Supporting Information

Effects of gradual oxidation of aromatic sulfur-heterocycle derivatives on multilevel memory data storage performance

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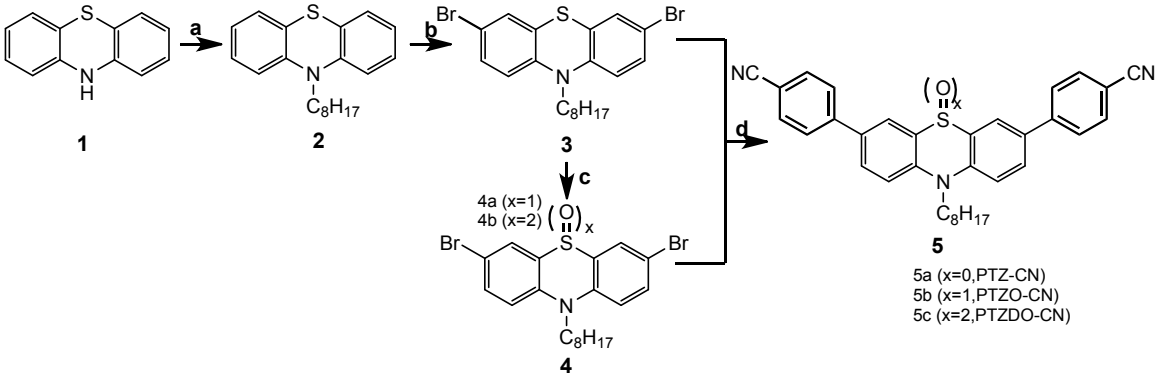
1. Preparation of PTZ-CN, PTZO-CN and PTZDO-CN.



Scheme 1. Synthesis scheme and molecular structure. Reagents and conditions: (a) $C_8H_{17}Br$, KOH, DMSO, 80°C, under nitrogen atmosphere; (b) Br_2, HOAc, $CHCl_3$, RT; (c) 4a, m-CPBA, DCM, 0°C; 4b,H_2O_2,HOAc, 90°C;(d) 4-Cyanophenylboronic Acid,$Pd(PPh_3)_4$, K_2CO_3, H_2O, dioxane, 80°C under nitrogen atmosphere.

All reactions were carried out under an air atmosphereunless otherwise stated. The following compounds were synthesized according to the procedures reported in the literature:10-octyl-10*H*-phenothiazine[1];3,7-dibromo-10-octyl-10H-phenothiazine[2];3,7-dibromo-10-octyl-10H-phenothiazine 5-oxide[3];3,7-dibromo-10-octyl-10H-phenothiazine 5,5-dioxide[4].

Synthesis of compound 2 (10-octyl-10*H*-phenothiazine). A dry flask (500 mL) was charged with phenothiazine (10.0 g, 50.2 mmol) and KOH (2.8 g, 50.2 mmol) under nitrogen at 80°C, after the system had been stirred for 20 min, *n*-octyl bromide (9.7 g, 50.2 mmol) was slowly added by syringe. The color of the reaction mixture changed from black to yellow, and the solution was stirred for 3 h. After completion of the reaction, the reaction mixture was diluted with H_2O and extracted with EtOAc (3 × 50 mL) by separatory funnel. The combined organic layer was washed with brine and dried over anhydrous sodium sulfate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using

petroleum as eluent to give **2** (14.0 g, 90%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J*=7.5, 4H), 6.86 (d, *J*=6.9, 4H), 3.84 (m, 2H), 1.97 – 1.71 (m, 2H), 1.33 (m, 10H), 0.86 (t, *J*=6.9, 3H).

Synthesis of compound 3 (3, 7-dibromo-10-octyl-10H-phenothiazine). In a two-necked flask with a dropping funnel under a nitrogen atmosphere, compound 2 (3.1 g, 10 mmol) was dissolved in trichloromethane (30 mL). Bromine (2.1mL, 40 mmol) dissolved in acetic acid (10 mL) and added dropwise to the solution, where upon it slightly warmed and its color turned dark red. After the system had been stirred for 2 hours at room temperature, another portion of bromine (1.0 mL, 19 mmol) was added to the reaction mixture and the color turned dark green. The solution was stirred for 2 hours at room temperature, and then a saturated aqueous solution of sodium sulfite (20 mL) and diethyl ether (20 mL) were added to the mixture and the system was stirred for 30 minutes.The organic phase was separated, and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried with sodium sulfate, and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (n-hexane/acetone 10:1) to give 3(4.2 g, 90 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.08 (m, 4H), 6.66 (d, *J*=8.5, 2H), 3.73 (t, *J*=7.1, 2H), 1.85 – 1.55 (m, 2H), 1.49 – 1.08 (m, 10H), 0.86 (t, *J*=6.8, 3H).

