Electronic Supplementary Information

Side-chain Engineering of Two-dimensional Polymer Thin Films for High-Performance Organic Non-volatile Memories

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Experimental Section

1.1 Two-dimensional polymer film Growth and Transfer.

First, 30 mL of deionized water was transferred into a glass weighing bottle (75 mm × 35 mm), which had been ultrasonically cleaned twice with ethanol, to serve as the liquid substrate for the growth of the two-dimensional polymer film. Next, 1.76 mg (5 μmol) of TAPB and 2.51 mg (7.5 μmol) of $TPOC_6$ [PDA (1 mg), TPOH (1.25 mg), TPF_4 (1.55 mg)] were dissolved in a mixed solution of 1,4-dioxane, mesitylene, and chloroform (volume ratio 1:1:2) with a total volume of 1 mL. The solution was sonicated at 25℃ and 100 Hz for 20 minutes and then filtered using a 0.22 μm pore size filter. Subsequently, 75 μL of acetic acid was rapidly added, and the mixture was shaken continuously to ensure even mixing. Using a micropipette, 50 μL of the prepared precursor solution was carefully deposited onto the surface of the deionized water, ensuring slow and steady evaporation for film growth. The container was then sealed and left undisturbed for 24 hours in an environment maintained at 16℃ and 30% humidity. After the solvent had completely evaporated, a floating two-dimensional polymer film was obtained on the surface of the water. SiO_2 (300 nm)/Si wafers were used as the substrates and were ultrasonically cleaned for 30 minutes in deionized water, acetone, and isopropanol, followed by a 10-minute soak. The floating two-dimensional polymer film was transferred onto the SiO_2/Si substrates by gently immersing the substrate from below the water surface. The substrates were then soaked in deionized water, acetone, and isopropanol for 20 minutes each to remove any unreacted monomers.

1.2 Two-dimensional molecular crystals Growth and Transfer.

A total of 30 mL of glycerol was transferred into a glass weighing bottle (75 mm × 35 mm), which had been ultrasonically cleaned twice with ethanol, to serve as the liquid substrate for the growth of two-dimensional molecular crystals (2DMCs). Using a micropipette, 80 μL of the prepared Ph-BTBT-C10 solution (1 mg mL^{-1} in toluene) was carefully deposited on the surface of the glycerol, ensuring a slow and steady evaporation process for crystal growth. The system was then sealed and placed in an environment maintained at 16°C and 30% humidity. After complete solvent evaporation, Ph-BTBT-C10 2DMC floating on the glycerol surface were obtained. SiO_2

(300 nm)/Si wafers were used as the substrates and were ultrasonically cleaned for 30 minutes in deionized water, acetone, and isopropanol, followed by a 10-minute soak. The floating Ph-BTBT-C10 2DMC were transferred onto the SiO_2/Si substrates by inverting the substrate and gently scooping the crystals. The substrate with 2DMC was then gently rinsed with deionized water to remove any excess glycerol from the surface.

1.3 Gold layer bonding technique.

The Au source and drain electrodes were prepared as follows: First, a 100 nm thick Au film was pre-deposited on a SiO_2/Si wafer through thermal evaporation. Afterward, the mask was removed, and a small piece of the Au film, approximately 35 mm × 180 mm, was delaminated from the SiO_2/Si wafer and transferred onto the Ph-BTBT-C10 2DMCs as the source or drain electrode. The Au layer adhered to the crystal via van der Waals forces. This technique is highly suitable for fundamental research, as it requires minimal equipment, avoids the inevitable damage caused by vacuum deposition or thermal evaporation on the crystal, and still allows for excellent device performance.

Additional Figures

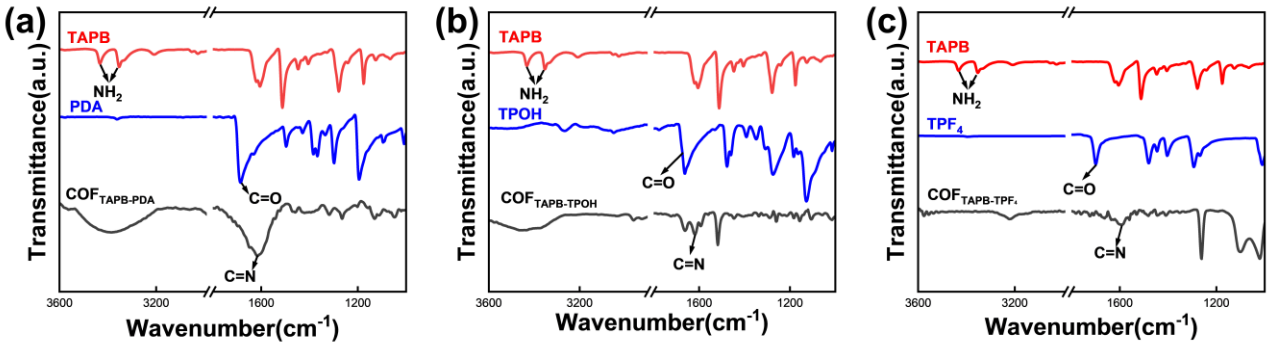

Fig. S1 Fourier transform infrared (FTIR) spectrum of 2DP thin films. (a) poly-TP (b) poly-TH (c) poly-TF.

