Flexible Pyrene/Phenanthro[9,10-d]imidazole-Based Memristive Devices for Mimicking Synaptic Plasticity

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Emulation of memory and learning functionalities of biological synapses using a two-terminal electronic device with bidirectional progressive conductance modulation is an indispensable move toward the development of bio-inspired neuromorphic networks. Herein, a small molecule 1-phenyl-2-(4-(pyren-1-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (pPPI) is synthesized, and an organic synaptic device is investigated with bipolar switching characteristics and bidirectional gradual conductance regulation for the first time. A facile solution-processing approach can be used to deposit a uniform active layer on flexible substrates. Our pPPI-based nonvolatile memory presents a superior electrical performance, such as relatively stable and reproducible bipolar resistive switching phenomena and a robust data retention capability. In particular, our device displays a remarkably large switching window of around $7.0 \times 10^4$, which is a record ON/OFF ratio compared with other small molecule-based memories up to now. In addition, comprehensive cognitive functions of chemical synapses, for example, the excitatory postsynaptic current (EPSC), paired-pulse facilitation/depression (PPF/PPD), spike-rate-dependent plasticity (SRDP), and spike-time-dependent plasticity (STDP) are successfully achieved. Our achievement of a synaptic device based on small molecules may boost the development of bio-inspired neuromorphic systems using organic electronics.

1. Introduction

Inspired by the diverse perceptive functions, such as memory, learning, attention, and visual sensing, as well as numerous advantages, for example, relatively low energy consumption and robustness of the biological brains, innovative artificial neuromorphic engineering with merits of good fault and error tolerance and massive parallelism has been developed.[11–19] Functional characteristics of the chemical systems can be emulated and hence break through the von Neumann bottleneck of the traditional computers.[11–13] In biological neural networks, a giant complex connection network of interior neurons ($\approx 10^{15}$) gives rise to its all-sided versatile functionalities, in which synapses ($10^{14}$–$10^{15}$) act as elementary cells of signal modulation and transmission.[14] The synapses can realize the generation and storage of information simultaneously by sending nerve signals from presynaptic neurons through synaptic cleft to the postsynaptic neurons, and the connection strength between neurons (known as synaptic plasticity) can be tuned.[15] Therefore, one crucial step for the construction of efficient neuromorphic systems lies in the implementation of a desired electronic synaptic component with analogous mimetic functions compared with chemical synapses.[16,17] For this purpose, it is highly demanded to investigate synapse-like electronic components.

By far, memristor,[14,18–21] ferroelectric memory,[22,23] phase-change memory,[24,25] resistive memory device,[11,26–30] field-effect transistor,[31–38] as well as the silicon-based complementary metal–oxide–semiconductor (CMOS) circuit[25,39] have been vigorously studied for realization of an ideal synaptic unit. However, device-level obstacles and barriers still exist. In particular, CMOS circuits using plenty of transistors and capacitors to mimic and capture various functions of a biological synapse require excessively large chip area with high energy dissipation and sophisticated integration. Consequently, attention has been paid to imitate synaptic behaviors in a single device with dramatic electrical properties. One of the most attractive components for the simulation of chemical synapses is a two-terminal nonvolatile memory device on account of their superior characteristics of fast speed of storage and access operations, relatively low power dissipation, simple fabrication process, and good integration capability at a high density and scalability as the 3D architecture.[40–45] The continuous electrical conductance modulation in the resistive memory device extremely resembles the consecutive
connection strength (synaptic weight) tuning in a biological synapse.\(^{[46,47]}\) Although the switch window, retention capability, endurance cycle, multibit data storage, and synaptic emulation of resistive memory devices have been extensively explored through application of various materials, including oxides,\(^{[48,49]}\) conjugated polymer,\(^{[49]}\) metal nanoparticles,\(^{[50,51]}\) and 2D materials\(^{[52–56]}\) in the past few decades, relatively less efforts have been made to investigate the dependence of linear conductance modulation, which plays a key role in increasing the precision of pattern recognition on various pulse parameters. On the other hand, it is essential to investigate an easy and simple preparation approach to build an efficient neuromorphic system.

Organic small molecules have been proverbially used in diverse electronic devices, for example, organic field-effect transistors (OFETs),\(^{[57]}\) organic photovoltaics (OPVs),\(^{[58,59]}\) and organic light-emitting diodes (OLEDs).\(^{[60]}\) They possess advantages of low cost and a simple solution fabrication process as well as favorable flexibility, indicating their underlying potential to be used in the resistive memory device for synaptic mimicry. Nevertheless, resistive memory based on organic small molecules for simulation of biological synaptic functionalities is rarely reported until now.

