

# Supplementary Information

## Morphology optimization of side-chain copolymers enables ternary memory device with high stability and reproducibility

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### A. Experimental Section

#### 1. Materials

Carbazole (Cz) (95%), Nitric acid (68%), azodiisobutyronitrile (AIBN) (98%), potassium hydroxide (KOH) (AR), 2-bromoethanol (98%), and methacryloyl chloride (95%) were all purchased from from Shanghai Chemical Reagent Co. Ltd. AIBN was used after the recrystallization from ethanol. All other reagents were used without further purification.

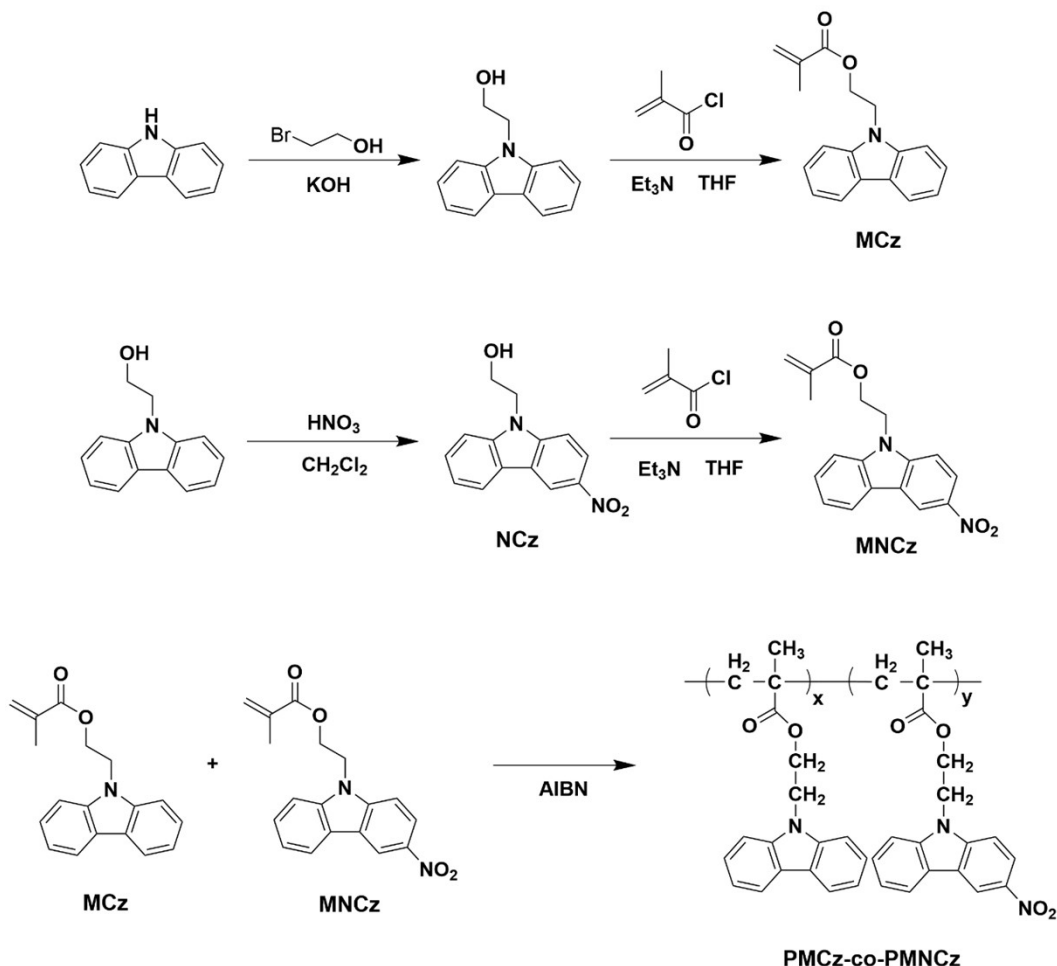
#### 2. Instrumentation and characterizations

<sup>1</sup>H NMR spectra were measured on an Inova 400 MHz FT-NMR workstation. All electrical measurements of the devices were characterized under ambient conditions without any encapsulation using a Tektronix Keithley 4200 semi-conductor parameter analyzer. The current–voltage (*I*–*V*) characteristics of the indium-tin oxide (ITO)/PMCz<sub>x</sub>-co-PMNCz<sub>y</sub>/Al sandwich memory devices are recorded at a scan speed of 0.01 V s<sup>-1</sup>. All electrical measurements of the device were taken at ambient conditions without any encapsulation. Ultraviolet-visible (UV-Vis) absorption spectra were obtained with the use of a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry was performed

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on a CorrTest CS Electrochemical Workstation analyzer at room temperature. X-ray diffraction (XRD) pattern was taken on an X'Pert-Pro MPD X-ray diffractometer. Atomic force microscopy (AFM) measurement was carried out by using a MFP-3DTM AFM instrument in tapping mode.

### 3. Synthetic procedures



**Scheme S1.** The synthetic routes of the designed monomers and target copolymers PMCz<sub>x</sub>-co-PMNCz<sub>y</sub>.

**(1) 9H-Carbazole-9-ethanol.** KOH (14.0 g), carbazole (6.68 g, 40 mmol) and 80 ml DMF solvent were added into a 250 ml round-bottom flask and the solution was stirred for about 45 min in room temperature. Then 2-bromoethanol (3.5 ml, 52 mmol) was added slowly to the above solution, and the mixture was stirred for another 10 h. After finishing the reaction, the mixture was poured into 200 ml dilute water and stirred for about 1h. Then the aqueous solution was stand for 6 h to precipitate the solid phase, filtrate, washed with ethanol for several times to get the product as a white needle (80%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.10 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.39 (t, J = 7.1 Hz, 2H), 7.14 (t, J = 7.0 Hz, 2H), 4.85 (t, J = 5.5 Hz, 1H), 4.39 (t, J = 5.7 Hz, 2H), 3.74 (d, J = 5.6 Hz, 2H).

**(2) 2-(9H-carbazol-9-yl)ethyl methacrylate (MCz).** Compound 1 (4.22 g, 20 mmol), Et<sub>3</sub>N (3.03 g, 30 mmol) and 40 ml THF were added into a 100 ml round-bottom flask, and the mixture solution was cooled to 0 °C in an ice-bath. methacryloyl chloride (3.12 g, 30 mmol) in 10 ml THF was added slowly to the above solution and reacted in 0 °C for about 2h, then the solution could be warmed to room temperature. After reacting for 6 h in room temperature, the mixture was poured into water, extracted 3 times with 20 mL of dichloromethane, dried with Na<sub>2</sub>SO<sub>4</sub>. After rotary evaporation under reduced pressure to remove the excess solvent, the residue was purified through column chromatography on a silica gel with hexane/ethyl acetate (2:1, v/v) as the eluent. The product was obtained as a pale powder (95%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.11 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.5 Hz, 2H), 7.41 (ddd, J = 8.3, 7.1, 1.2 Hz, 2H), 7.20 – 7.13 (m, 2H), 5.69 (dd, J = 1.6, 1.0 Hz, 1H), 5.47 (p, J = 1.5 Hz, 1H), 4.71 (t, J = 5.1 Hz, 2H), 4.42 (t, J = 5.1 Hz, 2H), 1.60 (t, J = 1.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 166.85, 140.56, 135.84, 126.59, 126.11, 122.61, 120.72, 119.43, 109.92, 63.35, 41.63, 18.29.

