

A two-dimensional polymer memristor based on conformational change with tunable resistive switching behaviours

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Electronic Supplementary Information

1. Experimental details

All of the chemicals were obtained from commercial sources and the synthetic route is shown in Figure S2.

1.1 Synthesis of 9-(3-bromopropyl)-9H-carbazole:

To a mixture of carbazole (5.0 g, 30 mmol), benzene (15 ml), benzyltriethylammonium chloride (BTEAC) (250 mg), and aqueous (50%) sodium hydroxide solution (15 ml), an excess amount (more than 10 times equivalent to carbazole) of alkyl dibromide was added with stirring. And then extracted with dichloromethane (3×50 mL). The organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether-dichloromethane (10:1) as eluent to afford the product as a colorless sugar (1.96 g, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 7.7 Hz, 2H), 7.54–7.40 (m, 4H), 7.26 (d, J = 7.2 Hz, 2H), 4.50 (t, J = 6.4 Hz, 2H), 3.38 (t, J = 6.0 Hz, 2H), 2.44 (p, J = 6.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.36, 125.86, 122.99, 120.46, 119.16, 108.63, 40.93, 31.98, 30.90.

1.2 Synthesis of 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde:

In a round bottom flask, 2,5-dihydroxyterephthalaldehyde (250 mg, 1.5 mmol) was dissolved in 7 ml of DMF, then 9-(3-bromopropyl)-9H-carbazole (1.96 g, 6.8 mmol), sodium iodide (1.4 g, 9.3 mmol) and potassium carbonate (843.6 mg, 6.1 mmol) were added. And the reaction mixture was stirred under argon at 40 °C overnight. And then extracted with ethyl acetate (3×60 mL). The organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether-dichloromethane (3:1) as eluent to afford the product as a yellow powder (562 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 10.41 (s, 2H), 8.10 (d, J = 7.7 Hz, 4H), 7.39 (t, J = 8.9 Hz, 8H), 7.28 (s, 2H), 7.23 (t, J = 7.2 Hz, 4H), 4.57 (t, J = 6.4 Hz, 4H), 4.09 (t, J = 5.3 Hz, 4H), 2.44 (s, 4H). ¹³C

NMR (101 MHz, CDCl_3) δ 188.52, 154.67, 140.25, 129.01, 125.82, 122.98, 120.56, 119.16, 111.78, 108.31, 66.19, 39.60, 28.48. HRMS calcd for: $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_4^+$ $[\text{M}+\text{Na}]^+$: 603.2254, found: 603.2256.

1.3 Synthesis of two-dimensional covalent organic polymer ($2\text{DP}_{\text{TPAK}+\text{TAPB}}$):

1,3,5-tris(4-aminophenyl)-benzene (TAPB, 1.4 mg, 0.004 mmol) and 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde (TPAK, 3.5 mg, 0.006 mmol) were dissolved in 2 mL DMF and then 40 μL of acetic acid were added. 50, 100, 200, 300 μL of this mixture solution were diluted by 300 μL chlorobenzol and then carefully dropped on the surface of the 20 mL deionized water, respectively. After the bottle was allowed to stand at room temperature for 48 h, a layered two-dimensional polymer film was finally obtained at the solution/air interface.

1.4 Device fabrication of $2\text{DP}_{\text{TPAK}+\text{TAPB}}$ film:

The indium-tin-oxide (ITO) glass substrates were sequentially cleaned with toluene, acetone, ethyl alcohol, isopropanol and deionized water. The synthesized $2\text{DP}_{\text{TPAK}+\text{TAPB}}$ films were first transferred onto the surface of water and DMF to remove unreacted precursors. Then, the $2\text{DP}_{\text{TPAK}+\text{TAPB}}$ films were picked up by the ITO glass substrates (For the flexible device, the films were transferred onto the flexible ITO substrates). The top electrode of Au (50 nm) were deposited on the $2\text{DP}_{\text{TPAK}+\text{TAPB}}$ with the help of copper mask. The memory characteristics of devices were measured using a probe station at room temperature.

1.5 STM structural characterization of $2\text{DP}_{\text{TPAK}+\text{TAPB}}$:

First, 1,3,5-tris(4-aminobenzene)benzene (TAPB) and 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde (TPAK) are dissolved in DMSO to make a solution with a concentration of 0.4 mg/g. Next, use caprylic acid to dilute it to 0.008 mg/g. Then mix 0.008 mg/g TAPB and 0.008 mg/g TPAK at a molar ratio of 1:3, and drop 10 μL of the mixture onto the newly cleaved HOPG surface. And then place it in a preheated oven at 90°C for 30 minutes, and finally use STM for structural characterization.

2. Characterization

NMR spectra were recorded with a 400-MHz spectrometer for ^1H NMR and a 101-MHz instrument for ^{13}C NMR using TMS as an internal standard. Chemical shifts (δ) are reported relative to TMS (^1H NMR), CDCl_3 or DMSO- d_6 (^{13}C NMR). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). High resolution mass spectroscopy (HRMS) using a quadrupole time of flight mass analyzer with electrospray ionization was used to analyze reaction products. Optical microscope images were taken by a Nikon ECLIPSE Ci-POL polarizing optical

microscope with a blue filter. AFM images were obtained in tapping mode by the Bruker Dimension Icon AFM instrument. SEM images were taken using a Hitachi SEM SU8010 field emission scanning electron microscope (FESEM). The UV-visible absorption spectrum was carried out at room temperature using a SHZMADZU UV-3600 Plus spectrophotometer. Attenuated total reflection FTIR (ATR FTIR) spectra of 2DP_{TPAK+TAPB} films were obtained using the Bruker vertex 70. Samples for transmission electron microscopy (TEM) examination were transferred to a porous copper TEM grid (i.e. coated with a carbon film) and all were highly resolved using Tecnai G2 F20 S-TWIN to obtain resolution TEM and SAED images. XPS measurements were performed on a Thermo Fisher Scientific ESCALAB 250Xi. CV curve of 2DP_{TPAK+TAPB} film were performed on the Au electrode in 0.1M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆)/CH₃CN solution with Ag/AgCl as the reference electrode and Pt wire as the counter electrode. The inset shows the CV curve of the ferrocene standard, swept in the same conditions as for the film. E_{FOC} was measured to be 0.44 eV vs. Ag/AgCl in CH₃CN. The concentration of ferrocene in CH₃CN is 0.1 mol/L. $E_{eg} = hc/\lambda = 1240/\lambda = 1240/500 = 2.48$ eV; $E_{HOMO} = -[E_{ox(onset)vsAg/AgCl} + 4.8 - E_{FOC}] = -(1.15 + 4.8 - 0.44)$ eV = -5.51 eV; $E_{LUMO} = E_{HOMO} + E_{eg} = (-5.51 + 2.48)$ eV = -3.03 eV. *I-V* measurements were made using a micromanipulator 6150 probe station connected to a Keithley 4200-SCS. All electrical measurements were made in an ambient air environment.

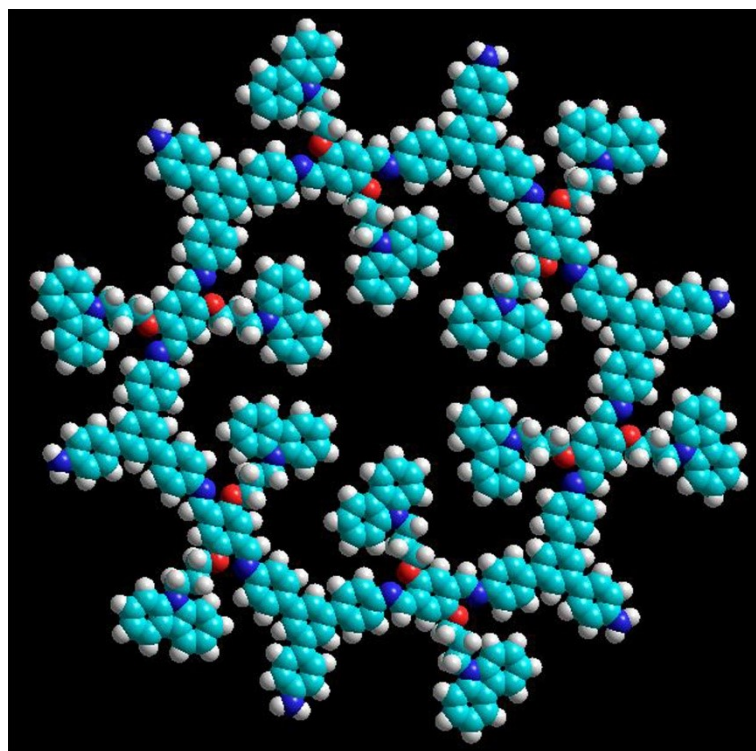


Figure S1. The simulated $2DP_{TPAK+TAPB}$ structure (White: hydrogen atom; Cyan: carbon atom; Blue: nitrogen atom; Red: oxygen atom).

