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Electronic Supplementary Information (ESI) for

Deriving Highly Oriented Organic Naonofibers and Ternary Memory Performance by Salification-Induced Effect

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Experimental

Materials

All the chemicals such as 9-phenyl-9H-carbazole, N-Bromosuccinimide, 4-Pyridineboronic acid and 4-Bromo-1,8-naphthalic anhydride were purchased from commercial source (TCI) and used without further purification. All the solvents were purchased from Sinopharm Chemical Reagent and Enox Co., Ltd.

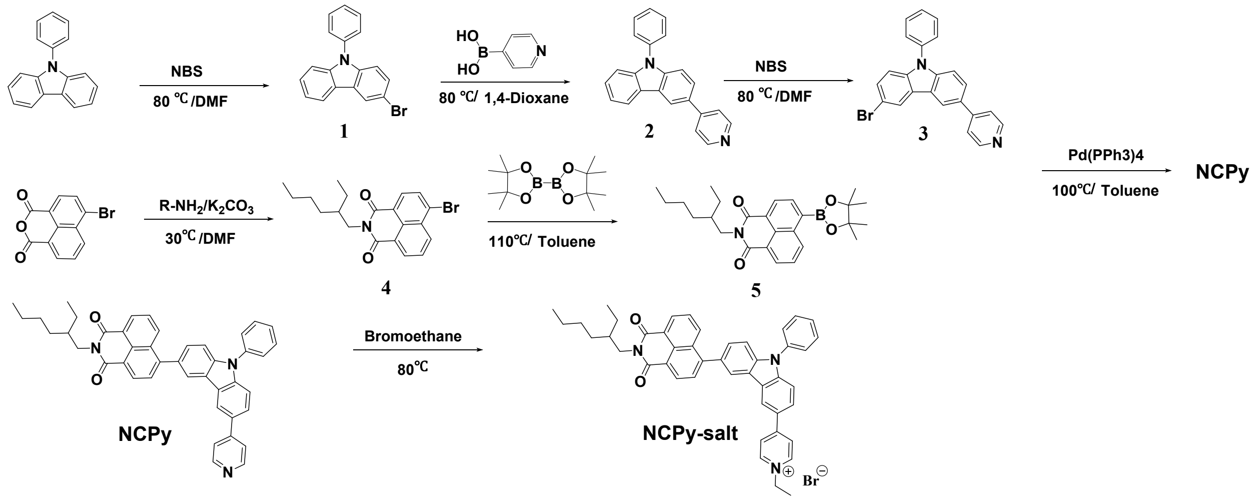
Characterization

All NMR spectra were obtained in chloroform-d ($CDCl_3$) containing 0.003% TMS as an internal reference with an Inova FT-NMR spectrometer (400 MHz for ^{1}H NMR and 300 MHz for ^{13}C NMR). The compounds were also characterized by a Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) in the positive mode without any matrix. Ultraviolet-visible (UV-vis) absorption spectra and cyclic voltammetry were obtained using the UV-3600 spectrophotometer (Shimadzu) and the CorrTest Electrochemical Workstation analyzer at room temperature, respectively. Atomic force microscopy (AFM) measurements were carried out by a MFP-3DTM AFM instrument. X-ray diffraction (XRD) patterns were performed using an X'Pert-Pro MPD X-ray diffractometer. All electrical measurements of the devices were performed under ambient conditions without any encapsulation using Keilthley 4200-SCS semiconductor parameter analyzer.

Fabrication of memory devices

The indium-tin-oxide (ITO) glass substrates were precleaned sequentially with water, ethanol, and acetone, in an ultrasonic bath for 20 min, respectively. A 10 mg/ml solution of the compounds was filtered through a membrane micro-filter with a pore size of 0.22 μm and then spin-coated onto the ITO substrates with the speed of 800 rpm for 10 s and 1300 rpm for 30 s. 100-nm-thickness top Al layer was thermally evaporated onto the film under 2×10^{-6} Torr through a shadow mask under N_2.

Synthetic procedures



Scheme S1. The synthetic routes of NCPy and NCPy-salt.

***3-bromo-9-phenyl-9H-carbazole (1)*：** 9-phenyl-9H-carbazole (2.00 g, 8.24 mmol) was added in 250 ml three-neck-flask and dissolved in 10 ml DMF under the ice bath. NBS (1.61 g, 9.05 mmol) was added slowly for about 30 min and stirred in dark for another 30 min. Then the reaction was heated to 80 ℃ and stirred overnight. The mixture was washed by brine and extracted by $CHCl_3$. The brown crude product 1 (2.03 g) was finally obtained and used directly without further purification.

***9-phenyl-3-(pyridin-4-yl)-9H-carbazole (2)*：** The crude compound 1 (1.77 g, 5.50 mmol), 4-Pyridineboronic acid (1.23 g, 10.0 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) were mixed with the component solvents of 1,4-dioxane (50 ml) and water (10 ml) in a round-bottom flask, and heated to 80 ℃ for 24 h under N_2 atmosphere. After cooling, the mixture was washed with brine and extracted by $CHCl_3$. The solvent was removed to give a crude mixture from the organic phase. The crude product was purified using column chromatography to afford the light yellow compound 2 (1.17 g, yield: 66.5%) (Eluent: hexane/CH_2Cl_2=1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (2H, s), 8.43 (1H, s), 8.21 (1H, s), 7.65 (5H, s), 7.59 (2H, s), 7.46 (4H, s), 7.34 (1H, s).

***3-bromo-9-phenyl-6-(pyridin-4-yl)-9H-carbazole (3)*：** Yellow Compound 3 was obtained by the same procedure as compound 1 (yield：93.3%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (2H, s), 8.38 (1 H, s), 8.32 (1 H, s), 7.72 (1H, d, J = 8.5 Hz), 7.64 (4H, s), 7.53 (3H, s), 7.47 (2H, d, J = 8.3 Hz), 7.29 (1H, d, J = 8.29 Hz).

6-bromo-2-(2-ethylhexyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4) and 2-(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[de]isoquinoline-

1,3(2H)-dione (5): The compound 4 and compound 5 were synthesized according to the previously-reported literatures[1-2].

2-(2-ethylhexyl)-6-(9-phenyl-6-(pyridin-4-yl)-9H-carbazol-3-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NCPy): Compound 3 (500 mg, 1.22 mmol), compound 5 (1.60 g, 3.66mmol), $Pd(PPh_3)_4$ (0.14 g, 0.122 mmol), and CsF (0.93 g, 6.10 mmol) were mixed in component solvents of toluene (50 ml) and H_2O (6.1 ml) under N_2. Then the mixture was heated to 100℃ and reacted for one night. After cooling, the mixture was washed with brine and extracted by $CHCl_3$. The crude product was purified using column chromatography to afford the light green compound NCPy (0.30 g, yield: 39.2%) (Eluent: hexane/ethyl acetate=1:2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (4 H, m), 8.57-8.20 (3 H, m), 7.67 (13 H, m), 4.21 (2 H, s), 1.76 (2 H, s), 1.29 (10 H, m), 0.88 (3 H, m). ^{13}C NMR (300 MHz, $CDCl_3$): δ 164.34, 164.16, 149.92, 149.00, 147.38, 141.94, 141.38, 136.99, 132.85, 131.12, 131.09, 130.79, 130.41, 130.34, 130.20, 128.80, 128.51, 128.23, 128.20, 126.92, 126.76, 125.59, 123.80, 123.53, 122.96, 121.93, 121.67, 121.45, 119.12, 110.79, 110.30, 40.55, 31.83, 29.37, 29.24, 28.17, 27.19, 22.65, 14.11. **MALDI-TOF MS**: calcd for $[C_{43}H_{37}N_3O_2]^+$, 627.2886; found, 627.2910.