To tackle the aforementioned issues, we report on a two-terminal bipolar resistive memory device using a compact active layer based on novel 1-phenyl-2-(4-(pyren-1-yl)phenyl)-1H-phenanthro[9,10-dj]imidazole (pPPI) with a simple solution processing approach and its promising application for biological synaptic simulation. The structure of pPPI is designed and contained the pyrene and phenanthro[9,10-dj]imidazole moiety. Pyrene moiety with four fused benzene rings is widely used as the hole-transporting materials because of the strong electron delocalization character, whereas the heteroatom-containing phenanthro[9,10-dj]imidazole can provide the excellent electron transporting ability. Therefore, the use of pPPI with such bipolar character is beneficial to the enhancement of hole and electron transporting properties. As a result, the pPPI-based devices using the solution process exhibit excellent bipolar resistive switching characteristics under different current limitations (CLS), steps and delay time, a good endurance ability, a robust data retention capability of \(\approx 10^5 \text{s}\), a high thermal stability under elevated temperatures, and favorable reproducibility. Especially, our device displays a remarkably large switching window of about \(7.0 \times 10^4\) \text{V}, which is a record ON/OFF ratio compared with other small molecule-based memories up to now. In addition, conductive atomic force microscopy (CAFM) and Kelvin probe force microscopy (KPFM) are conducted to verify that the resistive switching nature of pPPI-based device is ascribed to the trap-filled space charge-limited current (SCLC) mechanism. Furthermore, for the first time, the pPPI small molecule is introduced to an artificial synapse, in which various plastic synaptic functionalities, including excitatory postsynaptic current (EPSC), paired-pulse facilitation (PPF), paired-pulse depression (PPD), spike-rate-dependent plasticity (SRDP), and spike-time-dependent plasticity (STDP), have been successfully realized, and in particular, the connection between linear conductance modulation and diverse pulse parameters is revealed. Meanwhile, the energy dissipation for an individual electrical spike is under the \(\text{nJ}\) level for both positive and negative directions. These results provide a useful guideline of organic small molecules for two-terminal synaptic devices and imitation of regulatory artificial synapses.

2. Results and Discussion

The complete experimental fabrication procedures of pPPI are provided in the Experimental Section of Supporting Information. The UV–visible absorption spectra (Figure 1a) and photoluminescent (PL) spectra (Figure 1b) of pPPI were measured to investigate its optical characteristics at room temperature in the methylene chloride (\(\text{CH}_2\text{Cl}_2\)) solution with different concentrations ranging from \(10^{-5}\) to \(10^{-3}\) M. As indicated in Figure 1a, pPPI exhibits a strong absorption band within the UV light region in which the absorption peak of about 264 nm can be attributed to the \(\pi-\pi^*\) transition on the basis of the phenyl ring connected with the N atom, and the longer absorption regions located at around 337 and 365 nm are ascribed to the \(\pi-\pi^*\) transition resulted from the PPI unit, thereby existing intramolecular charge transport. In addition, the optical energy bandgap of pPPI is extracted to be 3.13 eV estimated from the onset of the absorption range (inset of Figure 1a). Subsequently, the experimental PL emission spectra of pPPI in the dilute \(\text{CH}_2\text{Cl}_2\) solution (Figure 1b) display a main emission peak at 446 nm, which is demonstrated by the blue light emission of the pPPI solution under sustained UV light irradiation (inset of Figure 1b). Cyclic voltammetry (CV) was also conducted to examine the oxidative electrochemical characteristics of pPPI (Figure 1c). Apparently, the oxidation process at about 0.9 V can be observed in the \(\text{CH}_2\text{Cl}_2\) solution; meanwhile, the highest occupied molecular orbital (HOMO) energy level evaluated from the onset of the oxidation potential and the lowest unoccupied molecular orbital (LUMO) level calculated from the difference between the HOMO level and the energy bandgap are 5.58 and 2.45 eV, respectively. To gain insight into the electronic states of pPPI, density function theory (DFT) calculation was performed (Figure 1d and Figure S1, Supporting Information). The result show that its HOMO is distributed mostly over the pyrene and phenanthro[9,10-dj]imidazole. On the other hand, the LUMO is localized mainly on the pyrene and phenanthro[9,10-dj]imidazole as well, and to a lesser extent over the N-phenyl ring of phenanthro[9,10-dj]imidazole. These results show that the electronic transition is mainly \(\pi\to\pi^*\) transition and to a lesser degree of charge transfer transition due to the introduction of the heteroatom cyclic phenanthro[9,10-dj]imidazole with pyrene. To verify the interface affinity of the pPPI solution and glass substrate, contact angle measurement and surface energy calculation were performed, as shown in Figure 1e. According to the contact angles of glycol and water drops after interacting with the pPPI active layer, the surface energy \((\gamma_s)\) of the pPPI thin film calculated by adding up the dispersion force component \((\gamma_{s,d})\) and polar force component \((\gamma_{s,p})\) of the surface energy is 32.655 mJ m\(^{-2}\) on the basis of the following equation\(^{[61]}\)

\[
1 + \cos \theta = \frac{2(\gamma_{s,d})^{0.5}(\gamma_{t,d})^{0.5} + 2(\gamma_{s,p})^{0.5}(\gamma_{t,p})^{0.5}}{(\gamma_t)^{0.5}}
\]

where \(\theta\) is the contact angle between the test liquid and the thin layer, and \(\gamma_{s,d}, \gamma_{s,p}, \) and \(\gamma_t\) represent the already known dispersion.
force component of the surface energy, polar force component of the surface energy, and total surface energy of the test liquid, respectively. The lower surface energy of the pPPI active layer reveals the favorability that the pPPI solution in chlorobenzene could spread out onto the glass substrate with a relatively large surface energy (about 250 mJ m\(^{-2}\)) and hence form a uniform layer. In addition, a contact angle of 10.332° is obtained by dropping the pPPI solution onto glass directly, which demonstrates good liquid adhesion ability and is in good agreement with the surface energy analysis.

pPPI-based memory devices have been fabricated, and the 3D configuration and fabrication procedure of the studied device are schematically shown in Figure 2a. This crossbar array began with the organic homogenous pPPI thin film spin-coated onto the glass substrate, which was precoated with parallel indium tin oxide (ITO) bottom electrodes (BE). Subsequently, the Al or Au top electrode (TE) was thermally evaporated onto the active layer under the assistance of a shadow mask. The top-viewed atomic force microscopy (AFM) image of the organic pPPI film manufactured by 10 mg mL\(^{-1}\) transparent yellow solution shown in Figure 2b verifies the smooth and dense film morphology with relatively low root-mean-square roughness (\(R_s\)) and average roughness (\(R_a\)). The cross-sectional scanning electron microscopy (SEM) image of the aforementioned device indicates that the active layer is composed of compact interconnected organic pPPI small molecules with a thickness of about 25 nm (Figure 2c).

