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A Multilevel Memory Based on Proton-Doped Polyazomethine with an Excellent Uniformity in Resistive Switching

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Supporting Information

ABSTRACT: The uniformity of operating parameters in organic nonvolatile memory devices is very important to avoid false programming and error readout problems. In the present work, we fabricated an organic resistive-switching memory based on protonic-acid-doped polyazomethine (PA-TsOH), which demonstrates an excellent operative uniformity and multilevel storage capability. The deliberate tuning of the resistance states can be attributed to the electric-field-controlled molecular doping of the imine-containing polymers.

Organic electronics has emerged as a rising technology because of its potential for large-area processability, mechanical flexibility, and light-weight and low-cost applications in roll-to-roll display, organic thin-film transistors (OTFTs), organic photovoltaics (OPVs), and organic nonvolatile memories (ONVMs).[1−4] Among these, ONVMs are promising candidates for next-generation data storage to which plenty of efforts, concerning organic materials and device architectures with a large ON/OFF ratio, good endurance, long retention time, low power consumption, and fast switching speed, have been devoted.[4a,5] However, the operation parameters of ONVM devices, in particular their switching voltages, usually suffer from severe fluctuations, which lead to false programming and error readout limitations that have hindered the practical implementation of ONVMs.[6] Therefore, obtaining reliable ONVMs with reproducible and uniform operation parameters is still a great challenge for both the scientific and engineering communities.[6] Unfortunately, because of the lack of an appropriate design principle, less improvement in the uniformity of the operation parameters in ONVMs has been achieved over the past decade. On the other hand, it is noteworthy that inorganic resistive memories with gradual resistance-change character usually exhibit better operative uniformity and controllability in comparison with their counterparts exhibiting sudden resistance-switching behavior, which can be ascribed to the controllable increase in resistance.[7] Inspired by these results, we focused on gradual and consecutive tuning of the resistance states of polymers by manipulating the doping level, aiming to achieve more reliable and controllable ONVM devices.

Poly(Schiff base)s are a family of conjugated polymers constructed from imine groups (C═N) in the backbone and exhibiting excellent thermal stability, good mechanical properties, metal-chelating ability, and molecular-doping-controlled electrical properties.[8,9] The imine groups in poly(Schiff base)s can act as effective atomic or molecular anchor sites for protonic acid dopants, while the reversible doping/dedoping of the conjugated polymer backbone can be consecutively controlled by applying an electrical field.[10] Consequently, it is expected that the resistance can be fine-tuned by modifying the doping level of the polymer. Nevertheless, a consecutive change in the device conductivity can be used for realizing multilevel storage, which is extremely important for increasing the data storage capacity exponentially.[5d,11]

In this work, we report ONVM devices based on a novel *p*-toluenesulfonic acid (TsOH)-doped poly(Schiff base) that has not been explored previously but has promising potential for resistive switching and information storage applications. The devices concurrently exhibit an excellent uniformity in resistance-switching parameters, multilevel storage states, and self-rectifying effects. The poly(Schiff base), polyazomethine (PA), was synthesized by polycondensation of diamine and dialdehyde monomers [Scheme 1; see the Supporting Information (SI) for detailed experiments and characterization] and was soluble in common organic solvents such as cyclohexanone, *N*,*N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidinone (NMP). The average molecular weight of the as-synthesized PA was 32.2 kDa, with a polydispersity index of 2.5 as measured by gel-permeation chromatography. The PA was found to have a thermal degradation temperature ($T_{d10\%}$) of 427 °C (Figure S1 in the SI) and a glass transition temperature (T_g) of 278 °C (Figure S2). TsOH-doped PA (PA-TsOH) was prepared by mixing PA and TsOH in cyclohexanone solution. The doping of PA with protons was confirmed by UV−vis spectroscopy (Figure S4) and cyclic voltammetry (CV) (Figure S5)