Synthesis of compound 4a (3,7-dibromo-10-octyl-10H-phenothiazine 5-oxide). To a solution of (2.3 g, 5 mmol) of compound **3** in 20 mL of DCM, a solution of meta-chloroperoxybenzoic acid (1.0 g, 5 mmol, 85%) in DCM (10 mL) was added dropwise over 30 min at 0°C. The reaction was completed within 2 h. The reaction mixture was washed with oversaturated aqueous of Na_2CO_3, and then the reaction mixture was extracted with DCM (3 × 20 mL) by separatory funnel and the combined organic layers were washed with brine and dried over anhydrous sodium sulfate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using petroleum ether/ethyl acetate (5/1; v/v) to offer compound **4a** as (1.93 g, 80%) as a pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, *J*=2.3, 2H), 7.70 (dd, *J*=9.0, 2.3, 2H), 7.26 (d, *J*=3.1, 2H), 4.13 (dd, *J*=22.6, 14.4, 2H), 1.93 – 1.88 (m, 2H), 1.45 – 1.22 (m, 10H), 0.90 (t, *J*=6.7, 3H). HRMS: Anal. Calcd. For $C_{20}H_{23}Br_2NOS$ $[M + H]^+$ 483.9867, 487.9826 found 483.9857,487.9834

Synthesis of compound 4b (3,7-dibromo-10-octyl-10H-phenothiazine 5,5-dioxide). To a solution of (2.3 g, 5 mmol) of compound **3** in 20 mL of acetic acid, a solution of Hydrogen peroxide (8 mL, 80 mmol, 30%) was added dropwise over 30 min at at room temperature. The reaction mixture was transferred to 90 0°C stirring overnight, After completion of the reaction, The reaction mixture was washed with oversaturated aqueous of Na_2SO_3, and then the reaction mixture was extracted with ethyl acetate (3 × 20 mL) by separatory funnel and the combined organic layers were washed with brine and dried over anhydrous sodium sulfate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using petroleum ether/ethyl acetate (8/1; v/v) to offer compound **4b** as (2.37 g, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J*=2.3, 2H), 7.69 (dd, *J*=9.1, 2.4, 2H), 7.21 (d, *J*=9.1, 2H), 4.16 – 4.06 (m, 2H), 1.91 – 1.88 (m, 2H), 1.37 – 1.23 (m, 10H), 0.88 (t, *J*=6.7, 3H). HRMS: Anal. Calcd. For $C_{20}H_{23}Br_2NO_2S$ $[M + H]^+$ 499.9816, 503.9775 found 499.9900,503.9765.

Synthesis of compound 5a (4,4'-(10-octyl-10H-phenothiazine-3,7-diyl)dibenzonitrile). compound 3 (1.0 mmol ratio), 4-Cyanophenylboronic Acid(4.0 mmol ratio),$Pd(PPh_3)_4$(0.03 mmol ratio) and Potassium carbonate (4 mmol ratio) in distilled 1,4-dioxane (15 mL),degassed deionized water (5 mL) were added by syringe under a nitrogen atmosphere, then the mixture was refluxed for 12 h. After being cooled to room temperature, the mixture was poured into 30 mL deionized water and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3*20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica column chromatography using petroleum ether/ethyl acetate (5/1; v/v) to offer compound **5a** as (462 mg, 90%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (dd, *J*=28.5, 8.1, 8H), 7.44 – 7.33 (m, 4H), 6.95 (d, *J*=8.4, 2H), 3.90 (t, *J*=6.5, 2H), 1.91 – 1.78 (m, 2H), 1.41-1.22 m, 10H), 0.86 (t, *J*=6.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.99, 144.09, 133.40, 132.59, 126.80, 126.26, 125.79, 124.77, 118.94, 115.73, 110.41, 47.68, 31.67, 29.14, 26.82, 26.68, 22.57, 14.07. HRMS: Anal. Calcd. For $C_{34}H_{31}N_3S$ $[M + H]^+$ 514.2239 found 514.2300

Compounds 5b and 5c were synthesized use using a similar procedure for compound 5a.