1-ethyl-4-(6-(2-(2-ethylbutyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-9-phenyl-9H-carbazol-3-yl)pyQridin-1-ium (NCPy-salt): NCPy (100 mg, 0.15 mmol) was added into 100 ml flask followed by injecting 3 ml bromoethane under N_2 atmosphere. The reaction was kept for 12 h at 80℃. Bromoethane was removed by evaporation and then recrystallized from methanol to give the pure compound as a yellow solid NCPy-salt (0.1 g, yield 98.0%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.13 (2 H, s), 8.49 (1 H, s), 8.40 (2 H, s), 8.31 (1 H, s), 8.14 (1 H, d, J = 6.3 Hz), 8.09 (2 H, d, J = 7.1 Hz), 7.65 (1 H, d, J = 8.1 Hz), 7.57 (2 H, d, J = 7.0 Hz), 7.48 (2 H, d, J = 6.3 Hz), 7.39 (3 H, d, J = 6.9 Hz), 7.21 (1 H, s), 7.17 (2 H, t, J = 7.3 Hz), 4.70 (2 H, s), 3.97 (2 H, s), 1.64 (3 H, s), 1.25 (10 H, m), 0.86 (5 H, m). ^3C NMR (300 MHz, $CDCl_3$): δ 163.75, 163.43, 155.13, 146.36, 143.94, 142.64, 140.82, 136.08, 132.42, 131.16, 130.36, 130.06, 129.97, 129.23, 128.81, 128.13, 128.03, 127.78, 126.77, 126.48, 125.60, 124.76, 124.24, 123.76, 123.11, 122.79, 121.99, 121.49, 120.42, 110.51, 109.95, 56.03, 40.36, 31.78, 29.66, 29.34, 29.22, 28.05, 27.17, 24.83, 22.61, 16.80, 14.07, 0.99. **MALDI-TOF MS**: calcd for $[C_{45}H_{42}N_3O_2]^+$, 656.3272; found, 656.3290.

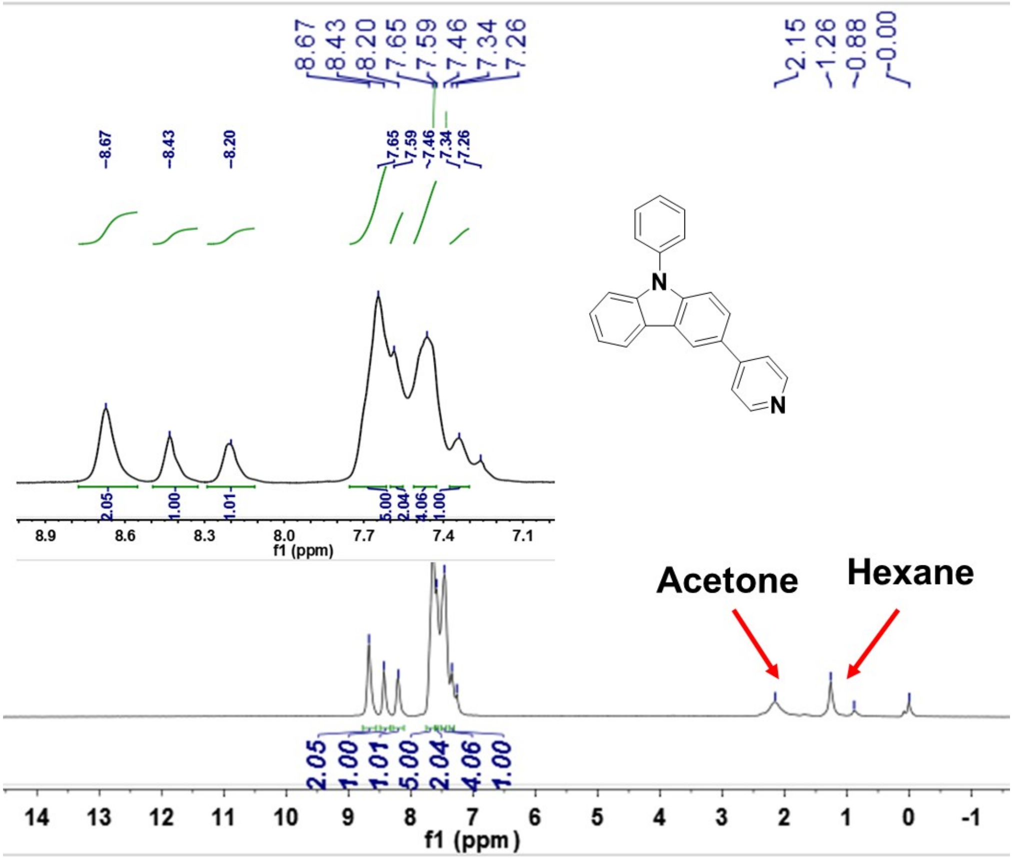


Fig. S1 The [1]H NMR spectrum of compounds 2 in $CDCl_3$.

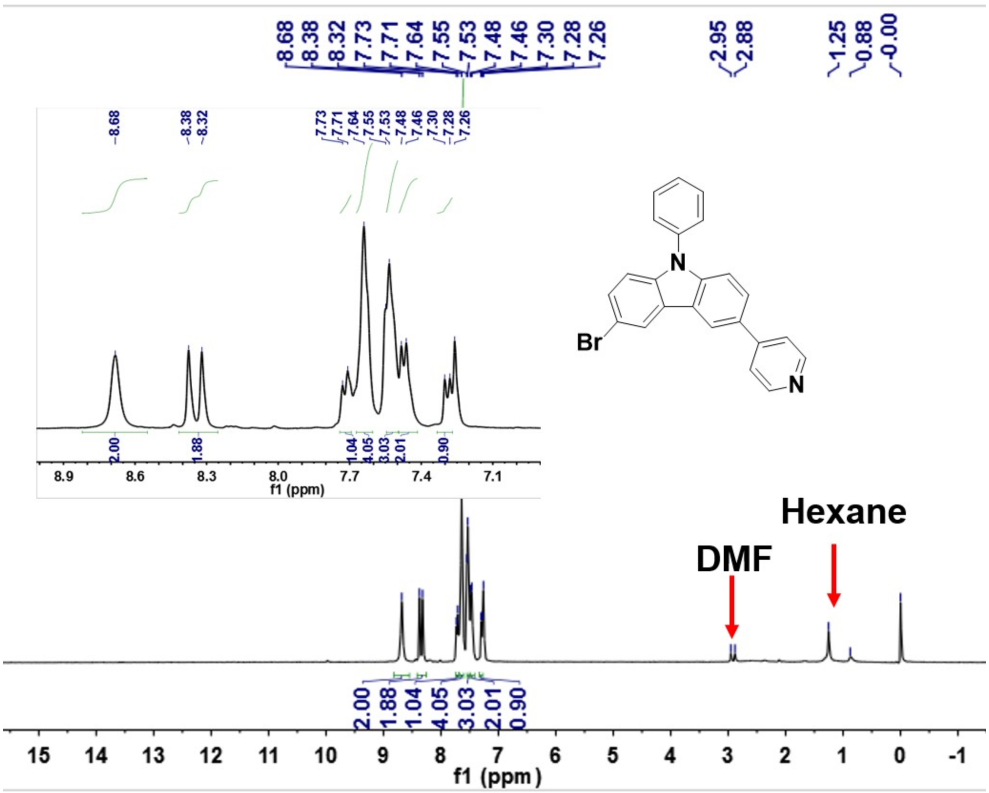


Fig. S2 The [1]H NMR spectrum of compounds 3 in $CDCl_3$.

