

Supporting Information

A Small-Molecule-based Device for Data-storage and Electro-optical Switch Applications

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Experimental Section

Materials: 4-bromo-1,8-naphthalic anhydride (97%) was purchased from Liaoning Liangang Dyes Chemical Co. Ltd, China. 1-Chloro-6-hydroxyhexane (99%) was purchased from Shandong Zouping Mingxing Chemical Co. Ltd., China. Carbazole, POCl₃ and other reagents and solvents were received from Sinopharm Chemical Reagent Co. Ltd, China. All the chemicals were used without further purification.

Preparation of 4-Hydrazino-N-butyl-1,8-naphthalimide (1)¹:

4-Bromide-1,8-naphthalic anhydride (2.5 g, 9 mmol) and butylamine (0.73 g, 10 mmol) were refluxed in 100 mL 1,2-dichlorobenzene with vigorous stirring for 3 hours. The mixture was cooled to 100 °C and sodium carbonate (0.045 g, 0.4 mmol) were added, whereupon the dichlorobenzene was removed in vacuum, the crude product was recrystallized from ethanol to give a pale yellow crystal: 4-bromide-N-butyl-1,8-naphthalic anhydride (2.6 g, 87%). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 8.64 (d, 1H), 8.55 (d, 1H), 8.40 (d, 1H), 8.02 (d, 1H), 7.84 (t, 1H), 4.17 (t, 2H), 1.71 (m, 2H), 1.43 (m, 2H), 0.97 (t, 3H)

4-bromide-N-butyl-1,8-naphthalic anhydride (2.6 g, 8 mmol) and 1.2 mL 85% hydrazine hydrate in 30 mL methoxyl ethanol were heated under reflux for 3 h. After

cooling to room-temperature, the precipitated solids were filtered, washed with ethanol and chloroform, then re-crystallized from methoxyl ethanol and dried in vacuum to give a brownish-red powdery product: 4-hydrazino-N-butyle-1,8-naphthalimide (1.69 g, 74.9%). ¹H-NMR (*d*₆-DMSO, 400 MHz) δ (ppm): 8.60 (d, 1H), 8.40 (d, 1H), 8.28 (d, 1H), 7.64 (t, 1H), 7.24 (d, 1H), 4.68 (s, 2H), 4.01 (t, 2H), 1.58 (m, 2H), 1.33 (m, 2H), 0.92 (t, 3H)

Preparation of (9H-carbazol-9-yl) hexanol (2): A mixture of potassium hydroxide (14 g, 0.25 mol) and DMF (80 mL) was vigorously stirred in a three-neck flask at room temperature till the potassium hydroxide had been dissolved totally. The carbazole (6.6 g, 40 mmol) was added into the mixture and continuously stirred for 45 minutes. 1-Chloro-6-hydroxyhexane (5.7 g, 42 mmol) was added dropwise in 30 minutes. The reaction mixture was heated to 50°C and refluxed for 24 h. The reaction mixture was poured into water and the precipitated product was filtered and purified through silica-gel column (CHCl₃/petroleum ether=2/1), the yield is 78% and the colour is white. Elemental analysis calculated for C₁₈H₂₁NO (wt%): C, 80.86, H, 7.92, N, 5.24; Found: C, 81.12, H, 8.00, N, 5.19. ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 8.10 (d, 2H), 7.44 (t, 2H), 7.37 (t, 2H), 7.20 (t, 2H), 4.23 (t, 2H), 3.52 (t, 2H), 1.84 (m, 2H), 1.46 (m, 2H), 1.39 (m, 4H)