Synthesis of compound 5b (4,4'-(10-octyl-5-oxido-10H-phenothiazine-3,7-diyl)dibenzonitrile).380 mg,72%,pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (dd, *J*=4.4, 2.2, 2H), 7.94 – 7.88 (m, 2H), 7.82 – 7.62 (m, 8H), 7.60 – 7.52 (m, 2H), 4.31 (t, *J*=5.8, 2H), 2.10 – 1.93 (m, 2H), 1.65 – 1.18 (m, 10H), 0.92 (d, *J*=4.5, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.30, 137.92, 132.91, 132.86, 131.51, 130.27, 127.13, 124.72, 118.72, 116.61, 111.14, 48.43, 31.72, 29.23, 26.82, 26.35, 22.60, 14.07. HRMS: Anal. Calcd. For $C_{34}H_{31}N_3OS$ $[M + H]^+$ 530.2188 found 530.2279.

Synthesis of compound 5c (4,4'-(10-octyl-5,5-dioxido-10H-phenothiazine-3,7-diyl)dibenzonitrile).502 mg,92%,pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (d, *J*=2.2, 2H), 7.91 (dd, *J*=8.9, 2.2, 2H), 7.83 – 7.73 (m, 8H), 7.51 (d, *J*=9.0, 2H), 4.30 – 4.24 (m, 2H), 2.05 – 1.96 (m, 2H), 1.59 – 1.27 (m, 10H), 0.91 (t, *J*=6.7, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.88, 140.39, 133.01, 132.88, 131.76, 127.23, 124.69, 122.19, 118.62, 116.98, 111.46, 48.71, 31.68, 29.16, 29.15, 26.80, 26.66, 22.57, 14.05. HRMS: Anal. Calcd. For $C_{34}H_{31}N_3O_2S$ $[M + H]^+$ 546.2137 found 546.2294.

References

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[2] G. Y.; Zou, Y. P. Li, Y. F. *J. Phys. Chem. C*. 2008, **112**, 12058−12064.

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[4] Xue, M; Xiao J; Hong H; Yi C; Cheng Z. *Synlett*. 2013, **24**, 1505.

2. The memory device image

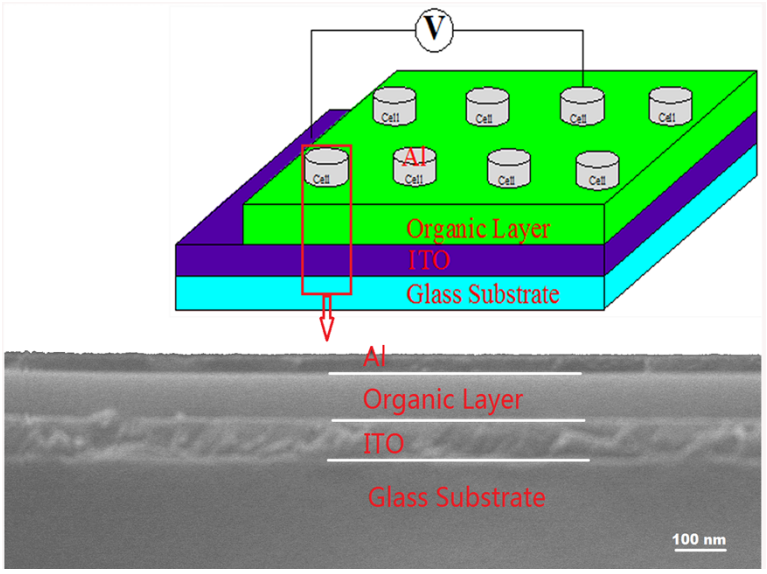

Fig. S1. (top) Illustration of the sandwich device; (bottom) SEM image of a cross-

