

Electronic Supplementary Information

Resistive Non-Volatile Memories Fabricated with Poly(vinylidene fluoride)/Poly(thiophene) Blend Nanosheets

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Materials.

PVDF ($M_n = 7.1 \times 10^4$, $M_w = 1.8 \times 10^5$) was purchased from Aldrich and was reprecipitated once before use. P3CPenT ($M_w = 5.5\text{--}6.5 \times 10^4$) was used as received from Rieke Metals, Inc. pDDA ($M_n = 3.0 \times 10^4$, $M_w = 8.9 \times 10^4$) was synthesized through free radical polymerization initiated by AIBN, referring to a method described in an earlier report.^{S1,S2} Solvents including *N*-methyl-2-pyrrolidone (NMP) and chloroform were commercially available and were used without further purification. Octyltrichlorosilane was purchased from Tokyo Chemical Industry Co. Ltd. for the hydrophobic treatment of the substrate surface.

Procedures of LB deposition.

PVDF in NMP and P3CPenT in NMP (1 mM) were prepared at room temperature. pDDA was dissolved in CHCl_3 (1 mM). PVDF and pDDA solutions are colorless and transparent. P3CPenT solution shows an orange color. Then, three co-solutions of PVDF and P3CPenT were prepared with different weight ratios of P3CPenT of 6, 9, and 23 wt% (relative to PVDF) by mixing different volumes of the pre-prepared PVDF and P3CPenT solutions in NMP. The pDDA solution and

PVDF-P3CPenT co-solution were then spread successively onto the water surface to form a stable mixed Langmuir film keeping molar mixing ratio of PVDF-P3CPenT:pDDA to be 50:1.^{S3} The water was purified using an ultrapure water system ($>17.5 \text{ M}\Omega \text{ cm}$, CPW-101; Advantec Toyo Kaisha Ltd.). Experiments to assess the surface pressure (π)-area (A) isotherms and preparation of the mixed LB nanofilms were conducted using an automatically controlled Langmuir trough (FSD-220&21; USI Co. Ltd.) at a compression rate of $14 \text{ cm}^2 \text{ min}^{-1}$ at $20 \text{ }^\circ\text{C}$. During deposition, the substrate holder was lifted at a dipping speed of 10 mm min^{-1} in both upstrokes and downstrokes. If not otherwise specified, the blend LB monolayers at varying P3CPenT weight percentages were deposited at $20 \text{ }^\circ\text{C}$ under surface pressure of 30 mN m^{-1} and dried under a nitrogen flow.

Device fabrication.

The memory devices were fabricated with a sandwiched structure of glass substrate/gold (Au)/blend LB nanofilms/aluminum (Al). A bottom Au electrode ($40\pm 5 \text{ nm}$) and top Al electrode ($30\pm 5 \text{ nm}$) with equal areas of $3 \text{ mm} \times 3 \text{ mm}$ were thermally evaporated through a metal mask at a rate of 1.0 \AA s^{-1} onto glass substrates and the surface of the blend nanosheets, respectively. The samples were cooled using liquid nitrogen at 77 K during the deposition of top Al electrodes.

Measurements.

UV-vis absorption spectra were obtained using a UV-vis absorption spectrometer (U-3000; Hitachi Ltd.). The Fourier transform infrared (FT-IR) transmission measurements were conducted at a spectral resolution of 4 cm^{-1} using FT-IR (FTIR 4200; Jasco Corp.) under a nitrogen atmosphere. Film surface morphologies were investigated using atomic force microscopy (AFM) measurements (SPA-400; Hitachi High-Tech Science Corp.) under a contact mode. A silicon nitride cantilever (0.08 N m^{-1} and 34 kHz , OMCL-TR400PSA-1; Olympus Corp.) was used during measurement. For Kelvin probe force microscopy, the contact mode was firstly carried out to polarize the mixed LB nanofilms on gold electrode under a bias voltage using a conductive Pt-coated silicon cantilever (OMCL-AC240TM-B2; Olympus Corp.). Then, the Kelvin mode (KFM) was used to obtain the polarized potential images using the same cantilever. The X-ray diffraction (XRD) pattern was measured using a diffractometer (D8 Advance; Bruker AXS K.K.) with a Cu-K α radiation source ($\lambda=0.154\text{ nm}$). The morphology and composition of the samples were examined by Hitachi S-3400N Scanning Electron Microscope (SEM) combined with energy dispersive X-ray spectroscopy (EDX). A multifunction synthesizer (WF1946B, NF Corp., Japan) was used to generate the polarization pulse signal with poling width of 2.5 s . The current density (J)-voltage (V) characteristics of the memory devices were measured using a semiconductor parameter analyzer (4155C; Agilent Technologies Inc.) under a vacuum condition. Substrates such as quartz, silicon wafers, and glass were used respectively for UV-vis, AFM, and J - V measurements. Their hydrophilic treatment was done using a UV-O $_3$ cleaner after being washed thoroughly using chloroform, acetone, and 2-propanol. Hydrophobic substrates were obtained by immersing the previously described hydrophilic substrates into an octyltrichlorosilane chloroform solution for 3 hr .