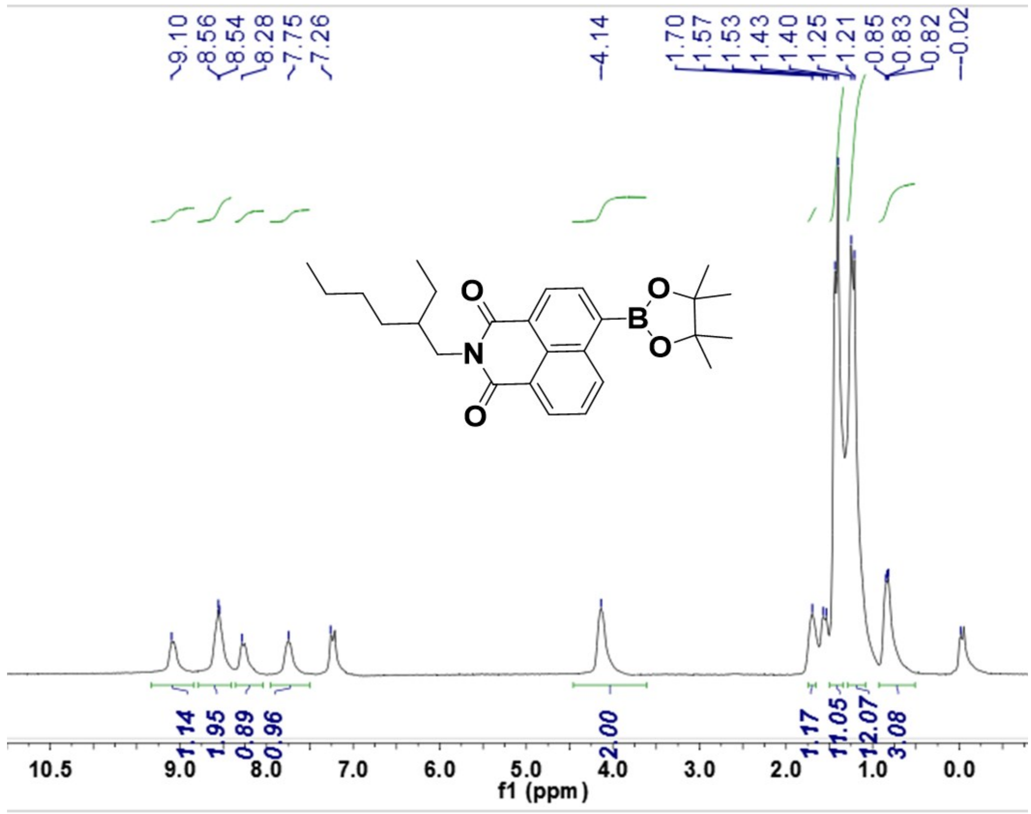


Fig. S3 The [1]H NMR spectrum of compounds 5 in $CDCl_3$.

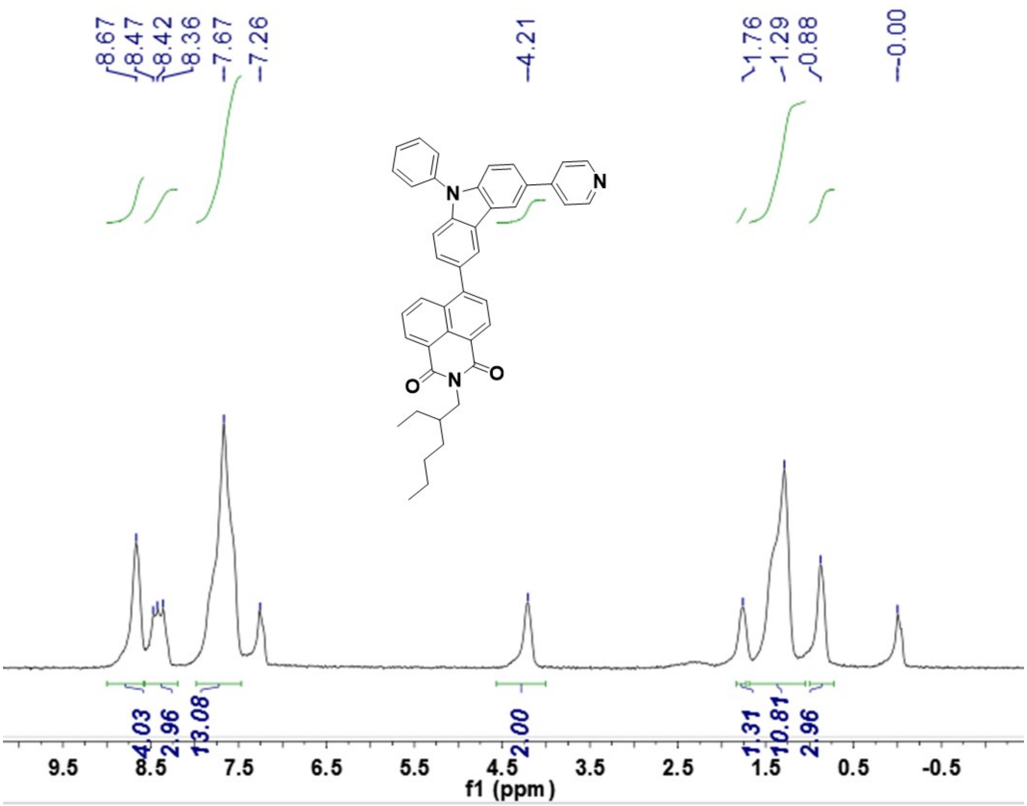


Fig. S4 The [1]H NMR spectrum of NCPy in $CDCl_3$.

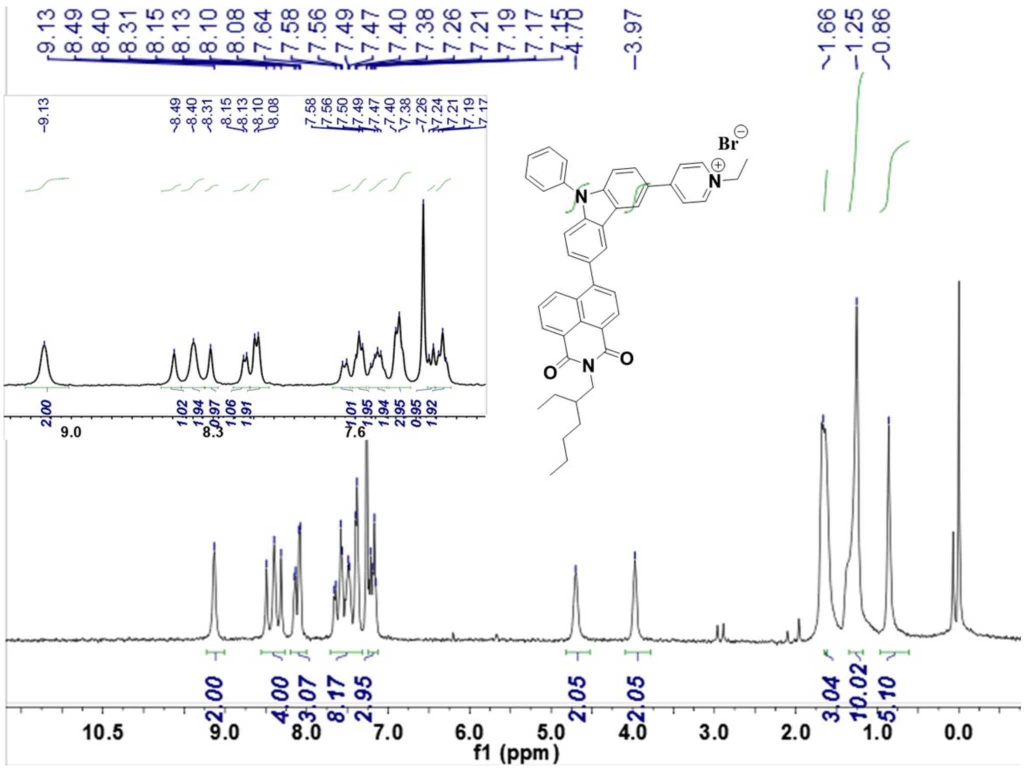


Fig. S5 The ^{1}H NMR spectrum of compound NCPy-salt in $CDCl_3$.