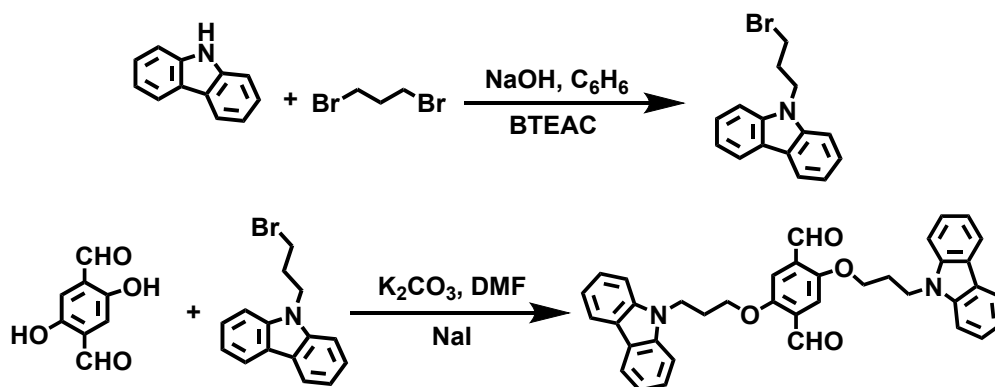


Figure S2. Synthetic route for 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde (TPAK)

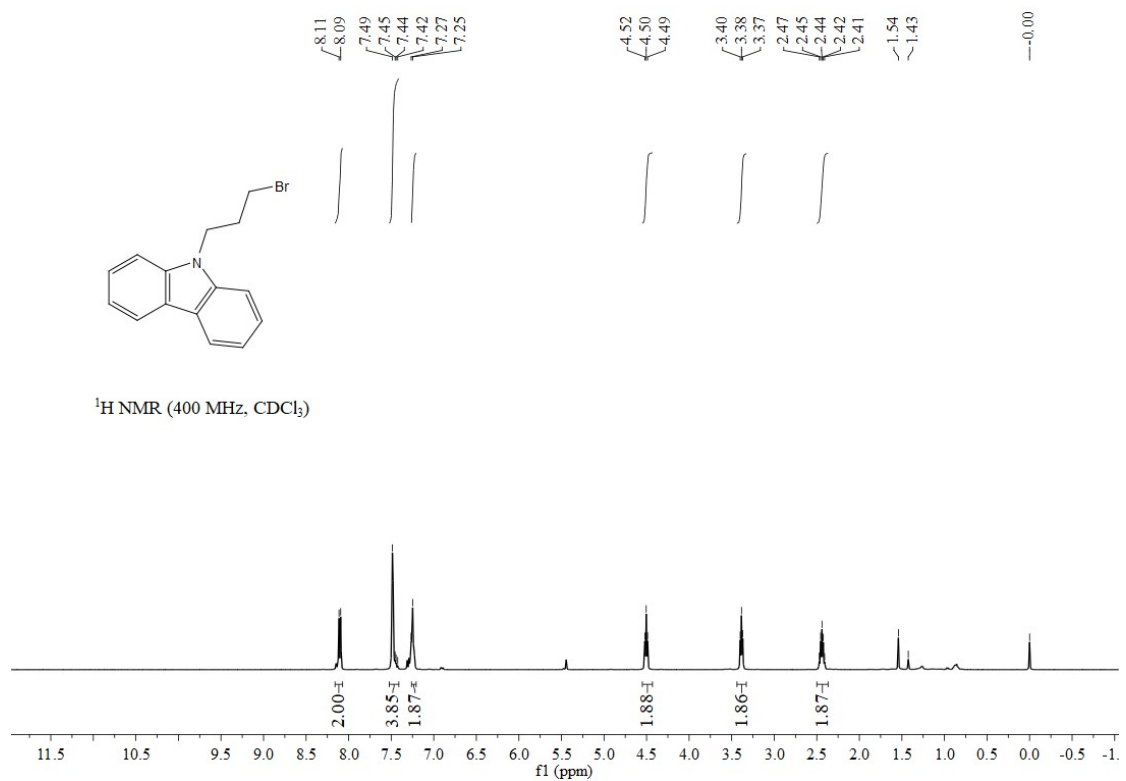


Figure S3. ¹H NMR spectrum of 9-(3-bromopropyl)-9H-carbazole in CDCl₃

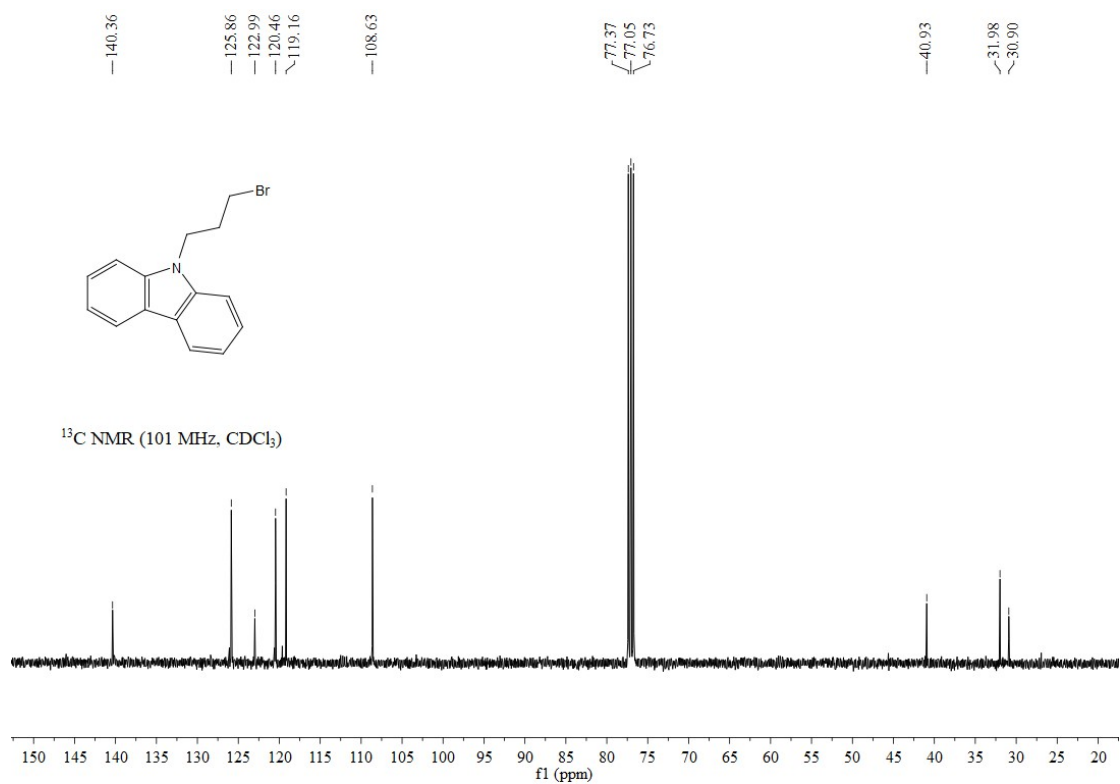


Figure S4. ¹³C NMR spectrum of 9-(3-bromopropyl)-9H-carbazole in CDCl₃.