section view of the device

2. Thermal properties image

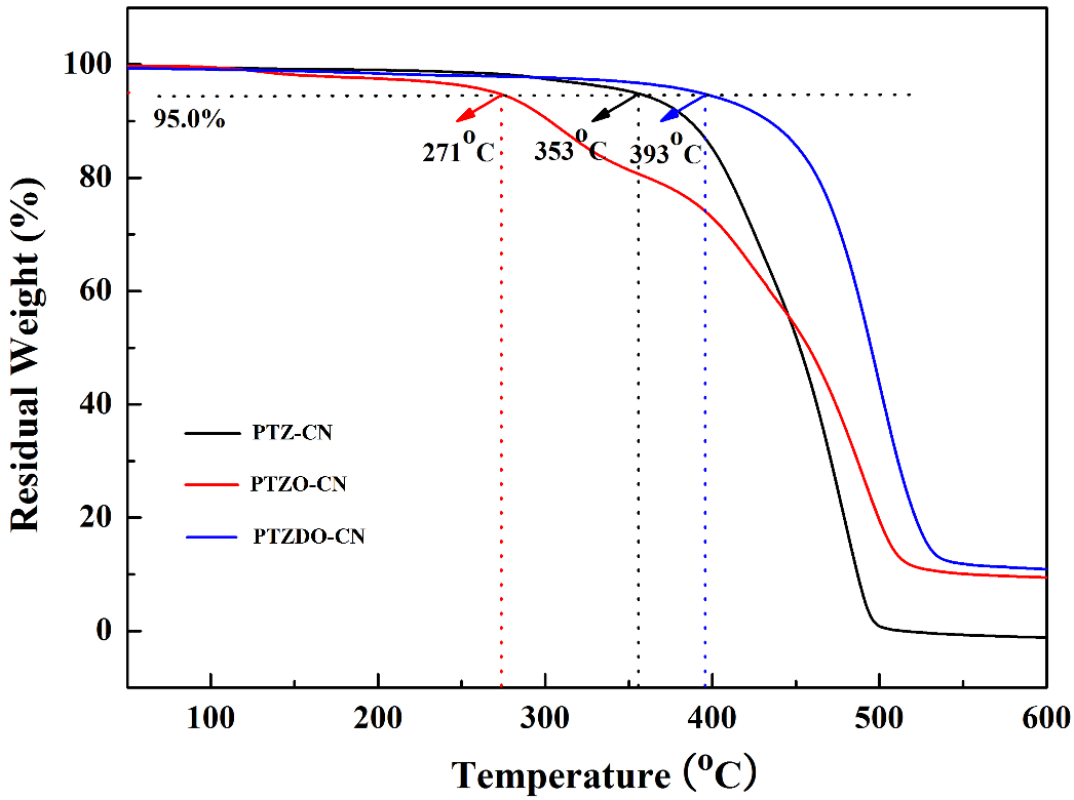

Fig. S2. TGA curves of the three molecules with a heating rate of 20°C min^{-1} under nitrogen