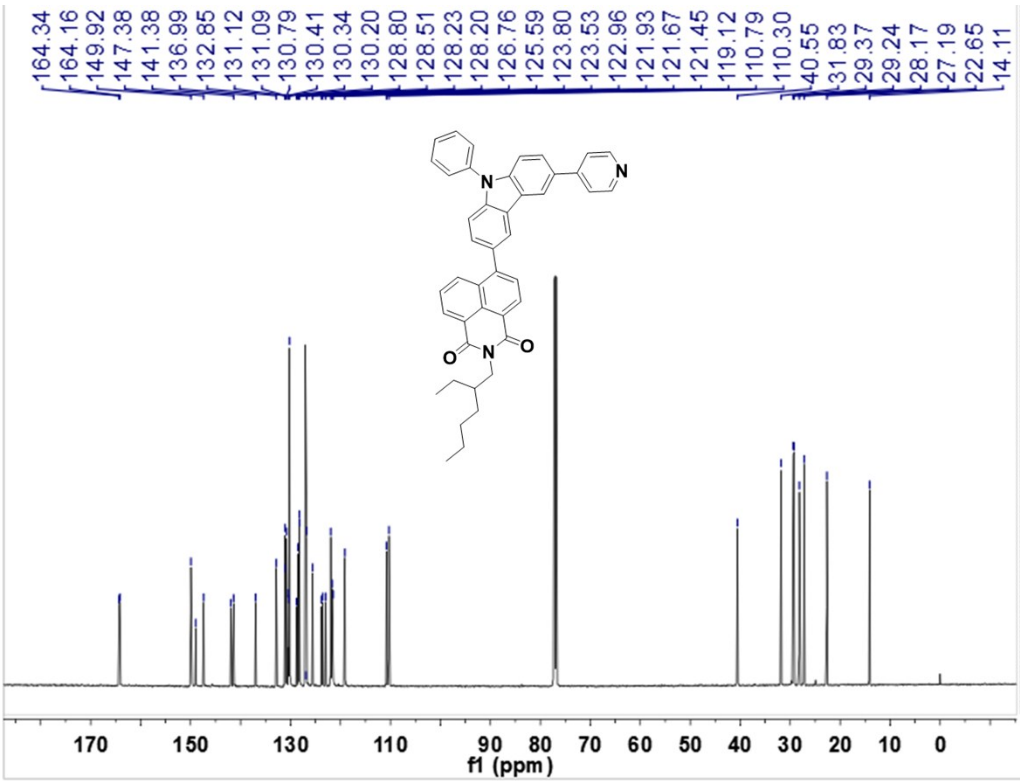


Fig. S6 The ^{13}C NMR spectrum of NCPy in $CDCl_3$.

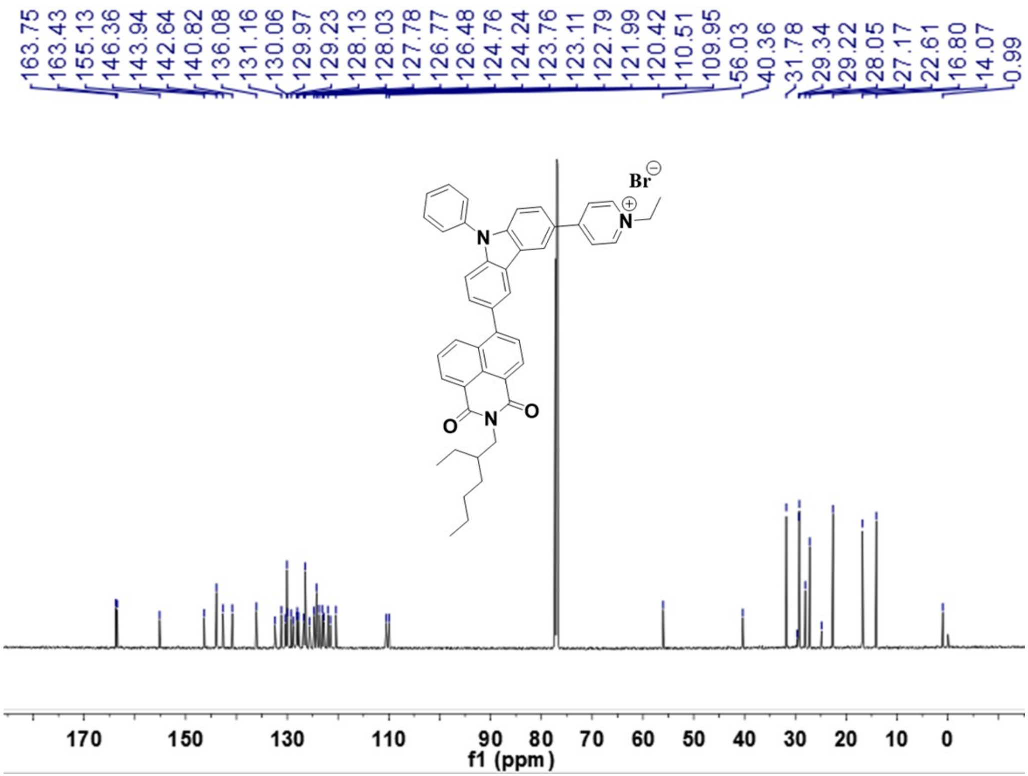


Fig. S7 The ^{13}C NMR spectrum of NCPy-salt in $CDCl_3$.

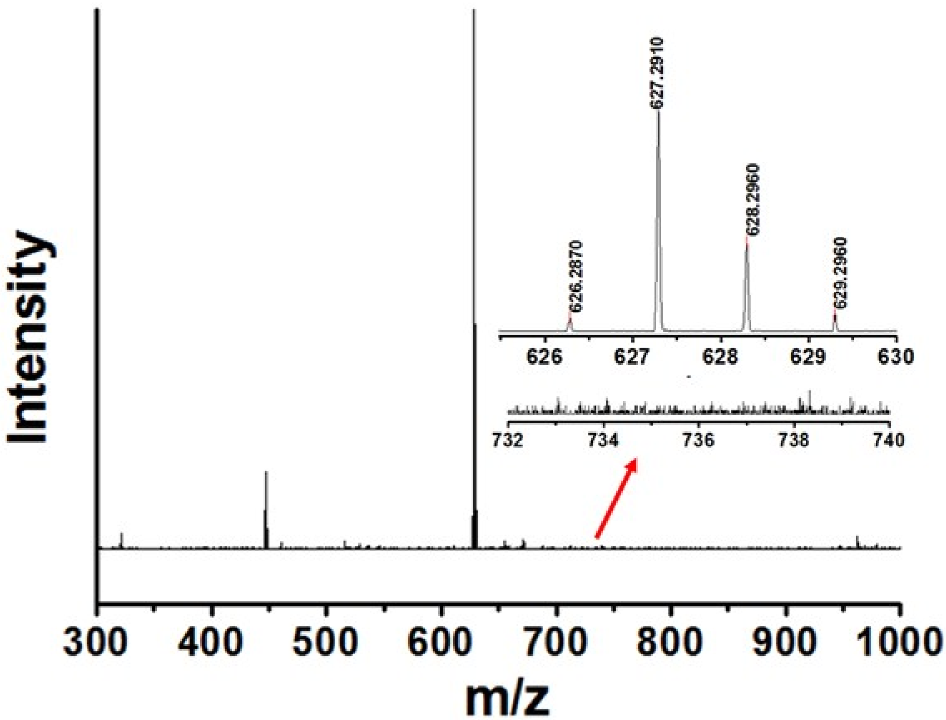


Fig. S8 The MALDI-TOF MS spectrum of compounds NCPy.

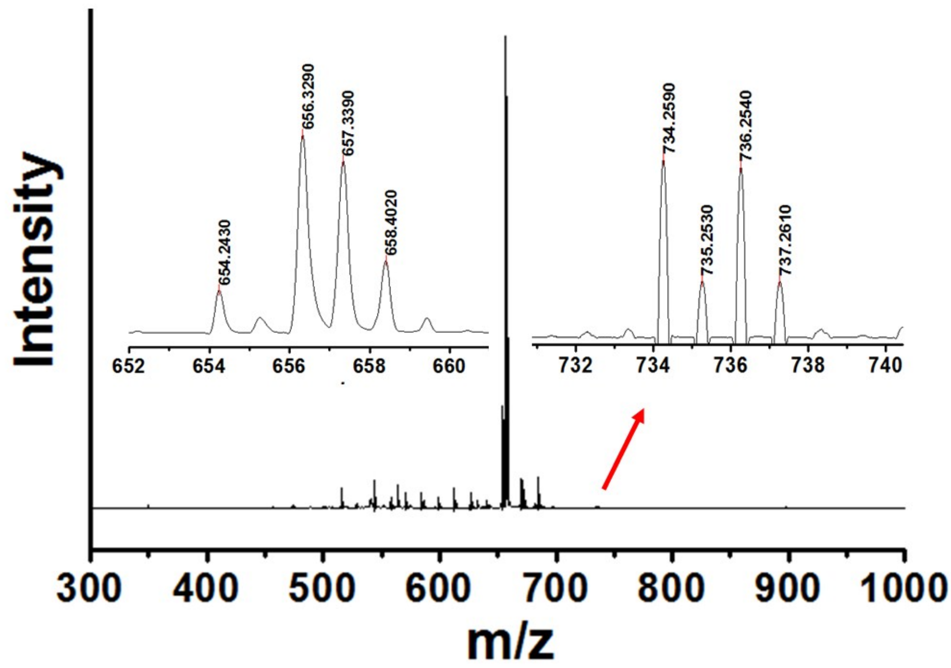


Fig. S9 The MALDI-TOF MS spectrum of compounds NCPy-salt.

