Supplementary Information

Molecular length adjustment for organic *azo*-based nonvolatile ternary memory devices

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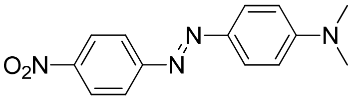
1. Experimental Section

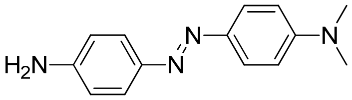
1.1 Preparation of DPAPIT and DPAPPD.

*Synthesis of N,N-dimethyl-4-((4-nitrophenyl)diazenyl)aniline (**2**).*



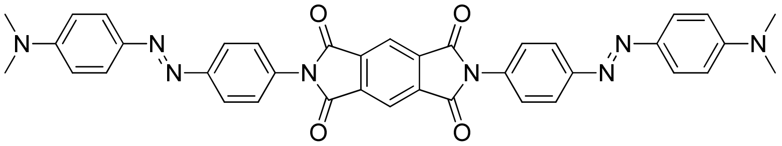
4-Nitroaniline **1** (2.76 g, 20.0 mmol) was partially dissolved in a mixture of deionized water (8 mL) and concentrated aqueous HCl (8 mL) by heating it in an water bath. The mixture was cooled by pouring it onto ice water. After additional cooling in an ice bath, a solution of sodium nitrite (1.38 g, 20.0 mmol) in deionized water (5 mL) was added; the mixture became homogeneous. After 1 h, an ice-cold solution of *N*,*N*-dimethylaniline (2.42 g, 20.0 mmol) in a mixture of deionized water (20 mL) and concentrated aqueous HCl (4 mL) was added dropwise for 30 min at 0~5 °C. After stirred in ice-water bath for 2 h, the mixture was neutralized with 1M KOH solution. Standing for a moment, the mixture was filtered and washed with deionized water. The red powder was dried in the vacuum oven overnight at 60 °C. Yield of **2**: 4.78 g, 89%

*Reduction of Azo compound 2 to amino derivative 4-((4-aminophenyl)-diazen-yl)-N,N-dimethyl -aniline (**3**).*[1~3]



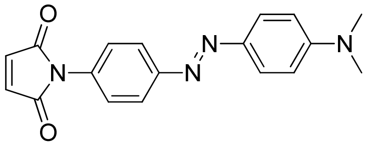
To a solution of **2** (0.54 g, 2.0 mmol) in dioxane (20 mL), $Na_2S\cdot 9H_2O$ (1.58 g, 6.6 mmol) in of H_2O (5 mL) was added in portions. The mixture was heated at 80 °C and stirred under nitrogen atmosphere until the TLC showed no starting material **2**. The mixture was cooled to room temperature, then poured into water. After standing for 2 h, the mixture was filtered and washed with deionized water. The crude product was dried in the vacuum oven and purified by recrystallization from 50% ethanol to afford **3** as brown solid (0.37 g, 77%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.65 (d, J = 9.1 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 9.1 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 5.78 (s, 2H), 3.01 (s, 6H).

*Synthesis of 2,6-bis(4-((4-(dimethylamino)phenyl)diazenyl)phenyl)pyrrolo[3,4-f]iso-indole-1,3,5,7-(2H,6H)-tetraone (**DPAPIT**).*



Reduction product **3** (0.30 g, 1.25 mmol) was dissolved in dimethylforamide (DMF, 5mL), a solution of pyromellitic anhydride (0.14 g, 0.63 mmol) in DMF (4 mL) was added dropwise into it. After refluxed for 12 h, the reaction mixture was cooled down to room temperature and poured into water. The precipitate was filtered and washed with water. Crude **DPAPIT** was obtained and purified by column chromatography on silica gel with ethyl acetate-petroleum ether as the eluent, yield 33%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.44 (s, 2H, Ar*H*), 8.33 (s, 1H, Ar*H*), 7.75 (m, 11H, Ar*H*), 6.82 (d, J = 9.0 Hz, 4H, Ar*H*), 3.05 (s, 12H, $4\times CH_3$). HRMS: calcd for $C_{38}H_{30}N_8O_4$ [M + H]$^+$ 663.2390, found 663.4539. Anal. calcd for $C_{38}H_{30}N_8O_4$: C, 68.87; H, 4.56; N, 16.91; O, 9.66; found: C, 68.69; H, 4.48; N, 16.78; O, 9.82.

