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Photoelectric Multilevel Memory Device based on Covalent Organic Polymer Film with Keto–Enol Tautomerism for Harsh Environments Applications

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Covalent organic polymers (COPs) memristors with multilevel memory behavior in harsh environments and photoelectric regulation are crucial for high-density storage and high-efficiency neuromorphic computing. Here, a donor–acceptor (D–A)-type COP film (Py-COP-3), which is initiated by keto–enol tautomerism, is proposed for high-performance memristors. Satisfactorily, the indium tin oxide (ITO)/Py-COP-3/Ag device demonstrates multilevel memory performance, even in high temperatures, acid-base corrosion, and various organic solvents. Moreover, the performance can be modulated by the photoelectric effect to maintain a great switching behavior. By contrast, Py-COP-0, with similar structure and chemical composition to Py-COP-3 but without keto–enol tautomerism, exhibits binary storage performance. Further studies unravel that both the formation of conductive filaments and charge transfer within D-A Py-COP-3 film contribute to the resistive switching behavior of memory devices.

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1. Introduction

There is a strong demand for the development of ultra-high density data storage materials and devices for the coming big data era,^[1,2] in which the design and synthesis of novel organic resistive switching materials have garnered intensive research interest. With a deeper understanding of small molecule and polymer memristors, organic polymers are widely studied to store electrical bits of information because of their excellent flexibility and electrical current switching capability.^[3,4] Nowadays, three or more conductive states could be realized in multilevel memristors employing small molecules, conjugated polymers, composite materials based on blends of polymers or polymers with small organic molecules, and nanoscale active materials.[5-11] Compared with the binary system, the capacity

of the ternary system has increased by a magnitude of 10⁶ per unit area.^[9] However, many organic active materials cannot withstand high temperatures and solvents, which significantly limits their application range, such as aerospace exploration, geothermal, oil and gas industries, etc.

Covalent organic polymers (COPs) thin films are promising memory materials owing to their excellent solution processability, light weight, outstanding uniformity, good stability, and mechanical flexibility.^[12-16] COPs feature a well-defined structure through rational molecular design and can attain a clearer understanding of the switching mechanism through theoretical simulations, which have led to a widespread research boom in the field of resistive switch memory. In particular, the adjustment in the molecular skeleton or substituents can significantly alter the storage performance.^[17–20] Recently, much effort has been devoted to exploiting COPs for resistive switching memory devices. However, these studies only have focused on implementing binary storage. To the best of our knowledge, there are no reports on COP materials structurally modulated by keto-enol tautomerism to achieve multilevel memory behavior tolerable in harsh environments.

Establishing donor–acceptor (D–A) configuration in polymerbased memristors is recognized as a reliable means to facilitate inner ion migration via adjusting the microstructure,^[21] which exerts an influence in the formation of conductive filaments of





Scheme 1. Synthetic process of Py-COP-3 film and the fabrication of the ITO/Py-COP-3/Ag device.

memory devices. Besides, it is believed that both the intensive electron delocalization and strong dipole moment of molecule in a D-A polymer would be capable of effectively stabilizing the conductive charge-transfer state and thus generating the nonvolatile nature of the high-conductivity state in an electronic memory device.^[22] In this regard, it is expected that both the physical properties and storage performance of the device could be promoted in a D-A-type COP. Here, the facile design of D-A-type Py-COP-3 film by introducing the β -ketoenamine moiety for realizing efficient photoelectric multilevel memory devices available in harsh environments is reported. Through the polycondensation of 1,3,6,8-tetrakis(4-aminophenyl)pyrene (PyTTA) with 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (THTA), followed by the keto-enol tautomerism, a D-A-type Py-COP-3 film was generated and successfully demonstrated for multilevel memory devices (Scheme S1, Supporting Information). Moreover, the indium tin oxide (ITO)/Py-COP-3/Ag memory device can be modulated by light illumination to maintain a great switching behavior. In contrast, Py-COP-0, with similar structure and chemical composition to Py-COP-3 but without keto-enol tautomerism, exhibits binary storage performance. Further studies unraveled that both the formation of conductive filaments and charge transfer within D-A Py-COP-3 film contributed to the resistive switching behavior of memory devices.