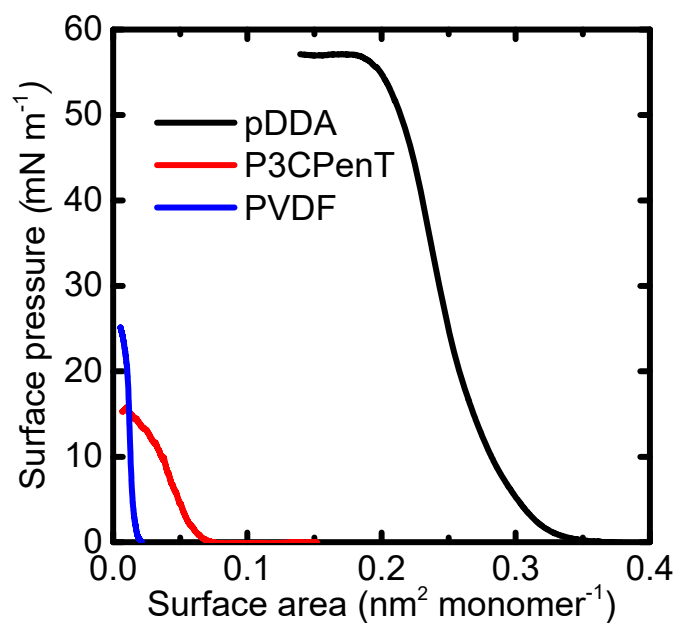


Figure S1. (a) Surface pressure (π)-area (A) isotherms of pure pDDA, P3CPenT, and PVDF monolayers.

Table S1. Limiting surface area (S_{aver}), collapse surface pressure (π_c), and the surface pressure (π^*), occupied area (A^*), and modulus (C_s^{-1*}) at the concentrated solid state

Content of P3CPenT	23 wt%	9 wt%	6 wt%
S_{aver} (nm ²)	0.0250	0.0230	0.0224
π_c (mN m ⁻¹)	51	49	50
π^* (mN m ⁻¹)	30	30	31
A^* (nm ²)	0.0196	0.0183	0.0178
C_s^{-1*} (mN m ⁻¹)	123	123	123

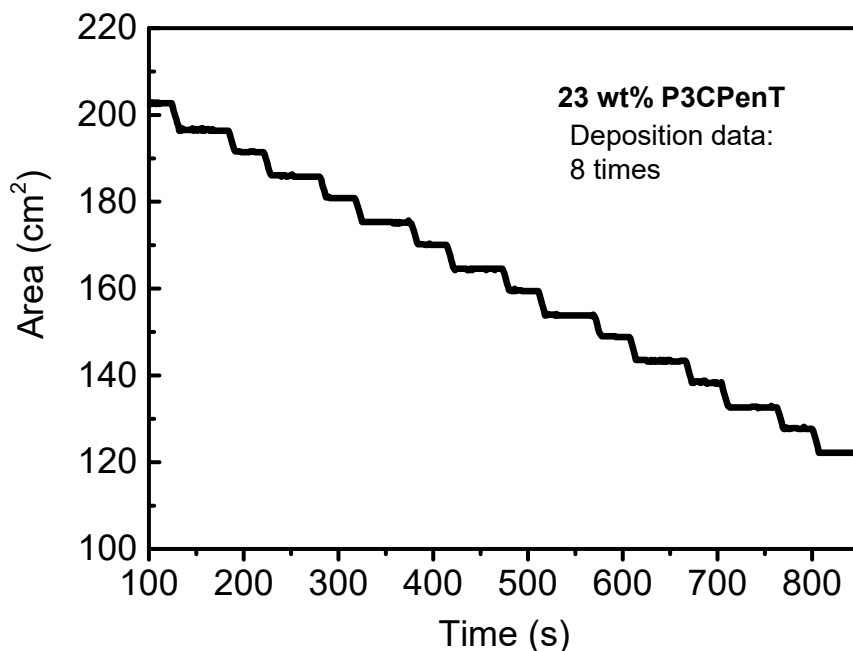


Figure S2. Deposition curves of PVDF-P3CPenT-pDDA LB blend nanosheets film at a P3CPenT content of 23 wt%.