The memory effect of the undoped-PA devices was explored first, and the current−voltage ($I-V$) characteristics are shown in Figure S6a (see the SI for detailed results and discussion). Compared with the memory behavior of Pt/PA/Pt devices,

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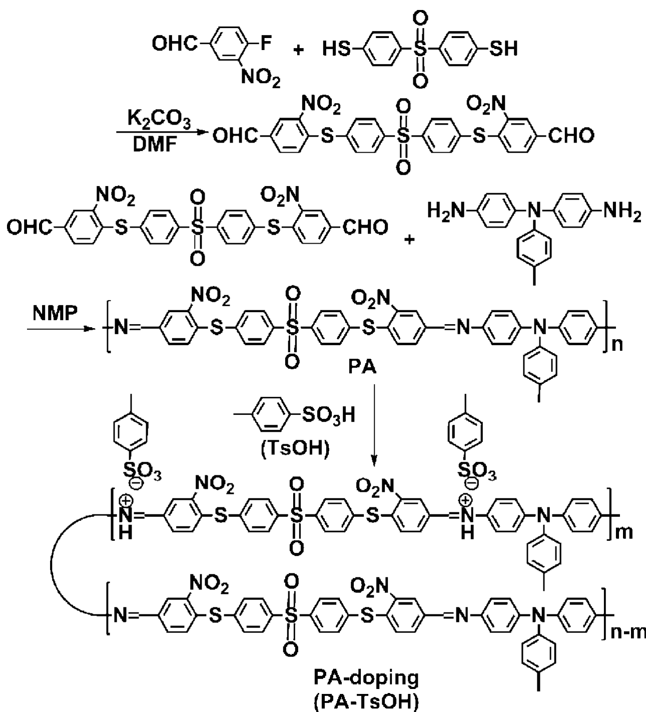
Scheme 1. Synthesis of Monomers and the Poly(Schiff base)



which showed a sharp resistive-switching effect, the Pt/PA-TsOH/Pt devices exhibited much smoother *I*−*V* characteristics during the resistive-switching process. As shown in Figure 1b,

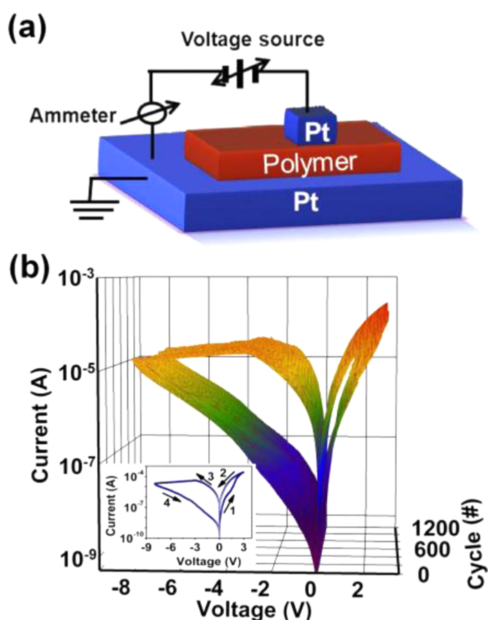


Figure 1. (a) Schematic illustration of the poly(Schiff base)-based ONVM devices. (b) Consecutive *I*−*V* cycles of a Pt/PA-TsOH/Pt device. The inset shows the first *I*−*V* cycle.