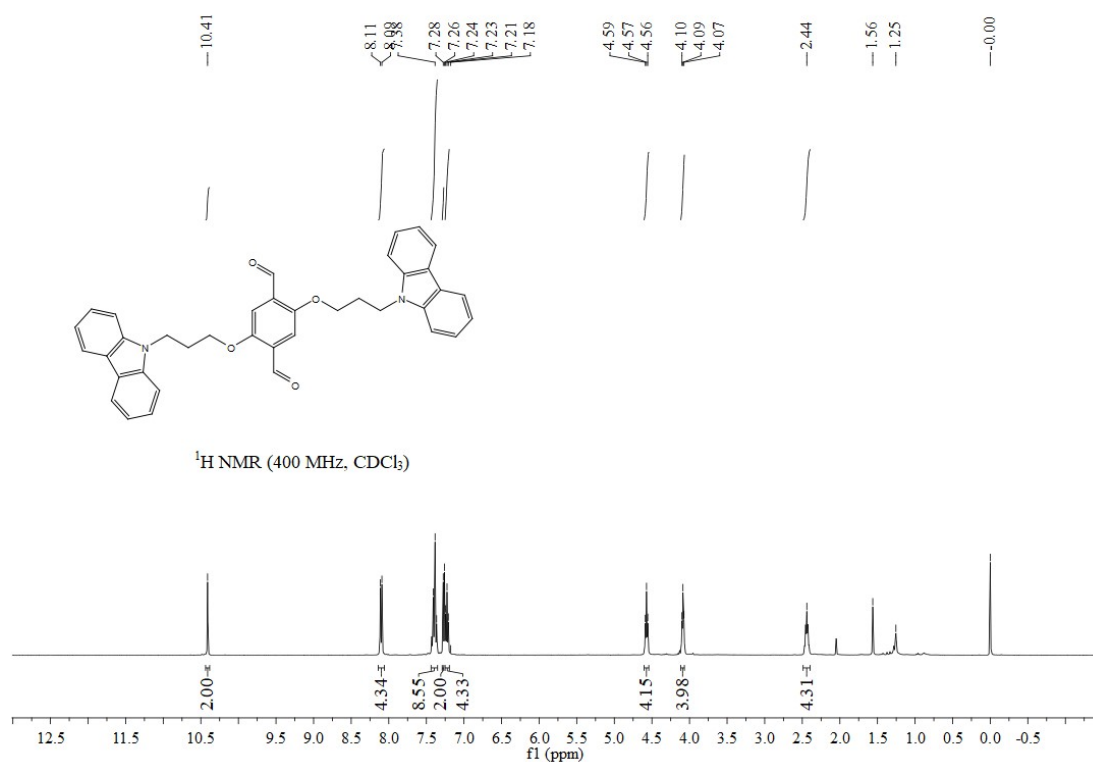


Figure S5. ¹H NMR spectrum of 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde (TPAK) in CDCl₃.

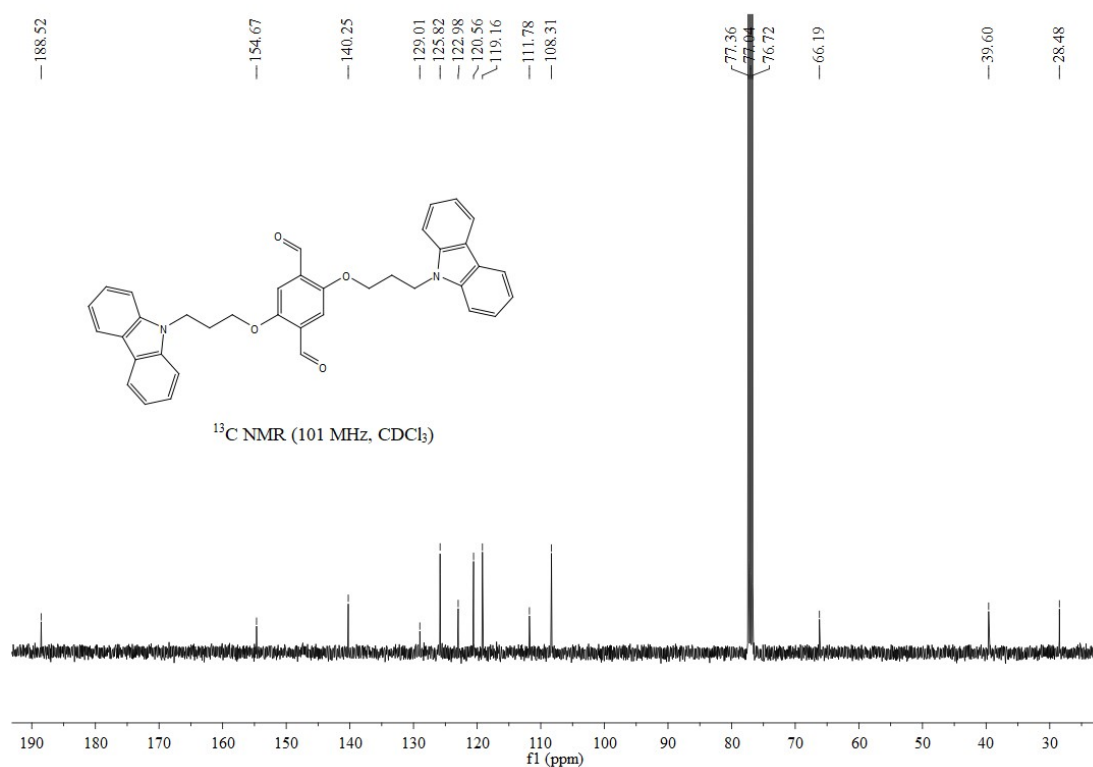


Figure S6. ¹³C NMR spectrum of 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde (TPAK) in CDCl₃.

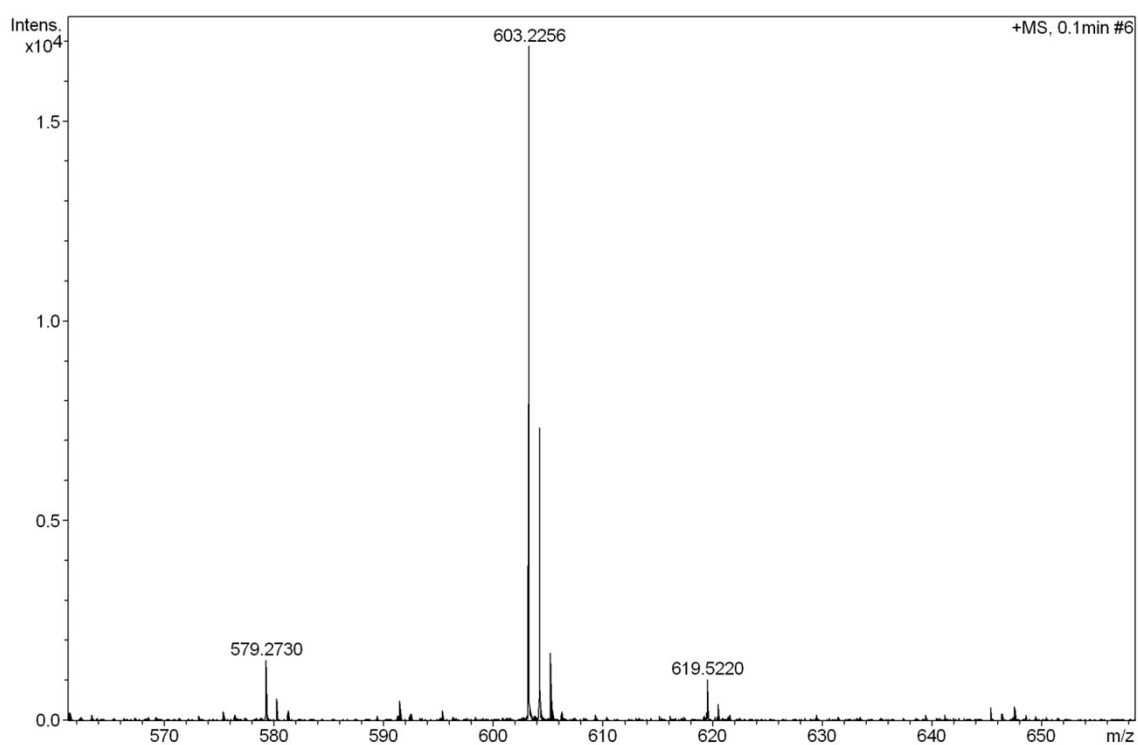


Figure S7. High resolution mass spectroscopy (HRMS) of 2,5-bis(3-(9H-carbazol-9-yl)propoxy)terephthalaldehyde (TPAK) in CH_2Cl_2 .

