Nonvolatile Flexible Memory Based on a Planar Zigzag-Type Nitrogen-Doped Picene

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The wearable information storage devices have aroused particular attention due to their great promise in smart electronics and healthcare service. These devices require all the memory circuit components to be flexible and stretchable, especially for the memory storage elements. Herein, a planar zigzag-structured nitrogen-doped picene is successfully constructed as the active layer to obtain resistive switching memory devices, which possess both robust mechanical flexibility and electrical reliability. Attributed to the large-area film morphological uniformity, the nonvolatile flexible memory devices exhibit highly reproducible resistive switching behavior, accompanying with concentrated distributions of switching voltages and resistance states under repetitive conformal deformation operation. The insight gained from this work may afford new opportunities for realizing high-performance wearable information storage electronics.

1. Introduction

Recently, flexible electronics have attracted considerable interests and emerged as an important topic due to their unique superiorities.[1–3] With the advantages of lightweight, softness, foldability, and shape diversity, flexible devices hold great promise for next-generation wearable artificial intelligent electronics, such as biosensors, e-skin, and robotics.[4–12] Among these promising fields, flexible resistive memory, which utilizes bistable resistance states to encode and store binary digital data, is considered as one of the most powerful contenders for the next-generation intelligent information storage technology.[13–26] Flexible resistive memory devices possess a simple two-terminal metal/insulator/metal (MIM) structure, which is conducive to repetitive conformal deformation. More intriguingly, they can succeed to mimic biological synaptic functions,[24–27] which satisfy the critical requirements for future neuromorphic computing systems.

To date, a versatile range of functional materials have been demonstrated for flexible resistive memory applications, including inorganic materials,[28–30] organic materials,[31–33] and inorganic–organic hybrid materials.[34–36] Compared to inorganic counterparts, organic active materials appear to be more suitable for flexible functionality, given their low cost, high scalability, and inherent compatibility with flexible substrates.[21,22] Their optoelectronic properties can be feasibly modulated by molecular design-cum-synthesis strategy, which endows them with superior stretchable and adaptable abilities.[16,33] However, despite these charming merits, the application of soft organic materials sometimes suffers from insufficient repeatability of behaviors.[2,37] which is closely correlated with the nonuniform morphology across the resistive switching film. Therefore, from a material perspective, seeking for organic components that are inert to processing technique and hold orderly film morphologies still deserves particular research endeavors.

Among the developed organic functional materials, nitrogen-doped acenes have emerged as an important platform for high-performance organic electronics.[38–43] Their properties can be feasibly modulated by the number/valence/position of nitrogen atoms, which afford possibilities of achieving exceptional solid-state microstructures and optoelectronic properties.[39,43] To date, nitrogen-doped acenes have demonstrated to be promising candidates for various fields such as organic solar cells (OSCs),[42,44] organic field-effect transistors (OFETs),[43,45] and organic light-emitting diodes (OLEDs).[46,47] Nevertheless, their applications in flexible memory devices remain rarely explored.

In this article, we designed a planar zigzag-structured nitrogen-doped picene (PBDN, Figure 1a, b) and explored its potential for flexible resistive memory. Compared with the
common isomer of linearly fused pentacene, the zigzag shape allows for engineering molecular electronic properties and intermolecular interactions, which are believed to be crucial for controlling film morphologies. Moreover, we successfully introduced azo acceptors into this zigzag-type picene through rational molecular design-cum-synthesis, which both realize nitrogen doping and offer an ideal symmetric donor–acceptor system for resistive memory application. The synthesis of PBDN is simple with high yield. Due to the high conjugation, PBDN shows poor solubility in most common organic solvents, such as CH₂Cl₂, toluene, and dichlorobenzene. Nevertheless, thermogravimetric analysis (TGA) test reveals that PBDN possesses satisfactory thermal stability, with an onset decomposition temperature over 330 °C (Figure S3, Supporting Information). Thus, we adopted thermal deposition technique for the fabrication of PBDN film. Figure 1c shows the photography of the as-prepared PBDN film. The film shows good optical transparency and large-area film uniformity over 2 × 2 cm² on the indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrate. Moreover, the scanning electron microscope (SEM) verifies the uniform film morphology at the microscale.

As expected, the MIM-type Al/PBDN/ITO/PET device demonstrates unipolar flexible resistive switching behavior with robust electrical reliability and mechanical stability, which is a promising contender for nonvolatile memory application.

2. Results and Discussion
2.1. Photophysical and Electronic Properties of PBDN

The UV/Vis absorption spectrum of PBDN in thin film state was first conducted to examine its optical property. PBDN shows two high-energy absorption peaks at 217 and 268 nm, and one broad low-energy absorption band including a major peak around 460 nm and two lower peaks at 557 and 615 nm (Figure 2a). The high-energy absorption peaks result from the molecular aromatic conjugation, whereas the broad low-energy absorption band corresponds to the intramolecular charge transfer (ICT) process. The onset of the optical absorption (λ_onset) is determined to be 660 nm. Thus, the optical bandgap (E_g) is calculated to be about 1.88 eV, according to the equation E_g = 1240/λ_onset.