the as-fabricated Pt/PA-TsOH/Pt memory cells was in the the high-resistance state (HRS) (i.e., the OFF state). When a positively biased potential sweep from 0 to 3 V was applied (sweep 1 in the Figure 1b inset), the current increased consecutively from ∼1 nA to ∼0.2 mA, indicating that the device had been set to the low-resistance state (LRS) (i.e., the ON state) by the positive forward sweep. This transition, which is defined as the "Write" (or "SET") process, was confirmed by the subsequent positive backward potential sweep from 3 to 0 V (sweep 2). In the following sweep from 0 to −3.3 V (sweep 3), the device remained in the LRS. The retention of the LRS of the Pt/PA-TsOH/Pt devices was retained for ∼4 min after the applied voltage was removed and could be further prolonged by refreshing the ON state with a constant-voltage stress of 1 V (Figure S8). In the "Erase" (or "RESET") process, the device was programmed back to the initial OFF state by applying a negative bias voltage of −3.3 V, and a value of 600 for the ON/OFF ratio (defined as R_{HRS}/R_{LRS}, where R_{HRS} and R_{LRS} are the resistance values in the HRS and LRS, respectively) was readily achieved. Moreover, a self-rectifying effect was also observed in the Pt/PA-TsOH/Pt devices, with rectification ratios of ∼100 and ∼10 in the HRS and LRS, respectively (Figure S9). Dedicated efforts are being made to enhance the self-rectifying effect further by exploring different protonic acid dopants with molecular volumes larger than that of TsOH. Though the present self-rectifying effect in the LRS is moderate, it still provides a simple but effective alternative to the incorporation of additional control elements as an approach to solve the cross-talking problem in crossbar-structured devices.[6b−d,12]

To investigate the uniformity of the resistance-switching parameters, cyclic programming operations of the Pt/PA-TsOH/Pt devices were performed. Highly reproducible memory *I*−*V* loops of more than 1000 consecutive cycles are shown in Figure 1b and Figure S10, and no obvious degradation was observed. We define the voltages inducing the sharpest change in the device current during the SET and RESET processes as the SET voltage (V_{SET}) and the RESET voltage (V_{RESET}), respectively. A narrow distribution of R_{HRS} (40.5 ± 17.5 MΩ), R_{LRS} (355 ± 38 KΩ), V_{SET} (2.65 ± 0.07 V), and V_{RESET} (−3.31 ± 0.15 V) was obtained. On the other hand, less consistent resistive-switching behavior was observed for the Pt/PA/Pt devices (Figure S6b), with R_{LRS} (1.0×10^2 to 4.6×10^4 Ω), R_{HRS} (1.9×10^5 to 8.2×10^6 Ω), V_{SET} (3.48 ± 2.12 V), and V_{RESET} (−1.61 ± 1.11 V) fluctuating in relatively wider ranges. To elucidate further the switching stability of the two devices, cumulative probability distributions for R_{LRS}, R_{HRS}, V_{SET}, and V_{RESET} are plotted in Figure 2. The statistical distributions for the operation parameters of the Pt/PA/Pt devices exhibit large fluctuations, while those of the Pt/PA-TsOH/Pt devices are very uniform. All of the operation parameters for the Pt/PA-TsOH/Pt devices featured a small standard deviation (Δ) to mean (μ) ratio, with Δ/μ values of 0.0391, 0.0966, 0.0255, and 0.0231, respectively, for the device resistances in the ON and OFF states and the corresponding SET and RESET voltages. Therefore, an excellent uniformity in the device performance, superior to those reported in the literature, was achieved in the Pt/PA-TsOH/Pt ONVM devices (Figure S11).[13] Nevertheless, the Δ/μ values for R_{LRS}, R_{HRS}, V_{SET}, and V_{RESET} of the Pt/PA/Pt devices (0.4671, 1.2241, 5.9015, and 2.1234, respectively) are 1−2 orders of magnitude larger than those of the Pt/PA-TsOH/Pt devices, again suggesting that controllable protonic doping is an effective way to optimize the uniformity of resistive-switching behaviors.