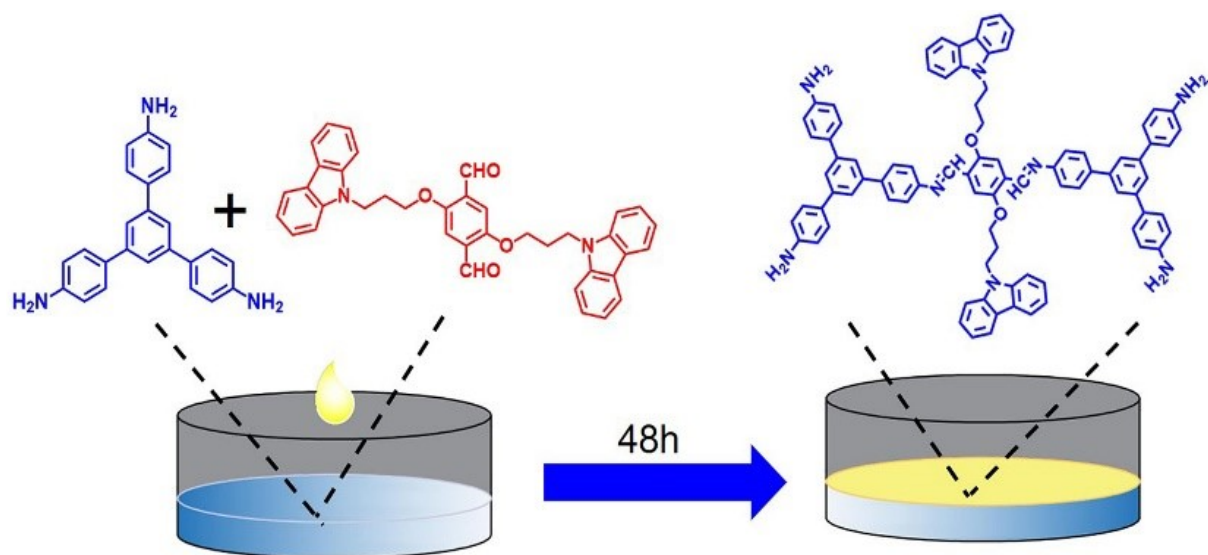


Figure S8. The preparation diagram of 2DP on the solution/air interface.

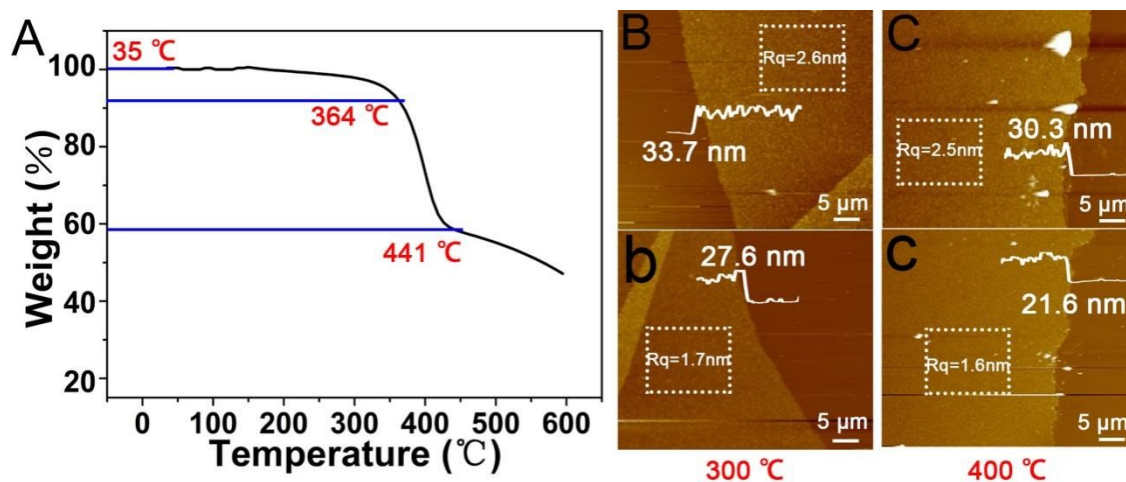


Figure S9. A. TGA curves of $2DP_{TPAK+TAPB}$. B(b)-C(c). AFM images of $2DP_{TPAK+TAPB}$ films before and after heating at 300 °C B(b) and 400 °C C(c) for 2 h.

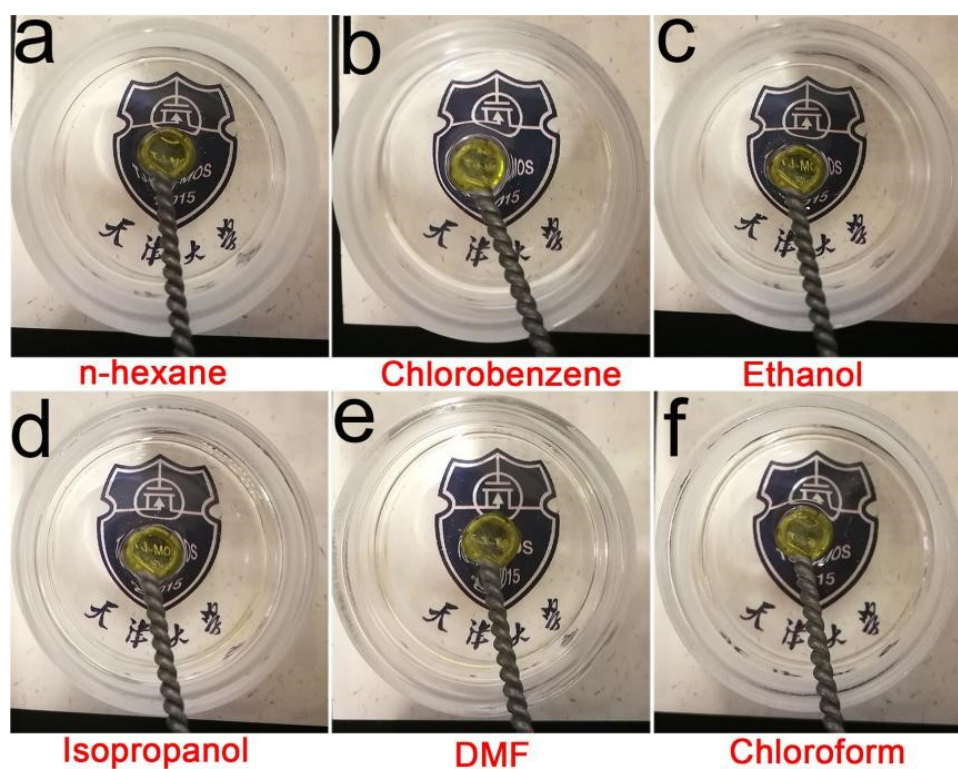


Figure S10. a-f. Digital images of $2DP_{TPAK+TAPB}$ films after soaking in different organic solvents for 5 minutes with the thickness of about 404 nm.