2. Results and Discussion

Py-COP-3 was chosen as an example for detailed elucidation. The Py-COP-3 film was fabricated on a conductive ITO glass substrate in a mixed solvent of *N*,*N*-dimethylacetamide (DMAc) and o-dichlorobenzene (o-DCB) at 120 °C for 3 days (Scheme 1, for details, see the Supporting Information). These as-prepared films and bulk powders were then characterized by Fourier transform infrared (FT-IR), solid-state ¹³C cross-polarization magic angle spinning NMR (¹³C CP-MAS NMR), UV-visible (UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), N₂ sorption isotherms, scanning electron microscopy (SEM), and contact angle tests (Figure 1 and Figures S1–S10, Supporting Information). Features originating from the imine bonds (C=N) (1622 cm⁻¹) in the FT-IR spectrum for Py-COP-0 evidence the occurrence of the Schiff base reaction (Figure S1, Supporting Information), which was further confirmed by the disappearance of the aldehyde (1664 cm⁻¹) and amine (3352 cm⁻¹) stretching signals. In contrast, C=C peaks at \approx 1574 cm⁻¹ were detected for Py-COP-3, clarifying that keto-enol tautomerism took place (Figure 1a). Moreover, the C=O peaks at \approx 1617 cm⁻¹ were merged with the C=C stretching band and appeared as a shoulder, indicating the coexistence of the two kinds of tautomers.^[23,24] The formation of the Py-COP-3 was also unraveled by ¹³C CP-MAS NMR (Figure 1b). Py-COP-3 showed distinctive signals at ≈184.6, 146.5, and 107.0 ppm, corresponding to the carbonyl (-C=O), the imine carbon (-C=N), and the enamine carbon (-C=C-N-), respectively, which is consistent with the reported β -ketoenamine-linked COFs.^[24–27] UVvis spectrum of as-synthesized Py-COP-3 indicates the successful polymerization of two monomers (Figure 1c): the absorption band of Py-COP-3 is broadened, and the degree of conjugation is enhanced after polymerization. Besides, the successful synthesis of Py-COPs was equally surveyed by XPS (Figure S4, Supporting Information). With regard to the C 1s XPS spectrum of Py-COP-0, the peaks at 285.74 and 284.70 eV corresponded to imine carbon and the conjugated structure of carbon, respectively (Figure S4b, Supporting Information). For the C 1s XPS spectrum of Py-COP-3 (Figure S4e, Supporting Information), three typical signals appear, which are attributed to the carbonyl carbon (287.40 eV), imine carbon (286.25 eV), and the conjugated structure of carbon (284.80 eV), respectively.^[28,29] TGA was employed to study the thermal stability properties of Py-COPs (Figure S5, Supporting Information). The results showed that both Py-COP-0 and Py-COP-3 can be thermally stable. The amorphous nature of Py-COP-3 was unveiled by the broad PXRD patterns (Figure S6, Supporting Information), which was further evidenced by the TEM results with no apparent fringes (Figure S7, Supporting Information). As revealed by the SEM images, Py-COP-3 exhibits a unique uniform morphology (Figure S8, Supporting Information). The uniformity in morphology suggests that Py-COP-3 has a homogenous composition throughout, without significant impurities or variations in its structure.^[30] The nitrogen sorption isotherms are assigned to type I isotherm, which indicates the microporous structure of Py-COP-3. The Brunauer-Emmett-Teller surface area of Py-COP-3 was evaluated to be 646.9 $m^2 g^{-1}$ (Figure S9, Supporting Information). The successful growth of Py-COP-3 could also be confirmed by the contact angle tests (Figure S10, Supporting Information), demonstrating significantly improved hydrophilicity upon the introduction of hydroxyl groups (Py-COP-0: 80.9° vs Py-COP-3: 50.0°).