![Figure 1](image1.png)

**Figure 1.** a) Molecular structure of zigzag-type PBDN. b) Optimized molecular conformation of zigzag-type PBDN. c) Optical photography of PBDN thin film. d) SEM image of PBDN thin film.

![Figure 2](image2.png)

**Figure 2.** a) Optical absorption spectra of PBDN in thin film state. b) Cyclic voltammogram curve of PBDN film at a scan rate of 50 mV s⁻¹.

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To study the molecular energy levels of PBDN, cyclic voltammetry (CV) was performed to inspect the electrochemical properties. As shown in Figure 2b, PBDN exhibits a quasi-reversible reduction peak at −0.80 V in the negative region. Using the onset reduction potential, the lowest unoccupied molecular orbital (LUMO) energy of PBDN is estimated to be −3.61 eV, according to the equation 
\[ E_{\text{LUMO}} = -(4.80 - E_{\text{Fc}} + E_{\text{red onset}}) \] eV. The highest occupied molecular orbital (HOMO) energy level of PBDN is thus calculated to be −5.49 eV, using the equation 
\[ E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{opt}} \]. Notably, the high molecular conjugation of PBDN can allow for efficient charge delocalization, which is beneficial for the charge conduction under external electric field.

2.2. Film Morphology and Uniformity of PBDN

The optical uniformity of PBDN pushes us to inspect its micro-morphology through the cooperation of atomic force microscope (AFM) and SEM measurements. As shown in Figure 3a,b, the AFM height and phase images reveal that PBDN film exhibits a regular nanoscale granular structure, with the root-mean-square roughness (R_RMS) of 1.88 nm. The roughness is small, which denotes a smooth surface. In addition, the 3D-AFM image of Py–Fc film shows a multihills-like nanopattern (Figure 3c) with preferential bottom–up orientation. This self-assembled molecular growth can facilitate the formation of charge transporting pathways along the vertical direction. Moreover, the SEM topography also shows a continuous surface morphology, which clearly suggests a high uniformity, and hence, guarantees a homogeneous interface between the organic layer and electrode. The homogeneous interface can both reduce the series contact resistance and enhance the entire device reproducibility. Therefore, the synergistic effect of oriented molecular self-assembly and uniform micromorphology endows PBDN film with a great potential in the fabrication of vertical MIM-type memory devices.

2.3. Flexible Nonvolatile Memory Performance of PBDN

Inspired by the optical transparency, intrinsic toughness, and large-scale uniform morphology of PBDN film, we explored its feasibility in the preparation of flexible memory devices. In this article, the MIM-type Al/PBDN/ITO devices on the flexible PET substrates were fabricated (Figure 4a). Figure 4b shows the photographic records of the device bending test on a mounted instrument. When a negative voltage bias from 0 to −5.0 V was applied to the pristine device, an abrupt current increase occurs at SET voltage (i.e., threshold voltage) of −1.55 V (sweep 1, Figure 4c), indicating that the device has been switched

Figure 3. a) AFM height image of PBDN-based film deposited onto ITO substrate. The scale bar is 5 × 5 μm. b) AFM phase image of the film. c) 3D-AFM image of the film. d) SEM image of the film.
from a low-conductivity (OFF) state to a high-conductivity (ON) state. This OFF-to-ON state transition can correspond to a digital “writing” process in data storage. The device can maintain its ON state during the upcoming negative and positive voltage pulse (sweep 2 and 3), and even after the removal of electricity. Moreover, the resistive switching properties of the device under bending state were measured. The flexible device was bended under the bending radius of 7.84 mm by controlling its chord length to be 15 mm, and repeated bending cycles up to 120 cycles were subsequently operated for a mechanical flexibility test. A drift was observed in the SET voltage, but overall, the electrical properties were similar with each other, which demonstrated the flexible nonvolatile memory nature. To clearly illustrate the device performance under bending state, the variation of ON/OFF current ratio as a function of different bending times was shown in Figure 4d. All of the ON/OFF current ratios remain over $10^2$, whereas the SET voltages locate in a narrow range from $-1.0$ to $+1.0$.
to −3.0 V. These results indicate that PBDN-based devices possess unipolar flexible resistive switching behavior with satisfactory electrical reliability and mechanical stability.

Moreover, we also evaluated the stability of PBDN-based device through retention test under a constant stress of −1.0 V. The ON and OFF states display no obvious change over 2.5 × 10^3 s (Figure 2c). This result shows that the device is endurable under external continuous voltage stress and read pulse. Overall, the reproducible and reliable nonvolatile resistive switching behavior was observed for PBDN-based flexible devices.

To shed more light on the resistive switching behavior of PBDN, the typical current–voltage (I–V) curve was replotted in double-logarithmic scale. As shown in Figure 4f, the ohmic region (I ∝ V^{1.01}) first appears at the low bias. As the voltage increases, the traps generated from PBDN are gradually filled and the Fermi level is raised to approach the conductive band. The I–V curve approximately follows a square law (I ∝ V^{1.86}), called by trap-filled space-charge-limited current (SCLC) conduction mechanism (namely, Child’s law).[50,51] When the voltage further increases to the threshold voltage, all traps are filled up and the conductivity rapidly improves to a higher level of ON state, which follows ohmic conduction behavior (I ∝ V^{1.02}), due to the thermal excitation of the filled traps. Thus, it is inferred that the trap-filled SCLC transport mode dominates the I–V characteristics.