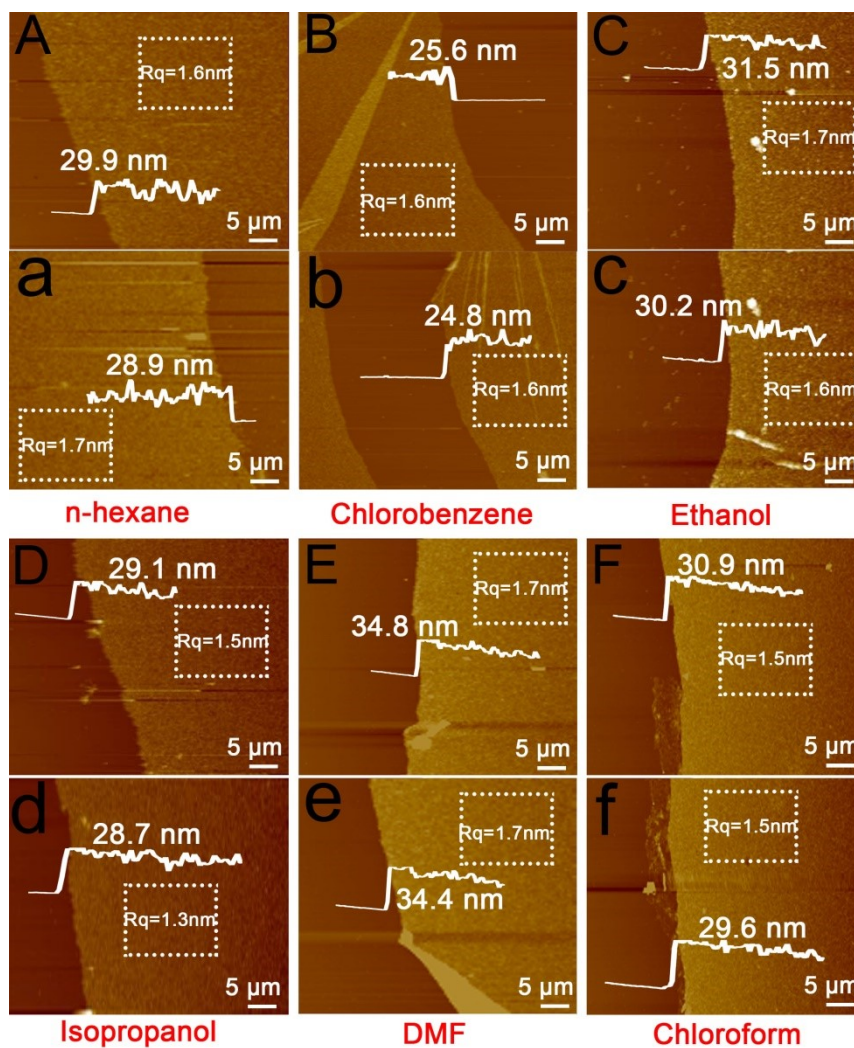


Figure S11. A(a)-F(f). AFM images of $2DP_{TPAK+TAPB}$ films before and after soaking in different organic solvents for 5 minutes.

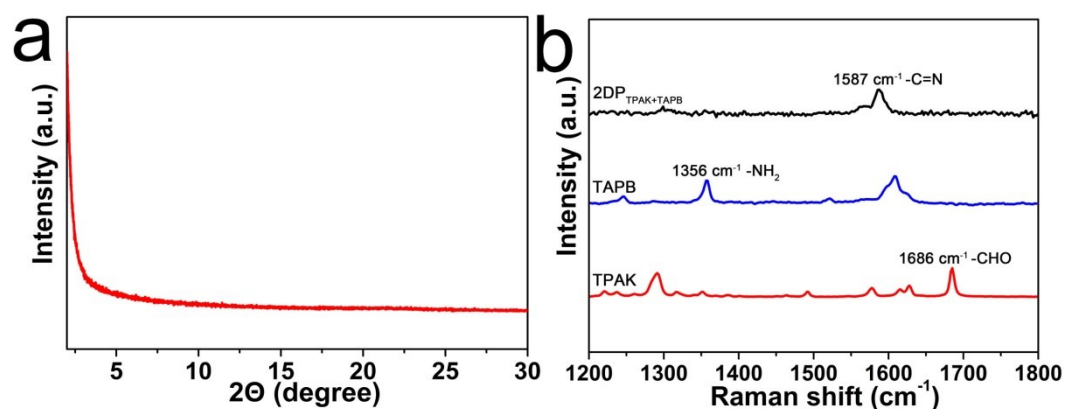


Figure S12. a. XRD spectra of $2DP_{TPAK+TAPB}$. **b.** Raman spectra of $2DP_{TPAK+TAPB}$, TAPB and TPAK.

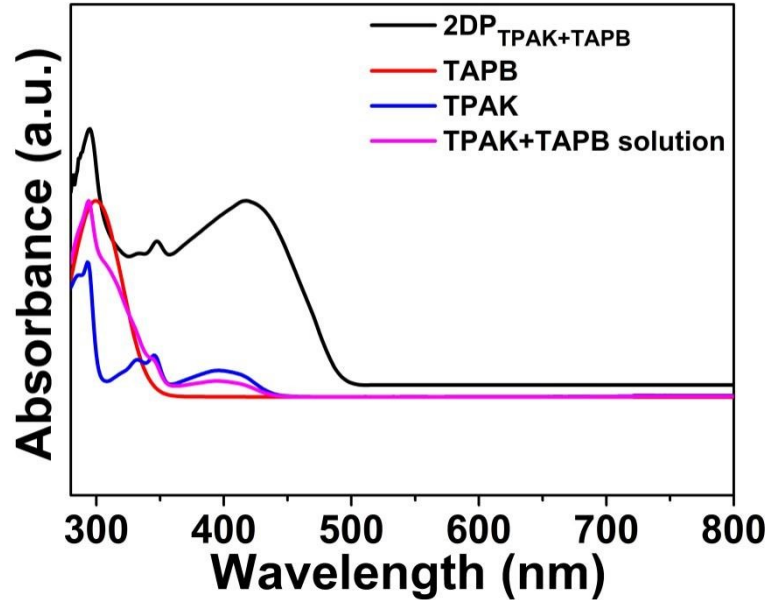


Figure S13. UV-Vis spectra of $2P_{\text{TPAK+TAPB}}$ film (black), TAPB (red) and TPAK (blue) in DMF solution and mixture solution of TAPB and TPAK (pink).

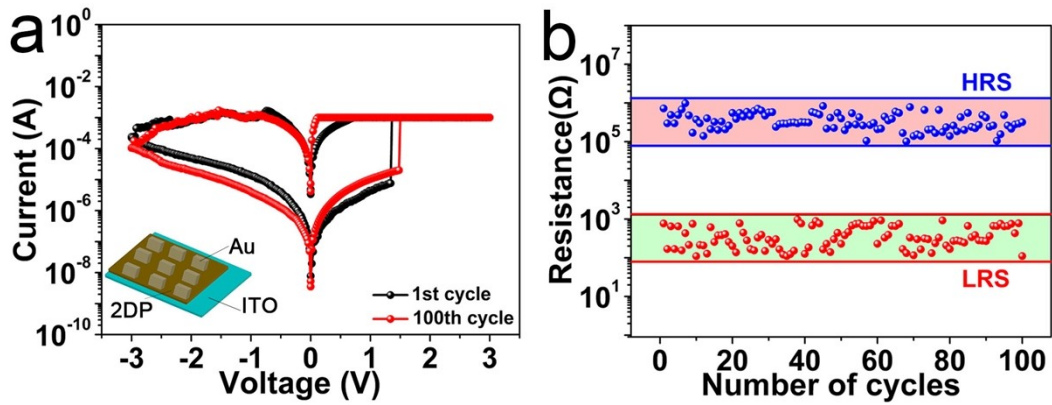


Figure S14. a. I - V characteristics of the 1st and 100th cycle of the Au/ $2P_{\text{TPAK+TAPB}}$ /ITO device. **b.** The cycle-to-cycle distributions of HRS resistance and LRS resistance (read at 0.1 V).