Figure 1. a) FT-IR spectrum of Py-COP-3; b) ¹³C solid-state NMR spectra of Py-COP-3; c) the UV-vis spectra of Py-COP-3; d,e) plane-view and crosssectional SEM images of the as-fabricated ITO/Py-COP-3/Ag (the Py-COP-3 film thickness: 50 nm; the Ag electrode thickness: 120 nm); f) the AFM image of ITO/Py-COP-3 film (R_q = 5.55 nm).

The plane-view and cross-sectional images by SEM unraveled that the Py-COP-3 film was uniform with an average thickness of ≈50 nm (Figure 1d,e and Figure S11d,e, Supporting Information). Furthermore, atomic force microscopy (AFM, Figure 1f and Figure S11a-c, Supporting Information) reveals a relatively smooth surface of the Py-COP-3 film with root mean square (rms) roughness of 5.55 nm. It has been reported that the uniform thickness and the smooth surface of the active layer films can facilitate the migration of charge carriers, and thus beneficial for reaching a lower threshold voltage and higher ON/OFF ratios.^[31] The current–voltage (I–V) characteristic curves of ITO/Py-COP-3/Ag memory devices under the compliance current (CC) of 0.5 A are shown in Figure 2a. When the positive bias sweeping (from 0 to +5.0 V) was applied, the device switched from the low-conductivity state (OFF, $\approx 10^{-6.4}$ A) to the intermediate-conductivity state (ON1, $\approx 10^{-3.9}$ A) and further to a high-conductivity state (ON2, $\approx 10^{-1.4}$ A). The threshold voltages were $V_{\rm th1}$ = +1.14 V and $V_{\rm th2}$ = +1.73 V, respectively. The ON2/ON1/OFF current ratio was 10^{5.0}/10^{2.5}/1. This device exhibited a typical ternary nonvolatile write-once read-many-times (WORM) memory behavior. The ternary stability of the ITO/Py-COP-3/Ag device can be validated by random 142 sweeping cycles (Figure 2b). The write and erase operations of the ITO/Py-COP-3/Ag device in pulse mode also can be measured under set pulses (+1.8 V/10 µs) and reset pulses (-2.0 V/1 ms). Figure S12 in the Supporting Information shows that the ON/OFF states can be maintained for 2×10^3 endurance cycles, suggesting good device reliability. Furthermore, the currents of "OFF", "ON1," and "ON2" states under the constant stress of +1.0 V are stable with neglectable degradations (Figure 2c). In contrast, the ITO/Py-COP-0/Ag memory device mainly exhibited WORM binary memory performances with a current ratio of $10^{3.3}/1$ (Figure S13d, Supporting Information). The ITO/Py-COP-0/Ag memory device remains stable under a constant voltage of +1.0 V for 1 \times 10⁴ s without degradation, indicating the good reliability of this device. Figure 2d shows the cumulative probability (CP) of the high and low resistance values for the ITO/Py-COP-0/Ag and ITO/Py-COP-3/Ag memory devices. The results revealed that the ON/OFF ratios of Py-COP-0 and Py-COP-3 were 1.73×10^5 and 5.06×10^5 , respectively, which suggests that these devices meet the requirements of memristor device applications and can be applied to big data storage.^[32] The first SET voltage (V_{th1}) of the Py-COP-3-based device was distributed in the range of 0.91–1.34 V, while the second SET voltage (V_{th2}) was mainly centralized between 1.69 and 1.89 V (Figure 2e). Compared to the broad V_{th1} distribution of Py-COP-0, Py-COP-3-based devices were more consistent with $V_{\rm th}$, suggesting the possibility for the Py-COP-3-based devices to be a candidate for multilevel resistive memory. Moreover, to explore the effect of β -ketoenamine moieties on the ternary yield of the devices, the test on a batch of individual devices (sample cells: 100) is conducted. The ternary yield was calculated by the number of ternary memory behaviors in 100 memory cell measurements. The ternary yield of the ITO/Py-COP-3/Ag device was 72%, while the ITO/Py-COP-0/Ag device can only present binary resistive states (Figure 2f).