The Langmuir films were transferred to substrates with a constant lifting rate of 10 mm min^{-1} at 30 mN m^{-1} at $20 \text{ }^\circ\text{C}$. The reduced area per deposition is uniform, as **Figure S2** shows. The transfer ratio for both downstrokes and upstrokes are calculated as almost unity according to **Equation S1**. Results show that the blend LB nanofilms own very regular layer structures.

$$\text{Transfer ratio } (R) = \text{reduced area } (A_r) \text{ per deposition/ substrate area } (A_s)$$

(Equation S1)

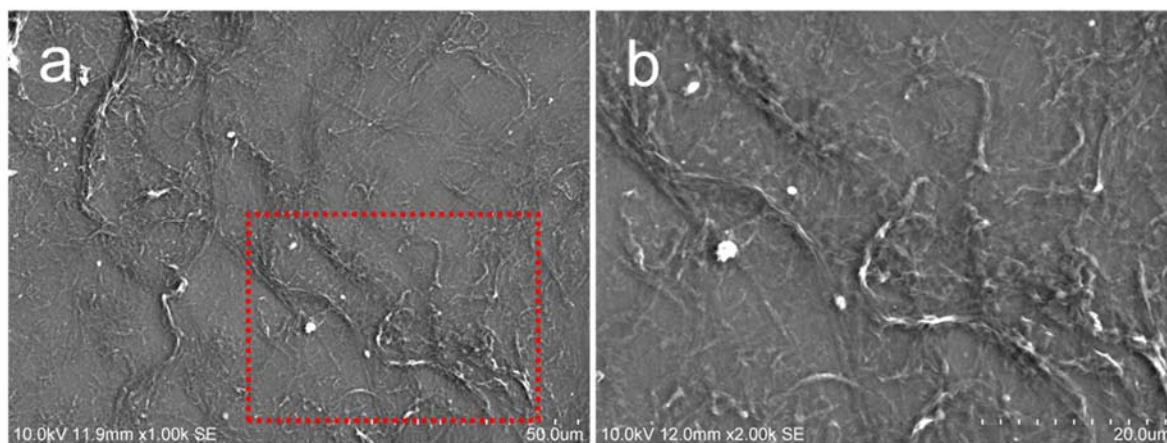


Figure S3. SEM images of PVDF-P3CPenT-pDDA LB blend nanosheets at a P3CPenT content of 23 wt%.

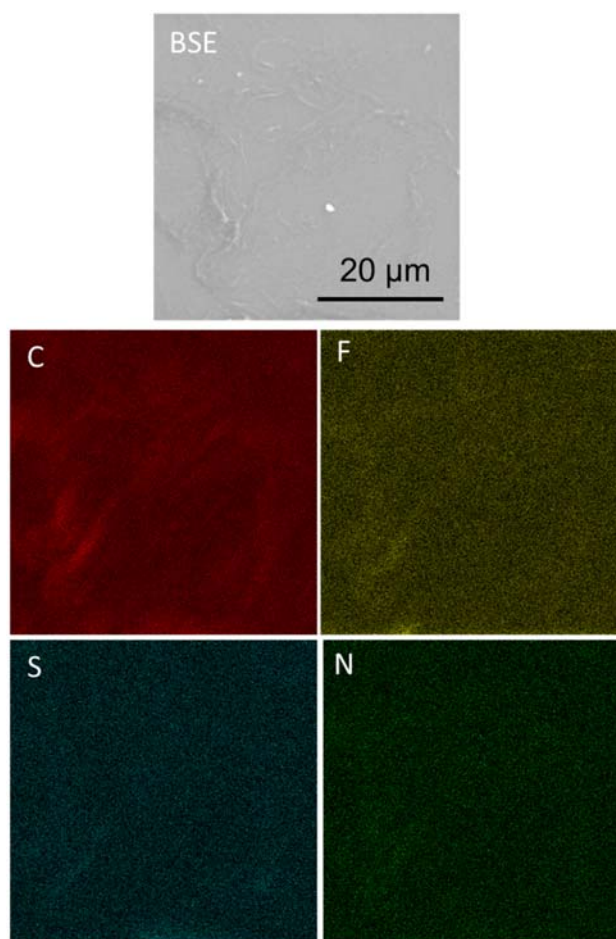


Figure S4. SEM image (top), and EDX mappings for elements of C, F, S, and N in PVDF-P3CPenT-pDDA LB blend nanosheets at a P3CPenT content of 23 wt%.

