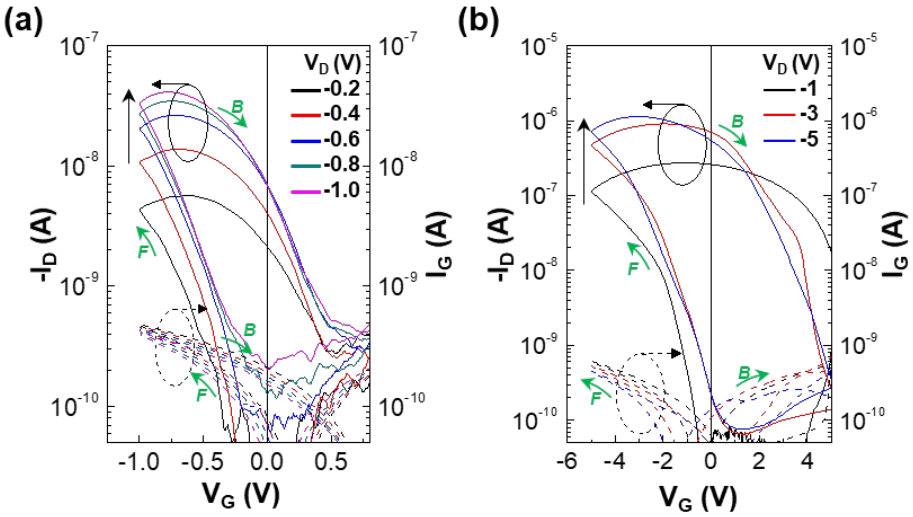

Fig. S16. Comparison between I_D-V_G and I_G-V_G curves for the OFETs with the PAMPSA-AN layers (AN ratio = 0.5, annealing at 150 ºC for 30 min): (a) V_G = -1 V ~ +1 V, (b) V_G = -5 V ~ +5 V. The I_G levels were significantly lower than the I_D levels, indicating good quality of devices with a low leakage current.