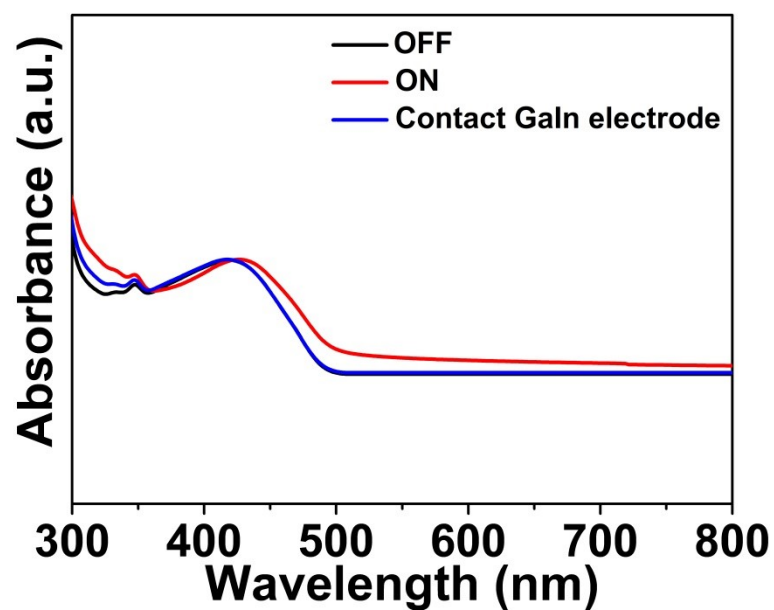


Figure S15. UV-Vis spectra of the device showing Flash memory behavior in the “ON” (red), “OFF” (black) states and the film in contact with the GaIn liquid electrode but without applying voltage (blue).

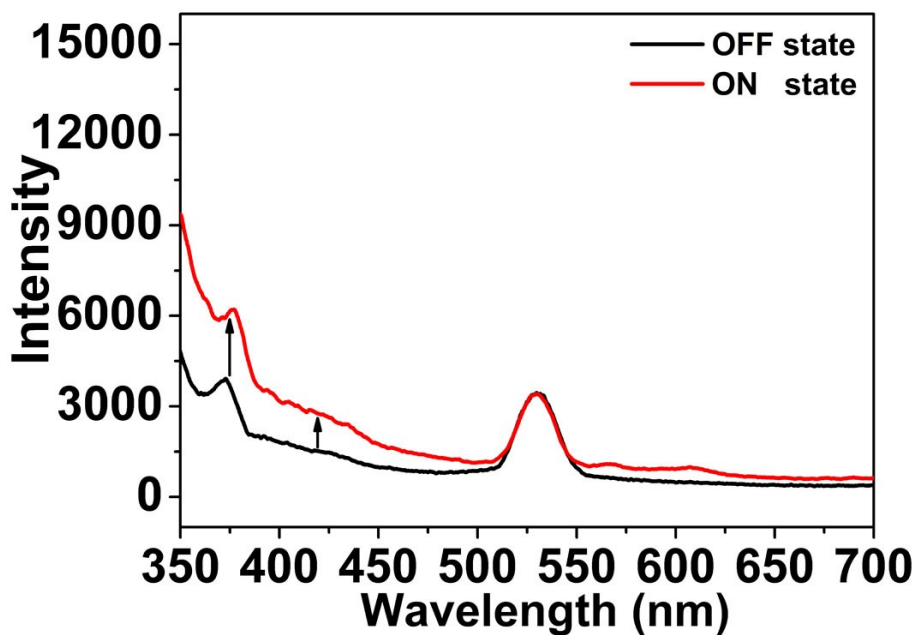


Figure S16. The fluorescence emission spectra of $2DP_{TPAK+TAPB}$ in different states, ($I_{CC}=10^{-3}$ A) ($\lambda_{ex} = 340$ nm).

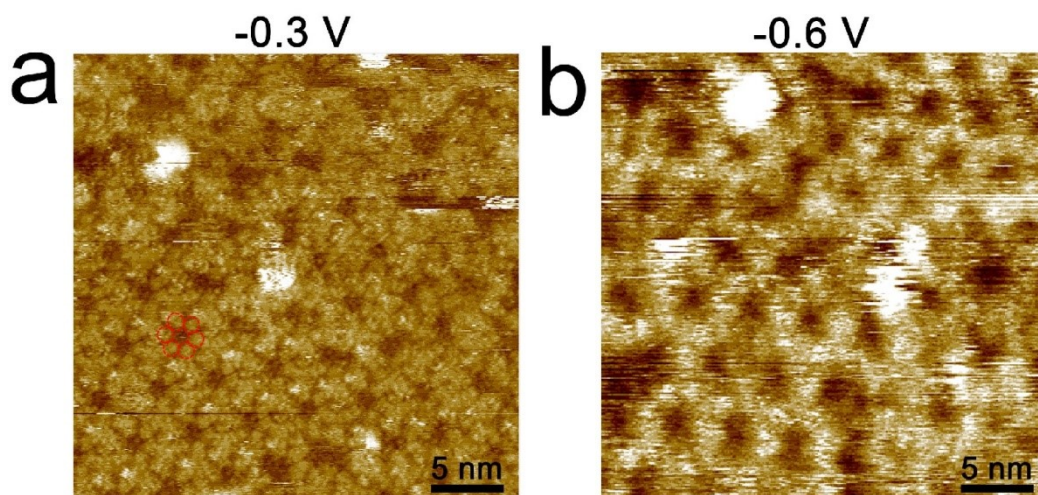


Figure S17. The STM image of $2DP_{TPAK+TAPB}$ synthesized at the octanoic acid/HOPG interface (The carbazole group parts have been marked with red circles). Imaging conditions: $I_{set} = 50.0$ pA, **a.** $V_{bias} = -0.30$ V, **b.** $V_{bias} = -0.60$ V.

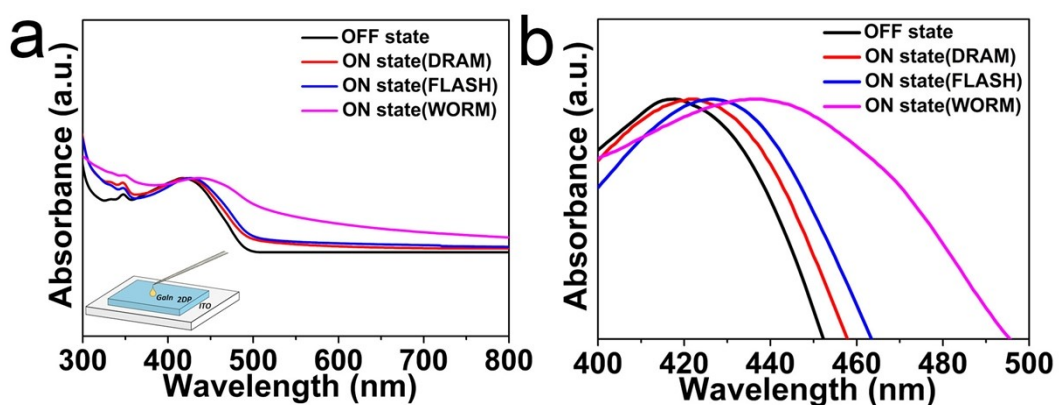


Figure S18. The UV-Vis spectra of the device in the three different ON/OFF states.