**(3) 2-(3-nitro-9H-carbazol-9-yl)ethan-1-ol (NCz).** Compound 1 (2.95 g, 14 mmol) was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred in an ice-water bath for 30 min. Then, 2.0 g of concentrated HNO<sub>3</sub> was added very slowly for approximately 1 h. Finally, the mixture was stirred at room temperature for 1 h, and a yellow solid was obtained by filtration (55%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 9.16 – 9.13 (m, 1H), 8.34 (dd, J = 30.9, 7.1 Hz, 2H), 7.73 (dd, J = 24.0, 8.7 Hz, 2H), 7.53 (s, 1H), 7.29 (s, 1H), 4.89 (t, J = 5.5 Hz, 1H), 4.50 (t, J = 5.4 Hz, 2H), 3.77 (d, J = 5.3 Hz, 2H).

**(4) 2-(3-nitro-9H-carbazol-9-yl)ethyl methacrylate (MNCz).** NCz (1.28 g, 5 mmol), Et<sub>3</sub>N (1.01 g, 10 mmol) and 80 ml DMF were added into a 100 ml round-bottom flask, and the mixture solution was cooled to 0 °C in an ice-bath. methacryloyl chloride (1.04 g, 10 mmol) in 10 ml DMF was added slowly to the above solution and reacted in 0 °C for about 2 h, then the solution could be warmed to room temperature. After reacting for 6 h in room temperature, the mixture was poured into water, extracted 3 times with 20 mL of dichloromethane, dried with Na<sub>2</sub>SO<sub>4</sub>. After rotary evaporation under reduced pressure to remove the excess solvent, the residue was purified through column chromatography on a silica gel with hexane/ethyl acetate (7:1, v/v) as the eluent. The product was obtained as a yellow solid (60%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 9.17 (d, J = 2.3 Hz, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.34 – 8.30 (m, 1H), 7.84 (d, J = 9.1 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.55 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.33 – 7.28 (m, 1H), 5.66 (dd, J = 1.6, 1.0 Hz, 1H), 5.47 (t, J = 1.6 Hz, 1H), 4.83 (t, J = 5.0 Hz, 2H), 4.46 (t, J = 5.0 Hz, 2H), 1.57 (t, J = 1.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 166.70, 144.01, 141.89, 140.60, 135.70, 127.87, 126.70, 122.70, 122.52, 121.94, 121.68, 121.26, 117.84, 111.08, 110.40, 63.13, 42.26, 18.26.

**(5) Random copolymer PMCz<sub>1</sub>-co-PMNCz<sub>1</sub>.** Under N<sub>2</sub> flow, MCz (558 mg, 2 mmol), MNCz (648 mg, 2 mmol), AIBN (1.6 mg, 0.01 mmol) and 3 ml cyclohexanone was added into a polymerization pipe, and reacted at 75 °C for 24 h. Then the solution was poured into 200 ml methanol, precipitate, and filtrate, dry in vacuum to get the polymer PMCz<sub>1</sub>-co-PMNCz<sub>1</sub>. Mn = 4231, Mw = 7278, PDI = 1.72.

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**(6) Random copolymer  $\text{PMCz}_2\text{-co-PMNCz}_1$ .** Under  $\text{N}_2$  flow, MCz (558 mg, 2 mmol), MNCz (324 mg, 1 mmol), AIBN (1.6 mg, 0.01 mmol) and 3 ml cyclohexanone was added into a polymerization pipe, and reacted at 75 °C for 24 h. Then the solution was poured into 200 ml methanol, precipitate, and filtrate, dry in vacuum to get the polymer  $\text{PMCz}_2\text{-co-PMNCz}_1$ . Mn = 6098, Mw = 9878, PDI = 1.62

**(7) Random copolymer  $\text{PMCz}_4\text{-co-PMNCz}_1$ .** Under  $\text{N}_2$  flow, MCz (558 mg, 2 mmol), MNCz (162 mg, 0.5 mmol), AIBN (1.6 mg, 0.01 mmol) and 3 ml cyclohexanone was added into a polymerization pipe, and reacted at 75 °C for 24 h. Then the solution was poured into 200 ml methanol, precipitate, and filtrate, dry in vacuum to get the polymer  $\text{PMCz}_4\text{-co-PMNCz}_1$ . Mn = 7593, Mw = 11618, PDI = 1.53.

#### 4. Memory device fabrication

The indium-tin-oxide (ITO) glass was pre-cleaned with water, acetone, and alcohol in an ultrasonic bath for 30 min, respectively. The solution of 12 mg polymer  $\text{PMCz}_x\text{-co-PMNCz}_y$  in 1 mL cyclohexanone was filtered through a micro filter equipped with a 0.22  $\mu\text{m}$  sized pinhole. The filtrates were spin coated on the ITO substrate at a speed of 500 RPM for 12 s, followed by 2100 RPM for 20 s. The solution was evaporated under high vacuum ( $10^{-3}$  Torr) overnight and the film thickness was controlled by the speed of the spin-coating machine. An aluminum layer was thermally evaporated and deposited onto the active film at about  $2 \times 10^{-6}$  Torr through a shadow mask to form the top electrode, and the deposit speed was controlled to be 2.5 Å per second. The sandwich-structured memory device area of about 0.0314  $\text{mm}^2$  was obtained. Subsequently, to obtain the film after voltage sweep, a liquid Hg droplet was deposited on the film and served as the top electrode, then Hg droplet was removed after the voltage sweeping on device  $\text{Hg/PMCz}_x\text{-co-PMNCz}_y/\text{ITO}$  to obtain the voltage-swept film.

#### 5. Computational details

The electrostatic potential (ESP) surfaces and the HOMO/LUMO orbital surfaces of Cz and NCz were performed with the Gaussian 09 suite of programs through density functional theory (DFT) using the Becke's three-parameter functional combined with the Lee, Yang, and Parr's correlation functional (B3LYP), along with the 6-31G basis set. (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T. J. A.; Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.;

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Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009)

## B. Figures

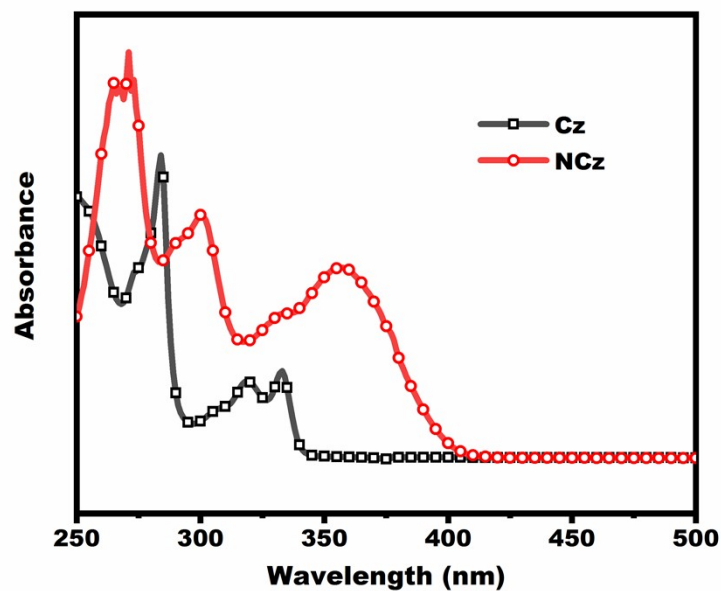


Figure S1. UV-vis absorption spectra of Cz and NCz monomers in solution.