The electrical switching property of the pPPI-based memory device was first measured with two-probe electrical measurements in which high force was exerted on the Al TE, whereas ITO BE was totally grounded under air atmosphere to reveal its memory characteristic. The representative current–voltage (I–V) curve of the aforementioned device is shown in a semilogarithmic scale in Figure 2d. No apparent electroforming procedure is necessary for activating the device performance, and a typical bipolar resistive switching nature with two distinct conductance states can be observed in the as-fabricated device. During the measurement, the current increases progressively by steadily increasing the imposed positive voltage from 0 to 2.4 V (stage I); but then, at the threshold bias of 2.4 V, a pronounced increase of the conductance from 0.795 nS to 0.417 mS arises with a CL of 1 mA. The abrupt transition from a high resistance state (HRS) to low resistance state (LRS) is termed as the SET operation (stage II). The LRS of the device stays unchanged by exceeding and then reversing the bias to \(-1.9\) V, indicating a nonvolatile characteristic (stages III and IV). Subsequently, RESET operation is realized with the CL of 100 mA by using the erasing bias of \(-1.9\) V to switch the device from LRS to HRS (stages V and VI). The switching window can be obtained by comparing the difference in resistance values between LRS and HRS, that is, \((R_{\text{HRS}} - R_{\text{LRS}})/R_{\text{LRS}} \approx R_{\text{HRS}}/R_{\text{LRS}}\) is approximately equal to \(7.0 \times 10^2\) at an electrical read bias of \(-1\) V, demonstrating the two distinguishable conductance states ("0" or "1") in the integrated circuit. Accordingly, to highlight the extraordinary resistive switching margin of pPPI-based cells, the switching window of previously reported resistive memory based on small molecules\(^{[62–70]}\) is summarized and compared with our work as shown in Figure 2e. Notably, our pPPI-based device exhibits the remarkably high window by far maybe due to the smooth surface morphology and excellent charge trapping/detrapping states of the pPPI layer, eliminating the misreading events in practical memory cell applications.

Figure 1. Characterization of the organic pPPI small molecule. a) UV–visible absorption and b) PL spectra of pPPI in the methylene chloride (CH\(_2\)Cl\(_2\)) solution with different concentrations ranging from \(10^{-3}\) to \(10^{-7}\) m. Inset of (a) exhibits the extracted energy bandgap of pPPI estimated from the onset of the absorption range, whereas the inset of (b) presents the induced blue light emission under sustained UV light illumination. c) Cyclic voltammogram of pPPI in the CH\(_2\)Cl\(_2\) solution. d) Spatial distributions of the HOMO and LUMO levels of pPPI according to DFT calculations. e) Contact angle images of seeding glycol (upper image) and water (middle image) droplets on the pPPI thin film and seeding pPPI droplets on the glass substrate (bottom image), respectively.
Then, a sequence of electrical parameters was adjusted successively to examine the changes of resistive switching property and furthermore investigate the switching mechanism of pPPI-based memory in an ambient condition. Figure 2f shows the SET/RESET functionality with respect to different CLs ranging from $10^{-5}$ to $10^{-1}$ A. Apparently, the switching threshold voltages of the SET and RESET process exhibit a noteworthy variation under different CLs. In the resistive memory device, based on the charge carrier trapping mechanism, the SET/RESET process is in accordance with the formation/rupture of conductive channels, which chiefly depends on the direction of electric field and Joule thermal energy induced by electrical current. Thus, more and thicker conductive paths formed under higher CL and hence harder rupture operation result in the gradually increasing SET and RESET bias in a high CL condition. Figure 2g shows the resistive switching bias as the dependence of the sweeping rate. Obviously, the SET and RESET bias increase systematically with steadily increasing sweeping rate ranging from 0.01, 0.03, 0.05, 0.07 to 0.1 V s$^{-1}$, which can be attributed to the formation of more conductive channels and larger Joule heat energy under the implementation of dense sweeping rate. In addition, it should be noted that the device with a sparse sweeping rate of 0.12 V s$^{-1}$ was switched from HRS to LRS when the applied electrical bias swept from 0 to +5 V to +4.52 V, signifying that a complete positive bias with an additional reverse positive sweep is sufficient enough to construct a full-trapped conductive path. In addition, measurement of the relation between the switching voltage and the delay time is conducted, as shown in Figure S2, Supporting Information. Shorter delay time, in other words, denser accumulation of bias voltages significantly improves the rate of conductive path formation and heat-induced channel rupture so that the SET/RESET switching voltages decrease gradually with decreasing delay time.