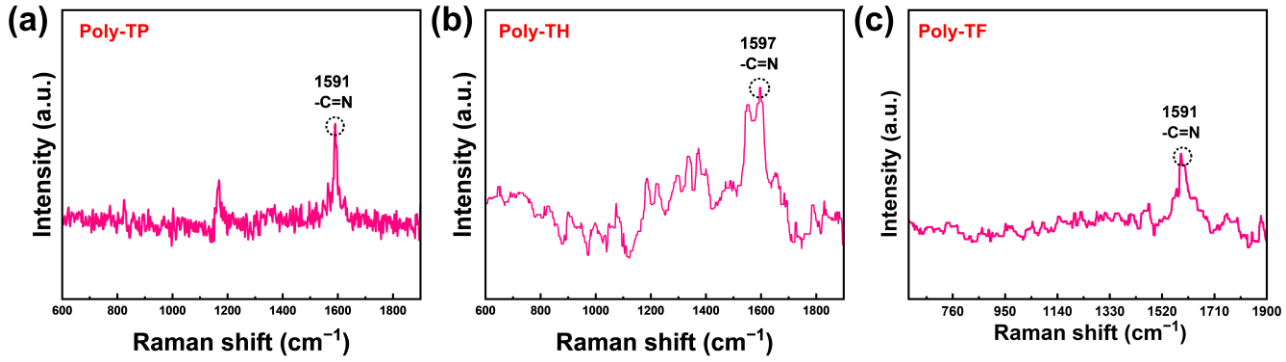

Fig. S2 Confocal laser Raman image of 2DP thin films. (a) poly-TP (b) poly-TH (c) poly-TF.

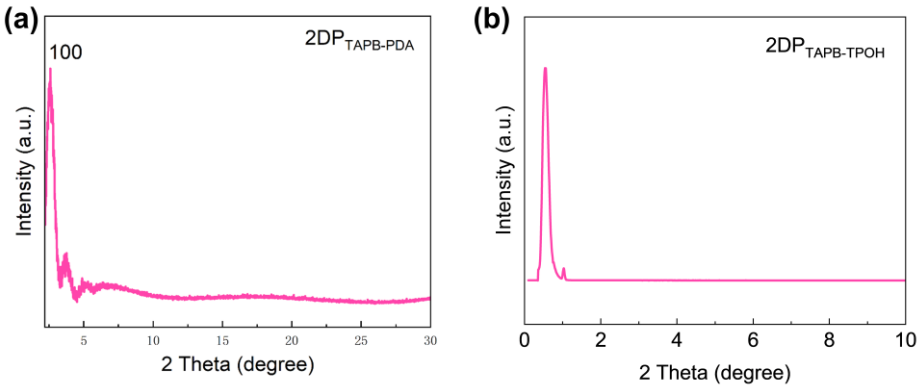

Fig. S3 XRD image of 2DP thin films. (a) poly-TP (b) poly-TH.

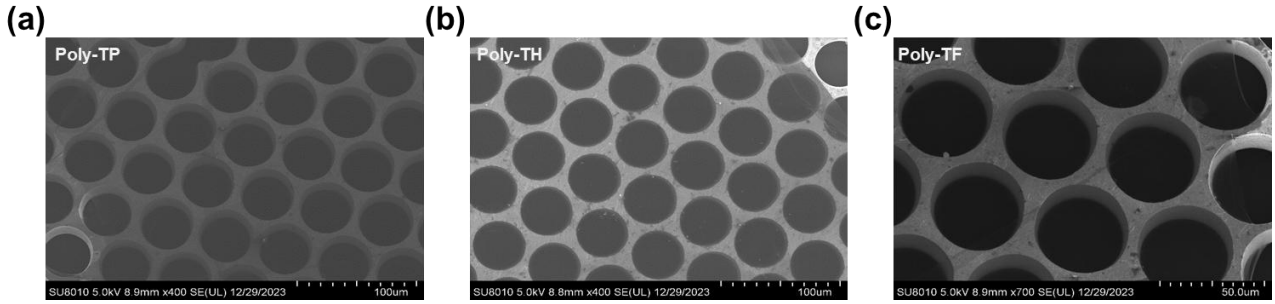

Fig. S4 SEM image of 2DP thin films. (a) poly-TP (b) poly-TH (c) poly-TF.

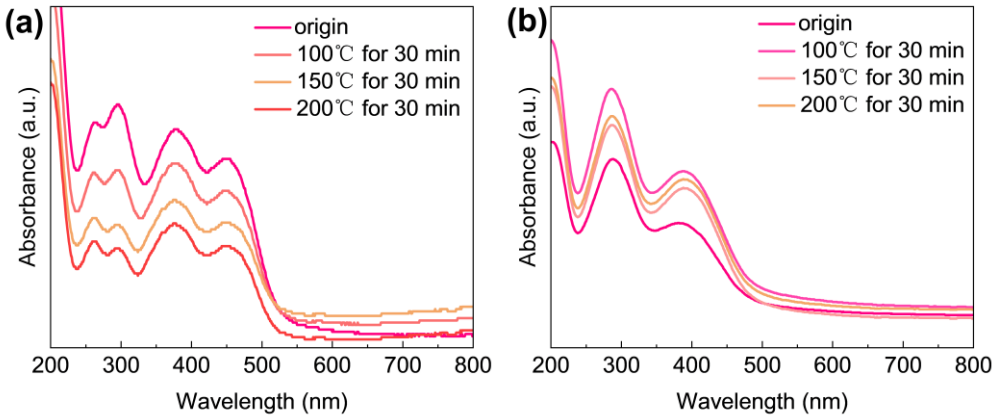

Fig. S5 UV-visible (UV-vis) absorption spectra of 2DP thin films after annealing at 100 °C, 150 °C, and 200 °C for 30 minutes, respectively. (a) poly-TH (b) poly-TF.