3. Energy levels image

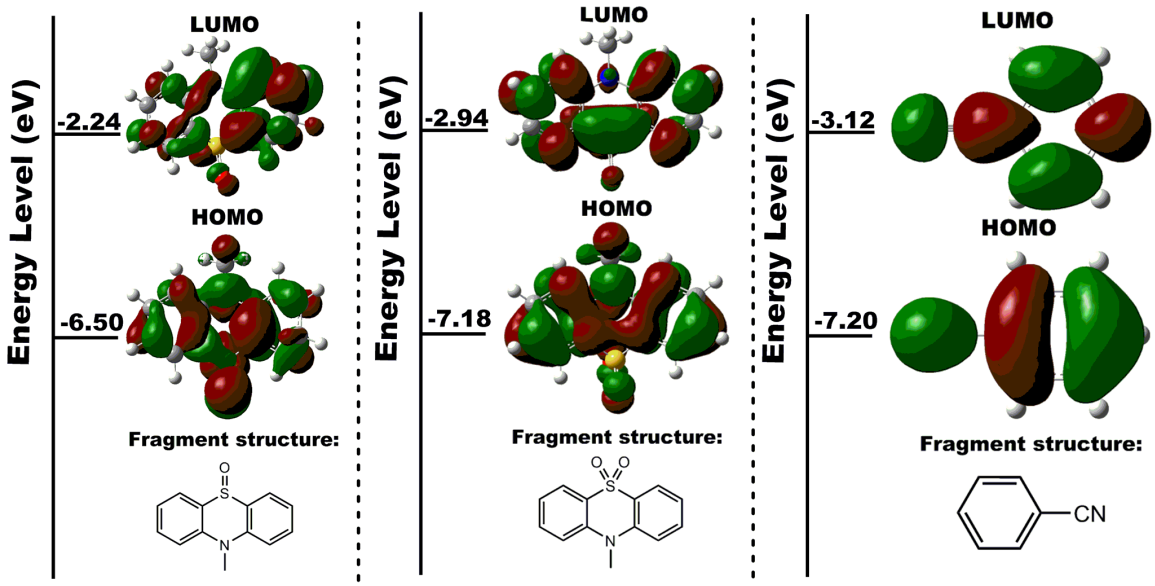

Figure S3. LUMO and HOMO energy levels for the three functional moieties (10-methyl-10H-phenothiazine 5-oxide moiety, sulphoxide; 10-methyl-10H-phenothiazine 5, 5-dioxide, sulfone; benzonitrile, cyan).

4. DFT molecular simulation results

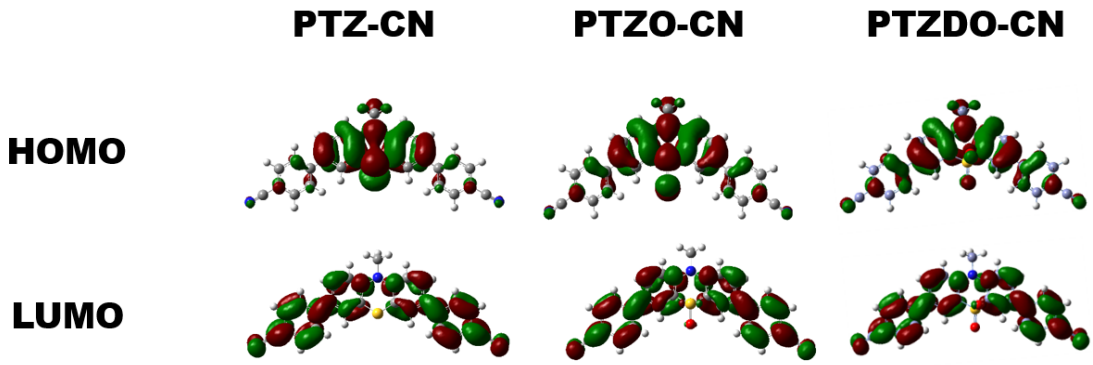

Figure S4. HOMOs and LUMOs of PTZ-CN, PTZO-CN and PTZDO-CN in their optimized ground-state structures.