*Synthesis of 1-(4-((4-(dimethylamino)phenyl)diazenyl)phenyl)-1H-pyrrole-2,5-dione (**DPAPPD**).*



Compound **3** (0.48 g, 2.0 mmol), maleic anhydride (0.20 g, 2.0 mmol) and acetone (10 mL) were added to a single-necked flask. After stirring for 8 h at 60 ^{o}C, intermediate product **4** was precipitated and collected by filtration. Washed the filter cake with ethyl acetate and dried under infrared lamp. Crude **4** was directly used to next step without further purification. Then **4**, triethylamine (0.19 g, 2.4 mmol) and acetone (10 mL) were stirring for 5 min at 60 °C. After dissolution of reactants, acetic anhydride (1.21 g, 11.6 mmol) and manganese acetate (0.01 g, as catalyst) were added and the mixture was continued to stir for 4 h at 60 °C. The reaction mixture was cooled to room temperature, then was poured into a large excess of water and isolated by filtration, the final yellow product was recrystallized from 95% ethanol. Yield of **DPAPPD**: 0.52 g, 78%. ^{1}H-NMR (400 MHz, DMSO-d_6), δ (ppm): 7.87 (d, J = 8.6 Hz, 2H, Ar*H*), 7.81 (d, J = 8.6 Hz, 2H, Ar*H*), 7.50 (d, J = 8.3 Hz, 2H, Ar*H*), 7.23 (s, 2H, C*H*CO), 6.85 (d, J = 8.8 Hz, 2H, Ar*H*), 3.07 (s, 6H, $2\times CH_3$). HRMS: calcd for $C_{18}H_{16}N_4O_2$ [M + H]$^+$ 321.1273, found 321.1347. Anal. calcd for $C_{18}H_{16}N_4O_2$: C, 67.49; H, 5.03; N, 17.49; O, 9.99; found: C, 67.55; H, 4.92; N, 17.39; O, 9.73.

1.2 Fabrication of the Memory Device

The indium-tin-oxide (ITO) glass was pre-cleaned with water, acetone, and alcohol, in that order, in an ultrasonic bath for 20 min. The active organic film was deposited under high vacuum about 10^{-6} Torr. The film thickness was about 80 nm. A layer of Al, about 100 nm in thickness was thermally evaporated and deposited onto the organic surface at about 5×10^{-6} Torr through a shadow mask to form the top electrode. The active device area of ~0.0314 mm^2 was obtained.

1.3 Measurement

NMR spectra were obtained on an Inova 400 MHz FT-NMR spectrometer. High-resolution mass spectra (HRMS) were determined on Micromass GCT-TOF mass spertrometer with ESI resource. Elemental analysis was performed using a Carlo-Erba EA-1110 instrument. UV-Vis absorption spectra were carried out at room temperature from 250 to 750 nm with a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry was performed at room temperature using an ITO working electrode, a reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 100mV/s (CorrTest CS Electrochemical Workstation analyzer). A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous *N,N*-dimethylformamide was used. SEM images were taken on a Hitachi S-4700 scanning electron microscope. Atomic force microscopy (AFM) measurements were performed by using a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument in tapping mode. All electrical measurements of the device were characterized under ambient conditions, without any encapsulation, using a HP 4145B semiconductor parameter analyzer equipped with HP 8110A pulse generator. TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from the Qingdao Ocean Chemicals.

1.4 References

[1] S. Yagai, T. Nakajima, T. Karatsu, K. Saitow, and A. Kitamura, *J. Am. Chem. Soc.* **2004**, *126*, 11500–11508.

[2] Y. Zhou, M. Xu, J. Wu, T. Yi, J. Han, S. Xiao, F. Li and C. Huang, *J. Phys. Org. Chem.* **2008**, *21*, 338–343.

[3] B.-C. Yu, Y. Shirai, and J. M. Tour, *Tetrahedron* **2006**, *62*, 10303–10310.

2. UV-Vis Absorption Spectra

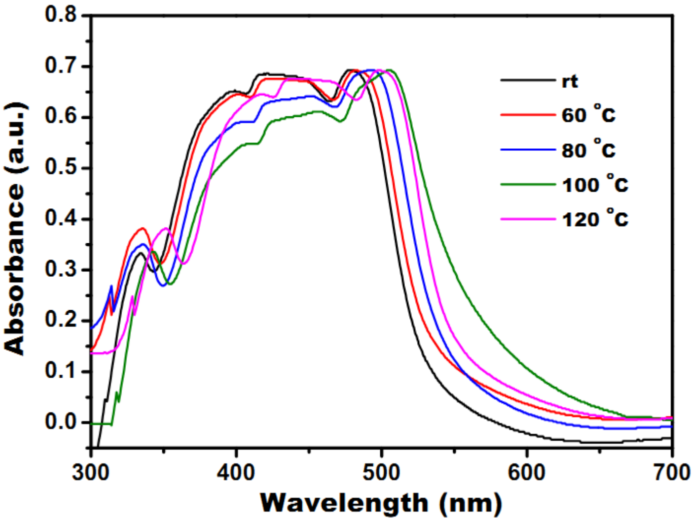


Figure S1. UV–vis absorption spectra of **DPPAIT** thin films of different annealing temperatures on ITO substrate