Preparation of (3-formyl-9H-carbazol-9-yl)hexyl acetate (3)²⁻³: A stirred solution of 2.4 g (9.0 mmol) of compound 2 in 30 mL of acetic anhydride was heated at reflux for 24 h. After cooling, the mixture was poured into water and the aqueous mixture was extracted with chloroform. The extract was dried with MgSO₄, and the solvent

was removed at reduced pressure. The crude product was chromatographed on a silica gel column (ethyl acetate: petroleum ether =1:4) to give the product (9H-carbazol-9-yl)hexyl acetate. The yield is 65%. To a stirred solution of 1.95 g (6.3 mmol) (9H-carbazol-9-yl)hexyl acetate in 30 mL of dry DMF was added dropwise 1.5 mL (1.6 mmol) of phosphorus oxychloride at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at 90 °C for ten hours. After cooling, the solution was poured into water. The resulting mixture was extracted with chloroform. The extract was dried with MgSO₄, and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column (ethyl acetate: petroleum ether =3:1) to give 1.08g white powder compound 3 (51%). Elemental analysis calculated for C₂₁H₂₃NO₃ (wt%): C, 74.75, H, 6.87, N, 4.15; Found: C, 74.79, H, 6.85, N, 4.13. ¹H-NMR (*d*₆-DMSO, 400 MHz) δ (ppm): 10.02 (s, 1 H), 8.54 (s, 1H), 8.01 (d, 1 H), 7.93 (d, 1H), 7.47 (t, 1 H), 7.40 (m, 2 H), 7.30 (t, 1H), 4.27 (t, 2 H), 3.54 (t, 2H), 1.95 (s, 3 H), 1.84 (m, 2H), 1.48 (m, 2H), 1.35 (m, 4H).

Preparation of 6, 6'-Di-(3-formyl-9H-carbazol-9-yl)-hexyl ether (4): POCl₃ (0.3 mol) was added slowly into a three-neck flask containing DMF (0.3 mol) at ice-bath condition. The reaction temperature was changed to room temperature and compound 2 (0.3 mol, 1,2-dichloroethane as solvent) was added into the mixture. The reaction temperature was raised to 90 °C and kept for 24 h. The reaction mixture was poured into the ice-bath and the product was extracted by CHCl₃. The yellow product was purified by silica-gel column (ethyl acetate: petroleum ether =3:1), the yield is 30%. Elemental analysis calculated for C₃₈H₄₀N₂O₃ (wt%): C, 79.69, H, 7.04, N, 4.89;

Found: C, 80.79, H, 7.00, N, 4.80. ¹H-NMR (CDCl₃, 400 MHz), δ (ppm): 10.02 (s, 2H), 8.62 (s, 2H), 8.15 (d, 2H), 8.01 (d, 2H), 7.49 (m, 6H), 7.32 (t, 2H), 4.36 (t, 4H), 3.50 (t, 4H), 1.93 (m, 4H), 1.74 (m, 4H), 1.50 (m, 8H).

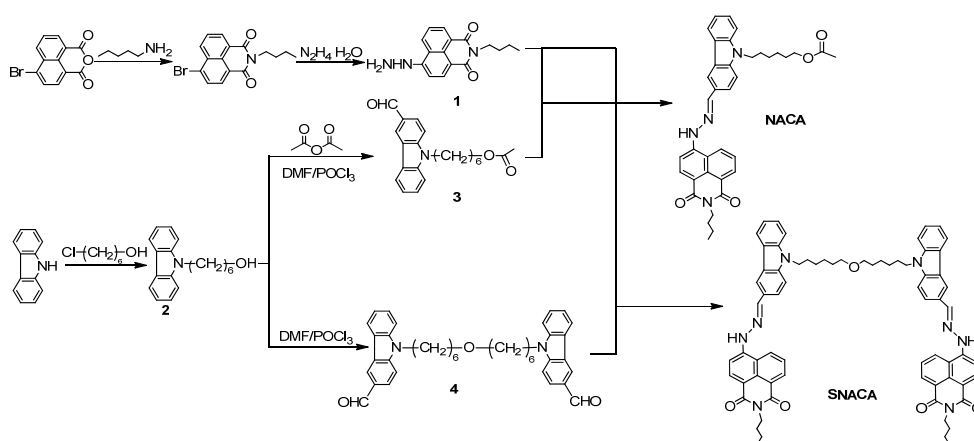
Preparation of SNACA: The mixture of compound 1 (0.1mol), compound 4 (0.12 mol) and glacial acetic acid (50 mL) was refluxed for 5 h. After cooling to room temperature, the precipitated product was purified through gel-silica column with acetic ether as the solvent. The product is brownish red and yield is 64%. Elemental analysis calculated for SNACA (wt%): C, 76.20, H, 6.39, N, 10.16; Found: C, 76.15; H, 6.30; N, 10.10. ¹H-NMR (CDCl₃, 400 MHz), δ (ppm): 8.61 (t, 6H), 8.40 (s, 2H), 8.23 (m, 6H), 7.95 (d, 2H), 7.90 (d, 2H), 7.68 (t, 2H), 7.51 (t, 2H), 7.44 (t, 4H), 7.30 (t, 2H), 4.34 (t, 4H), 4.19 (t, 4H), 3.98 (t, 4H), 1.93 (m, 4H), 1.75 (m, 4H), 1.46 (m, 12H), 0.98 (t, 6H).