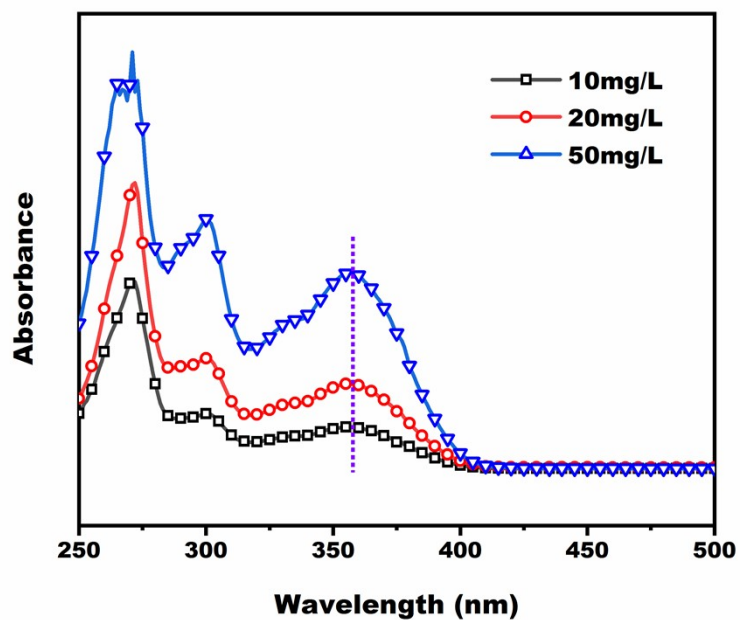
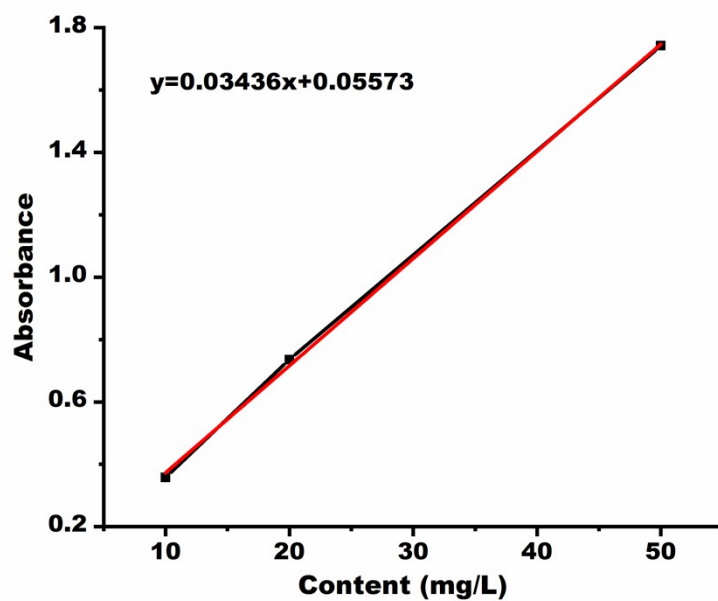
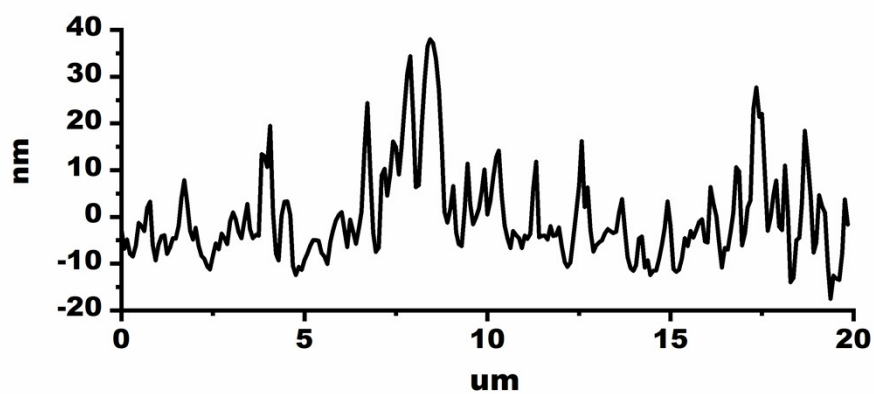


Figure S2. UV-vis absorption spectrum of monomer NCz with different contents in solution.



**Figure S3.** The linear relationship of the UV-vis absorbance intensity to the different contents of NCz in solution.



**Figure S4.** The cross-section profile of the corresponding tapping mode AFM image.

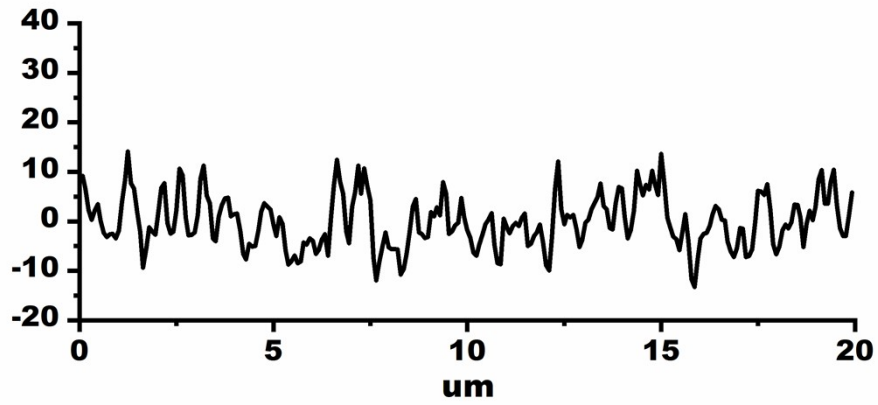


Figure S5. The cross-section profile of the corresponding tapping mode AFM image.

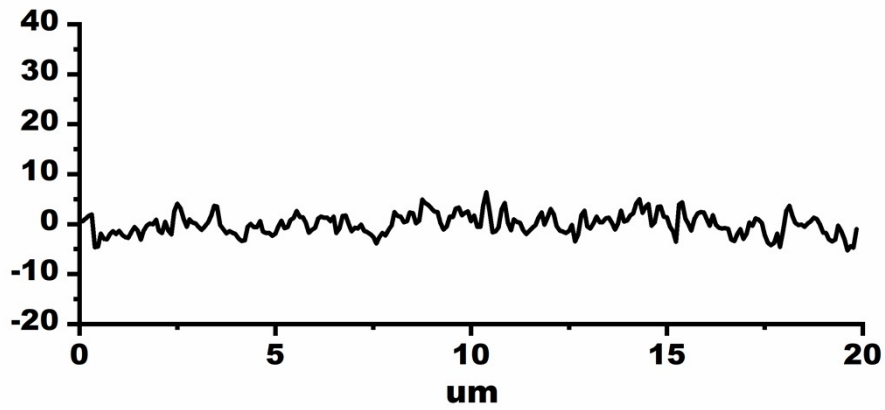


Figure S6. The cross-section profile of the corresponding tapping mode AFM image.

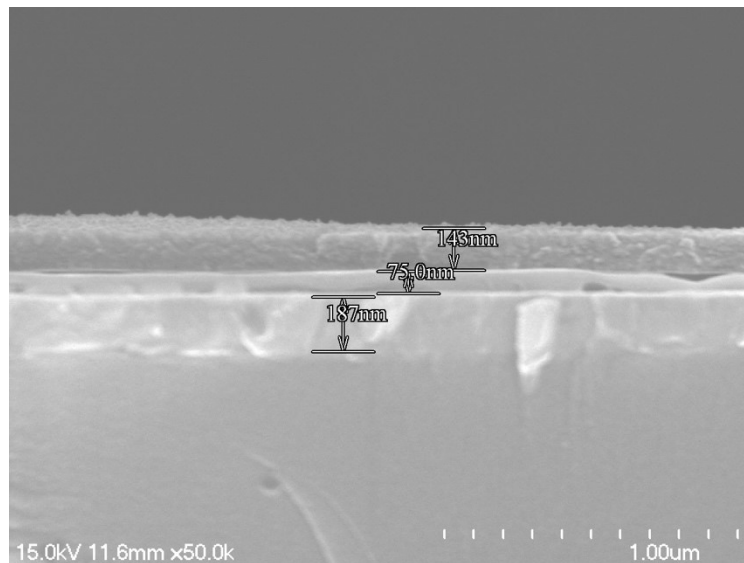


Figure S7. SEM image of a cross-section view of the sandwich device based on  $\text{PMNC}_x\text{-co-PMNC}_y$  polymers.