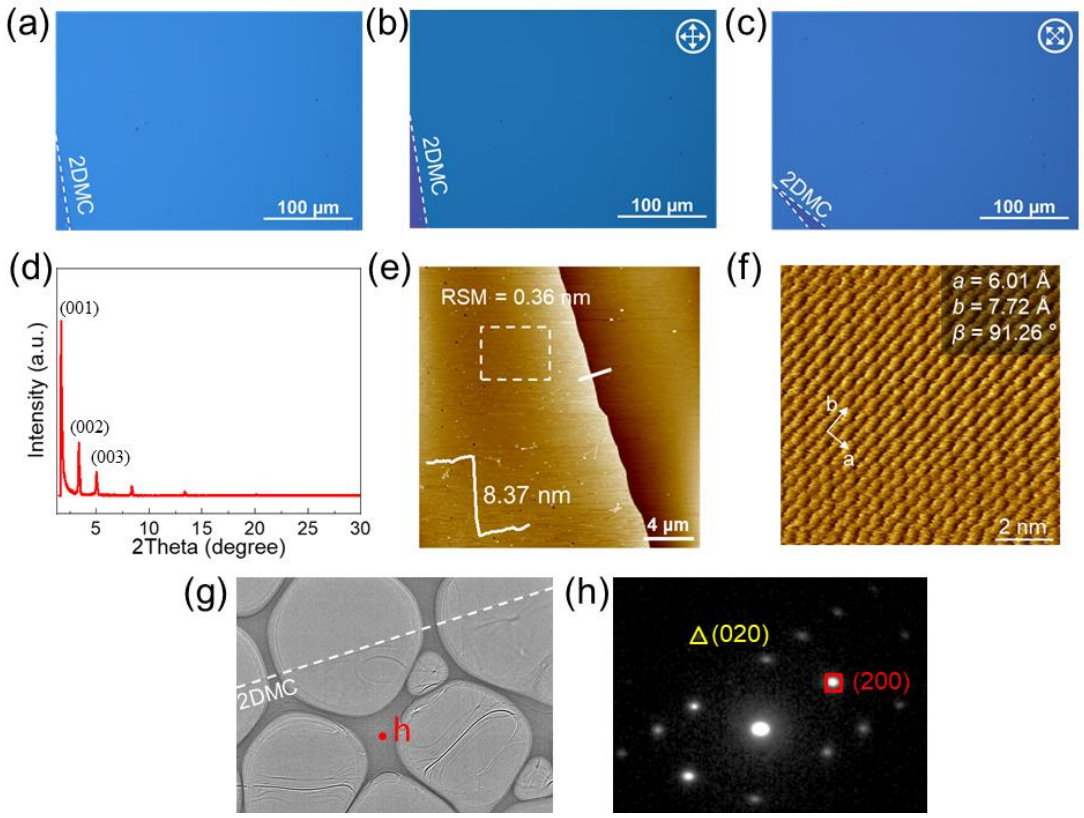

Fig. S6 (a) OM and (b, c) POM images of Ph-BTBT-C10 2DMC; (d) XRD pattern of Ph-BTBT-C10 2DMC; (e, f) AFM image and corresponding high-resolution AFM image of a typical Ph-BTBT-C10 2DMC; (g, h) TEM and the corresponding SAED pattern of individual Ph-BTBT-C10 2DMC.

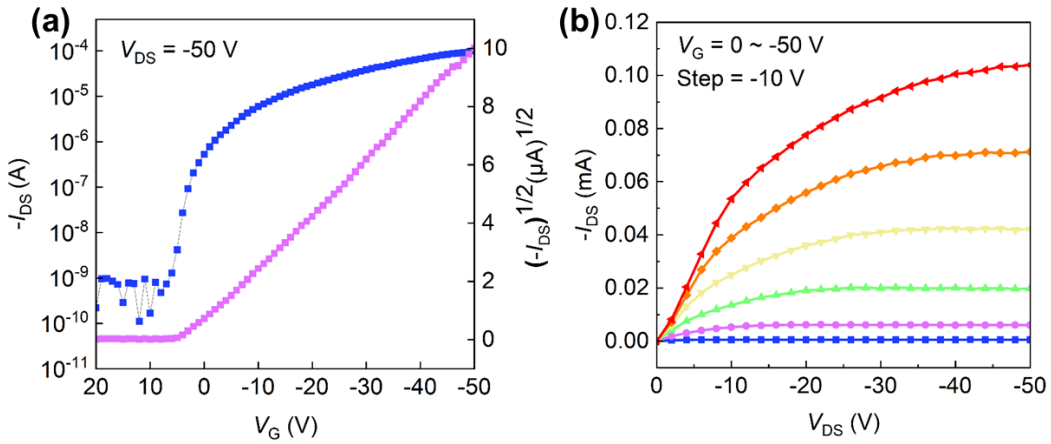

Fig. S7 Charge transport properties of the 2DMC. (a) Typical transfer and (b) output characteristics curves of the OFET based on 2DMC of Ph-BTBT-C10.

