Donor-acceptor-type poly[chalcogenoviologen-alt-triphenylamine] for synaptic biomimicking and neuromorphic computing

Zhizheng Zhao, Qiang Che, Kexin Wang, ... Yubin Fu, Bin Zhang, Yu Chen
chentangyu@yahoo.com (Y.C.)
amzhangbin@126.com (B.Z.)
yubin.fu@tu-dresden.de (Y.F.)

Highlights
Poly(chalcogenoviologen-alt-triphenylamine) (PCVTPA) has been synthesized
PCVTPA-based memristor exhibits excellent memristive performance
PCVTPA-based memristor is capable of executing arithmetic operations on decimal
PCVTPA shows great potential in constructing intelligent computing system

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Donor-acceptor-type poly[chalcogenoviologen-alt-triphenylamine] for synaptic biomimicking and neuromorphic computing

Zhizheng Zhao, Qiang Che, Kexin Wang, Mohamed E. El-Khouly, Jiaxuan Liu, Yubin Fu, Bin Zhang, and Yu Chen

SUMMARY
Polymer memristors are preeminent candidates for low-power edge computing paradigms. Poly[chalcogenoviologen-alt-triphenylamine] (PCVTPA) has been synthesized by direct coupling of chalcogeno-viologen as electron acceptor and 4-(bromomethyl)-N-(4-(bromo-methyl)phenyl)-N-phenylaniline as electron donor. The introduction of chalcogen atoms (S, Se, Te) into viologen scaffolds can greatly improve electrical conductive, electrochemical, and electrochromic properties of the materials when compared with the conventional viologens. Taking PTeVTPA as an example, the as-fabricated electronic device with a configuration of Al/PTeVTPA/ITO exhibits excellent multilevel storage and history-dependent memristive switching performance. Associated with the unique memristive behavior, the PTeVTPA-based device can not only be used to emulate the synaptic potentiation/depression, the human’s learning and memorizing functions, and the transition from short-term synaptic plasticity to long-term plasticity but also carry out decimal arithmetic operations as well. This work will be expected to offer a train of new thought for constructing high-performance synaptic biomimicking and neuromorphic computing system in the near future.

INTRODUCTION
The human memory mainly benefits from the natural evolution of neural networks that exhibit several outstanding properties such as massive parallel processing, in-memory computing architecture, event-driven operation and others. Since the discovery of the first real memristor at HP Labs in 2008 (Strukov et al., 2008), great efforts have been devoted to developing novel memristive functional materials and devices to construct artificial neural networks for neuromorphic computation and emulate the physiological functions (e.g., the learning, memorizing, forgetting, decision-making, and judging actions) of biological synapses (Chen et al., 2014; Zhang et al., 2018; Zhang et al., 2019, 2020; Zhang et al., 2021; Van De Burgt et al., 2018; Choi et al., 2018, 2020; Liu et al., 2016, 2018; Li et al., 2017; Wan et al., 2020; Kim et al., 2018; Wang et al., 2014, 2015; Ren et al., 2020; McFarlane et al., 2020). Recently, it was found that the negative photoconductance effect observed impressively in the high resistance state branch of the resistive switching memory enabled the memristor function to be extended to both memory logic display and multistate data storage (Zhou et al., 2021). The combination of multiple physical properties (memristive and capacitive) in a single device could also prefigure potential multifunctional applications (Sun et al., 2020). The memristor-based brain-like intelligent computing system not only can improve significantly the computing capability of modern computer systems via massive parallelism at very low power consumption but also can overcome the von Neumann bottleneck (i.e., the limited throughput between the memory and central processing unit) when dealing with data-intensive tasks.

A large number of inorganic materials are used to construct the memristor devices and still play a dominant role in fabricating memristors with superior processing efficiency and enormous storage capacity so far (Choi et al., 2018; Li et al., 2017; Wan et al., 2020; Kim et al., 2018). In comparison with the inorganic and organic small molecule counterparts, polymer materials show higher intrinsic flexibility and ease for solution processing. The solution processing capability allows them to be handled via low-cost techniques of dip coating, blade casting, spray coating, spin coating, roller-coating, and even ink-jet printing, making the...
fabrication procedure of electronic and optoelectronic devices potentially more economical without the involvement of vacuum deposition procedure (Chen et al., 2014; Liu et al., 2018; Ling et al., 2008; Lin et al., 2014; Liu and Chen, 2011). Since 2005, polymer memories have been proposed to revolutionize electrical applications by providing extremely inexpensive, lightweight, and transparent modules that can be fabricated onto plastic, glass, or the top layer of the complementary metal-oxide semiconductor circuits. Similar to these inorganic materials, some polymer functional materials, including metal-containing polymers, polymer-based multi-component redox systems, and pure polymers, have also been found to exhibit excellent memristive performance in recent years (Chen et al., 2014; Zhang et al., 2018, 2019, 2020, Zhang et al., 2021; Wang et al., 2014, 2015; Liu et al., 2016; Ren et al., 2020; McFarlane et al., 2020; Pincella et al., 2011; Bandyopadhyay et al., 2011). With these polymer memristors, one can observe nonlinear transmission characteristics similar to that of a biological synapse. More importantly, their memristive performance can be easily tuned through innovative molecular design cum synthesis strategy.