To further examine the impact of TE materials on the electrical performance and switching mechanism of the pPPI-based resistive random access memory (RRAM), a memory device with...
Au TE was also manufactured and typical I–V characteristics with different CLs, sweeping rates, and delay time were measured and exhibited in Figure S3, Supporting Information. Compared with the device with Al TE, the device with Au TE not only presents the alike nonvolatile rewritable bipolar resistive switching characteristic but also displays the same change patterns of SET/RESET functionality under different test parameters, including CL, sweeping step, and delay time. The similar switching characteristics of Au and Al top electrodes can be deciphered from two aspects. On the one hand, the whole fabrication process of pPPI-based RRAM devices is under nitrogen atmosphere/high-vacuum condition, and hence, relatively few aluminum oxides are formed at the interface between Al top electrode and pPPI function layer in spite of the specific ambient detecting environment, signifying a predominant pPPI-based switching active layer (as indicated in the cross-sectional SEM image in Figure 2c). On the other hand, the resistive switching mechanism in the AlOx-based RRAM device also originates from a variety of defects that alter electronic transport rather than a specific electronic structure of insulating materials. From this point of view, extremely few aluminum oxides also provide defects for channel formation, which is in congruence with the role of pPPI. Therefore, similar switching phenomena of Au and Al are observed. Nonetheless, it is worth noting that the conductive states of the memory device with Au TE at HRS is greater on account of the relatively low energy barrier of holes between the Au electrode and the pPPI active layer in the energy band alignment. On the other hand, as we all know, the inert metal electrode Au is extremely hard to be oxidized while readily oxidized active electrode Al can be constrained easily by the anions of the active layer and thereby is incapable of migrating to the BE to be reduced, precluding the metallic filament mechanism.

Next, 100 stochastic selected samples (cross-bar cells) of 20 pPPI-based devices were characterized to examine the device reproducibility, and the distributions of ON/OFF currents (I\text{ON} and I\text{OFF}) and SET/RESET bias (V\text{SET} and V\text{RESET}) have been summarized. The statistical distribution of ON/OFF currents read at 0.5 V bias is shown in Figure 2h. Evidently, the values of ΔI/(2ΔI)/I\text{mean} for the ON/OFF currents are approximately 28.87% and 68.90% according to the Gaussian fitting results. The variation range of currents basically has no change in comparison with the large ON/OFF ratio of more than 10⁶, precluding the probability of overlap between ON and OFF conductive states. In addition, the mathematical histogram and the statistics of the SET/RESET voltage bias shown in Figure 2i exhibit relatively dispersed electrical bias distributions, which is in contrast to the centralized switching voltage distributions of the carbon-rich filament mechanism due to the extremely localized carbon filaments within only one breakdown area. [77]

The endurance property and retention ability of pPPI-based memories were measured at ambient conditions. A bias of 1 V was chosen to realize the reading procedure due to two reasons: on the one hand, the SET and RESET voltage biases are mostly concentrated in the region of around 3 V; in this respect, selection of the reading bias at 1 V or a few tenths of 1 V both has no influences on the program and erase operations, thereby achieving the reading procedure successfully. On the other hand, the output current signals of ON/OFF states read at 1 V or a fraction of 1 V are basically within the same conductance order and the variety between them can be ignored in contrast to the unprecedentedly large switching window; therefore, a reading voltage of 1 V is exploited. Nevertheless, to realize relatively low power consumption for the practical applications of RRAM devices, indeed, much smaller electrical reading bias of a few tenths of 1 V is favorable and desirable. Figure 3a shows the endurance performance of the memory devices. As can be seen, the devices exhibit little fluctuation with the switching margin beyond 10⁷ after 2000 repeated voltage sweeps, suggesting the high controllability, reversibility, and reproducibility of the memory cells. No electrical bias was acquired to retain the conductance states after the cell was SET or RESET. Thus, we plot the ON/OFF resistance states as a function of cycled time to examine the retention capability of the device (Figure 3b). Note that little degradation of HRS/LRS and ON/OFF ratio is observed during the measurement period of ~105 s, ensuring the persistent preservation of stored information. To highlight the improved device characteristics of the as-fabricated pPPI-based RRAM, we have summarized different RRAM devices comprising various organic materials to compare their electrical performances, which indicate that the displayed electrical properties by exploiting pPPI as a functional layer are superior to most of the reported organic systems (Table S1, Supporting Information). Moreover, we have measured the SET and RESET switching speeds using voltage pulses (±5 V, 1 μs). A response time of 200/500 ns can be observed for program/erase operations (Figure S4, Supporting Information).

The electrical characteristics of the pPPI-based devices were also measured at elevated temperatures (303–393 K in step of 30 K) to examine its capability of withstanding the probable thermal shock. As shown in Figure 3c, the forming-free bipolar I–V curves exhibit little fluctuation under various heating temperatures especially at 393 K due to the relatively high glass transition temperature (Tg ≈ 413 K) of pPPI, excluding the possibility that the programming field is impacted notably by the high working temperatures. In addition, the direct current (DC) stress test of the memory cell within the time span of 1000 s was also conducted to verify the information preservation ability under augmented temperatures as shown in Figure 3d. Evidently, no significant degradation and fluctuation were observed among all retention curves of ON/OFF states under different working temperatures, suggesting good thermal stability and archival storage ability of the memory cell. Meanwhile, it should be noted that the electrical current at either the ON or OFF state both augments with increasing temperature and displays a proximate relation ln(I)∝T. This is in accordance with the representative semiconducting transport characteristics and is contrary to the typical metal feature with the conductive metallic filament mechanism. The dependence of electrical current on temperature in semiconductors can be adequately fitted using an exponential function expressed as

\[ I = I_t \exp(-\varphi_a/kT) \]  

and

\[ \ln(I) = \ln(I_t) - \varphi_a/kT \]

where \( \varphi_a \) and \( k \) represent the activation energy under heat and Boltzmann constant, respectively. Thus, according to the Arrhenius plot, by illustrating \( \ln(I) \) as a function of \( 1/T \) and
fitting the experimental data using a linear function (Figure 3e), two well-fitted straight lines can be observed, and the thermal activation energy of 30.9 and 121.3 meV for ON/OFF states can be calculated within the temperature range of 303–393 K on the basis of the straight gradients. Furthermore, note that the switching window maintains more than 10⁷ at a high temperature of 393 K, which endows the cross-bar cell with endurance to heating process. Subsequently, we further fabricated flexible pPPI-based memory cells to investigate the mechanical flexibility of the active layer. As shown in Figure 3f, the flexible pPPI-based devices present smooth SET/RESET operations and a large memory window beyond 10⁷, whose electrical performance is comparable with that on the rigid glass substrate. Moreover, the respective resistance states at ON/OFF states and the bipolar resistive switching functionality can be maintained with minor fluctuation after 100 bending cycles, indicating the good mechanical durability and possible practical flexible applications of pPPI.