4. Stability tests of the devices

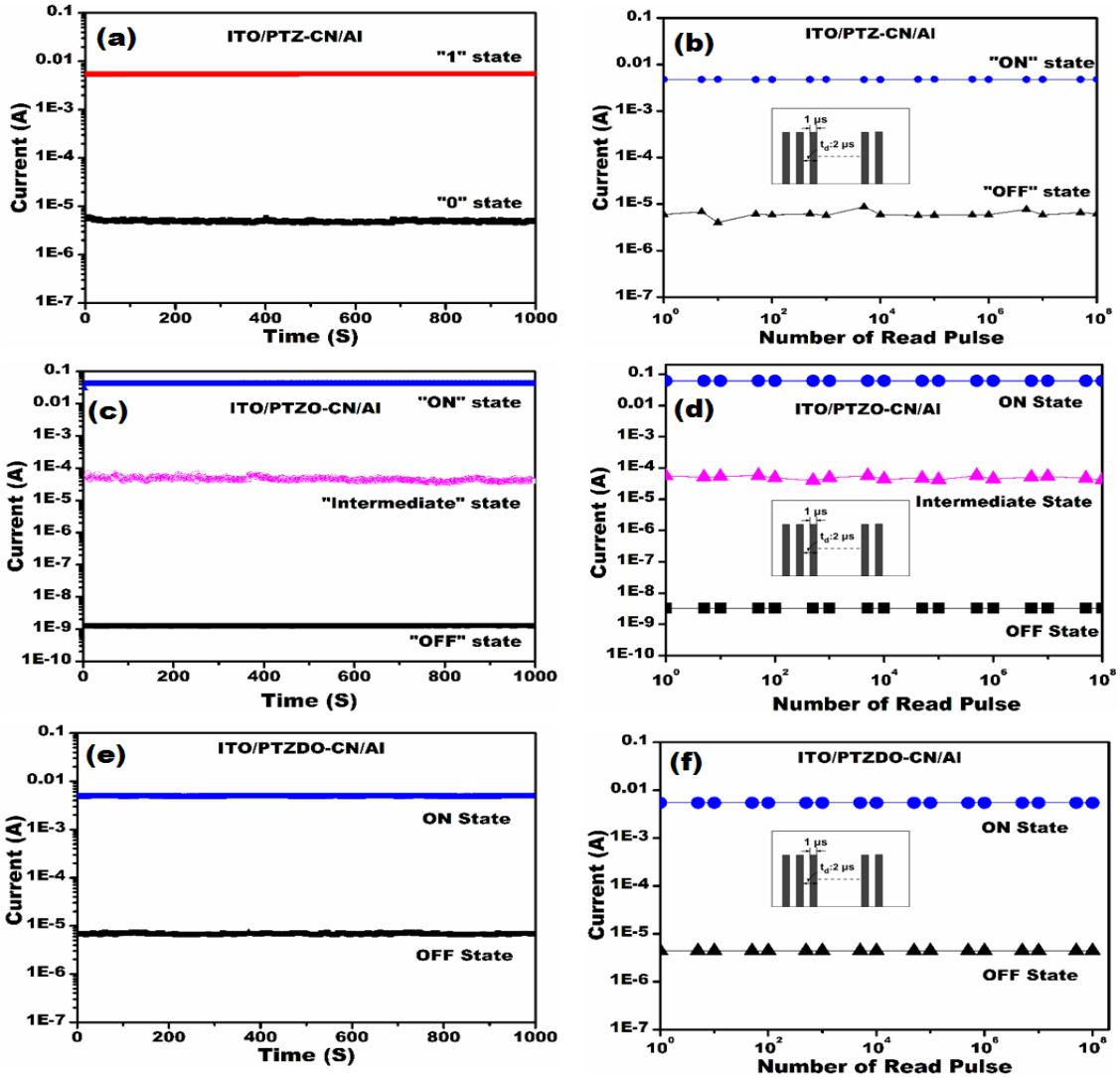

Figure S5. Stability tests of the fabricated ITO/PTZ-CN (a and b) or PTZO-CN (c and d) or PTZDO-CN (e and f)/Al memory device: (a, c and e) retention time measurement for the ON-, intermediateand-, OFF-states with a constant reading voltage of -1 V; (b, d and f) effect of read pulse of -1 V on the ON-, intermediate-

and OFF-states. The inset shows the pulse shape employed

5. I-V Curve

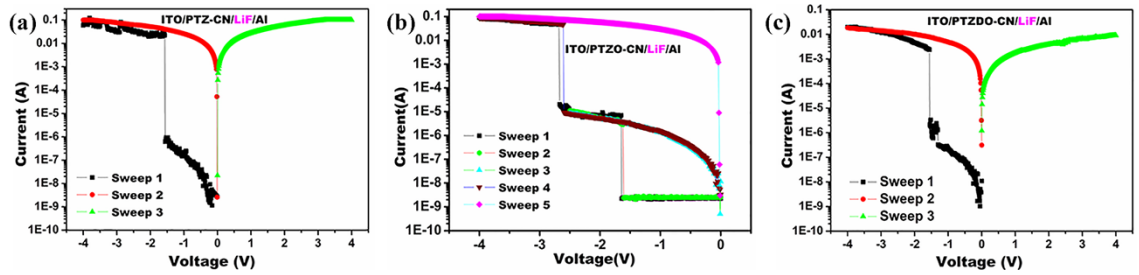

Figure S6. Current-voltage (I-V) characteristics of the memory device with the structure of **ITO/compound/LiF(5nm)/Ag**: (a)**PTZ-CN**; (b) **PTZO-CN**; (C) **PTZDO-CN**.