Preparation of NACA: Synthetic pathway to the compound NACA is same with the SNACA. The product is red powder and yield is 56%. Elemental analysis calculated for NACA (wt%): C, 73.73, H, 6.35, N, 9.30; Found: C, 73.65; H, 6.32; N, 9.25. ¹H-NMR (CDCl₃, 400 MHz), δ (ppm): 8.65 (t, 3H), 8.36 (s, 1H), 8.23 (m, 3H), 7.95 (d, 1H), 7.87 (d, 1H), 7.65 (t, 1H), 7.51 (t, 1H), 7.43 (t, 2H), 7.30 (t, 1H), 4.32 (t, 2H), 4.18 (t, 2H), 4.02 (t, 2H), 2.0 (s, 3H), 1.90 (m, 2H), 1.73 (m, 2H), 1.59 (m, 2H), 1.44 (m, 6H), 0.97 (t, 3H).

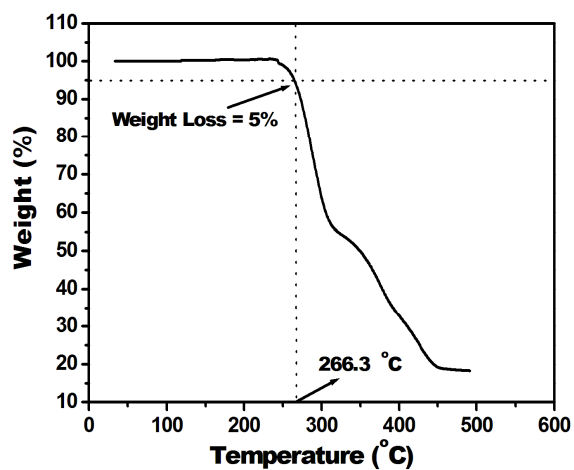
Fabrication of the Memory Device: The indium-tin-oxide (ITO)/glass or Pt substrate was pre-cleaned with water, acetone, and alcohol, in that order, in an ultrasonic bath for 20 min. The DMF solution of SNACA (12 mg/mL) was spin-coated onto ITO and

the solvent was removed in a vacuum chamber at 10^{-3} Torr and 50°C for 8h. The thickness of the polymer film was about 75 nm. A layer of Al, about 300 nm in thickness was thermally evaporated and deposited onto the organic surface at about 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 HP 4145B semiconductor parameter analyzer equipped with HP 8110A pulse generator.

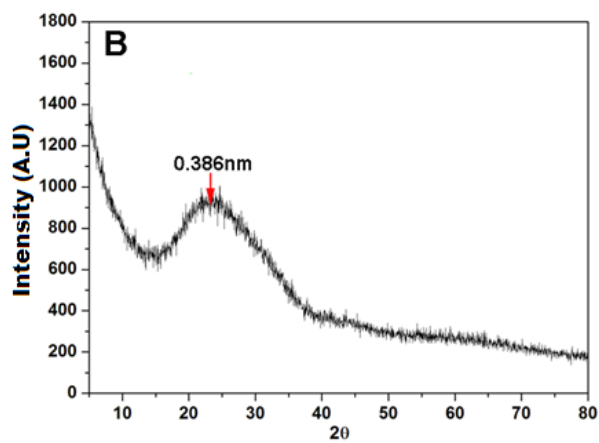
Characterization: The elemental analysis was performed by Italian 1106 FT analyzer. ¹H-NMR spectra were obtained on an Inova 400 MHz FT-NMR spectrometer. UV-vis absorption spectra were carried out at 25°C in the 650–300 nm spectral region with a Perkin–Elmer Lambda spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a TA instrument Dynamic TGA 2950 at a heating rate of 10°C/min and under an air flow rate of 50 mL/min.