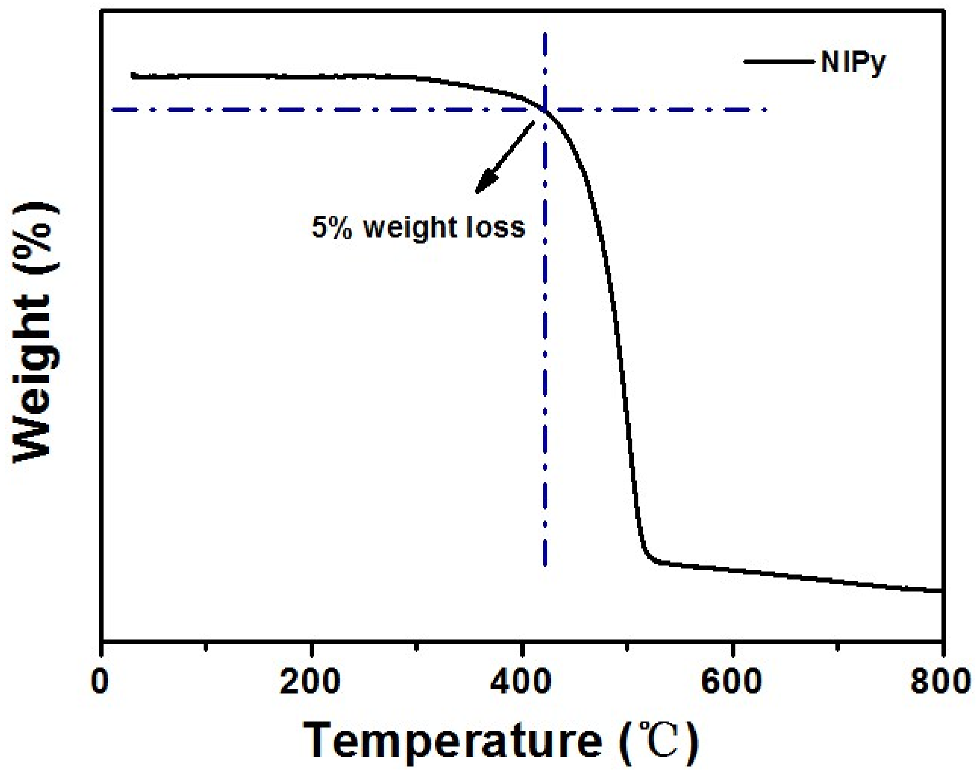


Fig. S10 TGA plot of the molecule NCPy, with a heating rate of 10℃/min under N_2 atmosphere.

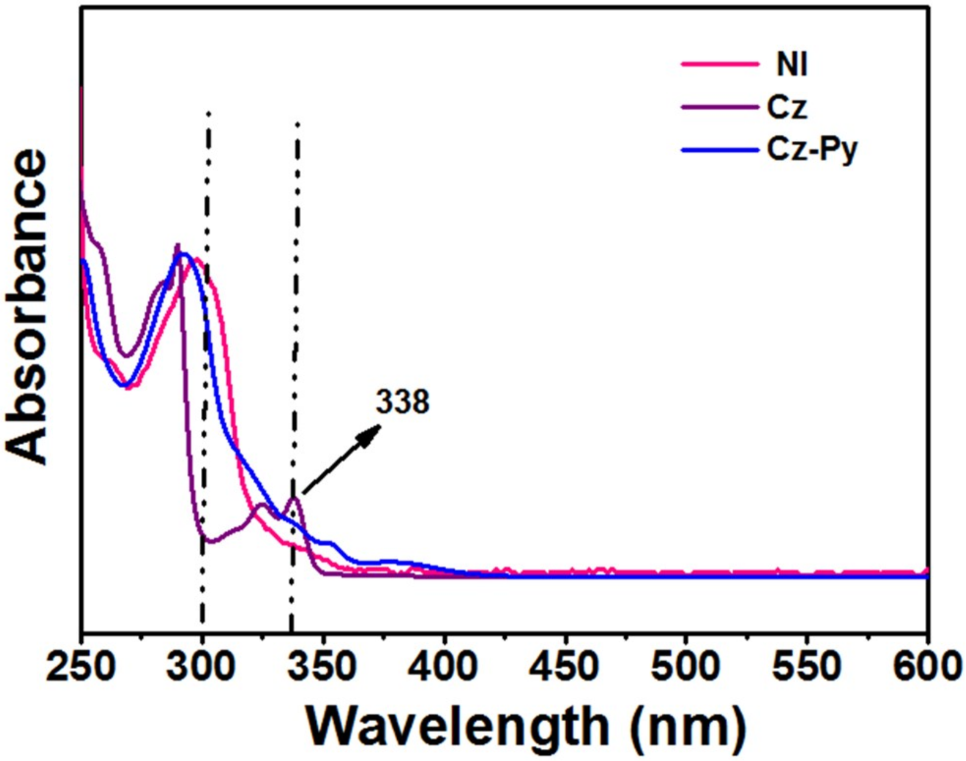


Fig. S11 Uv-vis absorption spectra of Cz and NI in acetonitrile solution.

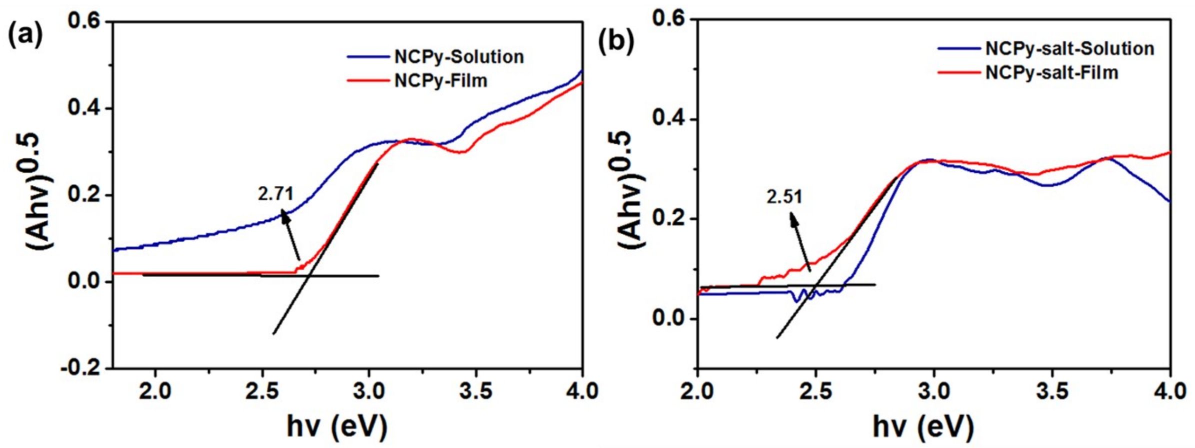


Fig. S12 $(Ahv)^{0.5}$-hv spectra of NCPy and NCPy-salt in DCM solution and in film states.

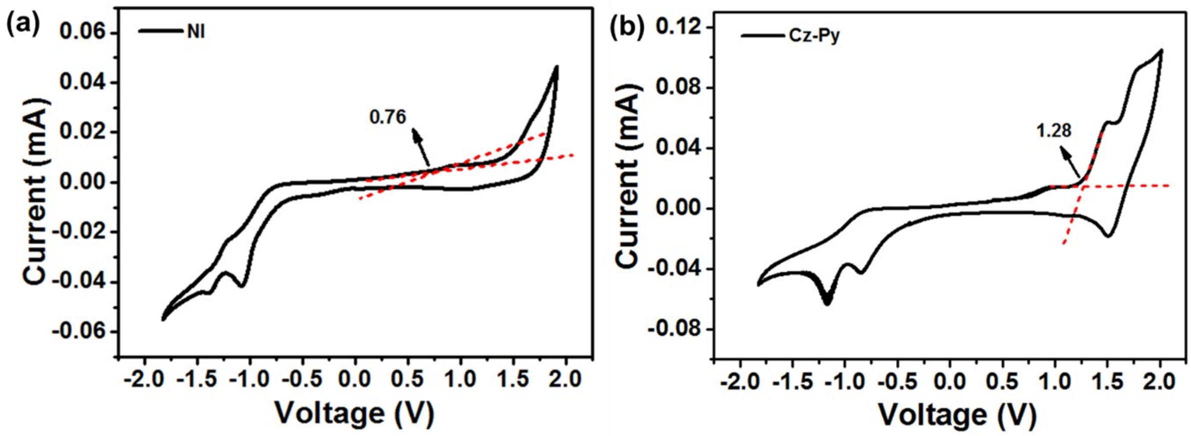


Fig. S13 Cyclic voltammograms of NI and Cz-Py films on the ITO glass substrate.