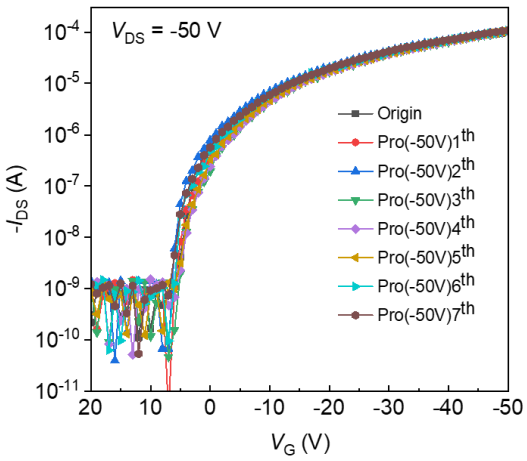

Fig. S8 A -50V programmed voltage transfer curve is applied multiple times to 2DMC (excluding 2DP).

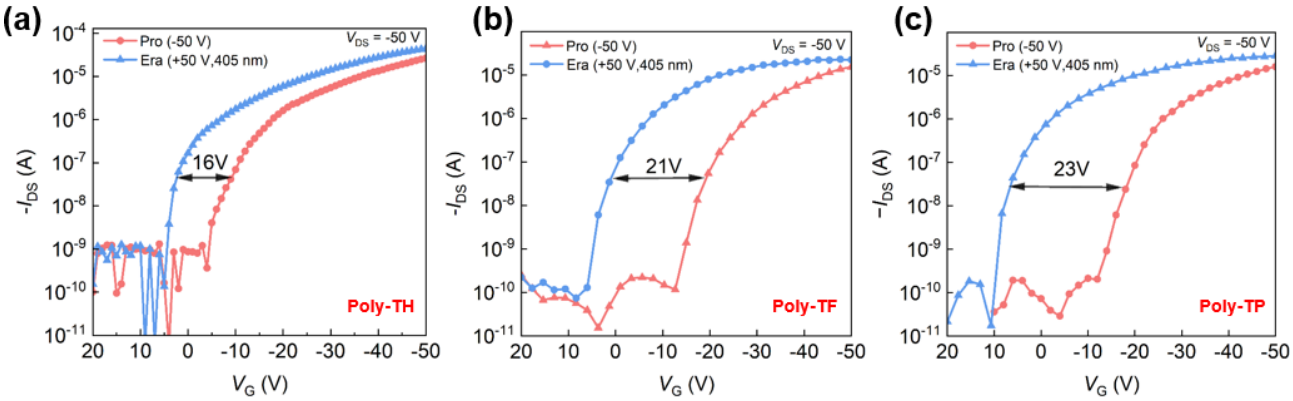

Fig. S9 2DP based OFET memory window changes after applying -50V programming instruction and +50V, 405nm light erase instruction. (a) poly-TH (b) poly-TF(c) poly-TP.

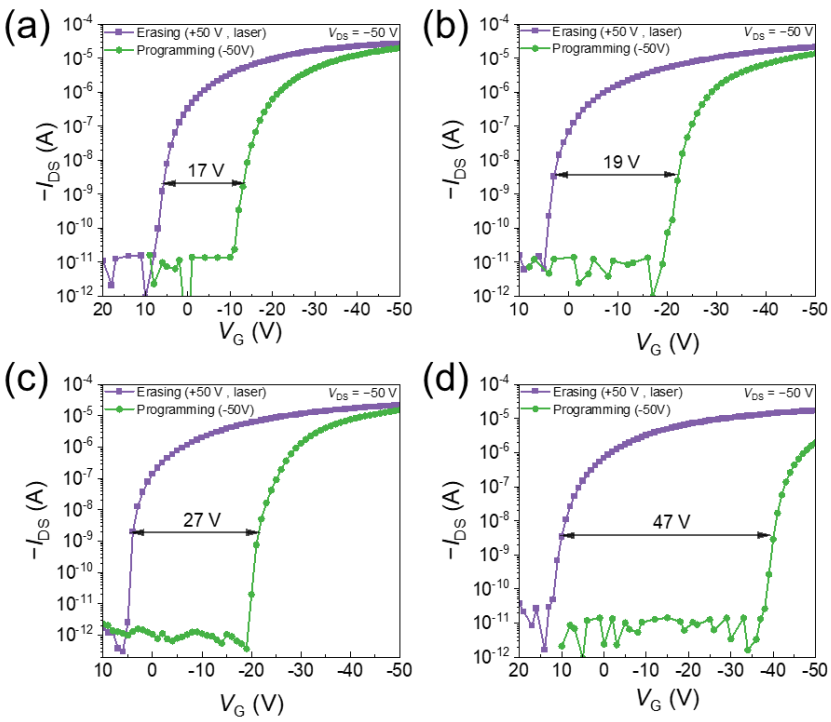

Fig. S10 Memory window of 2DP-based OFET devices under the application of −50 V programming voltage and a +50 V, 405 nm light erasing signal. (a) poly-TH, (b) poly-TF, (c) poly-TP, (d) poly-TT.