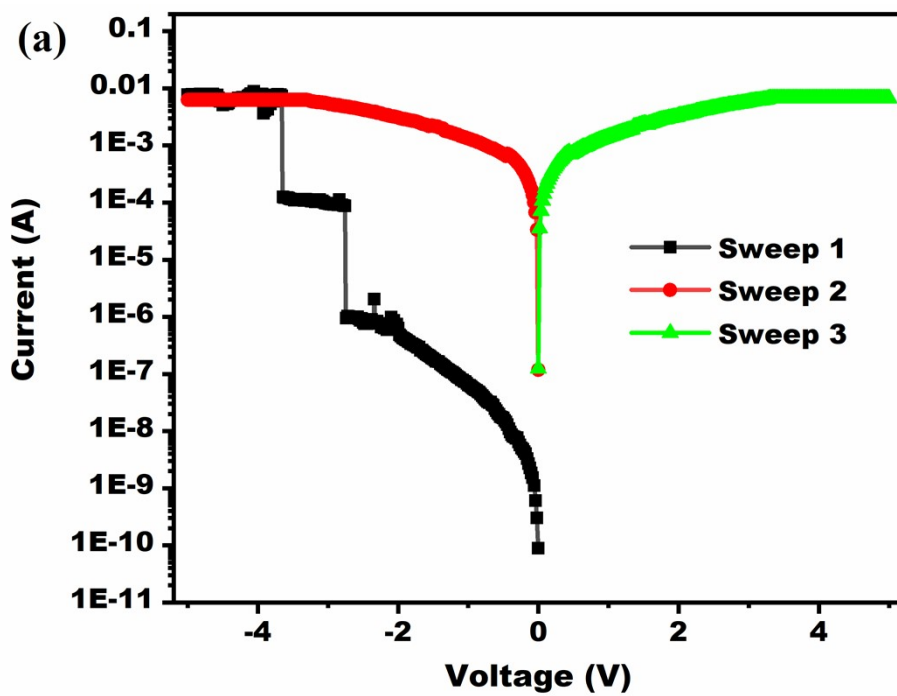


Figure S8. I-V curves for devices fabricated from PMNC<sub>1</sub>-co-PMNC<sub>1</sub>.

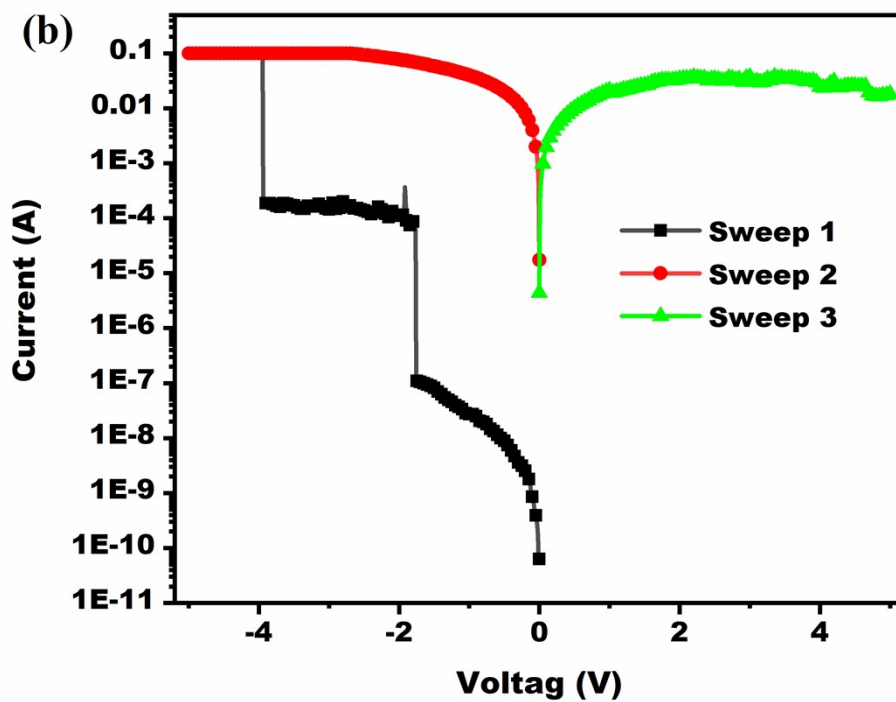


Figure S9. I-V curves for devices fabricated from PMNC<sub>2</sub>-co-PMNC<sub>1</sub>.



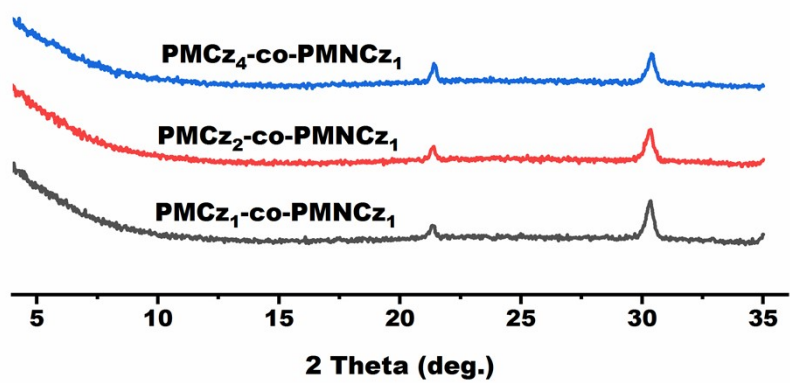


Figure S10. X-ray diffraction patterns of the three-polymeric films before voltage sweeping.

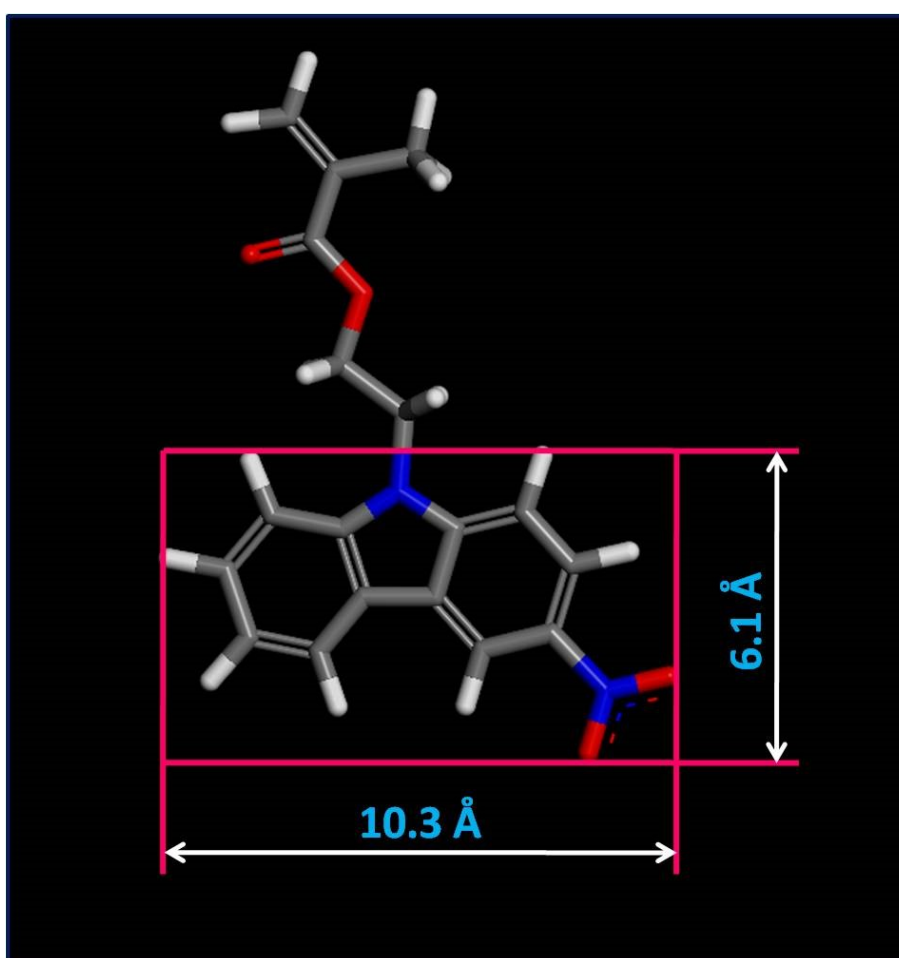


Figure S11. The optimized structure of MNCz monomer obtained from theoretical calculation.