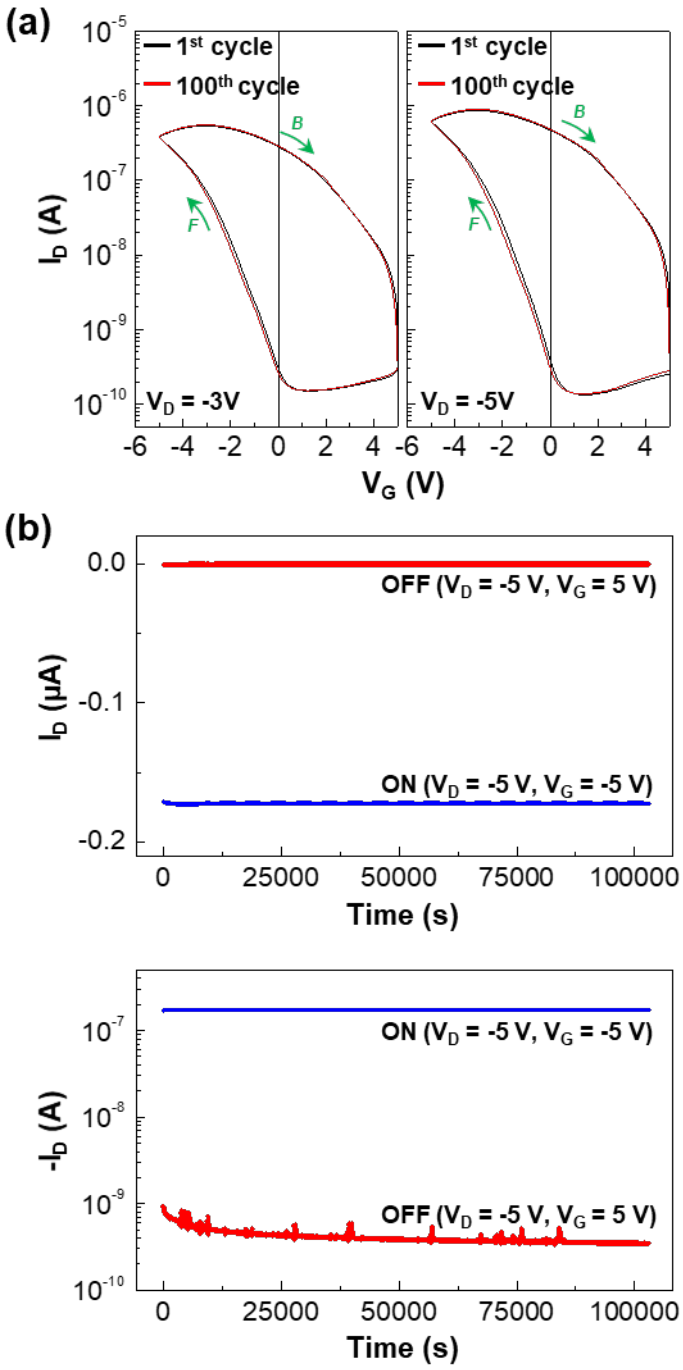

Fig. S17. (a) Transfer curves for the OFETs with the PAMPSA-AN layers (AN ratio = 0.5, annealing at 150 °C for 30 min) before (1st cycle) and after (100th cycle) repeated hysteresis sweeping tests from V_G = +5 V to V_G = -5 V (note that the deviation of drain current (V_G = -5 V) between the 1st and 100th cycles was only 3 %). (b) Charge retention characteristics during 101,880 s operations in the ON and OFF states of devices (top: linear scale; bottom: semi-logarithmic scale).

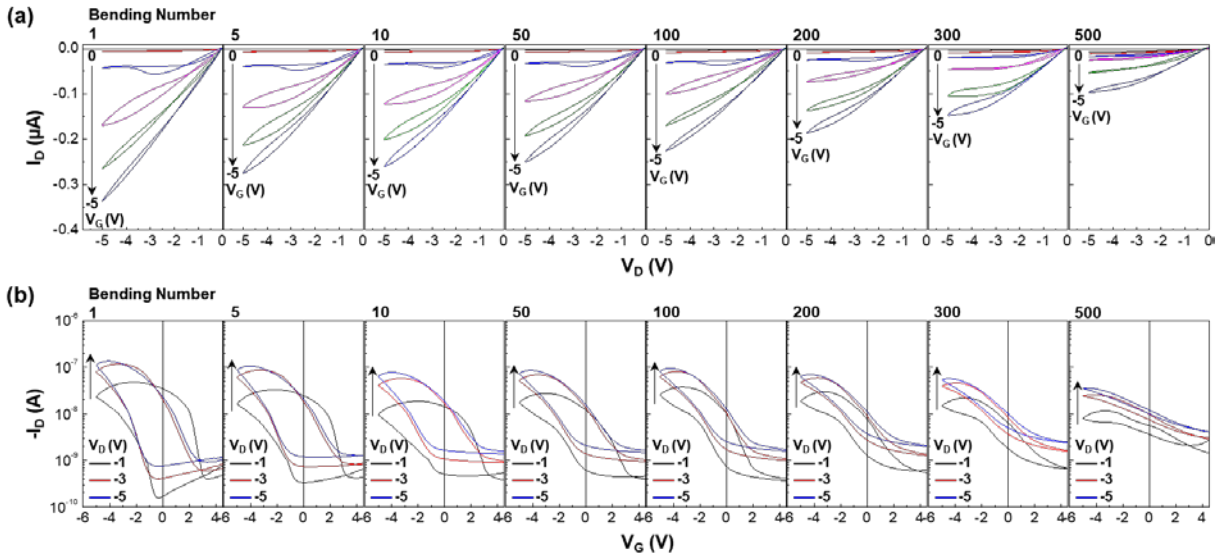

Fig. S18. (a) Output and (b) transfer curves for the flexible OFETs with the PAMPSA-AN layers (AN ratio = 0.5, annealing at 150 ºC for 30 min, colorless polyimide film substrates) according to the number of repeated bending test (0º ~ 30º).