To clarify the effect of the thickness of the Ag electrode and Py-COP-3 film on the ITO/Py-COP-3/Ag memory device performance, Py-COP-3 films with different thicknesses (18–240 nm)

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Figure 2. ITO/Py-COP-3/Ag memory device at 25 °C: a) *I*–V characteristics under the positive scan showing the corresponding OFF-to-ON1 and then to ON2 transitions; b) stabilities of the device showing 142 cycles at 25 °C; c) retention stability of ITO/Py-COP-3/Ag memory device at "OFF," "ON1," and "ON2" states under a constant "read" voltage of +1.0 V; d) the resistance values cumulative probability of Py-COP-0- and Py-COP-3-based device; e) SET voltage distribution of Py-COP-0- and Py-COP-3-based devices.

were prepared by varying the reaction time (1, 3, 5, and 7d), while the thicknesses of Ag electrode were controlled by sputtering time. Notably, the device with 50 nm film thickness exhibits the best multilevel-memory performance when the thickness of the Ag electrode (≈120 nm) is fixed (Figure S14, Supporting Information). The ON and OFF currents increased inversely with the film thickness, which may result from the enhanced conductance of Py-COP-3 films.^[33] It is worth noting that when the thickness of the Py-COP-3 films was less than 18 nm or greater than 240 nm, the ON/OFF ratio of the devices was generally low. Then, we fabricated devices with varied Ag electrode thickness while fixing the thickness of Py-COP-3 film (≈50 nm) (Figure S15, Supporting Information). Interestingly, the ON/OFF ratios and turn-on voltage showed clear independence in the thickness of the Ag electrode, demonstrating that the turn-on voltage is more likely to depend on the intrinsic properties of the Py-COP-3 films.^[17]

We also investigated the multilevel data storage performance of the as-fabricated ITO/Py-COP-3/Ag memory device by adjusting the compliance currents (I_{CC}) value during the SET process. By adjusting the I_{CC} value (ranging from 5 to 0.01 mA), the SET voltage was found to be dependent on the I_{CC} , which decreased from 0.72/0.87 to 0.46/0.64 V (**Figure 3**a and Figure S16a–d, Supporting Information), implying the multilevel information storage can be realized. Figure S16e–h in the Supporting Information shows the cumulative probability of the LRS and high resistive state (HRS) when the I_{CC} is 5, 1, 0.5, and 0.1 mA, respectively. The results revealed that the ON/OFF ratios were 2.75 × 10⁵, 3.24 × 10⁴, 2.95 × 10⁴, and 4.59 × 10², respectively. The device also could be stably erased to an intermediate resistance state, which

the state can be maintained over 3.6×10^3 s (Figure S17, Supporting Information). Moreover, I_{CC} is positively correlated with V_{RESET} , which is beneficial to the practical application of the lowpower consumption device. Besides, the current values can be maintained well during 20 cycles under different I_{CC} (Figure 3b). The statistical distribution and Gaussian fitting curves of the I_{LRS} with different I_{CC} also supported the multilevel information storage performance of Py-COP-3 resistive random access memory (RRAM, Figure 3c). The effect of the sweeping rate (V_{step}) on the Py-COP-3 memory device has also been investigated, where the shorter V_{step} results in a lower V_{SET} , as illustrated in Figure 3d. Subsequently, we explored the multilevel resistive switching (RS) behavior by regulating the RESET stop voltage. Figure 3e and Figure S18 in the Supporting Information show the multilevel I-V properties with gradually varied RESET stop voltages (-5, -4, -3, -2, and -1 V) and fixed SET stop voltage (+5 V). Notably, high RESET stop voltages implied a reduction in residual CF and extra rupture of CF, generating higher HRS.^[34,35] This device can achieve precise voltage control and switches of different resistance states by adjusting the I_{CC} , V_{step} , and RESET stop voltage, which promotes the practical application of the memristor device.^[36,37] Figure 3f presents a comparison of the device in this work and other COPs-based devices.[17-20,38-40] Compared to other reported works, the COP-3-based memristor features an excellent ON/OFF current ratio and V_{SET} (Table S1, Supporting Information).