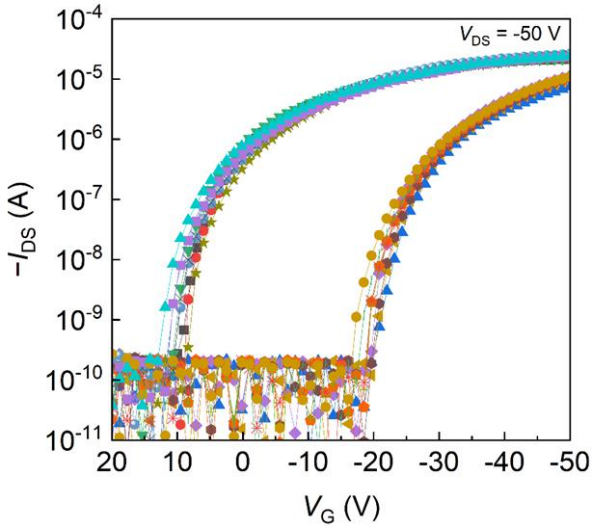

Fig. S11 Memory window changes of poly-TT 2DP thin films based OFET devices by applying multiple programming/erasing pulses.

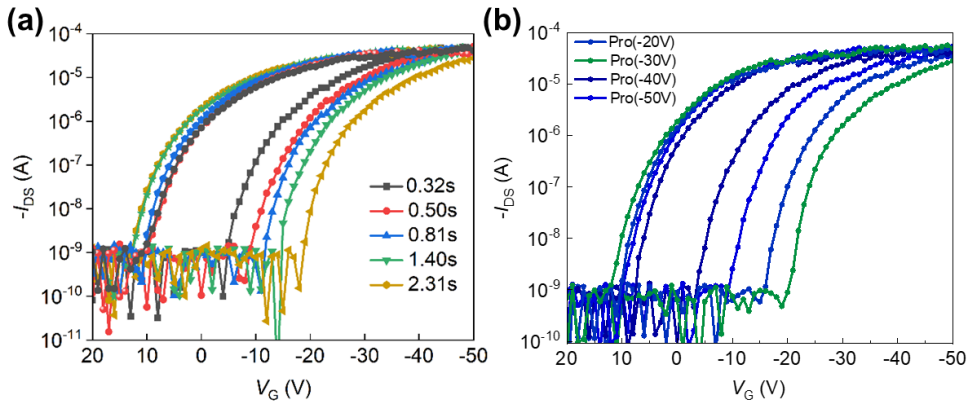

Fig. S12 (a) The memory window of the device under the same pulse time and different pulse voltages. (b) The memory window of the device under the same pulse voltage and different pulse time.

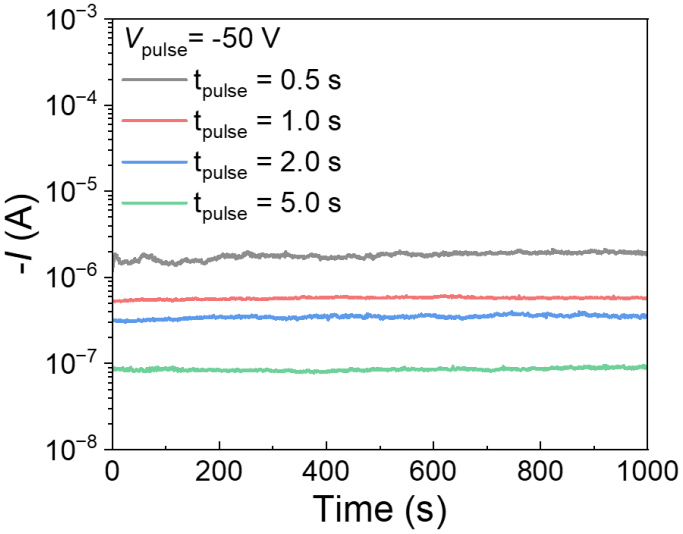

Fig. S13 *I-t* stability of poly-TT-based organic non-volatile memory devices.

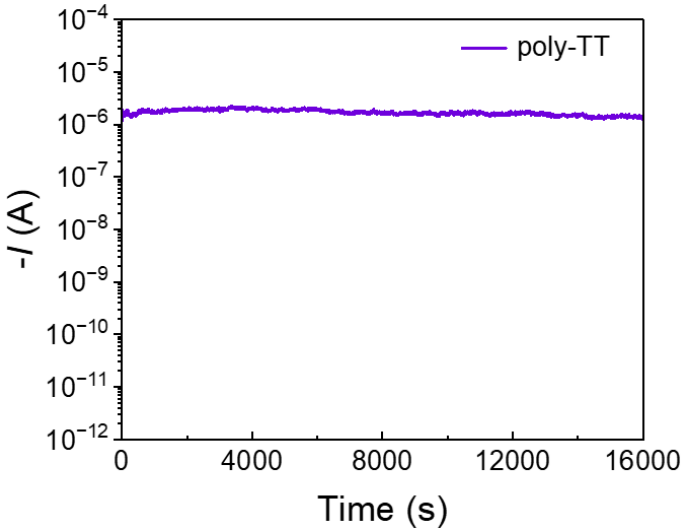

Fig. S14 Retention time of poly-TT-based organic non-volatile memory devices.

