Supplementary Information

Isomerization Change and Electron Trap Double Mechanisms

Induced Ternary Data Storage Performance

Huan Cao¹, Qijian Zhang²*, Hua Li¹*, Jianmei Lu¹*

College of Chemistry, Chemical Engineering and Materials Science, Innovation Center of Suzhou Nano Science and Technology, Soochow University, *Soochow University, Suzhou 215123, P. R. China. Fax: +86 512 65880367; Tel: +86 512 65880368; *E-mail: lujm@suda.edu.cn*

1 Experimental Section

Synthesis details

9-butyl-3-[(4-nitrophenyl)diazenyl]-9H-carbazole (NACB). 4-Nitroaniline (1.55 g, 11.2 mmol) was dissolved in a solution of concentrated HCl (8 mL) in water (50 mL). The mixture was cooled in an ice bath until temperature was below 4 °C. Then a solution containing sodium nitrite (0.9 g, 13.44 mmol) in water (10 mL) was added slowly to the above solution. The mixture was allowed to stir in the ice bath for 1 h. While the mixture was kept in the ice bath, the phase transfer catalyst, sodium dodecyl sulfate (60 mg), was added. To this solution was added 9-butylcarbazole (1.25 g, 5.6 mmol) in dichloromethane (50 mL), and then the resultant mixture was stirred vigorously at room temperature for 48 h. The mixture was heated to remove the dichloromethane layer. The red precipitate was filtered, washed with water, and air-dried. The solid was recrystallized from ethanol to yield 1.4 g of red solid. ¹H NMR (400 MHz, CDCl3, δ): 8.77 (s, 1H), 8.39 (d, 2H), 8.19 (m, 2H), 8.05 (d, 2H), 7.50 (m, 3H), 7.34 (m, 1H), 4.37 (t, 2H), 1.92 (m, 2H) 1.44 (m, 2H), 0.99 (t, 3H). Elemental analysis calculated for C₂₂H₂₀N₄O₂ (wt%): C, 70.95; H, 5.41; N, 15.04. Found: C, 70.10; H, 5.05; N, 15.10.

3-[(4-nitrophenyl)diazenyl]-9H-carbazole (NAC). 4-Nitroaniline (2.76 g, 20 mmol) was dissolved in a solution of concentrated HCl (8 mL) in water (8 mL). The mixture was cooled in an ice bath until temperature was below 4 °C. Then a solution containing sodium nitrite (1.66 g, 24 mmol) in water (8 mL) was added slowly to the above solution. The mixture was allowed to stir in the ice bath for 1.5 h. While the mixture was kept in the ice bath, the phase transfer catalyst, sodium dodecyl sulfate (210 mg), was added. To this solution was added 9-butylcarbazole (3.34 g, 20 mmol) in dichloromethane (100 mL), and then the resultant mixture was stirred vigorously at room temperature for 48 h. The mixture was heated to remove the dichloromethane layer. The resulting product was chromatographed on a silica gel column (chloroform: petroleum ether =5:1). ¹H NMR (400 MHz, DMSO-d6 , δ): 11.90 (s, 1H), 8.85 (s, 1H), 8.44 (d, 2H), 8.31 (d, 1H), 8.08 (t, 3H), 7.65 (d, 1H), 7.57 (d, 1H), 7.48 (t, 1H), 7.27(t, 1H). Elemental analysis calculated for C₁₈H₁₂N₄O₂ (wt%): C, 68.35; H, 3.82; N, 17.71. Found: C, 68.27; H, 3.95; N, 17.77.

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 75 nm. A layer of Al, about 150 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 about 0.0314 mm² was obtained. All electrical measurements of the device were characterized under ambient conditions, without any encapsulation, using a semiconductor characteristic testing set (Keilthley 4200-SCS).

2 Figures



Figure S1. The effect of the operation time (a read pulse of -1 V) on the ITO/NACB/Al device current in the "0", "1", and "2" states were measured with the heating plate at (A) 20 °C, (B) the high-intensity irradiation by a 300 W Xe lamp (C), 60 °C, (D) 100 °C.



Figure S2. XRD patterns of large-scale single crystal derived from methanol solution and vacuum-deposited thin films of NACB: (A) Vacuum-deposited film without annealing; (B) Vacuum-deposited film with 12 hours annealing at 80 °C; (C) Single crystal derived from methanol solution.



Figure S3. I-V characteristics of un-annealed NACB film based sandwiched device.



Figure S4. (A) AFM topography images of single crystal domains of NACB on ITO glass substrate; (B) The angle between the NACB molecule and the vertical direction was measured by mercury CCD soft.



Figure S5. AFM height images of nanoscale single crystal domain by using C-AFM tip perform morphology scan with different voltages at -1 V (A), -4 V (B), and -6 V (C), the below is the cross-section profile of the single crystal height corresponding to the upper image, respectively.



Figure S6. The single crystal CCD diffraction indicates the molecule stand on the substrate and the oblique angle with the vertical direction is about 134.24°.

The height of each layer of single crystal measured by AFM is about 4.3 nm. It can be calculated that the selected crystal ribbon is composed of 11-layer (the layers=47.4/4.3=11 layers) lamellar organic single crystals. Therefore, according to the change of height (in **Figure 7**), the each layer of single crystal consists of three molecules (in **Figure 5**C) and according to the angle between the molecule and the vertical direction is 134.24° which measured by mercury CCD soft (in **Figure 56**), the changed length for one molecule is (47.4-42.5)/(11×3) /cos (180°-134.24°) =2.1 Å, which is just consistent with the theoretical calculation result that NACB molecule length from trans-formation (the length of single molecule is about 16.0 Å) to cis-formation (the length of single molecule is about 13.8 Å) shortened about 2.2 Å.



Figure S7. UV-visible absorption spectrum of NACB films before and after applying electric field.



Figure S8. I-V characteristics of "0", "1" and "2" states from the red line of the insert, the inset represent a conductive atomic force microscopy tip with different voltages (-1 V, -4 V and -6 V) is first used to perform the morphology scan on the NACB film at the different area and then to read out the electrical characteristics with -1 V.