Next, to reveal the resistive switching and conduction nature of the pPPI-based memory cell, the plot of cell area versus device resistance is first shown in Figure S5, Supporting Information, and exhibits the fact that the resistance displays a negative correlation with the cell area in the case of HRS, whereas the resistance in LRS is irrelevant to the cell area, suggesting that the local conducting path exists in the LRS of the RRAM device originating from the formation of conductive channels inside the functional layer. Subsequently, the positive I–V curve plotted in the logarithmic scale and the corresponding fitting using a linear function for different portions. h,i) Resistive switching mechanism of the pPPI-based memory consisting of formation and rupture of conductive channels composed of defect-captured holes.
viewed. To analyze and understand these phenomena, the energy band alignment of the pPPI with electrodes is schematically shown in Figure S6a, Supporting Information. The work functions of Al and ITO are 4.3 and 4.8 eV, respectively, according to a previous work, whereas pPPI possesses an HOMO of 5.58 eV and an LUMO of 2.45 eV. It is worth noting that the injection barrier of electrons is much larger than that of holes based on the energy discrepancy between the electrodes and the pPPI active layer, signifying the hole carriers dominant behavior. Subsequently, according to the fitting results, \( \text{In}(I) \) is approximately linearly dependent on \( \text{In}(V) \) (slope \( \approx1.1 \)) during the OFF state ranging from 0 to 0.5 V. In this region, the small bias together with the injection barrier gives rise to the poor injection effect and induces thermionic emission of the holes from Al to the HOMO level of pPPI, which is also attributed to ohmic conduction (process I; \( I \propto V \)). Next, another linear correlation with the gradient of \( \approx2.1 \) is viewed by imposing the DC voltage from 0.5 to 4.4 V. The injection rate of holes augments significantly on account of the sensitive Schottky barrier under external electrical stress in which the depth of injection barrier declines with increased voltage bias (Figure S6b, Supporting Information). Then, most hole carriers generated by the synergistic effect between the decreased Schottky barrier and the thermionic emission are trapped gradually by the defects existing in the pPPI active layer, leading to the space-charge-limited current (SCLC obeying the Child law) predominant transport characteristics (process II; \( I \propto V^n \)). The already captured hole charge carriers result in an inner electrical field that can promote the trapping operation of more holes by defects. Along with the persistent augment of voltage sweep exceeding the threshold bias (\( \approx4.4 \) V), the injection and capture rates of holes increase rapidly, and thereby the pPPI defects are fully filled with the passage of time, resulting in the complete trapped conductive paths and hence the SET operation (process III; \( I \propto V^n, n > 2 \); Figure 3h). After the electrical bias exceeds the threshold voltage and sweeps back to 0 V, the relation between \( \text{In}(I) \) and \( \text{In}(V) \) is in good agreement with Ohm’s law, and the slope of the fitted straight line is extracted to be 1.1, demonstrating ohmic-conduction-based LRS (process IV; \( I \propto V \)). Moreover, the captured holes by defects in pPPI are maintained during the outage process, indicating a good trapping stability of holes in pPPI-based devices. Conversely, the extrusion of holes from defects (detrapping process) can be obtained by sending a reverse negative voltage sweep to the device, and hence, the inner electric field generated by captured holes also vanishes. In this process, the multiple conductive channels formed by trapped holes are ruptured, and erasing operation of the stored information is performed (Figure 3i and Figure S4c, Supporting Information). [78]

The Au devices exhibit a similar energy band alignment and thereby analogous resistive switching nature to that with Al TE, whereas Au owns a relatively large work function in contrast to Al, which leads to comparatively large electrical current at the OFF state due to the lower Schottky barrier and larger tunnelling rate of holes.

To examine the microscaled charge carriers (holes) trapping and detrapping ability and the trapping retention capability of the pPPI active layer, the in situ KPFM composed of carrier injection and surface potential monitoring was further performed to observe real-space imaging based on the charge capture operation. [79] As shown in Figure 4a, the charge carriers were injected longitudinally into a contact mode by scanning the pPPI active layer with platinum-/iridium-coated positive-/negative-biased conductive tip. During the measurement, 6 V biased tip first scanned a 1 \( \mu m \times 1 \mu m \) sample area; meanwhile, the positive holes were injected and trapped by the existing defects in the pPPI thin film, which increased the surface potential of this region. Then, the surface potential evolution within a 3 \( \mu m \times 3 \mu m \) scanning area was monitored by KPFM at once. The protrusion in the center of the 3D potential image shown in Figure 4b confirms the good hole trapping ability of the pPPI active layer, which is similar to the SET operation (holes trapping in positive DC bias) of the memory device. Subsequently, −6 V tip bias was sent to scan the same sample area (1 \( \mu m^2 \)) to immit electrons followed by the detection of the surface potential in the KPFM mode while retaining other parameters unchanged (Figure 4b). Note that the surface potential decreases a lot and returns to the original state basically due to holes dissipation under electron–hole recombination, which is analogous to the RESET process (holes detrapping in reverse negative stress). The retain capability of holes trapping was also evaluated by scanning another 1 \( \mu m^2 \) sample area with 6 V biased tip and then monitoring the contact potential difference (CPD) of 3 \( \mu m^2 \) scanning area in the KPFM mode with respect to time (Figure 4c,d). The augmenting surface potential of 0.215 V within the middle area after 5 min can be observed due to vast hole infusion, indicating a good hole injection and trapping efficiency. On the other hand, the original captured holes exhibit 86% release after 35 min, implying a proper maintenance ability of trapped holes in the pPPI film.