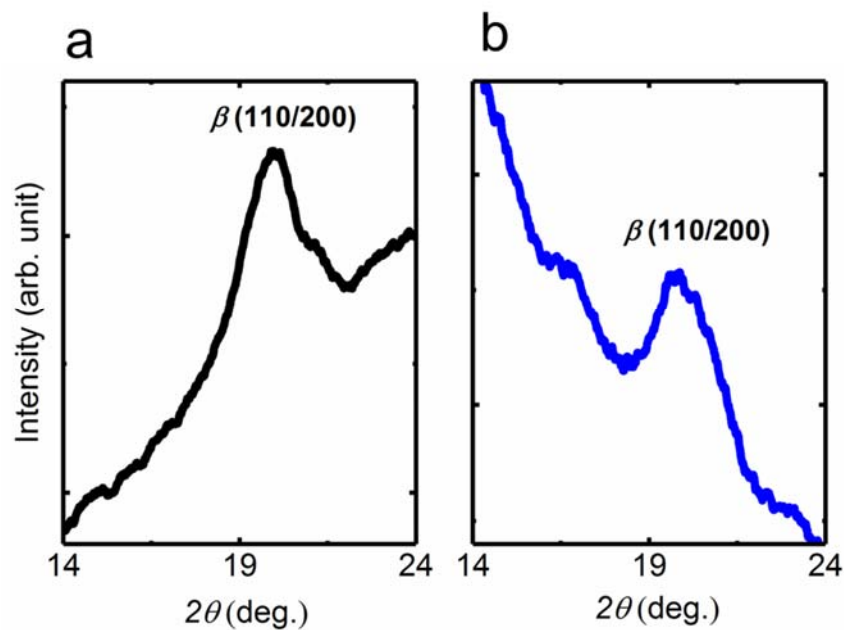


Figure S5. XRD spectra of the blend LB nanosheets: (a) PVDF-pDDA (black line) and (b) PVDF-P3CPenT-pDDA at 23 wt% P3CPenT.

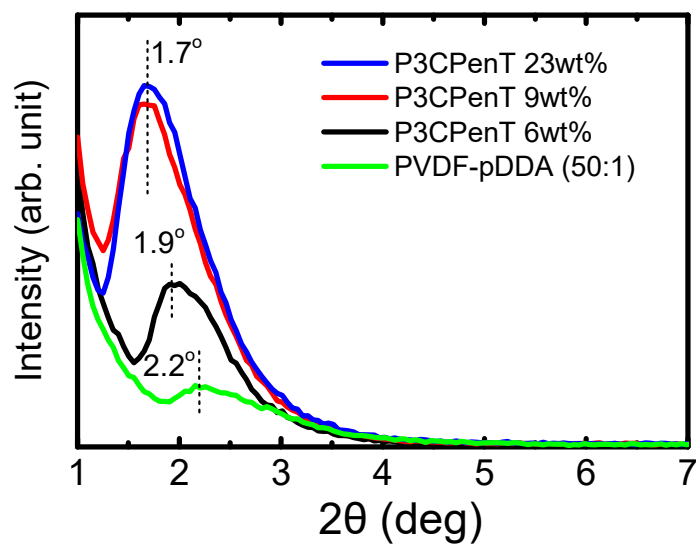


Figure S6. XRD spectra of the blend LB nanofilms at different content of P3CPenT: 0 (light green line), 6 (black line), 9 (red line), and 23 wt% (blue line).

$$F(\beta) = \frac{X_\beta}{X_\alpha} = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right)A_\alpha + A_\beta} \quad \text{Equation S2}$$

Here, A_α and A_β are the absorbance at 765 and 840 cm^{-1} , respectively, K_α and K_β are the absorption coefficients at the respective wavenumbers of 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$.^{S4}

Table S2. Monolayer thickness calculated from the Bragg law

Monolayer	pDDA*	PVDF-pDDA (50:1)	P3CPenT 6 wt%	P3CPenT 9 wt%	P3CPenT 23 wt%
Thickness (nm)	1.7	2.0	2.3	2.6	2.6