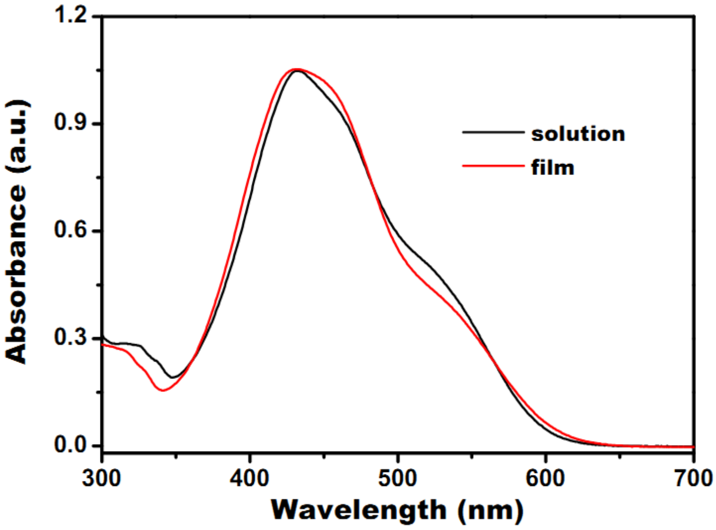


Figure S2. UV–vis absorption spectra of THF solution and the solid thin film of **DPAPPD**.

3. AFM Images

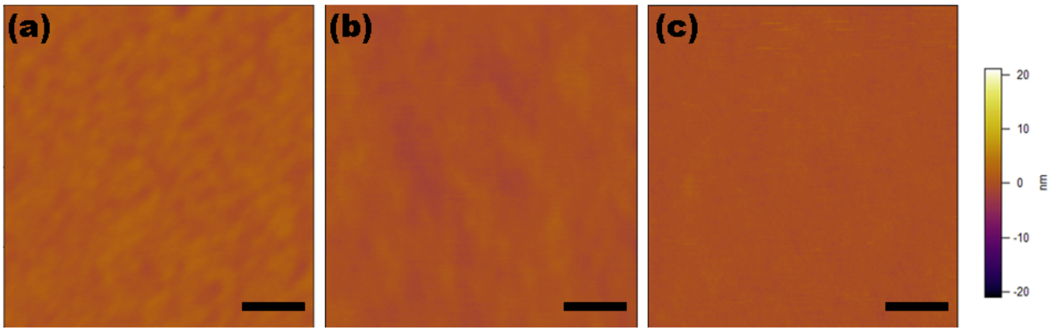


Figure S3. Tapping-mode AFM image of **DPAPPD** thin films deposited onto ITO substrate of different annealing temperatures: (a) without annealing, (b) 60 °C, and (c) 90 °C. The color bar of the three images were displayed in the right of (c). The scale bar corresponds to 1 μm.

4. XRD Pattern

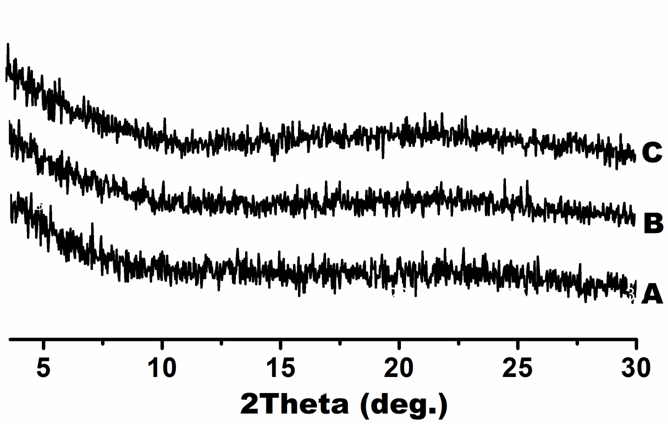


Figure S4. XRD pattern of **DPAPPD** films annealed at different temperatures: A) without annealing, B) 60 °C, and C) 90 °C.