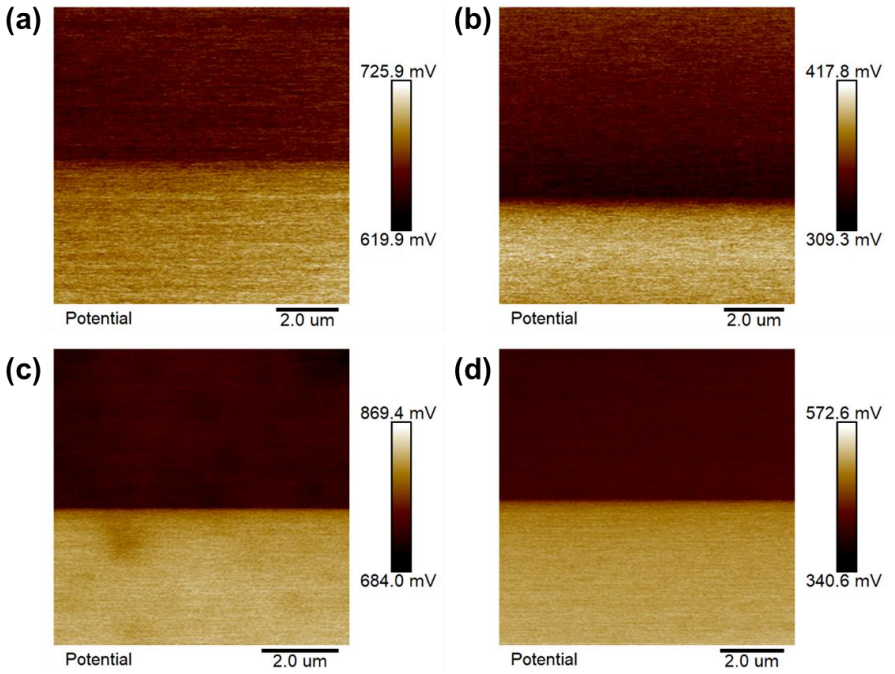

Fig. S15 The surface potential of OFET memory observed using KPFM mode, and the change diagram of Ph-BTBT-C10 2DMC surface potential before and after programming/erasing. (a) poly-TH (b) poly-TF (c) poly-TP (d) poly-TT.

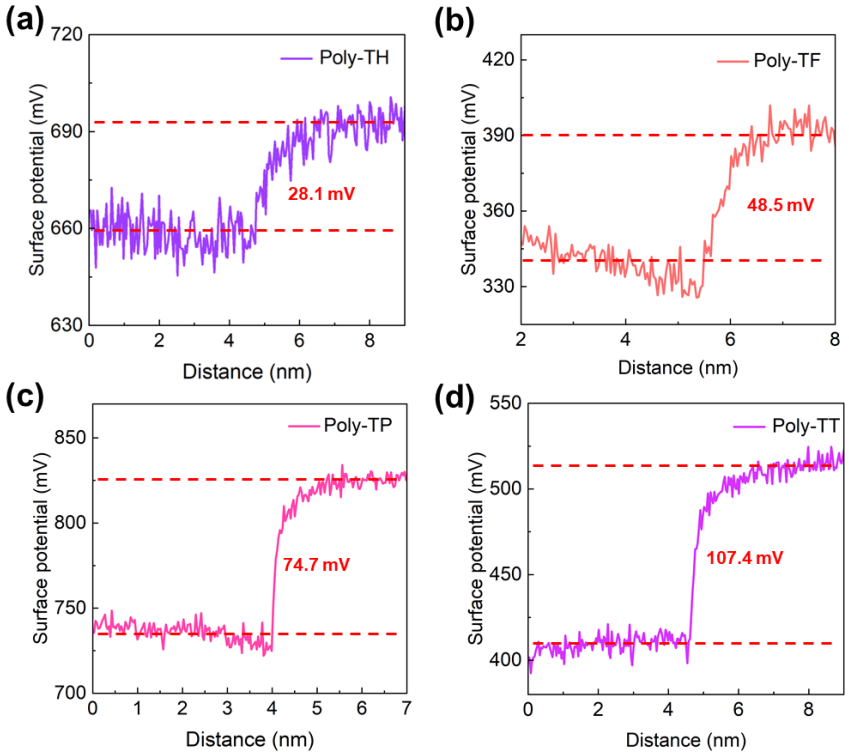

Fig. S16 Surface potential changes of Ph-BTBT-C10 2DMCs before and after programming/erasing. (a) poly-TH (b) poly-TF (c) poly-TP (d) poly-TT.

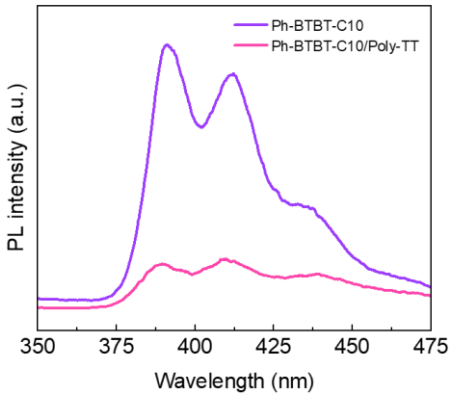

Fig. S17 Photoluminescence spectra of Ph-BTBT-C10 and Ph-BTBT-C10/poly-TT.