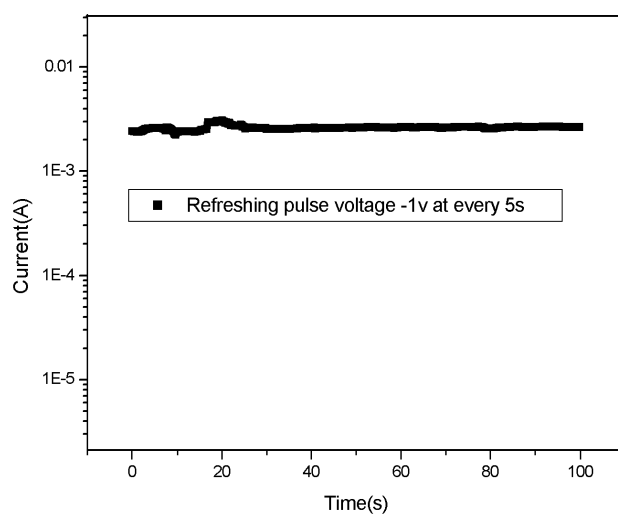
Scheme 1. Synthesis routes and molecular structure of SNACA and NACA



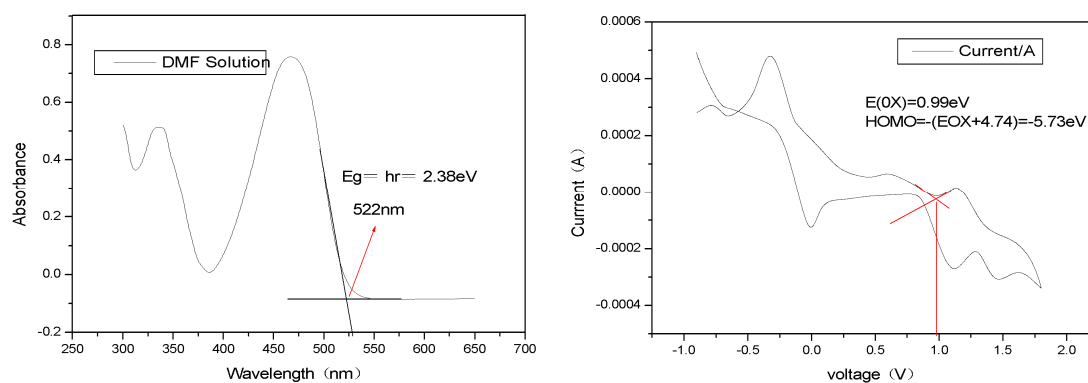
SI 1. TGA curves of NACA under an air flow rate of 50 ml/min. (Heating rate: 10 °C/min)



SI.2 X-ray diffraction (XRD) pattern of the thin film



SI 3. The ON state was maintained by refreshing at -1V every 5s.