Table S1 Theoretical HOMO1/LUMO1 calculated by DFT and practical HOMO2/LUMO2 of NCPy and NCPy-salt.

Compound	HOMO1	LUMO1	HOMO2	LUMO2
NCPy	-5.10 eV	-3.00 eV	–5.19 eV	–2.48 eV
NCPy-salt	-4.95 eV	-3.26 eV	–5.10 eV	–2.59 eV

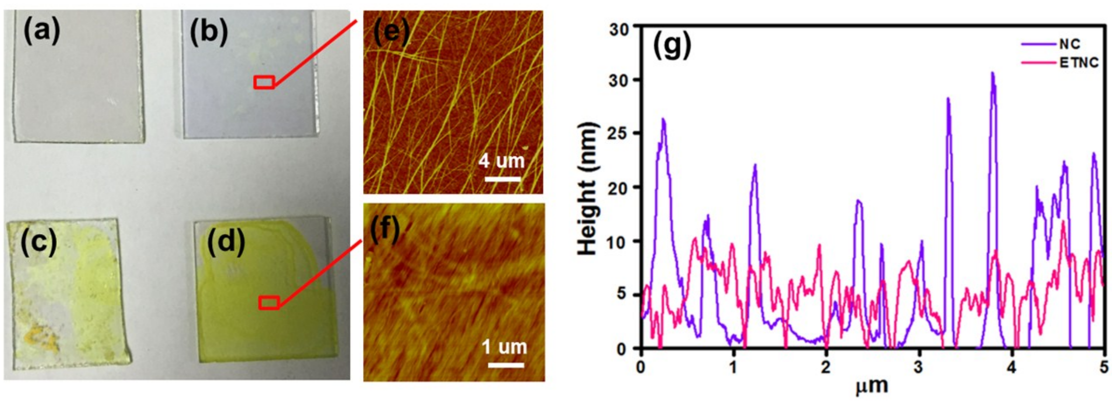


Fig. S14 (a-d) The optical photographs of the NCPy (a,c) and NCPy-salt (b,d) thin films spin-coated on ITO substrates at different rates：(a,b) 2000 r/min；(c,d) 300 r/min. (e-g) AFM images of NCPy-salt thin films (e,f) and their corresponding cross-section profiles (g).

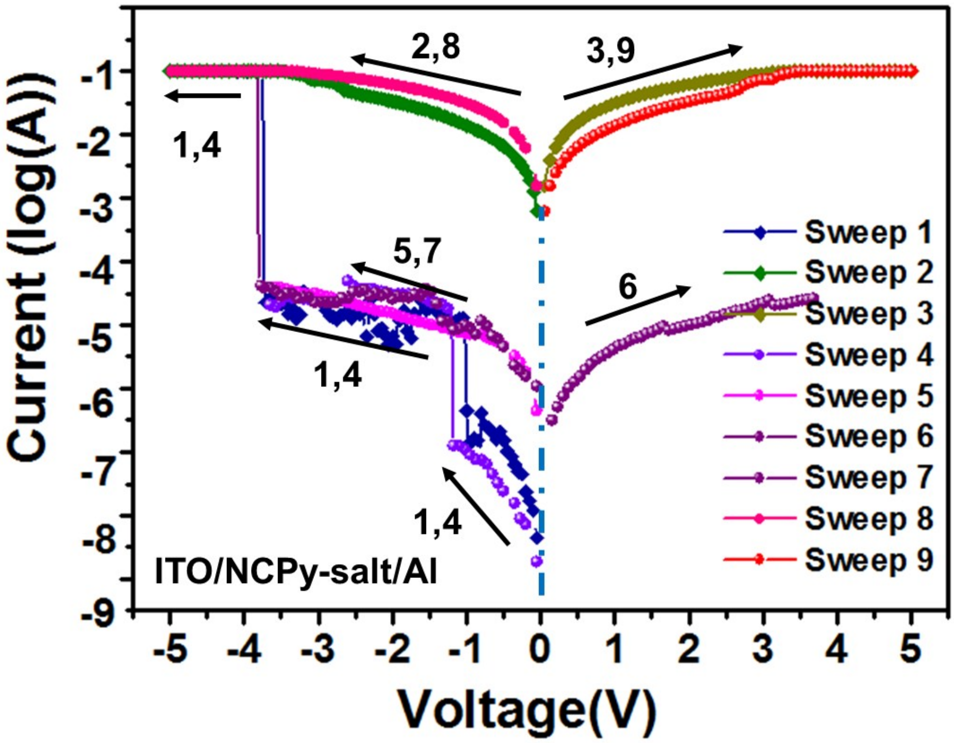


Fig. S15 Characteristic current–voltage (I–V) curves of NCPy-salt based memory devices. Sweep 1–3 are conducted on one cell of the device, and sweep 4–9 are conducted on another cell.

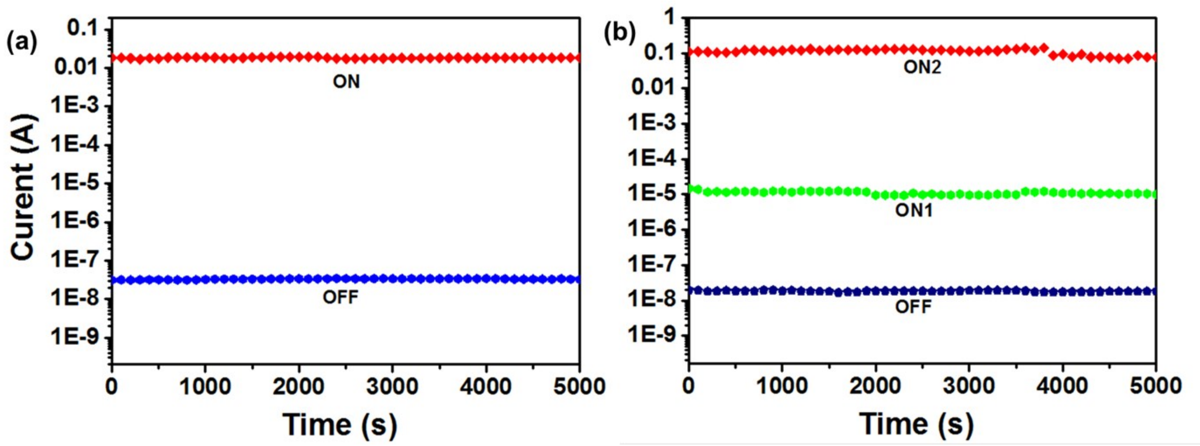


Fig. S16 Stability tests of the fabricated device: (a) NCPy; (b) NCPy-salt.

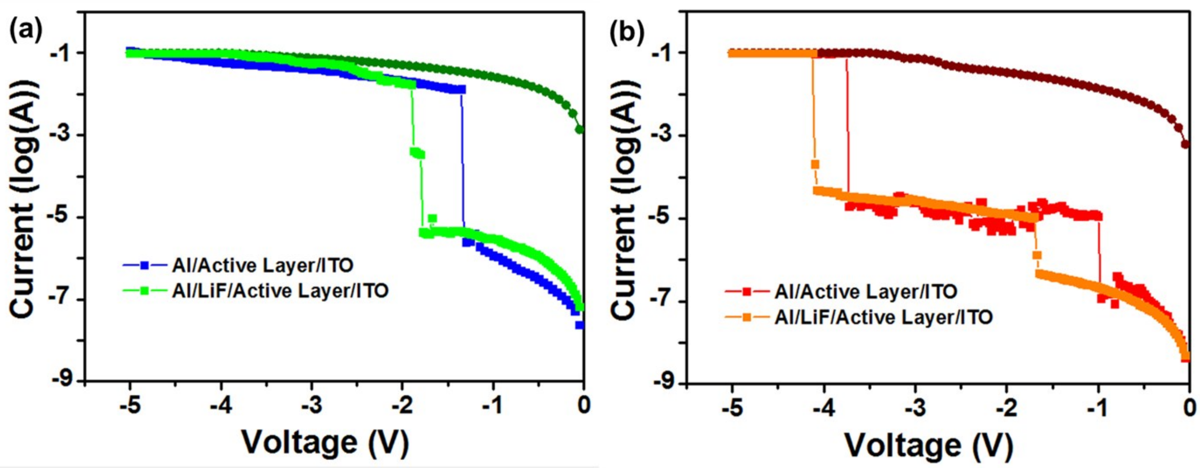


Fig. S17 Current–voltage (I–V) characteristics of (a) NCPy and (b) NCPy-salt based memory devices with ITO/Active Layer/LiF/Al structure.