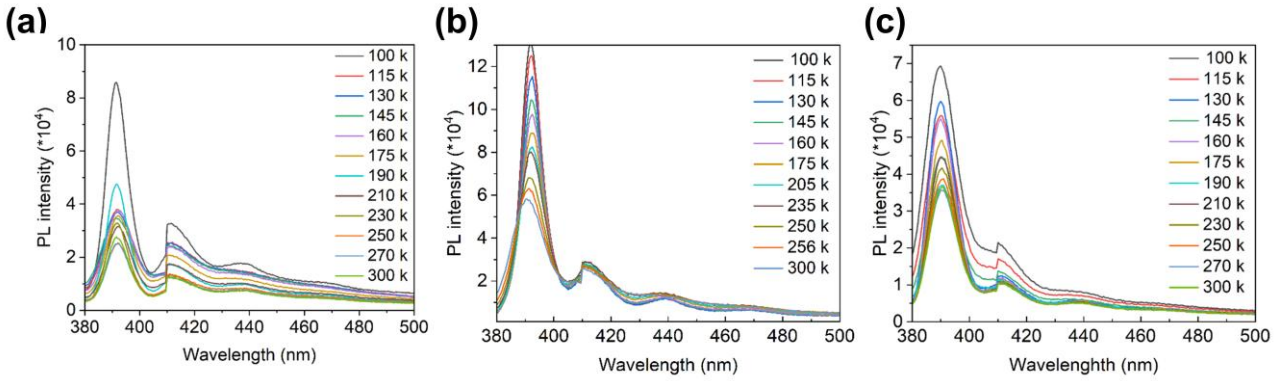

Fig. S18 Temperature-dependent photoluminescence (PL) spectra of PH-BTBT-C10/2DP thin films, respectively: (a) poly-TH (b) poly-TF (c) poly-TP.

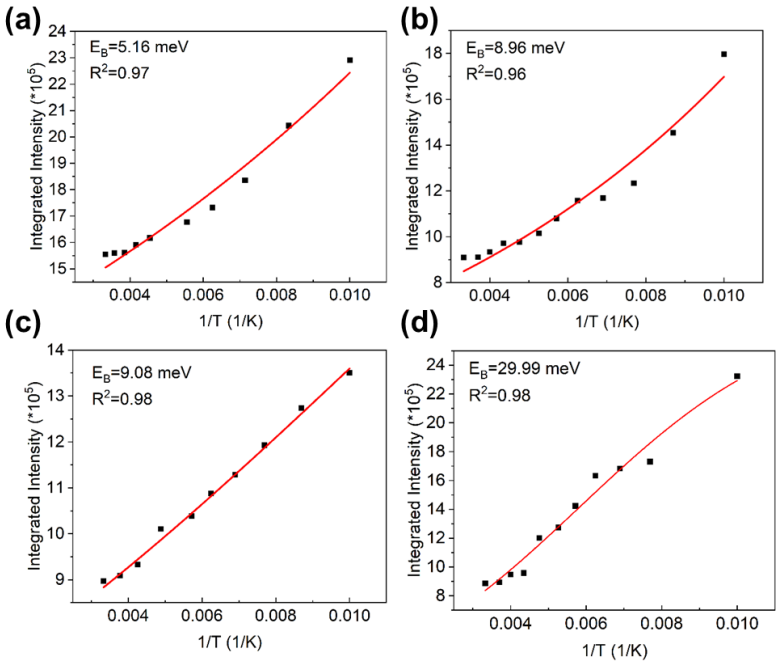

Fig. S19 The integral strength of PH-BTBT-C10/2DP thin films varies with temperature. respectively: (a) poly-TT (b) poly-TP (c) poly-TF (d) poly-TH.

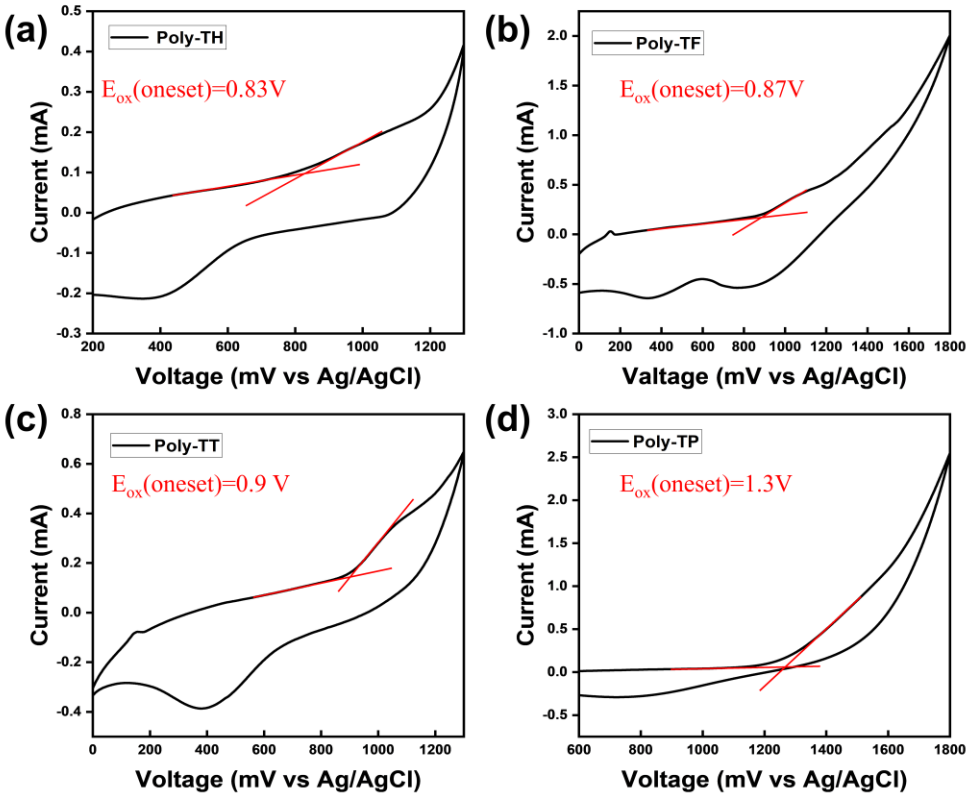

Fig. S20 Electrochemical *C-V* spectra of 2DP thin films. (a) poly-TH (b) poly-TF (c) poly-TT (d) poly-TP.