Multifunctional RRAM is a class of important electronic devices to implement photo-driven or photon-programming by photoelectric regulation.^[41] To explore the impact of light stimuli

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Figure 3. a) The *I*–V curves of the Py-COP-3-based device under different I_{CC} (5, 1, 0.5, and 0.1 mA); b) 20 cycles with various I_{CC} ($V_{read} = 0.1$ V); c) the distributions of the currents under different I_{CC} of LRS; d) the *I*–V curves of the Py-COP-3-based device under different V_{step} (0.003, 0.005, 0.007, 0.009, 0.01, and 0.03 V); e) the *I*–V curves of the Py-COP-3-based device under different RESET stop voltage (-5, -4, -3, -2, and -1 V); f) comparison of the ON/OFF ratios and SET voltage for the COPs-based memristors with other works.

on switching behavior, the *I–V* curves of the ITO/Py-COP-3/Ag memory devices that were irradiated by light-emitting diodes (LEDs) with different wavelengths were recorded, as displayed in Figure 4a,b and Figure S19 in the Supporting Information. Under dark conditions, the set voltage required to switch the device to the ON state was 0.78 V. In contrast, the set voltage gradually increased to 0.93, 1.05, and 1.41 V under illumination at 628, 520, and 394 nm LEDs, suggesting that photoinduced excitedstate intramolecular proton transfer can enable enol-imine to keto-enamine tautomerization and interfere with proton transfer, which affects the formation of conductive paths.^[25,42,43] In detail, when the light is applied to the Py-COP-3-based memristors in an HRS, the photogenerated carriers in COPs move toward the electrode under the effect of the electric field. However, this movement was hindered by the built-in electric field induced by the enol-imine to keto-enamine tautomerization, which ultimately exhibited an increase of $V_{\rm SET}$ in light conditions.^[44] Therefore, we further investigated the effect of keto-enol tautomerism structure on the photoenhanced RS behaviors of Py-COP-3 and Py-COP-0 by using photoluminescence (PL), transient photocurrent response measurements, and ultraviolet photoelectron spectroscopy (UPS). Compared with Py-COP-0, Py-COP-3 features a much lowered PL intensity that could originate from the retarded electron-hole recombination in Py-COP-3 (Figure S20, Supporting Information). As expected, Py-COP-3 displays a higher photocurrent response, demonstrating that Py-COP-3 with keto-enol tautomerism experiences a higher photogenerated carrier migration efficiency (Figure S21, Supporting Information). To understand the electronic properties of Py-COPs films-based memory

devices, the optical band gaps ($E_{\rm g}$) of the Py-COPs films were derived from UV-vis spectroscopy analysis (Figure S22, Supporting Information). The bandgaps were calculated through Tauc plots to be 2.29 and 2.47 eV for Py-COP-3 and Py-COP-0, respectively. The Py-COP-3 demonstrates a narrower bandgap than Py-COP-0, suggesting that the introduction of hydroxy group and keto–enol tautomerism lead to an enhanced conjugation, thereby reducing the bandgap energy, which is beneficial to the reduction of the energy required for photoelectric transition. Furthermore, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were determined by UPS measurements (Figure S23 and Table S2, Supporting Information). Reversible keto–enol tautomerism may induce electron push–pull effects and proton transfer, resulting in the deeper HOMO energy level (-5.82 eV) of Py-COP-3.^[45]

Moreover, to investigate the electronic structures and surface charge distributions of enol and ketone form of Py-COP-3, we conducted density functional theory calculations based on two fragment models (i.e., enol mode and ketone mode, Scheme 1 and Figure S24, Supporting Information). As demonstrated in Figure S24a-d in the Supporting Information, the HOMO mainly concentrated on the pyrene cores, while the LUMO was confined in the imine linker and its surrounding phenyl rings for both enol and ketone form, enabling efficient charge transfer from HOMO to LUMO in Py-COP-3. However, these two forms have quite different surface charge distributions (Figure S24e,f, Supporting Information), in which the lone pairs of oxygen in ketone lead to negatively charged THTA units and also a more polar framework.