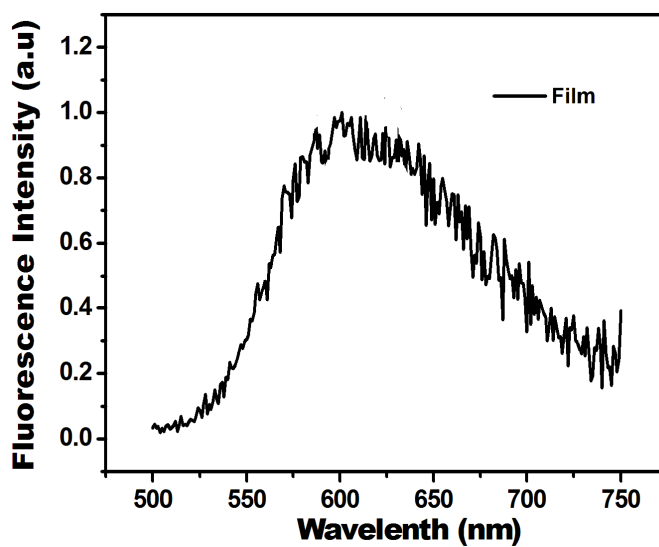
SI 4. The experimental results of HOMO and LUMO through cyclic voltammetry and UV/vis method

The HOMO energy levels can be calculated from the onset oxidation potential ($E_{\text{ox}}(\text{onset})$):

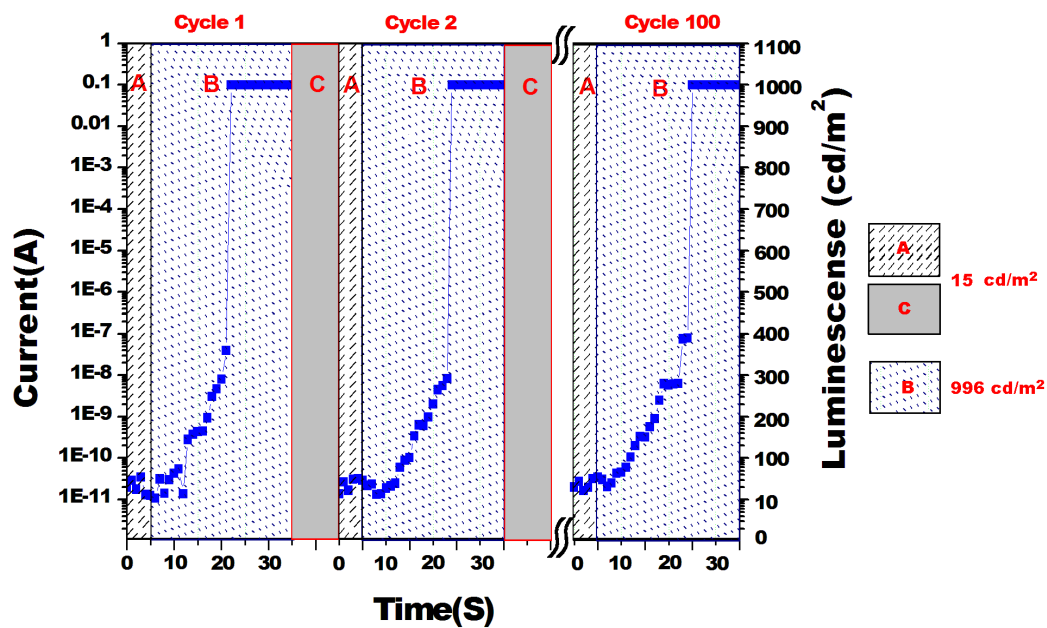
$$\text{HOMO} = -(E_{\text{OX}} + 4.74)(\text{eV})$$

$$\text{LUMO} = \text{HOMO} - E_{\text{UVedge}}(\text{bandgap})(\text{eV})$$

Wherein 4.74 is the corrector factor when the calomel electrode is the reference electrode.



SI 5. The fluorescence spectrum of SNACA film



SI.6 Electro-optical switch performance of the device, A and C areas mean the light intensity is 15 cd/m^2 , B area means the light intensity is 996 cd/m^2

Reference:

- (1) Gan, J. A.; Song, Q. L.; Hou, X. Y.; Chen, K. C.; Tian, H. *J. Photochem. Photobio. A.* **2004**, *162*, 399-406.
- (2) Huang, J.; Sohn, J.; Park, S. Y. *Macromolecules*, **2003**, *36*, 7970-7976.
- (3) Moon, H.; Hwang, J.; Kim, N.; Park, S. Y. *Macromolecules*, **2000**, *33*, 5116-5123.