5. *I-V* Curve

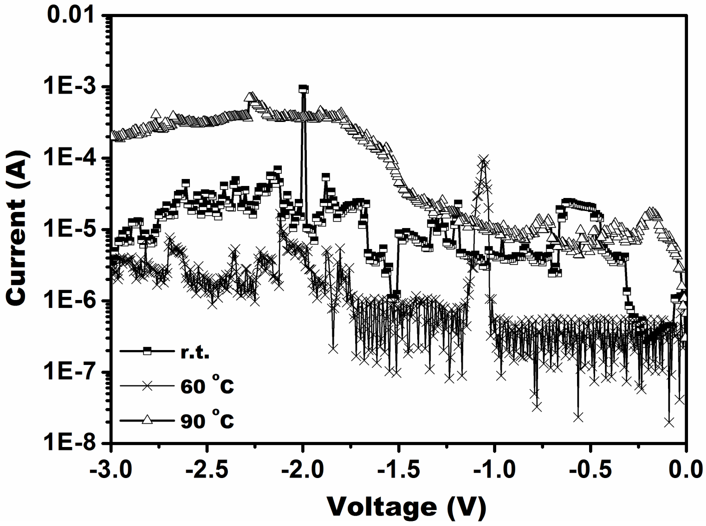


Figure S5. *I–V* characteristics of the memory devices fabricated with **DPAPPD** films annealed at different temperatures.

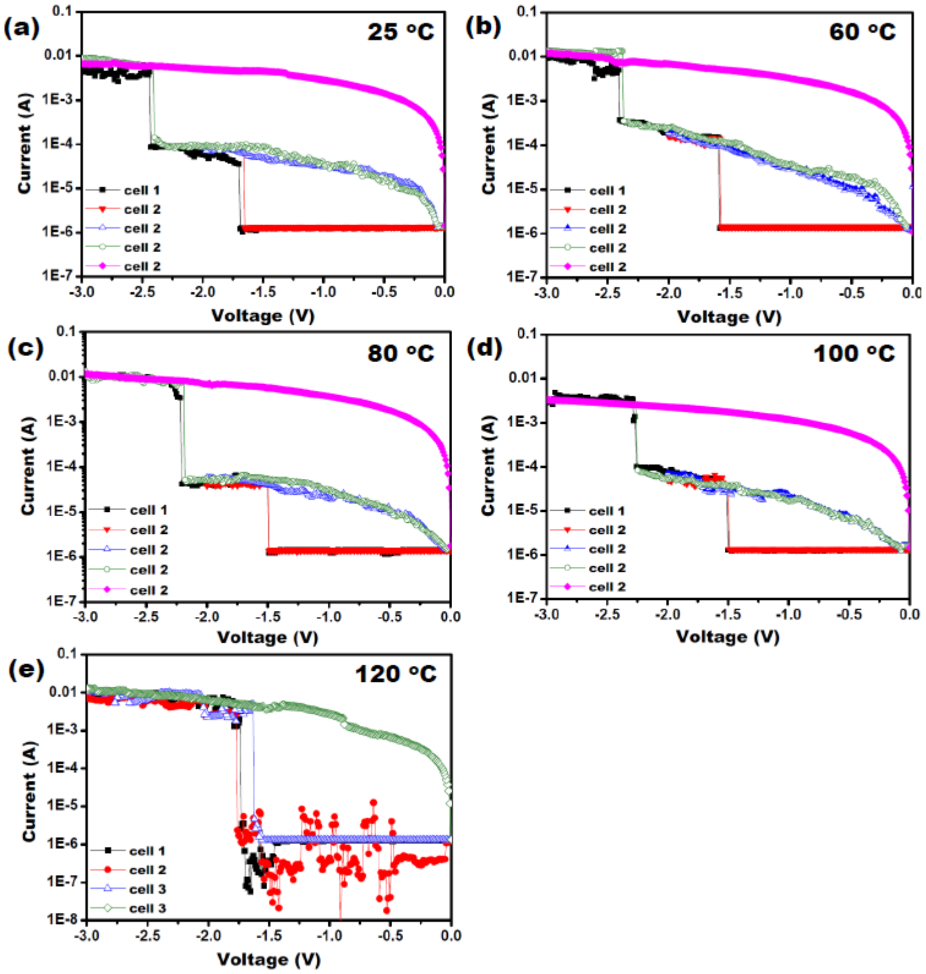


Figure S6. *I*–*V* characteristics of the memory device fabricated with **DPAPIT** annealed at different temperatures: a) without annealing, b) 60 °C, c) 80 °C, d) 100 °C, e) 120 °C, respectively.