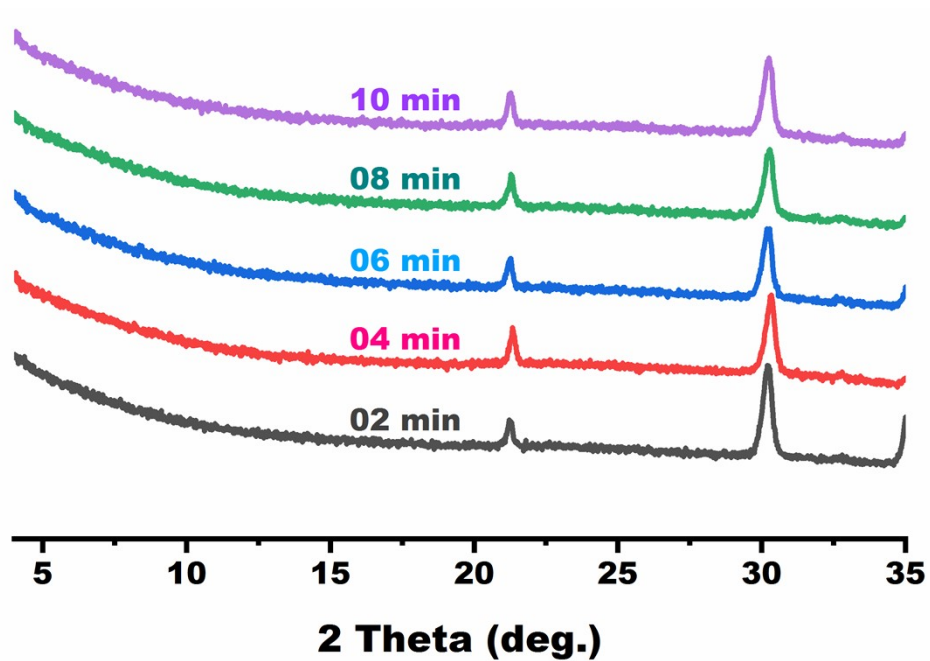


Figure S12. XRD patterns of PMCz4-co-PMNCz1 film after voltage stimulation.

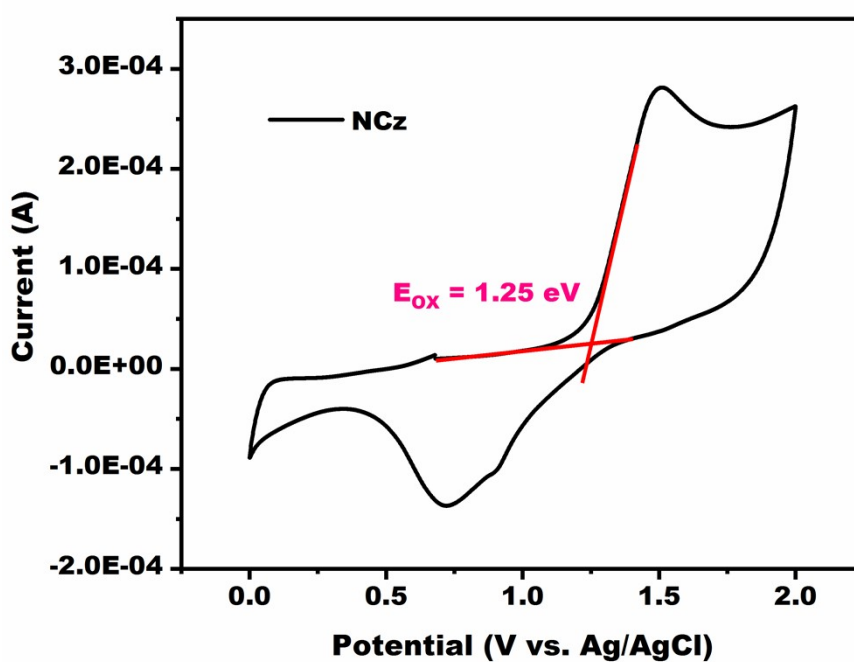


Figure S13. Cyclic voltammogram of MNCz in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) with  $n\text{-Bu}_4\text{NBF}_4$  (0.1 M) as electrolyte.

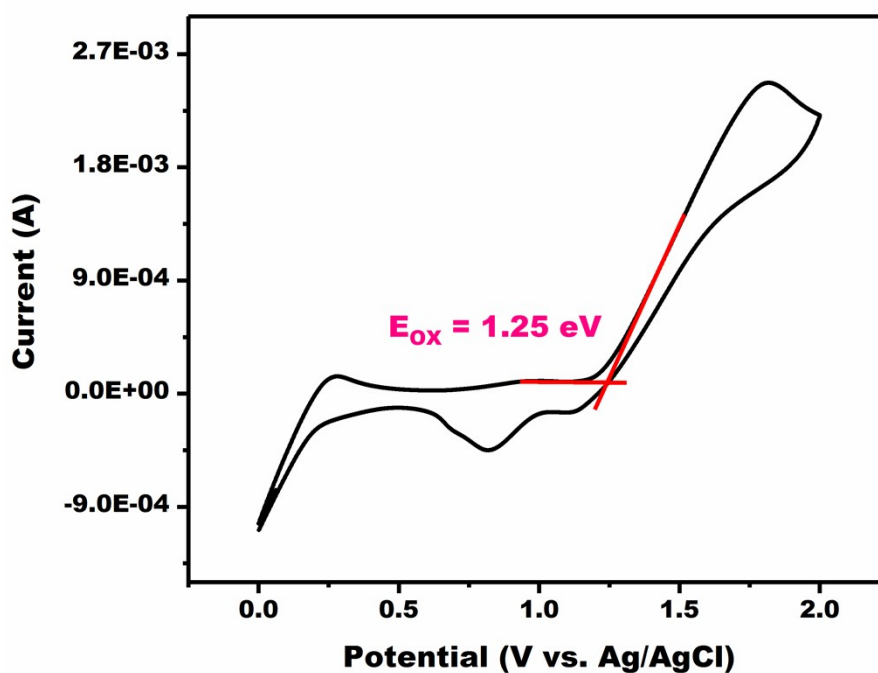


Figure S14. Cyclic voltammogram of MCz in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) with  $n\text{-Bu}_4\text{NBF}_4$  (0.1 M) as electrolyte.