### 2.4. Resistive Switching Mechanism of PBDN

It has been reported that the metal electrode can exert an influence on the resistive memory device performances (e.g., metal filamentary conduction and intermediate oxide formation).[12,19,52,53] To examine whether the Al metal electrode affected the flexible memory behavior, the top Al electrode was altered into inert gold (Au) and the device with structure of Au/PBDN/ITO/PET was fabricated and measured for comparison. Au is inert and can avoid the formation of metal filaments and/or interface oxide layer during device operation.[48,51] As shown in Figure S4a,b, Supporting Information, the fabricated device exhibits similar irreversible electrical switching behaviors with that using Al as electrode, which indicates that the resistive switching phenomenon is independent of Al electrode and belongs to the interior property of the molecule PBDN.

Moreover, the trap-filled SCLC transport mode observed in I–V curves reveals that charge trapping process may form among the PBDN layer. To get insight into the underlying memory mechanism of PBDN, we further took advantages of density functional theory (DFT) to understand their electrical properties. The calculated HOMO and LUMO isosurfaces of PBDN are shown in Figure 5a. As noted, the HOMO and LUMO surfaces are different. Compared with HOMO, the electrons of LUMO are more evenly distributed over the zigzag conjugated backbone. These electron density distributions generally indicate that the ICT process occurs upon undergoing the HOMO to LUMO transition, which is closely correlated with the electron acceptor among the molecular structure.[54]

The molecular electrostatic potential (ESP) of PBDN was calculated to examine the effect of electron acceptor. As shown in Figure 5b, there is a continuous positive ESP (in yellow–green) throughout the zigzag-type molecular skeleton, which forms an open channel for charge carrier migration. However, negative ESP region (in blue) caused by the electron acceptors of azo also exists. This negative region can act as “trap” to impede the motion of charge carriers.[51,55] Under a low negative bias, charge carriers cannot get adequate energy to overcome the injection barrier between the donor and acceptor. Thus, the device remains in the OFF state. When the SET voltage is approached, charge carriers acquire sufficient activation energy and inject from the donor to acceptor, which gradually fill up the azo traps.

![Figure 5.](image_url)

**Figure 5.** a) DFT calculated HOMO and LUMO isosurfaces of PBDN. b) The calculated molecular ESP of PBDN. c) Scheme of HOMO and LUMO energy levels of PBDN and the work function of ITO and Al.
Therefore, the device shows higher conductivity and switches from OFF to ON state, leading to a “trap-free” environment.[14,56] Moreover, Figure 5c shows the detailed energy levels of PBDN molecular orbitals. The energy bandgap between HOMO and LUMO was determined to be 1.88 eV, which is approximate to the average SET voltage of the flexible memory devices. This result suggests that when the SET voltage is applied, the HOMO to LUMO transition can be triggered, which verifies that the field-induced charge transfer process occurs at the excited state.[57] It has been reported that azo is a strong electron-withdrawing group, which can form a trap with large depth and hold the trapped charge carriers strongly.[58] Accordingly, the charge carriers trapped by the electron acceptor of azo can be stabilized by the intramolecular or intermolecular charge transfer effect at the excited state, forming a charge-separated state.[19,59] These trapped carriers cannot be easily released after removing the power supply or under reverse electric field. Therefore, the resulting ON state can be long-time maintained, indicating nonvolatile memory characteristics.

3. Conclusions

In summary, we have developed a flexible resistive switching memory device using a planar zigzag nitrogen-doped picene as active element. The PBDN-based films are optically continuous, thermally stable, and large-scale uniform. The intrinsic flexibility of the film makes it an ideal platform for application in flexible electronics. Reproducible nonvolatile resistive memory behavior, which can be sustained under the repetitive conformal deformation operation, is observed in the fabricated MIM flexible devices. This article may provide a good candidate for application in wearable resistive memory electronics. Future studies on the stretchable electrodes such as intrinsically conductive polymers, which may further extend the deformation capability of the organic devices, are now under progress.

4. Experimental Section

Flexible Thin-Film Deposition and Device Fabrication: The ITO-coated PET substrates were cleaned with distilled water, acetone, and ethanol via ultrasonication in sequence. Then PBDN was thermally deposited onto PET substrates under a pressure of $10^{-6}$ Torr, with the deposition rate of 1 Å s$^{-1}$. Afterward, the substrates were transferred into another evaporation chamber and pumped down to a vacuum of about $10^{-6}$ Torr. An array of Al electrodes with a thickness of about 100 nm were thermally deposited onto the organic film through a shadow mask of circular patterns. Under ambient air condition, electrical switching behaviors of the as-fabricated devices were measured using a Keithley 4200-SCS semiconductor characterization system at DC voltage/current sweep mode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

data storage, flexible memory, nitrogen-doped materials, nonvolatile memory, organic electronics

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