*value from reference S1

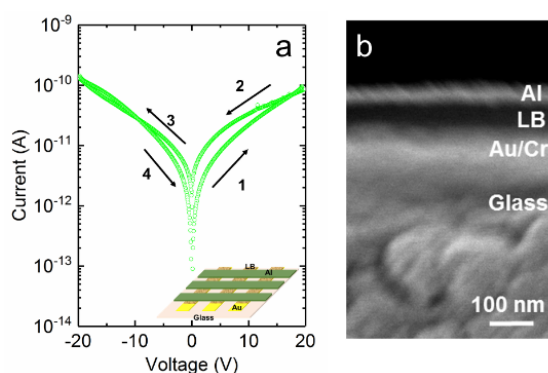


Fig. S7 (a) Current-voltage characteristic of the blend LB nanosheets (P3CPenT23 wt%, 30 layers, 78 nm). The inset presents the device structure; and (b) Cross-sectional SEM image of the memory device: Al (40 nm)-LB (78 nm)- Cr(3 nm)/Au (42 nm).

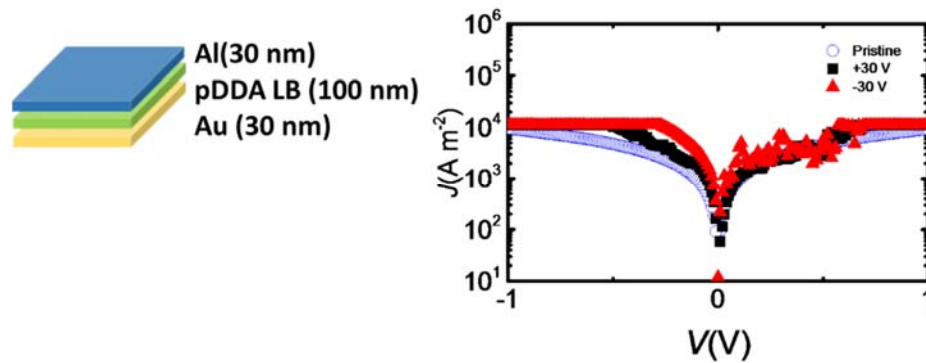


Figure S8. Schematic structure of control sample (left), and current density (J)-voltage (V) characteristics of the control sample in pristine and polarization states.

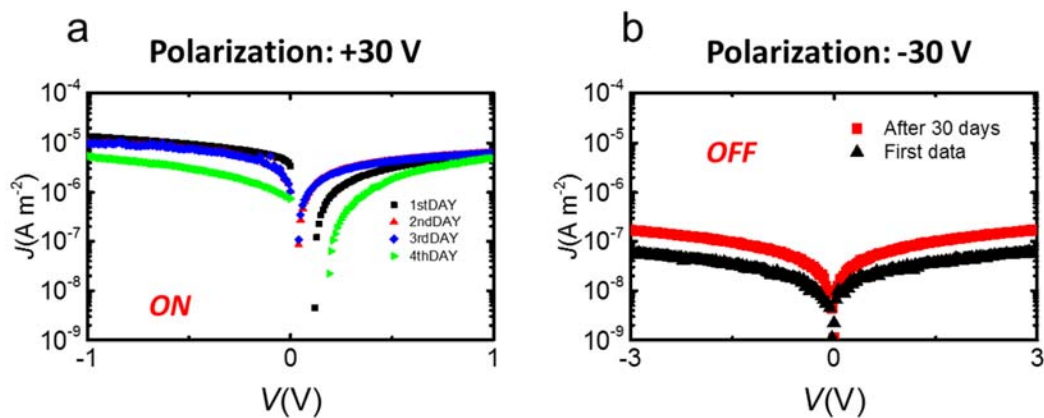


Figure S9. Current density (J)-voltage (V) characteristics of the blend LB nanofilms at (a) ON-state and (b) OFF-state varying with time.

References

- S1 T. Miyashita, Y. Mizuta and M. Matsuda, *Br. Polym. J.*, 1990, **22**, 327-331.
- S2 T. Miyashita, *Prog. Polym. Sci.*, 1993, **18**, 263-294.
- S3 H. Zhu, M. Mitsuishi and T. Miyashita, *Macromolecules*, 2012, **45**, 9076-9084.
- S4 R. Gregorio and M. Cestari, *J. Polym. Sci., Part B: Polym. Phys.*, 1994, **32**, 859-870.