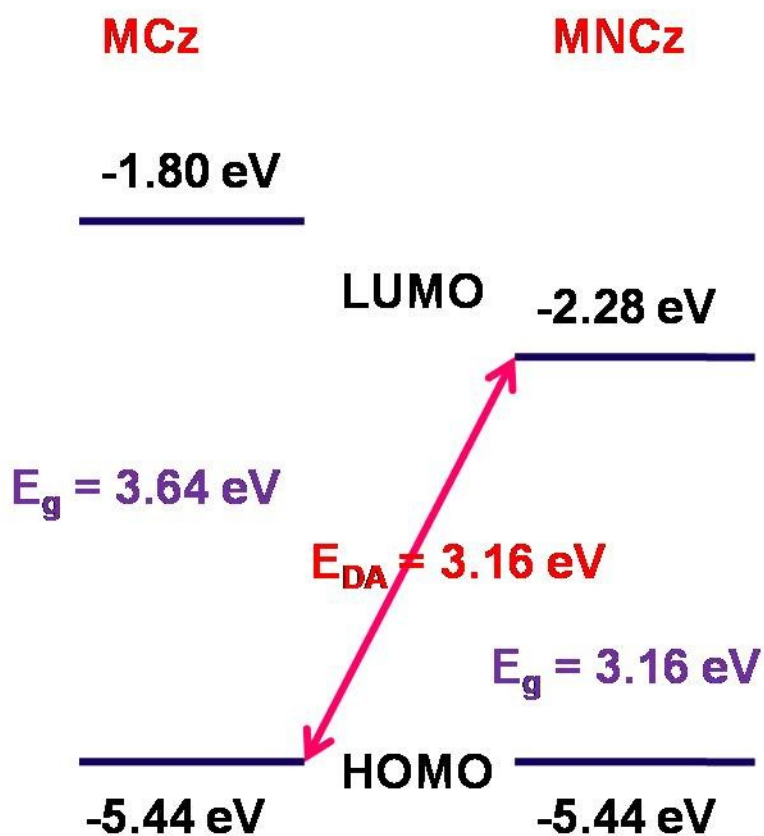


Figure S15. The experimental energy level diagram of MCz and MNCz.

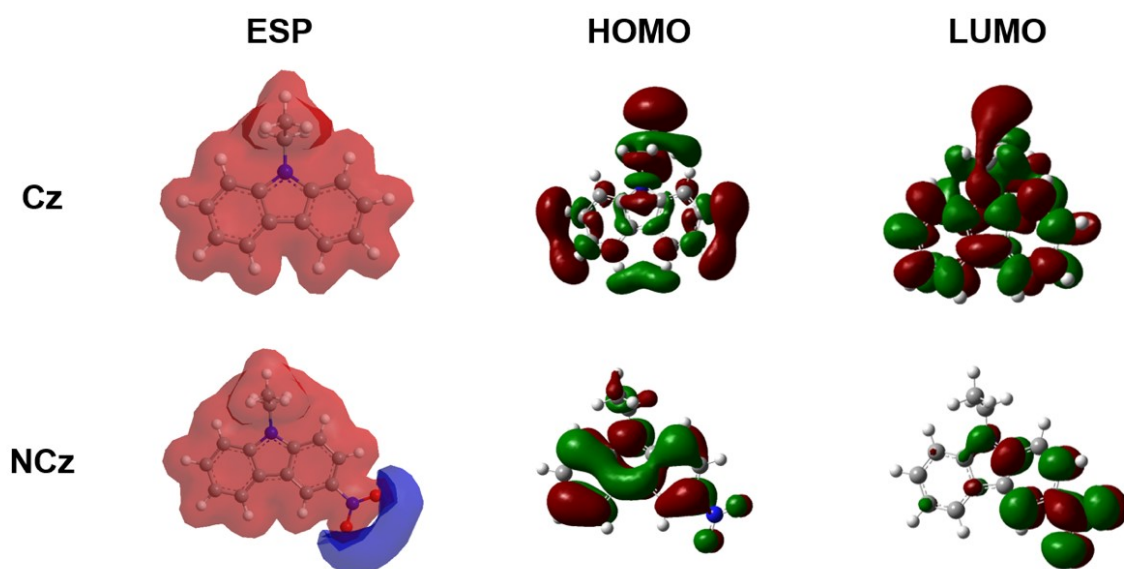


Figure S16. Molecular electrostatic potential (ESP) surfaces and molecular orbital energy levels of Cz and NCz.

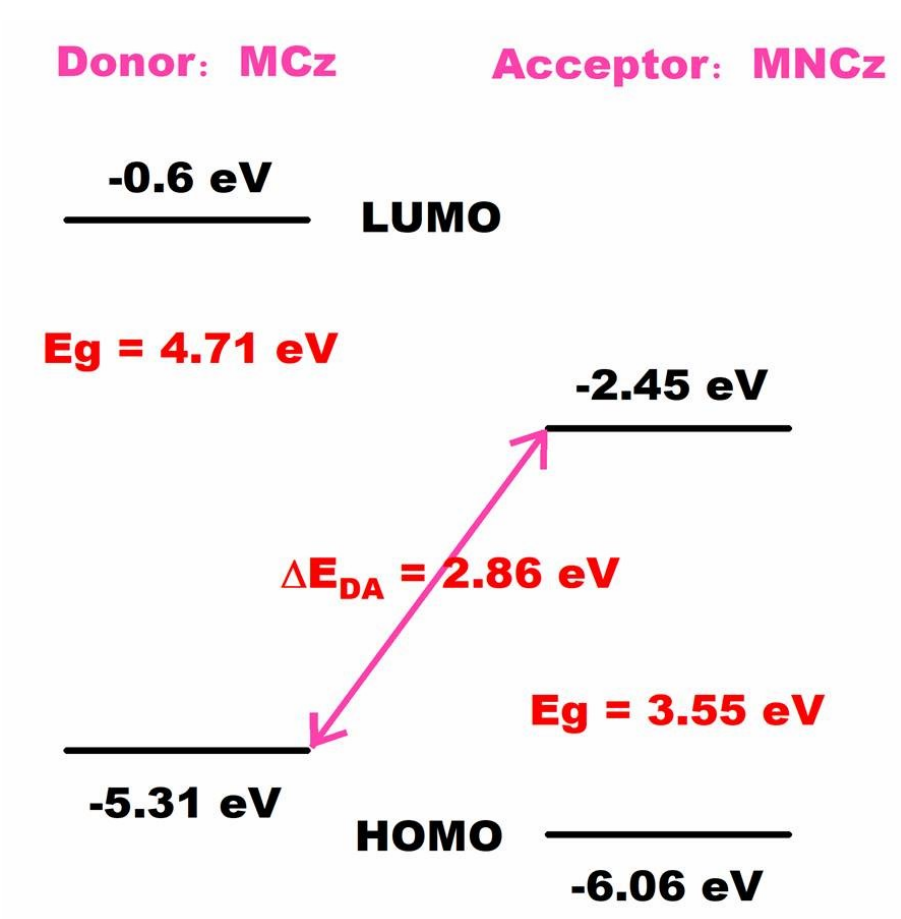


Figure S17. The theoretical energy level diagram of MCz and MNCz.