Moreover, CAFM was implemented to reveal the microscopic operation nature of the nanoscale pPPI-based resistive memory composed of the AFM conductive tip/pPPI active layer/ITO/glass structure. [80] The nanoscale current profiles under electrical bias with various operation amplitudes and polarities are shown in Figure 4e,f. For region A, the loop current in scale of tens of picoampere can be obtained without the SET process. However, large current signal up to 4.5 nA is acquired in region B after applying electrical stress with a magnitude of 6 V to the surface of the pPPI thin film, demonstrating that the state of the nanoscale device has been transferred from OFF to ON. Subsequently, a read bias of 1 V was exerted to the pPPI layer in region C and negligible degradation of nano-ampere current can be observed, indicating a good retention capability and nonvolatile characteristic of the nanoscaled devices. Finally, the device can return to its original HRS when bearing a reverse negative voltage of 6 V (region D). The microcosmic SET/RESET behaviors are in good agreement with the macroscopic resistive switching process of our fabricated devices.

The charge carrier (holes) trapping and detrapping processes of the pPPI-based devices under positive and negative voltage bias are extremely analogous to the transmission of chemical neurotransmitters between biological synapses. When external action potentials and nerve impulses are transmitted through axon to synaptosome, the permeability of calcium ions across the presynaptic membrane is significantly enhanced and calcium ions in the synaptic cleft enter the synaptosome simultaneously, prompting synaptic vesicles to tightly fuse with the presynaptic membrane and thereby rupture. The neurotransmitters in the
vesicles are released to the synaptic space and transmit across synapse to bind to the protein receptor on the subsynaptic membrane, which alters the osmosis of ions passing through the subsynaptic membrane and further gives rise to sudden excitatory or inhibitory potential changes in the postsynaptic membrane. Correspondingly, the successive electrical pulse trains that are equivalent to nerve impulses are imposed onto the Al TE that imitates presynaptic membrane to stimulate the diffusion and trapping/detrapping of holes in the pPPI active layer and, hence, modulate the device conductance monotonically, whereas the grounded ITO BE is used to mimic the dendrite of the subsynaptic membrane, which monitors ephemeral signals via connection strengths between neurons (Figure 5a). In neurobiology, the released neurotransmitters that have docked with protein receptors under a presynaptic spike can induce excitatory or inhibitory postsynaptic current denoted as EPSC or inhibitory postsynaptic current (IPSC). Thus, the current change between initial current and EPSC/IPSC induced by a battery of electrical stimulation with the fixed potentiating value (±5 V), reading bias (±1 V), and diverse durations (0.01, 0.05, 0.1, and 0.5 s) is shown in Figure 5b. Obviously, the amplitudes of current change increase from $1.8 \times 10^{-4}$ A to $9 \times 10^{-4}$ A during positive spike potentiation and augment from $2.55 \times 10^{-4}$ A to $1.03 \times 10^{-3}$ A under negative bias depression while increasing the durations from 0.01 to 0.5 s. This phenomenon may be originated from increased conductive paths and heat-induced channel rupture with increased pulse widths. This behavior extremely resembles the temporary enhanced/attenuated synaptic weight or excitatory/inhibitory postsynaptic potential (EPSP/IPSP) in chemical synapses.

Subsequently, the modulating synaptic connection arose from a single action potential acquires prescribed time for calcium ions and neurotransmitters to recover to a steady state; therefore, an enhanced synaptic response can be observed by imposing a second same impulse soon after the prior one. This physiological behavior is known as PPF/PPD, which belongs to short-term plasticity (STP) and controls decoding and processing of temporal data [81, 82]. As shown in Figure 5c,d, such a characteristic can also be achieved in our device by sending consecutive two stimuli (±5 V, 0.1 s) with inter-spike separation of 0.1 s to the Al electrode. Note that the triggered enhanced and subdued postsynaptic current (PSC) can be observed, respectively, after a pair of potentiating (positive) and depressing (negative) impulses arrive in a rapid sequence (see the inset of Figure 5c,d).
In addition, the PPF/PPD index with the relation \((\Delta I_2 - \Delta I_1)/\Delta I_1 \times 100\%\) (\(\Delta I_1\) and \(\Delta I_2\) represent the relative current of the pre- and post-spike responses) is introduced to describe and calculate the synaptic weight change quantitatively. Apparently, the synaptic weight change systematically augments with decreased time interval, which can be well fitted by a double-phase exponential function

\[
\text{PPF/PPD} = B + C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2)
\]

where \(B\), \(C_1\), \(C_2\), \(t\), \(\tau_1\), \(\tau_2\) refer to fitting constant, initial phase potentiation amplitudes, inter-pulse interval, and signal decay constants, respectively. For positive voltage pulses, the representative signal relaxation constants of the fast and slow decay terms correspond to 43 and 1077 ms, respectively, whereas the two respective fitting time constants equal to 56 and 1213 ms for negative bias spikes. These results agree well with the time frame of the chemical synapses. \(^{13,12,81,82\text{a}}\) It might be comprehended in the view that the smaller positive inter-spike time intervals allow slight holes detrapping process and less Joule heat but lead to more effective formed conductive channels so that the enhanced electrical conductance of the device occurs. Nonetheless, the smaller negative intervals induce less hole-trapping operation but gives rise to much more Joule thermal energy, vast detrapping of holes, and serious rupture of conductive paths, which finally results in the decreased device conductance.