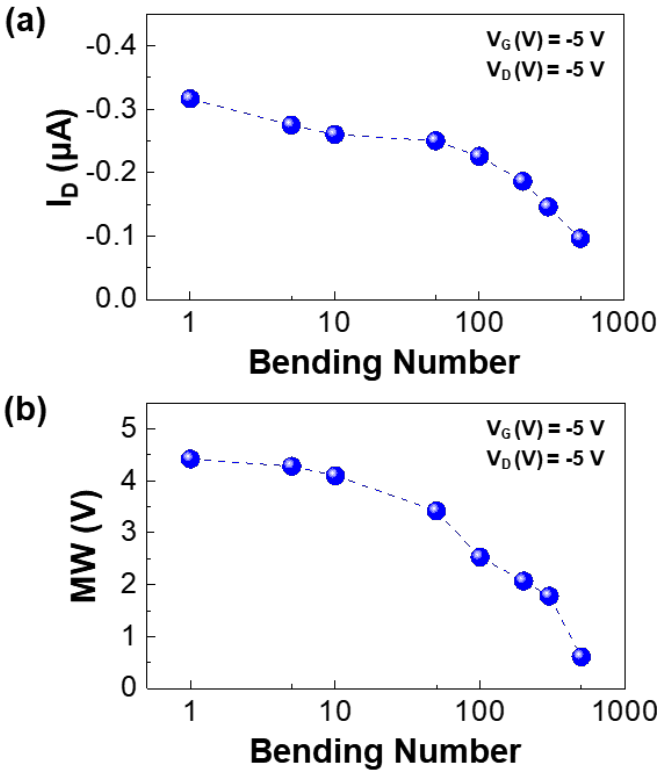

Fig. S19. Change of (a) drain current (I_D) and (b) memory window (threshold voltage difference) for the flexible OFETs with the PAMPSA-AN layers (AN ratio = 0.5, annealing at 150 ºC for 30 min). Data are taken from the transfer curves in Fig. S13.

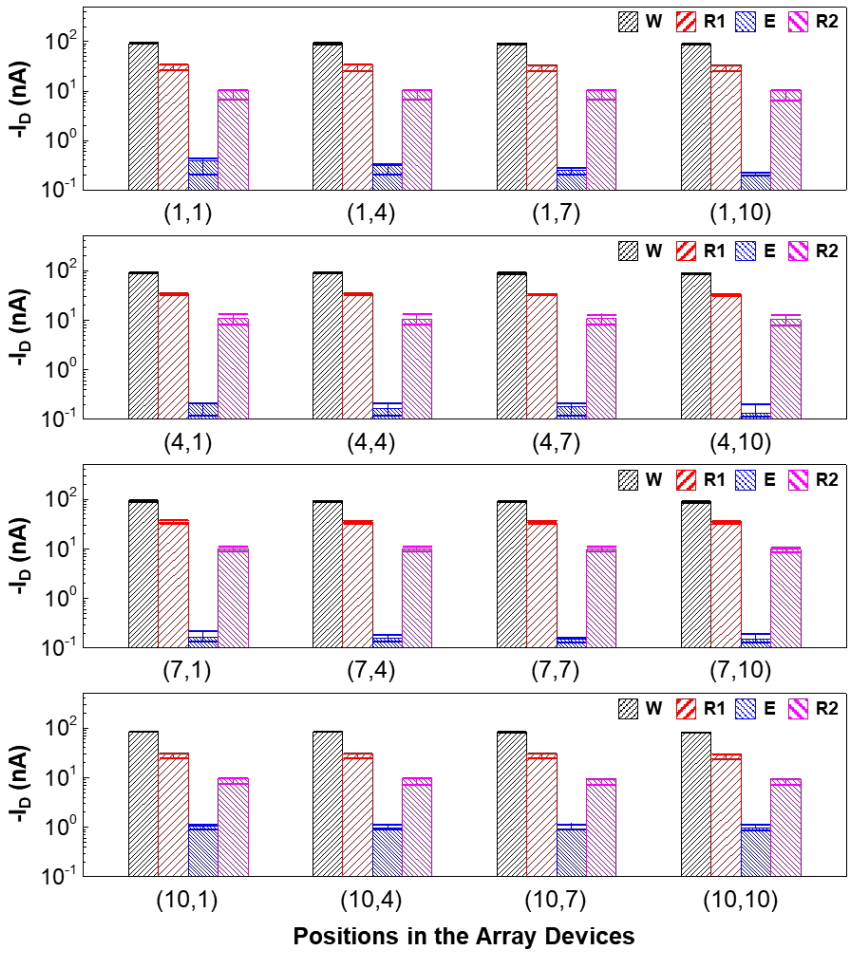

Fig. S20. Change of drain current (I_D) according to the position of sub-cells in the flexible array memory device during writing-reading-erasing-reading (WRER) operations (W: V_G = -5 V and V_D = -5 V; R: V_G = -1 V and V_D = -5 V). The deviations in I_D are marked with error bars for the individual operation cases.