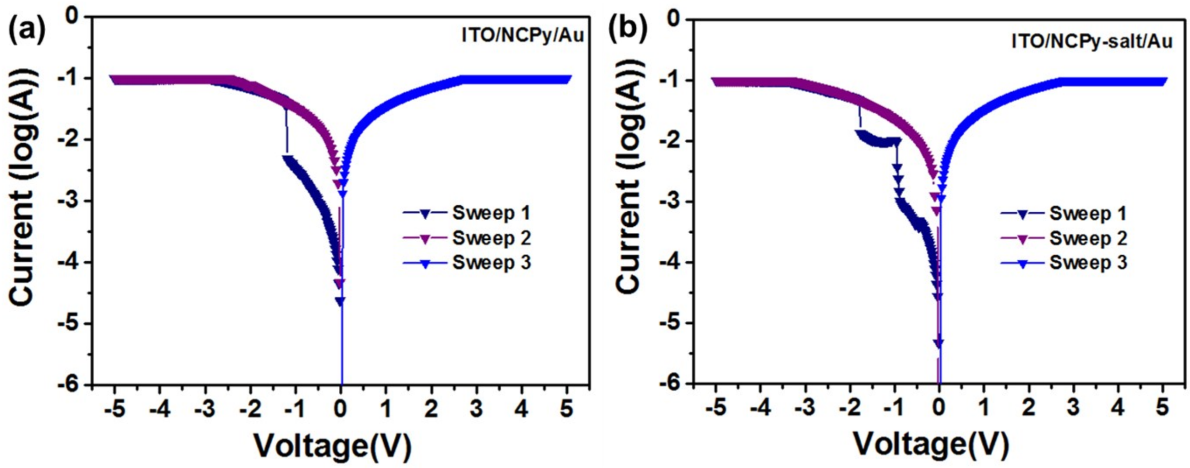


Fig. S18 Current–voltage (I–V) characteristics of (a) NCPy and (b) NCPy-salt based memory devices with ITO/Active Layer /Au structure.

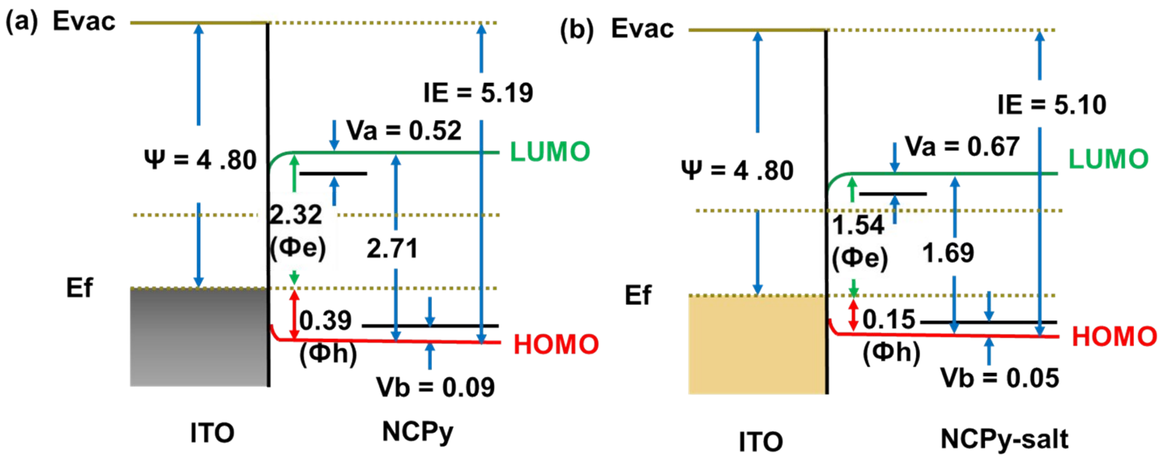


Fig. S19 Diagrams of the energy levels at the interfaces of a) ITO/NCPy, b) ITO/NCPy-salt. (Ψ is the work function, IE is the ionization energy, Φh is the hole injection barrier, and Φe is the electron injection barrier, Va and Vb are the band bending, respectively. Unit: eV)

Table S2 Excitation energies and oscillator strengths (138 HOMO, 139 LUMO) for NCPy calculated by time-dependent density functional theory (TD-DFT). The TD-DFT is simulated by td=(nstates=20) ucam-b3lyp/6-31++g.

Excited State 1:

3.000-A 1.9862 eV 624.23 nm f=0.0000 <S**2>=2.000

133A ->146A	-0.12837
136A ->139A	-0.42547
137A ->139A	0.38947
138A ->139A	0.32786
133B ->146B	0.12837
136B ->139B	0.42547
137B ->139B	-0.38947
138B ->139B	-0.32786
136A <-139A	-0.10858
136B <-139B	0.10858

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1699.01546158

Copying the excited state density for this state as the

1-particle RhoCI density.

Excited State 2:

3.000-A 2.9020 eV 427.23 nm f=0.0000 <S**2>=2.000

134A ->140A	0.19102
134A ->142A	-0.11516
136A ->140A	0.33789
137A ->140A	0.31438
137A ->142A	0.15839
138A ->141A	0.14449
138A ->142A	-0.17297
138A ->154A	-0.10792
134B ->140B	-0.19102
134B ->142B	0.11516
136B ->140B	-0.33789
137B ->140B	-0.31438
137B ->142B	-0.15839
138B ->141B	-0.14449
138B ->142B	0.17297
138B ->154B	0.10792

Excited State 3:

3.000-A 3.2058 eV 386.75 nm f=0.0000 <S**2>=2.000

134A ->139A	-0.10684
134A ->142A	-0.11791
136A ->141A	0.13270
137A ->141A	-0.14788
138A ->139A	0.14369
138A ->140A	0.41208
138A ->141A	-0.14581
138A ->142A	-0.15245
134B ->139B	0.10684
134B ->142B	0.11791
136B ->141B	-0.13270
137B ->141B	0.14788
138B ->139B	-0.14369
138B ->140B	-0.41208
138B ->141B	0.14581
138B ->142B	0.15245

Excited State 4:

3.000-A 3.3758 eV 367.27 nm f=0.0000 <S**2>=2.000

124A ->139A	-0.19289
126A ->139A	-0.15567
127A ->139A	-0.11826
133A ->139A	0.20792
136A ->141A	0.24661
137A ->140A	0.18641
137A ->141A	-0.21100
138A ->140A	-0.29113
138A ->141A	-0.15561
124B ->139B	0.19289
126B ->139B	0.15567
127B ->139B	0.11826
133B ->139B	-0.20792
136B ->141B	-0.24661
137B ->140B	-0.18641
137B ->141B	0.21100
138B ->140B	0.29113
138B ->141B	0.15561

Excited State 5:

3.000-A	3.4096 eV 363.64 nm f=0.0000 <S**2>=2.000
129A ->142A	0.14908
129A ->144A	0.10072
129A ->145A	0.22604
130A ->143A	-0.16727
130A ->144A	0.24640
130A ->145A	-0.21703
138A ->140A	-0.19302
138A ->142A	-0.20513
138A ->144A	-0.17642
138A ->145A	-0.10118
129B ->142B	-0.14908
129B ->144B	-0.10072
129B ->145B	-0.22605
130B ->143B	0.16727
130B ->144B	-0.24640
130B ->145B	0.21703
138B ->140B	0.19302
138B ->142B	0.20513
138B ->144B	0.17642
138B ->145B	0.10118

Excited State 6:

3.000-A	3.5709 eV 347.20 nm f=0.0000 <S**2>=2.000
125A ->142A	0.11064
127A ->142A	0.14898
132A ->149A	-0.39415
134A ->142A	-0.21286
136A ->140A	-0.15734
137A ->140A	-0.14180
137A ->142A	0.12296
138A ->140A	-0.22156
138A ->142A	-0.17187
125B ->142B	-0.11064
127B ->142B	-0.14899
132B ->149B	0.39414
134B ->142B	0.21286
136B ->140B	0.15734
137B ->140B	0.14180
137B ->142B	-0.12296
138B ->140B	0.22155
138B ->142B	0.17187

Excited State 7:

1.000-A	3.6273 eV 341.81 nm f=0.6351 <S**2>=0.000
136A ->139A	-0.24675
137A ->139A	0.33773
138A ->139A	0.55047
136B ->139B	-0.24675
137B ->139B	0.33773
138B ->139B	0.55047

Excited State 8:

3.000-A	3.6796 eV 336.95 nm f=0.0000 <S**2>=2.000
126A ->141A	-0.19059
128A ->139A	-0.50752
128A ->155A	-0.10379
128A ->156A	0.18141
129A ->139A	0.15242
131A ->141A	-0.22071
126B ->141B	0.19059
128B ->139B	0.50752
128B ->155B	0.10379
128B ->156B	-0.18141
129B ->139B	-0.15243
131B ->141B	0.22071

Excited State 9:

3.000-A 3.7664 eV 329.19 nm f=0.0000 <S**2>=2.000

126A ->139A	-0.17491
128A ->141A	-0.31897
129A ->139A	-0.11823
131A ->139A	-0.45562
131A ->156A	0.14691
126B ->139B	0.17491
128B ->141B	0.31897
129B ->139B	0.11823
131B ->139B	0.45562
131B ->156B	-0.14691

Excited State 10:

3.000-A 3.7737 eV 328.55 nm f=0.0000 <S**2>=2.000

133A ->139A	-0.59526
137A ->140A	0.13301
138A ->139A	0.13440
138A ->141A	-0.10852
133B ->139B	0.59526
137B ->140B	-0.13301
138B ->139B	-0.13440
138B ->141B	0.10852

Excited State 11:

3.000-A 3.8359 eV 323.22 nm f=0.0000 <S**2>=2.000

135A ->142A	-0.52241
135A ->144A	0.18935
135A ->145A	0.12508
135A ->152A	-0.11916
135A ->154A	0.18855
135A ->170A	0.11887
135B ->142B	0.52241
135B ->144B	-0.18934
135B ->145B	-0.12508
135B ->152B	0.11916
135B ->154B	-0.18855
135B ->170B	-0.11887

Excited State 12:

3.000-A 3.9235 eV 316.00 nm f=0.0000 <S**2>=2.000

126A ->139A	-0.17033
133A ->139A	-0.20231
134A ->139A	0.10064
136A ->139A	-0.12773
136A ->140A	-0.10129
136A ->141A	0.15463
137A ->140A	-0.26916
137A ->141A	-0.12479
138A ->139A	-0.29784
138A ->144A	0.10016
138A ->152A	0.12412
138A ->154A	-0.13751
126B ->139B	0.17033
133B ->139B	0.20230
134B ->139B	-0.10064
136B ->139B	0.12773
136B ->140B	0.10130
136B ->141B	-0.15463
137B ->140B	0.26917
137B ->141B	0.12479
138B ->139B	0.29784
138B ->144B	-0.10016
138B ->152B	-0.12412
138B ->154B	0.13751

Excited State 13:

3.000-A 4.0565 eV 305.65 nm f=0.0000 <S**2>=2.000

125A ->142A	0.11334
127A ->140A	-0.12535
132A ->149A	-0.27768
134A ->140A	-0.10665
137A ->140A	0.17884
138A ->140A	0.19987
138A ->142A	0.27517
138A ->156A	-0.10114
125B ->142B	-0.11335
127B ->140B	0.12535
132B ->149B	0.27768
134B ->140B	0.10665
137B ->140B	-0.17885
138B ->140B	-0.19987
138B ->142B	-0.27518
138B ->156B	0.10114

Excited State 14:

1.000-A 4.1401 eV 299.47 nm f=0.0108 <S**2>=0.000

126A ->141A	0.15146
128A ->139A	0.44004
128A ->156A	-0.13576
129A ->139A	-0.15744
131A ->141A	0.15620
136A ->139A	-0.14152
138A ->139A	-0.11740
138A ->140A	-0.31312
126B ->141B	0.15146
128B ->139B	0.44004
128B ->156B	-0.13576
129B ->139B	-0.15744
131B ->141B	0.15621
136B ->139B	-0.14152
138B ->139B	-0.11741
138B ->140B	-0.31312

Excited State 15:

1.000-A 4.1507 eV 298.71 nm f=0.0464 <S**2>=0.000

128A ->139A	0.25885
137A ->139A	0.10571
138A ->140A	0.53997
128B ->139B	0.25885
137B ->139B	0.10572
138B ->140B	0.53997

Excited State 16:

3.000-A 4.2404 eV 292.39 nm f=0.0000 <S**2>=2.000

125A ->140A	-0.12413
131A ->139A	0.10449
134A ->140A	-0.17319
137A ->139A	0.14440
137A ->140A	0.17071
138A ->139A	-0.36865
138A ->141A	-0.12180
138A ->154A	0.10775
125B ->140B	0.12413
131B ->139B	-0.10449
134B ->140B	0.17319
137B ->139B	-0.14440
137B ->140B	-0.17071
138B ->139B	0.36865
138B ->141B	0.12180
138B ->154B	-0.10775

Excited State 17:

1.000-A	4.2517 eV 291.61 nm f=0.0095 <S**2>=0.000
126A ->139A	0.17427
128A ->139A	-0.13506
128A ->141A	0.21234
131A ->139A	0.33246
134A ->139A	0.11401
136A ->139A	-0.21331
137A ->139A	0.27162
138A ->139A	-0.20982
138A ->141A	0.13227
126B ->139B	0.17427
128B ->139B	-0.13505
128B ->141B	0.21233
131B ->139B	0.33246
134B ->139B	0.11402
136B ->139B	-0.21331
137B ->139B	0.27163
138B ->139B	-0.20982
138B ->141B	0.13227

Excited State 18:

3.000-A	4.2709 eV 290.30 nm f=0.0000 <S**2>=2.000
123A ->139A	0.12996
126A ->141A	0.12857
131A ->141A	-0.19965
133A ->141A	-0.10334
136A ->139A	-0.24814
137A ->139A	-0.31889
137A ->141A	0.10147
137A ->144A	0.10344
137A ->152A	0.11345
137A ->154A	-0.11428
138A ->142A	-0.10248
123B ->139B	-0.12997
126B ->141B	-0.12858
131B ->141B	0.19965
133B ->141B	0.10334
136B ->139B	0.24814
137B ->139B	0.31890
137B ->141B	-0.10148
137B ->144B	-0.10344
137B ->152B	-0.11345
137B ->154B	0.11429
138B ->142B	0.10247

Excited State 19:

1.000-A 4.2729 eV 290.16 nm f=0.0094 <S**2>=0.000	
126A ->139A	-0.19558
128A ->139A	-0.12614
128A ->141A	-0.23810
129A ->139A	-0.10003
131A ->139A	-0.25731
133A ->139A	-0.11041
134A ->139A	0.10189
136A ->139A	-0.16382
137A ->139A	0.32032
137A ->140A	0.10875
138A ->139A	-0.26518
126B ->139B	-0.19557
128B ->139B	-0.12614
128B ->141B	-0.23810
129B ->139B	-0.10003
131B ->139B	-0.25731
133B ->139B	-0.11041
134B ->139B	0.10189
136B ->139B	-0.16383
137B ->139B	0.32031
137B ->140B	0.10875
138B ->139B	-0.26518

Excited State 20:

3.000-A 4.2987 eV 288.42 nm f=0.0000 <S**2>=2.000	
123A ->139A	0.13324
126A ->139A	0.10966
126A ->141A	0.16572
131A ->141A	-0.28391
133A ->141A	-0.10483
133A ->146A	0.10382
136A ->139A	0.16316
137A ->139A	0.26682
123B ->139B	-0.13325
126B ->139B	-0.10967
126B ->141B	-0.16573
131B ->141B	0.28392
133B ->141B	0.10483
133B ->146B	-0.10382
136B ->139B	-0.16315
137B ->139B	-0.26682

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