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Figure 4. a) *I–V* characteristics of ITO/Py-COP-3/Ag memory devices under light irradiance with different light wavelengths (light intensity: 180 mW cm⁻²); b) statistical distribution of SET voltages under light illumination with different light wavelengths; c) temperature tolerant performance of ITO/Py-COP-3/Ag memory device in the temperature range of 25–450 °C; d) device stability of "OFF" and "ON" at different temperatures; e) various solvents tolerant performance of ITO/Py-COP-3/Ag memory device.

In recent years, most of the attention has been focused on improving device performance under normal conditions, while the reliability of memristors in harsh environments such as high temperatures, acid-base corrosion, and organic solvents, has yet to be explored. Exploring high-density memories in harsh environments is significant for special industries such as geothermal, oil, and aerospace industries. Here, the temperature-tolerant performance of ITO/Py-COP-3/Ag and ITO/Py-COP-0/Ag memory devices has been appraised. As a proof of concept, the memristors based on Py-COP-3 films (≈50 nm thick) were selected and evaluated as examples. Excitingly, when elevating temperature from room temperature to 100, 200, 300, and 400 °C, the ternary memory behaviors of the ITO/Py-COP-3/Ag device can be retained (Figure 4c), and the cycle stabilities at different temperatures are illustrated in Figure 4d and Figure S25 in the Supporting Information. However, if the temperature reaches 450 °C, Py-COP-3 has undergone about 20% weight loss, which might be caused by the slight collapse of channels and loss of some functional groups in the framework (Figure S26a,b, Supporting Information). Therefore, its memory performance changes from ternary into binary behavior, and the ON/OFF ratio decreased to 10². Besides, the tolerant temperature of the ITO/Py-COP-3/Ag device was obviously higher than ITO/Py-COP-0/Ag (400 °C) (Figure S27, Supporting Information). The ITO/Py-COP-3/Ag memory devices also demonstrate high compatibility against H2O, various organic solvents, and acid-base aqueous solutions (Figure 4e and Figure S28, Supporting Information). In summary, the ITO/Py-COP-3/Ag memory device not only exhibits organic solvents tolerance, but also good durability in acidic and alkaline solutions.

To study the conduction mechanism of fabricated ITO/Py-COP-3/Ag memory devices, the double logarithm of the I-V curves under positive voltage sweep is first replotted (Figure 5a).^[46,47] The low voltage bias region exhibits the Ohmic conductivity characteristic $(I-V^{1.16})$. When the voltage gradually increases, the existing traps are gradually filled. This region obeys the trap-filled limited current rule $(I-V^{1.72})$. With the external electric field further increasing to $V_{\rm th1}$, all the traps were filled, and the I-V curve obeys space charge limited current mode (I- $V^{2.45}$). As the bias voltage reaches $V_{\text{th}2}$, the carriers accumulate to form a conductive path, and a linear I-V relationship is followed $(I-V^{0.99})$. Besides, the I-V curve for the ITO/Py-COP-0/Ag device was investigated in a log-log scale (Figure S29, Supporting Information). Second, the schematic diagram of the initial and set states of the Py-COP-3-based device is depicted in Figure 5b. In the positive sweeping, Py-COP-3 could trap the injected carriers from electrodes. The surface potential change of Py-COP-3 film was examined by in situ Kelvin probe force microscopy (KPFM) to detect charge trapping inside the active layer. The positive bias $(3.0 \times 3.0 \,\mu\text{m}^2, +5 \,\text{V})$ was applied following the negative bias (5.0 \times 5.0 μ m², -5 V), and the surface potential variation is displayed in Figure 5c-e. The potential differences between the charge-trapped and nontrapped regions are 27.7 eV, indicating that the bright regions in surface potential correspond to areas of increased surface potential. It is possible that the injected charge carriers cause an intramolecular charge-transfer (ICT) effect due to the enol-imine to keto-enamine tautomerization induced by the voltage bias.^[48,49] Clearly, the trapped charge carrier could be released by the employment of the positive bias, which is