Energy levels are calculated based on electrochemical spectrum and optical band gap. The optical band gap (*E*g) was measured by UV-vis absorption spectroscopy. LUMO levels of 2DP thin films are calculated as follows:

$$E_{\mathrm{HOMO}} = -\left[E_{\mathrm{OX}}(\mathrm{oneset}) + 4.8 - E_{\mathrm{FOC}}\right]$$

$$E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{eg}}$$

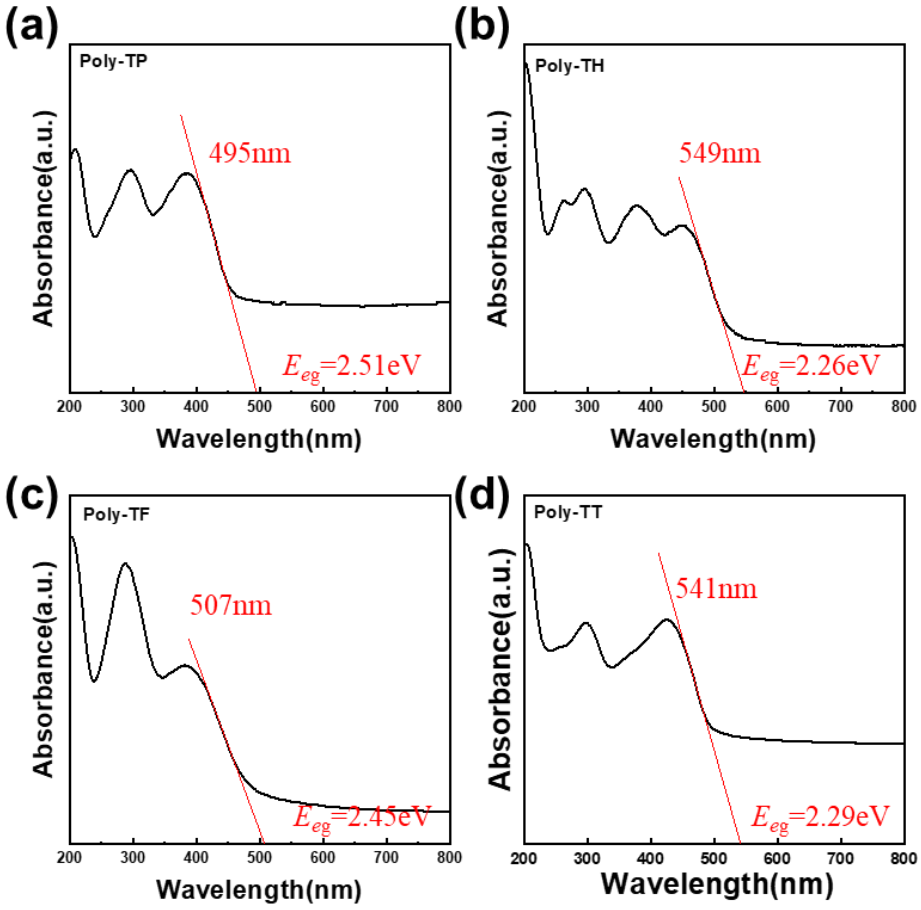

Fig. S21 UV-visible (UV-vis) absorption spectra of 2DP thin films. (a) poly-TP (b) poly-TH (c) poly-TF (d) poly-TT.

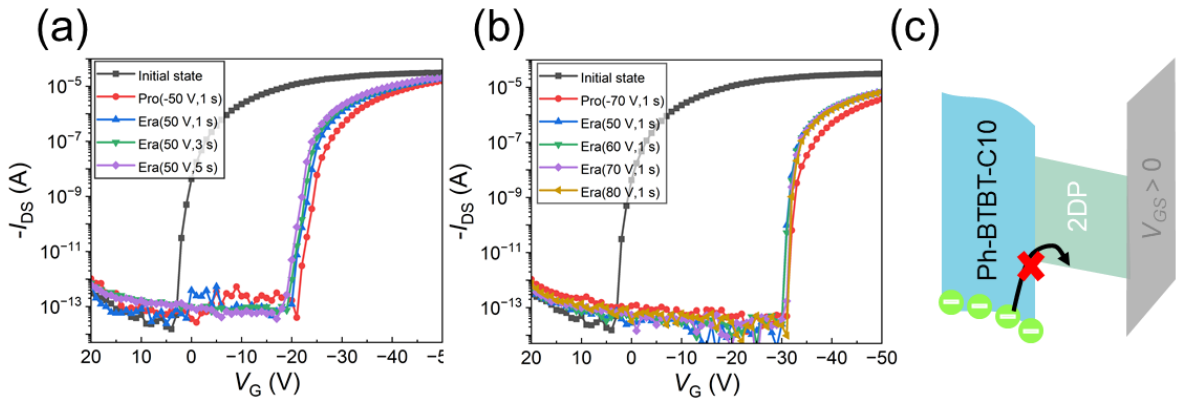

Fig. S22 (a) Electrical erasion of poly-TT-based OVNM under a fixed erase voltage of 50 V and varying erase durations. (b) Electrical erasion of poly-TT-based OVNM under a fixed erase duration and varying erase voltages. (c) Schematic illustration of the constraints on the electrical erasure process.