Neurobiologically, learning and memory functions in the human brain are related to synaptic plasticity, which is the connection strengths between different neurons. In addition, the intensification and deterioration of synaptic plasticity can be tuned via the various diffused ionic fluxes, such as \(\text{Ca}^{2+}\), \(\text{Na}^+\), \(\text{Mg}^{2+}\), and \(\text{K}^+\), and thereby the injected drifted neurotransmitters. As a vital property of synaptic plasticity, SRDP describes a physiologic behavior in which regulating the pre-spike stimulus rates results in the modulation of connection strengths. \(^{83\text{b}}\) Therefore, 15 identical voltage pulses (\(\pm 5\) V, \(0.1\) s) with fixed bottom bias (\(\pm 1\) V) and various spike frequencies (from 1.67 to 9.09 Hz) are used onto pPPI-based electronic synapse to confirm the...
frequency-dependent synaptic weight (Figure S7, Supporting Information). Apparently, the consolidation/deterioration of the electrical conductance is enhanced steadily with increasing stimulation frequency, validating the dependency of the synaptic plasticity on the bias spike rate. On the other hand, as indicated in the figure, the electrical current is excited or inhibited significantly under the imposed first several spikes, whereas the current modulation become more saturated during the subsequent stimulation pulse trains, indicating the nonlinear relation of current change and pulse number. Nonetheless, it is noteworthy that a smaller time interval gives rise to a larger step of current change with bigger jumps under identical potentiating amplitude ($\pm 5\, \text{V}$) and pulse width (0.1 s). Especially, the current change of pPPI-based synapse is approximately linearly proportional to the spike number and presents smooth potentiation or depression trend with a time interval of 0.5 s. This almost linear correlation between spike number and conductance modulation is highly appealing for the implementation of backpropagation algorithm that uses electronic devices with memristive behaviors for highly efficient vector-matrix multiplication calculation in image processing. To investigate the influences of pulse trains on the linear current regulation, electrical measurements by varying the potentiating amplitudes from $\pm 3$ to $\pm 6\, \text{V}$ are conducted to the synaptic device, as shown in Figure 5e,f. Similar as before, under a fixed time interval, greater potentiating bias brings about larger change rate of the device conductance and faster saturation rate of the electric current so that proximate linear connection can be achieved using consecutive impulses with lower spike voltages. This correlation between spike bias and current change could be depicted by the Butler–Volmer equation, which describes the electric current of the synaptic device before saturation under consecutive pulse stimulation\textsuperscript{[84]}

$$J = J_0 \left[ e^{\frac{e \varepsilon V}{kT}} - e^{\frac{e \varepsilon V V}{kT}} \right] \text{ (Butler–Volmer equation) } \quad (5)$$

where $J$, $J_0$, $e$, $\varepsilon$, $k$, $T$, and $V$ represent the electrode current density, exchange current density, electronic charge, number of charges related to the electrode reaction, cathodic charge transfer coefficient, Boltzmann’s constant, absolute temperature, and electric potential, respectively. Subsequently, this complex exponential equation can be transformed and simplified into the relatively simple expression at a tiny numerical value of $V$ and hence extremely small exponents in the Butler–Volmer equation (limit condition: $e^x \approx x + 1$ when $x$ is very small)

$$J \approx J_0 \left[ \left( \frac{e \varepsilon V}{kT} \times V + 1 \right) - \left( - \frac{(1 - \epsilon) e \varepsilon V}{kT} \times V + 1 \right) \right] \quad (6)$$

$$J \approx J_0 \left( \frac{e \varepsilon V}{kT} \right) \quad (7)$$

Evidently, on the basis of the limit condition of the Taylor series expansion, the expression of $J$ could be simplified and exhibits a linear relation to $V$ under infinitesimal exponents (infinitesimal $V$). That is to say, more linear relationship between the current change and the pulse number can be observed before the saturation of device conductance while stimulating the electronic synapses using successive pulse trains with smaller potentiating bias. Moreover, this linear dependence between $J$ and $V$ also accounts for the approximate linear variation of the electrical current under the continuous spikes regulation with suitable voltage/time parameters. Furthermore, what is noteworthy is that the change of the electric current at a steady state (saturation) augments with increased potentiating voltage bias and decreased time interval. In neurobiology, the connection strengths of the Hebbian rule are described as

$$W_{ij} = \frac{1}{p} \sum_{k=1}^{p} x_i^k x_j^k \quad (8)$$

where $W_{ij}$ is the synaptic weight between $i$ neuron and $j$ neuron, $p$ is the number of training mode, $x_i^k$ is the $k$th input of $i$ neuron, and $x_j^k$ is the $k$th output of $j$ neuron. It is apparently observed that the connection strength modification is in direct proportion to the multiplication of import strength and export intensity, and the reductive stimulation trains can reinforce the synaptic weight. Nonetheless, the connection strengths between neurons have a finite plasticity on account of the intrinsic constraint according to the Hebbian rule. Correspondingly, the electrical current of the synaptic device reaches a stable state after imposed numerous spikes, which can be explained that the trapping sites including defects are fully filled by holes and multiple conductive channels are constructed for positive potentiating voltages. Meanwhile, some shallow trapped holes are released, and thereby some fragile conductive paths are ruptured by induced heat energy for reverse negative bias, giving rise to a stabilized saturation state.