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Figure 5. a) The log *I* – log *V* fitting curves of ITO/Py-COP-3/Ag memristor under positive voltage sweep; b) schematic diagram of the initial state of the Py-COP-3-based device; c) schematic electrical writing operation in KPFM; d) KPFM surface potential distribution of Py-COP-3 film under a bias of $-5 V (5.0 \times 5.0 \mu m^2)$ followed by a positive voltage (+5 V, $3.0 \times 3.0 \mu m^2$); e) the randomly selected lines profile of KPFM from (d); f) TEM image and elemental distribution maps of a cross-sectional slice of the ITO/Py-COP-3/Ag memory device in its LRS; g,h) HRTEM images of a single nanoparticle in the filaments; i) EDS element analysis of the Ag filament in (h).

beneficial for the rupture of conductive filaments (CFs).^[10,50] Besides, in comparison with the UV-vis spectra of the Py-COP-0, the absorption peak of Py-COP-3 was red-shifted. It means that the Py-COP-3 would be beneficial for ICT due to the effective π -extension and D–A interaction. As a result, the resistive switching from OFF to ON1 state at this voltage could be attributed to the enol–imine to keto–enamine tautomerizationinduced charge transfer. Finally, to verify the filament penetration process, the cross-sectional TEM morphology of the ITO/Py-COP-3/Ag device in the LRS state was prepared by the focused

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ion beam (Figure 5f and Figure S30, Supporting Information). The high-resolution TEM (HRTEM) image enables a direct observation of Ag NPs distributed on the Py-COP-3 film. The energy-dispersive spectroscopy (EDS) measurements were also performed to analyze the chemical composition of the Ag NPs (Figure 5g-i).^[19] The CFs composed of Ag NPs connect with the top (Ag) and bottom (ITO) electrodes. To further understand the effect of the Ag electrode on memory switching performances, the top Ag electrode was replaced by an air-stable Au electrode.^[51,52] During the measurements of ITO/Py-COP-3/Au, the device cannot exhibit resistive switching behaviors, indicating the resistive switching phenomenon is dependent on the appropriate work function of Ag electrodes (Figure S31, Supporting Information). This finding further verified that the memory behavior is correlated more with the top electrode. Therefore, the ternary memory mechanism of the ITO/Py-COP-3/Ag memory device is most likely due to the combination of the enol-imine to keto-enamine tautomerization-induced charge transfer and the CFs, as confirmed by KPFM, TEM, and UV-vis absorption spectra measurements as well as theoretical calculations.

3. Conclusion

In summary, we put forward a proof-of-concept study based on Py-COP-*n* (n = 0, 3) films for realizing efficient multilevel memory devices in harsh environments by adjusting the content of β -ketoenamine moieties readily. The ITO/Py-COP-3/Ag device demonstrates excellent ternary memory performances in harsh environments such as high-temperature environments, acidbase corrosion, and organic solvents. Moreover, the ITO/Py-COP-3/Ag memory device can be modulated by the photoelectric effect to maintain a great switching behavior. The ternary memory mechanism of this ITO/Py-COP-3/Ag device can be recognized as the combination of the enol–imine to keto–enamine tautomerization-induced charge transfer processes and the CFs. This work may serve as the base for the design of high-density multilevel memristors that can work under extreme conditions.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Keywords

covalent organic polymers, harsh environments, keto-enol tautomerism, memristors, resistive random access memory

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