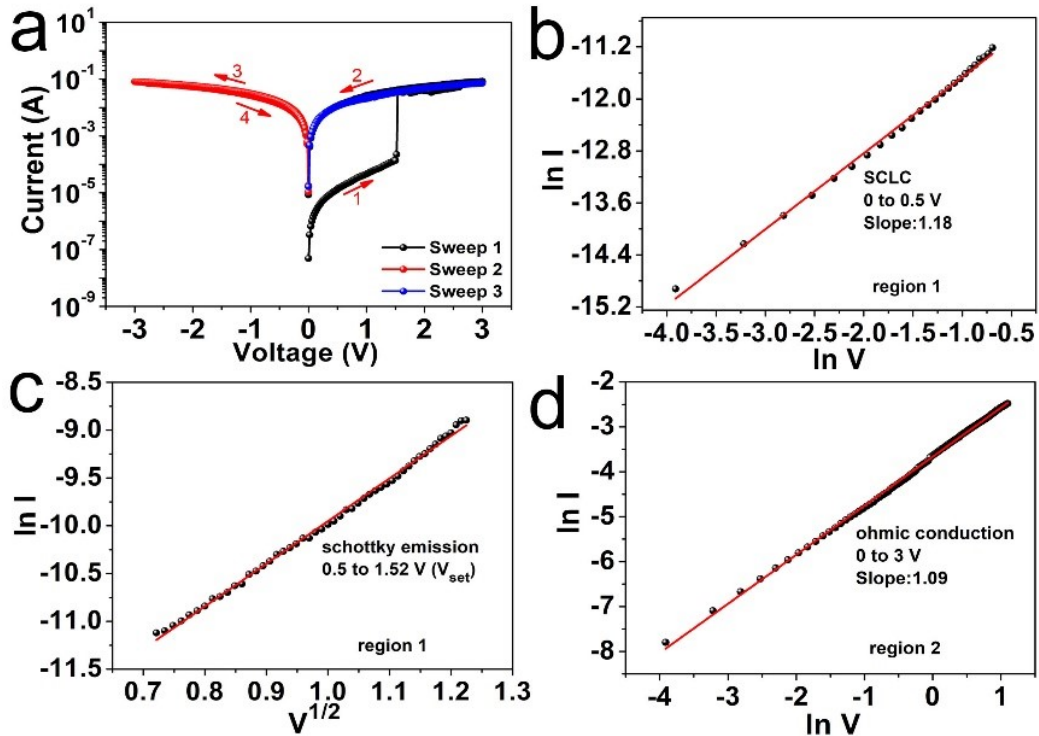


Figure S19. **a.** I - V characteristics of the device with the I_{CC} is 10^{-1} A. **b.** $\ln(I)$ vs $\ln(V)$ (SCLC) from 0 to 0.5 V before switching (region 1). **c.** $\ln(I)$ vs $V^{1/2}$ (schottky emission) from 0.5 to 1.52 V (V_{set}) before switching (region 1). **d.** $\ln(I)$ vs $\ln(V)$ (Ohmic conduction) from 0 to 3 V (ON state, region 2). Red lines are the theoretically fitted lines.

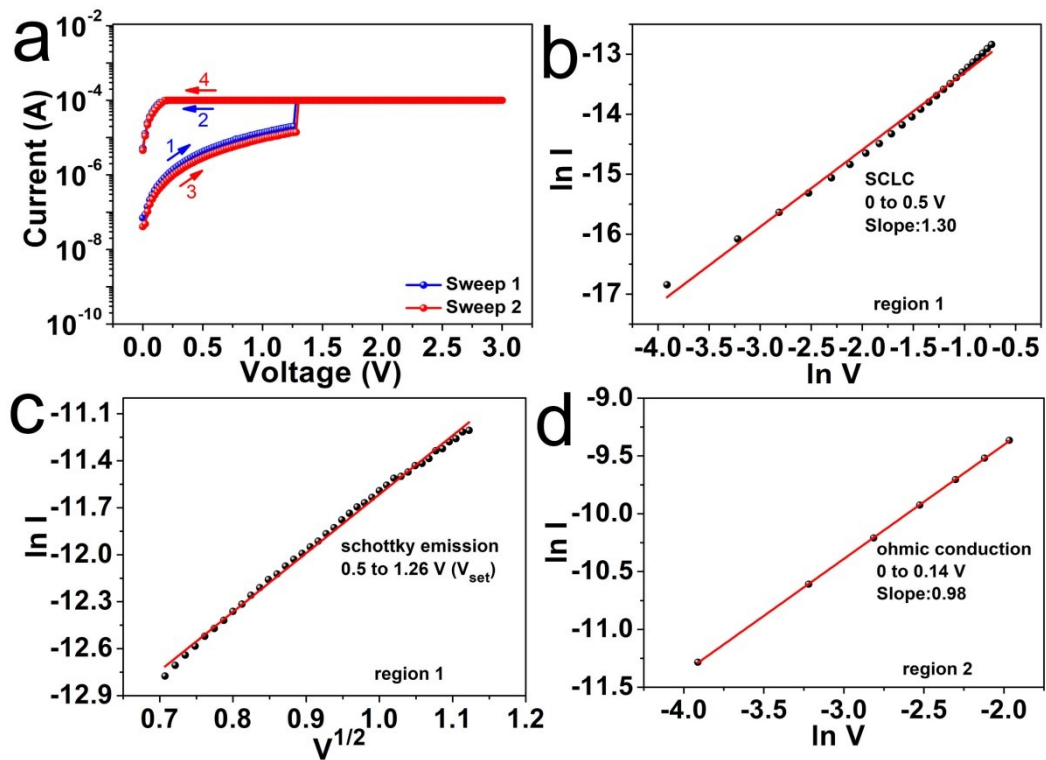


Figure S20. **a.** I - V characteristics of the device with the I_{CC} is 10^{-4} A. **b.** $\ln(I)$ vs $\ln(V)$ (SCLC)

from 0 to 0.5 V before switching (region 1). **c.** $\ln(I)$ vs $V^{1/2}$ (schottky emission) from 0.5 to 1.26 V before switching (region 1). **d.** $\ln(I)$ vs $\ln(V)$ (Ohmic conduction) from 0 to 0.14 V (ON state, region 2). Red lines are the theoretically fitted lines.

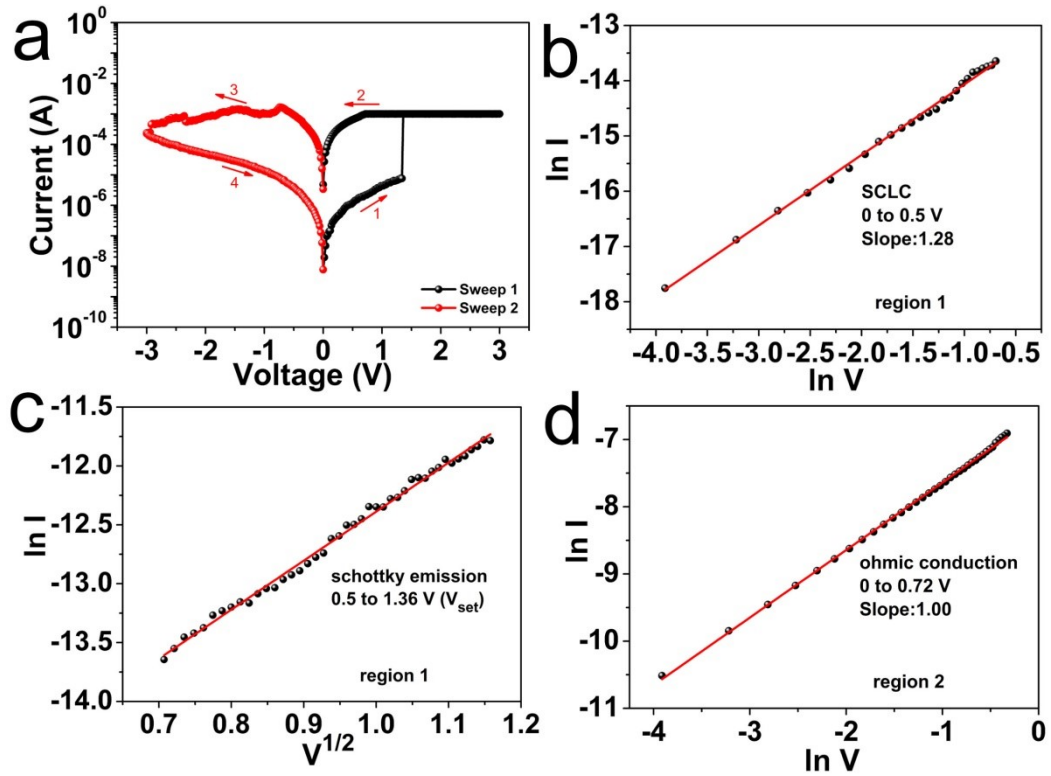


Figure S21. **a.** I - V characteristics of the device with the I_{CC} is 10^{-3} A. **b.** $\ln(I)$ vs $\ln(V)$ (SCLC) from 0 to 0.5 V before switching (region 1). **c.** $\ln(I)$ vs $V^{1/2}$ (schottky emission) from 0.5 to 1.36 V before switching (region 1). **d.** $\ln(I)$ vs $\ln(V)$ (Ohmic conduction) from 0 to 0.72 V (ON state, region 2). Red lines are the theoretically fitted lines.