More importantly, multilevel resistive states can be achieved by applying different RESET voltages to the Pt/PA-TsOH/Pt devices (Figure 3). After the Pt/PA-TsOH/Pt device was set to the LRS, it could be reset to four different HRSs by applying negative voltage sweeps with maximum voltages of −5, −6, −7,

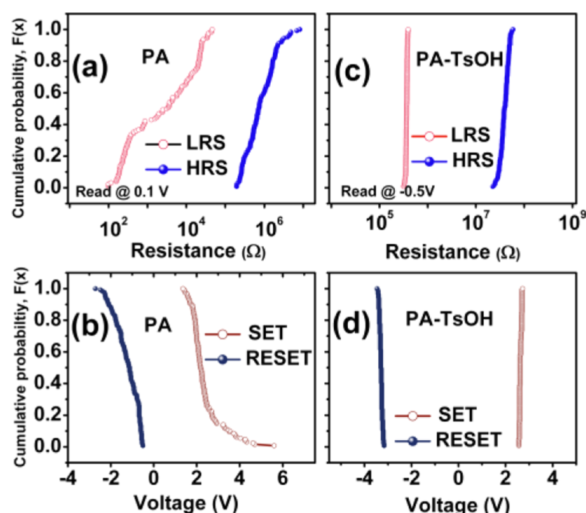


Figure 2. Statistical distribution/cumulative probability of the operation parameters for the (a, b) Pt/PA/Pt and (c, d) Pt/PA-TsOH/Pt devices.

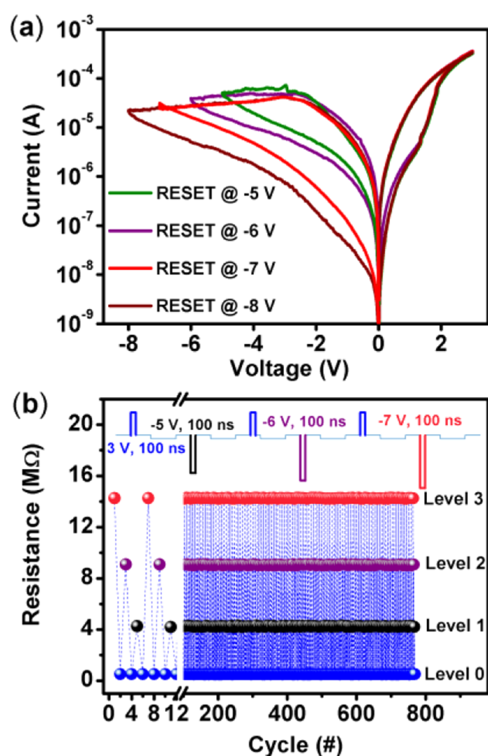


Figure 3. Multilevel operation of the Pt/PA-TsOH/Pt devices in (a) a dc sweeping mode and (b) a pulse mode. The inset of (b) illustrates the voltage pulse utilized for the device programming. The reading voltage is −0.5 V.

and −8 V (Figure 3a). The results suggest that the resistive states of the devices can be well-modulated by controlling the RESET voltage amplitude. We explored the multilevel data storage capability by applying voltage pulse stimuli (Figure 3b). Initially, voltage pulses with an amplitude of 3 V were employed to set the device to the LRS. For the RESET process, multilevel HRSs were achieved by varying the RESET pulses (−5, −6, and −7 V, respectively) in consecutive operations. The memory device was programmed between four resistive states consecutively for more than 700 switching cycles. The narrowly distributed resistances and small Δ/μ values for each state (0.007, 0.0092, 0.0039, and 0.0027 for levels "0", "1", "2", and "3", respectively) therefore promise an excellent uniformity of the Pt/PA-TsOH/Pt ONVM device in pulsed operation mode. Similar to the retention test of a two-state device (Figure S8), the LRSs (levels 0, 1, and 2) of a multilevel device gradually relaxed to the HRS (level 3; Figure S12). Furthermore, the retention ability of the multilevel device decreased with decreasing state resistance, in accordance with the fact that doping of a poly(Schiff base) with a protonic acid is energetically unfavorable, with the material becoming less stable at higher doping levels.