In biology, a significant characteristic of chemical synapses is plasticity where the connection strength between neurons can be regulated by adjusting the time lag between presynaptic action potential and postsynaptic impulse stimulus. This phenomenon is known as STDP, which depicts the neuromorphic learning process in a biological synapse on the basis of the Hebbian rule and is closely related to the shape of stimulated spikes.\textsuperscript{[85]} Triggering the presynaptic action potentials ahead of postsynaptic impulse stimulus results in augmented connection strengths and hence long-term potentiation, whereas using the postsynaptic impulse antecedent to presynaptic stimulus gives rise to declined synaptic weight and thereby persistent depression. In addition, the minor time lag between pre- and postsynaptic spikes can induce a large synaptic connection change, whereas negligible weight modification can be observed under a relatively long time interval. To examine the probability of realizing STDP learning operation based on the pPPI-based electronic synapse, pre-pulses were applied to the Al TE, which is taken for the presynaptic membrane, and post-spikes were used to the ITO BE, which is deemed as the postsynaptic membrane. Meanwhile, two pairs of spikes (Figure S8, Supporting Information) in which the time delay $\Delta t$ is defined as the interval between the beginning of two separated pulses were imposed to the synaptic device. Thus, the synaptic weight change $\Delta W = (I_a - I_b) / I_0$ under variable time intervals can be obtained and recorded by extracting the initial current $I_a$ before stimulus and the electric current $I_b$ after stimulation with an increased timescale ranging from 1 to 150 s. The plots of the relation between synaptic weight change and time delay in the symmetric Hebbian rule and symmetric anti-Hebbian rule are shown in Figure 5g,h, respectively. Apparently, the variation of time delay has a significant influence.
on the sign and amount of the synaptic weight change. These two
STDP learning rules can be well fitted using the exponential
Gaussian function as follows:\[96]\[87\]
\[
\Delta W = C \exp \left( -\frac{\Delta t^2}{\tau} \right) + W_0
\]
where \(\Delta W\), \(C\), \(\Delta t\), \(\tau\), and \(W_0\) represent change of synaptic weight,
fitting constant, time delay, fitting time value, and synaptic
weight constant, respectively. The fitting time values of our
synaptic device are on the same millisecond scale as the chemical
synapses, indicating the successful implementation of STDP.\[87\]
Last but not the least, energy efficiency and relatively low
power consumption for artificial synaptic emulation and subse-
quent neuromorphic computing are also extremely important.
Thus, we finally measured synaptic behaviors of newly fabricated
devices (area of crossbar: 15 \(\mu\)m \(\times\) 15 \(\mu\)m) using shadow mask
with 15 \(\mu\)m interval and discovered the same potentiation and
depression phenomena under positive and negative (read volt-
age: \(\pm\)1 V, potentiation voltage: \(\pm\)5 V and duration of 0.1 \(\mu\)s)
directions (Figure 5i). Meanwhile, the energy dissipation
(5.6 \times 10^{-12} J and 5.1 \times 10^{-12} J for positive and negative biases,
respectively) calculated from \(E = \int (V \times I) dt\) meets the require-
ment for neuromorphic computing. In addition, the energy
consumption can be further reduced when using technology
with the nanometer scale, which indicates promising synaptic
applications based on our RRAM device with a low power
consumption.

3. Conclusions
In summary, we have reported an organic small molecule pPPI-
based memory device, which can be used to mimic the different
functions of chemical synapses in a nonvolatile and reversible
manner. The aforementioned device exhibits remarkably large
switching window, good endurance ability, robust data record
retention capacity, as well as favorable thermal stability. In addi-
tion, the holes trapping and detrapping processes of the pPPI
film under positive and negative voltage bias are extremely anal-
ogous to the transmission of chemical neurotransmitters in bio-
logical synapses. Therefore, bio-inspired synaptic phenomena,
including EPSC, PPF, PPD, SRDP, and STDP, have been imple-
mented in the synaptic device.

What is noteworthy is that the test condition of our pPPI-
based RRAM devices is ambient atmosphere, and hence, the
existence and influences of water on our cells are inevitable.
Moisture (water molecules) possesses noteworthy influences
on the defect-chemical and electrochemical performance of the
RRAM devices on the basis of valence change and electro-
chemical metallization mechanisms because it can simply
produce electrode chemical reactions and thereby generate a
series of products, for example, oxygen, hydrogen, protons, or
other mediate ionic charges (mobile species), which finally
can result in an augment of the total device conductance.\[88,89\]
In particular, water molecules can function as the source for
the counter electrode reaction and impact the forming process,
SET and RESET kinetics, density, composition of the active layer,
etc.\[90]\] In addition, water molecules can also serve as corrosive
agents and thereby corrode the metal electrodes easily (Gibbs
free energy of oxides is negative, and thus, the reaction is spon-
taneous), which can give rise to a poor retention capability and
hence short service life of the RRAM devices.\[91\] Therefore, with
respect to our pPPI-based RRAM devices, prolonged exposure
to humidity might also induce various mobile ionic species (pro-
tons) originating from the electrochemical reaction of water and
hence affect the device conductance, program and erase opera-
tions and electrode corrosion, etc. These relations will be further
investigated in our future work using diverse methods, such as
CV,\[92\] isotope labeling, time-of-flight secondary-ion mass spectrometry,\[93\] etc. In addition, encapsulation layers, such as TiN,
Pt, or Al2O3, can be exploited for the short-term efficient protec-
tion of the RRAM cells from moisture and can improve the
device retention ability.

On the whole, our study offers an avenue to implement con-
ductance tuning of the two-terminal memory by the solution-
processing organic small molecule and accelerates the evolution
of electronic synapses using organic electronics.

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.

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