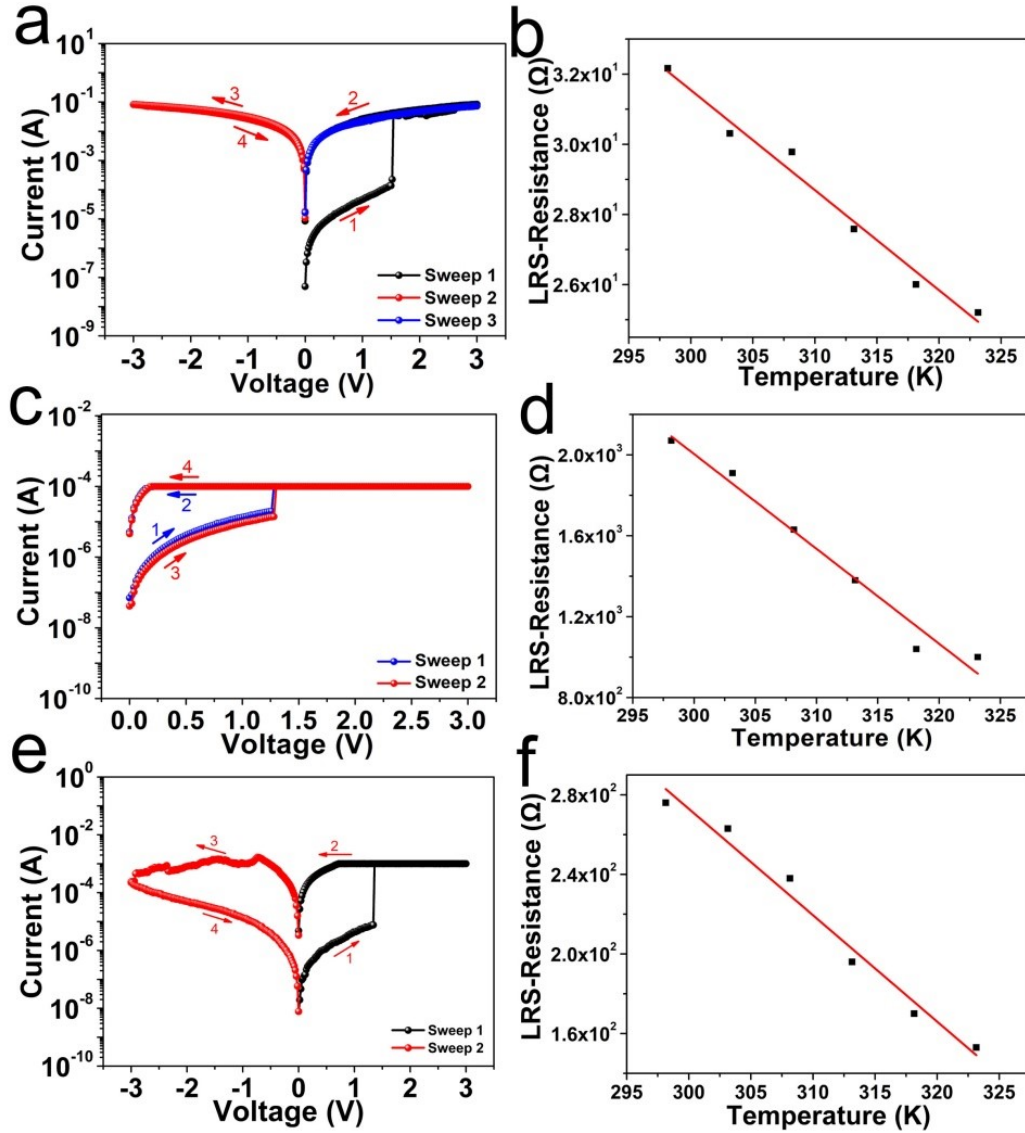


Figure S22. a, c and e. $I-V$ characteristics of the device with the I_{CC} are 10^{-1} A, 10^{-4} A and 10^{-3} A, respectively. b, d and f. Temperature dependence of the resistances of the LRS with the I_{CC} are 10^{-1} A, 10^{-4} A and 10^{-3} A, respectively.

Table S1 The degrees of red shift in the three different ON/OFF states of the device.

Memory behavior	DRAM	FLASH	WORM
Peak position	OFF state: 417 nm	OFF state: 417 nm	OFF state: 417 nm
	ON state: 422 nm	ON state: 426 nm	ON state: 436 nm
Degrees of red shift	5 nm	9 nm	19 nm

Table S2 Comparison of the devices properties in this work with devices based on other methods for modulating memory behavior.

Methods for	Material	Memory	Set voltage	ON/OFF	Mechanism	Same	Reference
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modulating memory behavior	type	type		ratio		device		
Different electrode types	Perovskite	FLASH/WORM	4.7 V/4.7 V	$10^2/10$	Vacancy/Metal	Conductive filament	No	33
Different electrode types	Metal oxide	FLASH/DRAM	-3 V/ \pm 3.5 V	$10^2/10^2$	Conductive filament	Conductive filament	No	34
Doping	Metal oxide	FLASH/DRAM	No	$10/10^2$	Trapping-detrapping	Trapping-detrapping	No	35
Doping	Polymer	DRAM/WORM	-3.4 V/-2.8 V	$10^7/10^5$	Charge transfer	Charge transfer	No	36
Different molecular structures	Polymer	DRAM/FLASH	-1.47 V/-2.07 V	$10/10^2$	Charge transfer	Charge transfer	No	37
Different active layer thickness	Polymer	DRAM/WORM	1.8 V;-2 V/1.55 V;-1.75 V	$10^2/10^6$	Conductive filament	Conductive filament	No	38
Different electrode thickness	Metal oxide	FLASH/DRAM	1.7 V/2.5 V	$10^2/10$	Conductive filament	Conductive filament	No	39
Different compliance currents (Degree of conformational change)	2D Polymer	DRAM/FLASH/WORM	1.26 V/1.36 V/1.52 V	$10^2/10^3/10^3$	Conformation change	Conformation change	Yes	This work

Table S3 Comparison of the devices properties in this work with devices based on conformational change mechanism.

Material type	Memory type	Active layer thickness	Set voltage	ON/OFF ratio	Temperature stability	Flexibility	Multiple memory types in Same device	Reference
1D Polymer	Polymer PMCz: WORM Polymer PVBCz: SRAM	50 nm	-1.8 V/-2 V	$10^6/10^3$	Not mentioned	Not mentioned	No	12
1D Polymer	Polymer P4VPCz2: WORM	80 nm	-3.3 V	10^7	Not mentioned	Not mentioned	No	17
1D Polymer	Polymer PMANA2: FLASH	80 nm	-2.20 V	10^4	285 °C(M)	Not mentioned	No	18
1D Polymer	Polymer PCz: WORM	50 nm	-1.8 V	10^6	120 °C(D)	Not mentioned	No	19
1D Polymer	Polymer PVK-PF: FLASH	50 nm	2.2 V	10^4	150 °C(D)	Not mentioned	No	20
1D Polymer	Polymer PVCz: WORM	75 nm	-1.7 V	10^6	370 °C(M)	Not mentioned	No	21
Small organic molecule	Rose Bengal: FLASH	50 nm	5.0 V	10^2	Not mentioned	Not mentioned	No	22

2D Polymer	$2P_{\text{TPAK}+\text{TAPB}}$ DRAM/FLASH/WORM	20-30 nm or 2.7 nm	1.26 V/1.36 V/1.52 V	$10^2/10^3/10^3$	300 °C(D)	500 th	Yes	This work
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Note: **M**: Material temperature stability; **D**: Device temperature stability.