The mechanism of the resistance-switching effects of the present poly(Schiff base) ONVM devices can be understood on the basis of the charge transfer effect and the electric-field-induced doping/dedoping effect. In the chemical structure of the PA backbone, the triphenylamine (TPA) moieties are electron donors, while the 4,4′-bis(3-nitro-4-formylphenylthio)-biphenyl sulfone moieties and imine groups are electron acceptors. The resistive switching in undoped PA can be attributed to the charge transfer interaction between the TPA donors and the sulfone/nitro/imine acceptors (the conduction mechanisms of the HRS and LRS are shown in Figure S13). On the other hand, the electronic scenario in the Pt/PA-TsOH/Pt device is completely different. Similar to polyaniline, molecular doping of the poly(Schiff base) with a protonic acid leads to an increased concentration of the effective charge carriers in the bulk heterojunction blend of the polymer hosts and small-molecule dopants.[14] However, with the relatively lower content of imine moieties in comparison with that in polyaniline, only a partial/low doping level is achieved in the PA-TsOH thin film, and the Pt/PA-TsOH/Pt device does not exhibit a significant enhancement in the HRS conductivity. Nevertheless, the molecular doping with the protonic acid (protonation) is responsible for the p-type self-rectifying behavior of the Pt/PA-TsOH/Pt devices. Because of the electrostatic interaction between the positively charged PA backbone and the negatively charged TsOH units, a more ordered stacking with enhanced $\pi-\pi$ conjugation is established in the PA-TsOH system (XRD, Figure S14). The extended conjugation system, as evidenced by the significant red shift of the optical absorbance (Figure S3), favors the transport of charge carriers. Under external electric fields, electromigration of the TsOH dopants toward the imine groups of the PA backbone gives rise to an enhanced doping level of the poly(Schiff base).[5a,15] As a consequence, the gradually increased concentration of charge carriers leads to a consecutive increase in the device conductivity. As the field-induced doping/dedoping process of the PA-TsOH system occurs throughout the entire thin film, the very uniform cyclic operation over 1000 consecutive cycles is thus expected with the delocalized tuning of the effective charge carrier concentrations. In comparison, the localized charge transfer due to intra- and/or interchain donor−acceptor interactions in undoped PA or other D−A polymer devices is usually of less controllable, resulting in random formation of conductive pathways and severe device-to-device variations. In the Pt/PA-TsOH/Pt devices, the transport behavior of the charge carrier keeps changing consecutively, making it difficult to fit the conduction mechanism directly using the existing models.[16] The field-assisted doping of the poly(Schiff base) by the protonic acid was also confirmed by the polarization properties of the Pt/PA-TsOH/Pt devices (Figure S15), wherein the dielectric polarization ($D-E$) hysteresis loop follows the

programming pattern (I−V characteristics) of the Pt/PA-TsOH/Pt ONVM devices. Moreover, since field-induced migration of dopants is energetically unfavorable, the resultant doped state of the PA-TsOH thin film decays with time, and the device eventually returns to its initial HRS after the electric field is removed. When a constant voltage is applied, the doped system can retain the LRS. Under a reverse electric field, the doped system is disrupted, and deprotonation of the poly(Schiff base) results in a decrease in charge carrier concentration and therefore a gradual increase in the device resistance. In addition, we have found that doping of the poly(Schiff base) by a protonic acid with larger molecular volume can further enhance the retention ability of the high-conductivity states; the corresponding research is still in progress. In addition, the doping level of the poly(Schiff base) can be deliberately controlled by the applied voltage pulses, and therefore, multilevel resistive switching can be achieved by varying the RESET voltage.

In summary, memory devices based on a protonic-acid-doped poly(Schiff based) have been developed, and they exhibit excellent uniformity of their operation parameters, self-rectifying behavior, good endurance, and multilevel storage capability. The promising resistive-switching properties of the Pt/PA-TsOH/Pt devices are attributed to the controllable doping/dedoping of the poly(Schiff based) under electrical fields. It has been demonstrated that electric-field-controllable doping of polymers is an effective approach for tuning the resistive-switching effect and provides an important opportunity for the development of high-performance ONVMs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental procedure; TGA, DSC, UV−vis, and CV data; AFM image; and retention times of PA and PA-TsOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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