### C. <sup>1</sup>H NMR

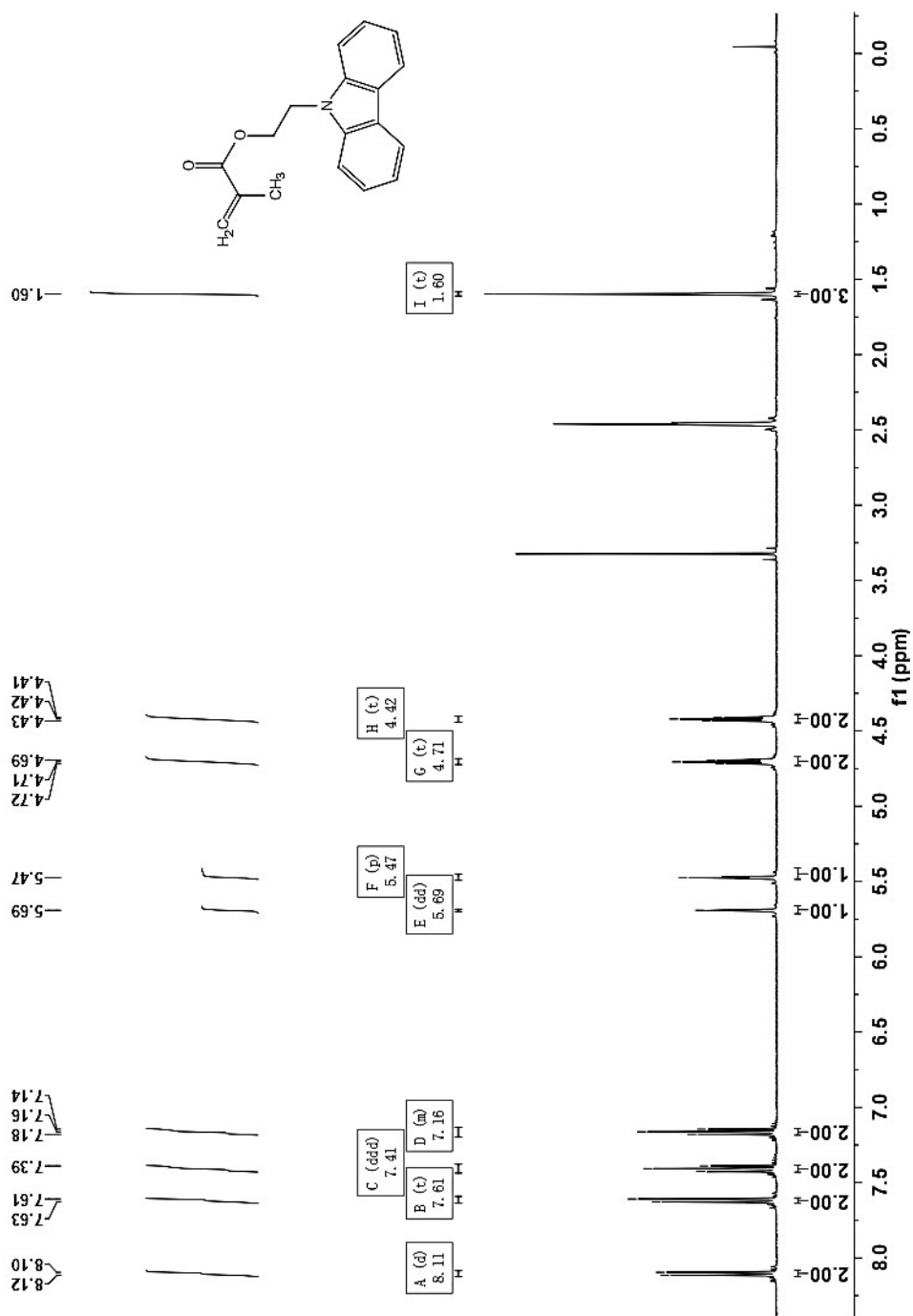


Figure S18. <sup>1</sup>H NMR spectra of the monomer MCz.

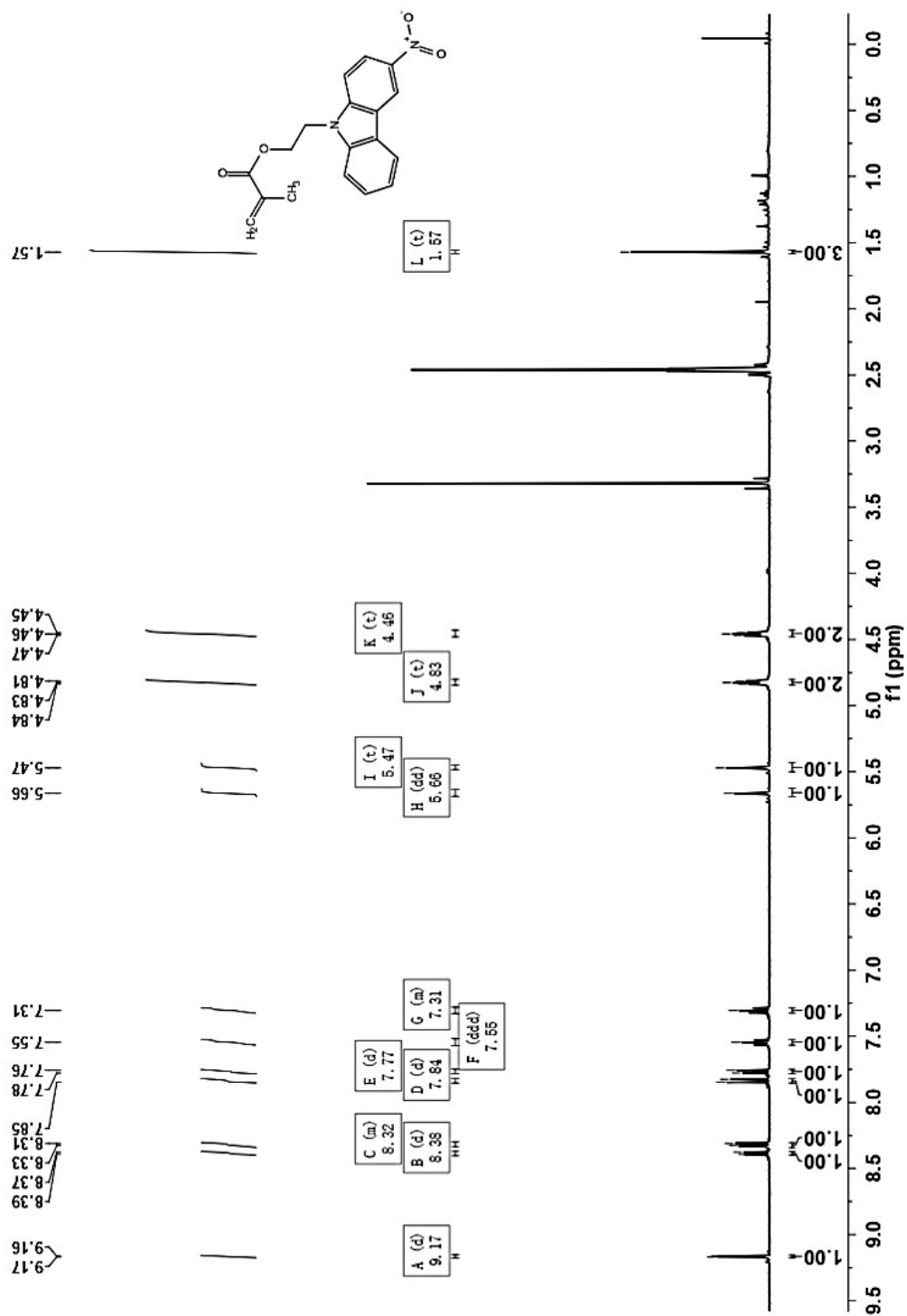
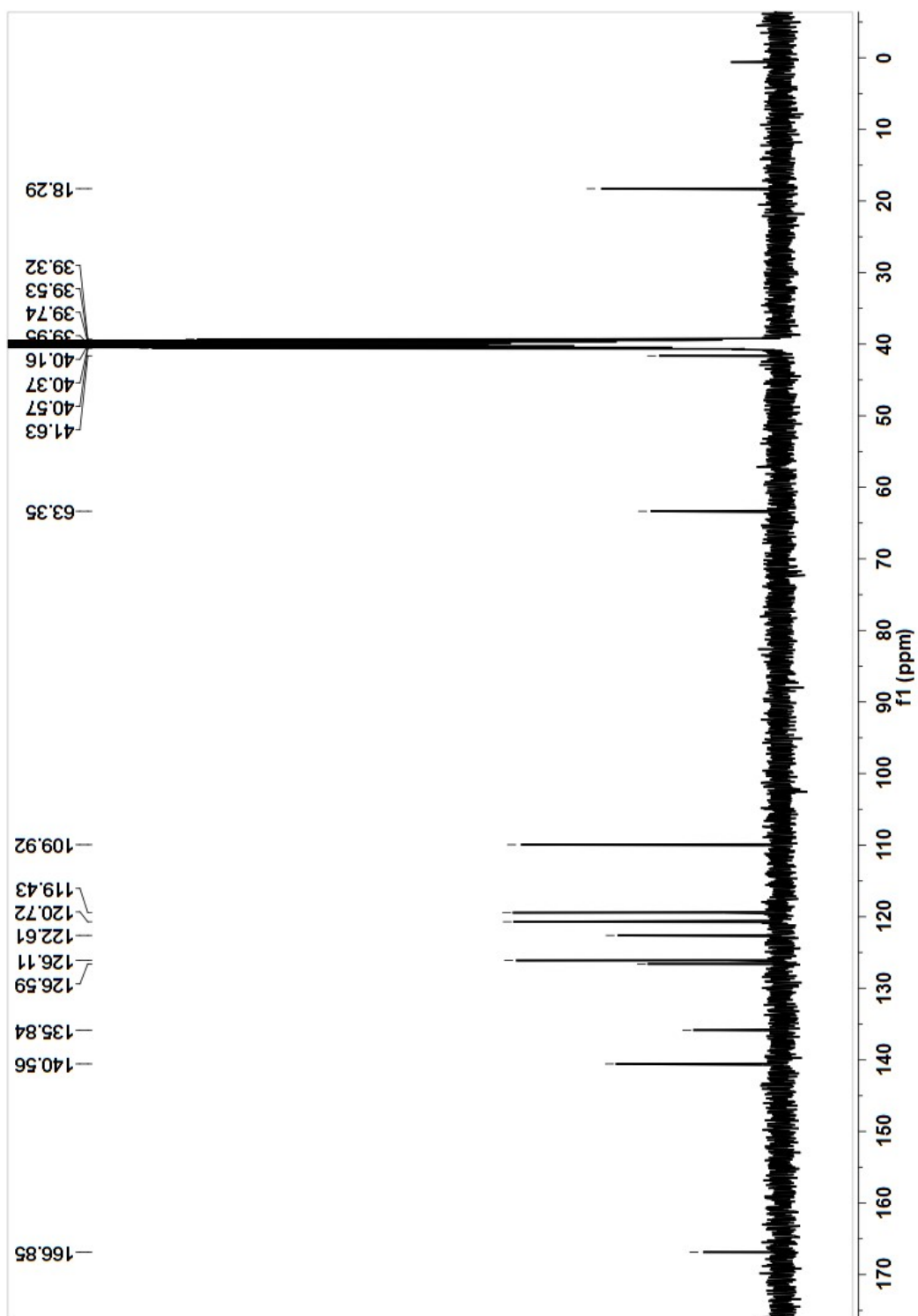
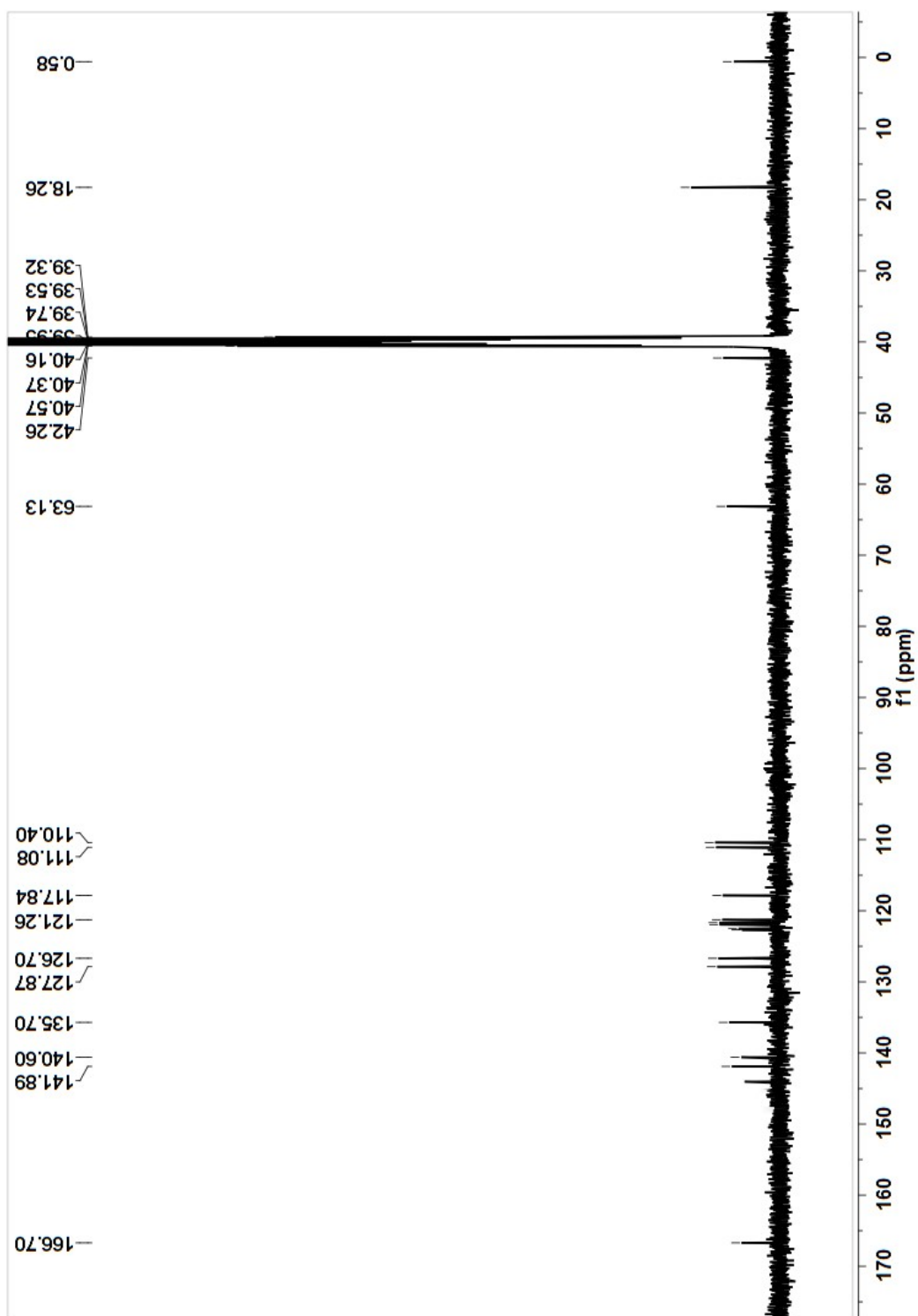


Figure S19. <sup>1</sup>H NMR spectra of the monomer MNCz.



**Figure S20.**  $^{13}\text{C}$  NMR spectra of the monomer MCz.



**Figure S21.**  $^{13}\text{C}$  NMR spectra of the monomer MCz.



## D. Tables

**Table S1.** The threshold voltage ( $V_{th}$ ), long-time stability (LTS) and device reproducibility (DRP) of previous reported memory devices.

Compound	$V_{th}$ (V)	LTS (s)	DRP	Ref.
PMCz <sub>4</sub> -co-PMNCz <sub>1</sub>	-1.14	20500	86%	<b><i>This work</i></b>
2-DPTZ	-1.60	14000	82%	<i>ACS Appl. Mater. Interfaces</i> 2022, 14, 8218–8225
<i>p</i> -BQBTZ	-2.50	10000	70%	<i>Mater. Chem. Front.</i> , 2021, 5, 3176–3183
CAPyNI	-3.50	12000	48%	<i>Adv. Funct. Mater.</i> <b>2018</b> , 28, 1800568
SPMA-AbDMA	-1.80	10000	64%	<i>J.Mater.Chem.C</i> ,2019,7,4863--4869
Ni <sub>2</sub> T <sub>2</sub> DPP	-3.00	10000	70%	<i>Chem. Asian J.</i> 2016, 11, 2078 – 2084
NACzBTz	-2.80	10000	78%	<i>ACS Appl. Mater. Interfaces</i> 2019, 11, 37973–37980
SA-Bu	-4.10	10000	82%	<i>Chem. Sci.</i> , 2017, 8, 2344–2351