Polymer memristors are preeminent candidates for low-power edge computing paradigms. In our pioneering works, we reported a proof-of-concept polymer memristive processing-memory unit that demonstrates programmable information storage and processing capabilities (Zhang et al., 2019). Using polyfluorene functionalized with triphenylamine and ferrocene moieties side chains as an active layer, the as-fabricated electronic device, which shows excellent memristive switching and multilevel memory performance, is capable of executing multilevel memory; decimal arithmetic operations of addition, subtraction, multiplication, and division; as well as simple Boolean logic operations. Recently, we designed and synthesized a two-dimensional conjugated polymer PBDTT-BQTPA (Zhang et al., 2021). This material-based electronic device exhibited a rapid transition from the OFF state to the ON state within ~32 ns. More importantly, we successfully achieved a record high 90% production yield of polymer memristors with low power and miniaturization potentials. The reliability of the as-fabricated memristor was greatly enhanced by the delocalized resistive switching, making downscaling of the device to 100-nm scale possible for low-power edge computing applications. We also observed for the first time the self-rectified memristive effect in a metal-free soluble organic oligomer PFD-BCN (Wang et al., 2015).

It would be quite desirable to integrate programmable multilevel storage, synaptic biomimicking, and neuromorphic computing in the same electronic device. As one of the most promising candidates for energy, electrochromism, gas separation and storage, and electronic and optoelectronic applications, viologens (Vs) composed of conjugated bi-/multipyridyl groups show a number of unique properties such as reversible redox behavior, ionic and localized conjugation, bio-sensitive response, and electrochromic and radical-rich features (Mi et al., 2019; Kortz et al., 2019; Ding et al., 2019; Zhang et al., 2017; Yang et al., 2021; Sluymans et al., 2020; Lipke et al., 2017; Li et al., 2018, 2019). For reduction of Vs, all of their three reductive states (neutral, radical cation, and dication) are thermodynamically stable. Also, Vs can be used as a strong electron-withdrawing unit to construct donor-acceptor-type organic/polymeric functional materials. On the other hand, triphenylamine (TPA) and its derivatives have been widely applied in the fields of optoelectronics and electronics owing to their 3D steric profile, low ionization potentials, inner redox activity, and excellent UV light-harvesting ability (Fang and Yamamoto, 2004; Zhang et al., 2018; El-Khouly et al., 2009; Ego et al., 2002). Based on these backgrounds, in this work, we designed and synthesized a novel conjugated donor-acceptor polymer, poly[chalcogenoviologen-alt-triphenylamine] (PCVTPA, including PSVTPA, PSeVTPA, and PTeVTPA), by direct coupling of 4-(bromomethyl)-N-(4-(bromomethyl)phenyl)-N-phenylaminaline as electron donor and chalcogenoviologen as electron acceptor, as shown in Scheme 1. The introduction of chalcogen atoms (S, Se, Te) into viologen scaffolds can greatly improve electrochemical, electrical conductive, and electrochromic properties of the materials (Lipke et al., 2017; Li et al., 2019). Like Vs, poly (chalcogenoviologen) (PCV) also exhibits good electron-withdrawing characteristics (Lipke et al., 2017; Li et al., 2019; Stolar et al., 2016). As a result, the as-prepared AI/PCVTPA/ITO sandwich structure device exhibited excellent history-dependent memristive switching performance. With this device one can not only easily realize the biological stimuli of the “learning→forgetting→re-learning→re-forgetting” processes associated to the human’s learning/memory functions but also execute decimal arithmetic operations of addition, subtraction, multiplication, and division. These results demonstrate that this material shows the great potential in constructing artificial neural networks for neuromorphic computation. As comparison, we also synthesized poly[4,4-bipyridine-alt-triphenylamine] (PBPTPA) under the same experimental conditions. Unlike PCVTPA, PBPTPA did not show any apparent memristive effect.
RESULTS AND DISCUSSION

Both the PCVTPA and PBPTPA polymers are highly soluble in acetonitrile and N,N-dimethylformamide (DMF). Their weight-average molecular weights/polydispersity indexes, which were determined with a gel permeation chromatograph PL-GPC50 using polystyrene standards eluting with DMF, are $4.7 \times 10^3/1.00$ for PSVTPA, $6.4 \times 10^3/1.05$ for PSeVTPA, $5.9 \times 10^3/1.21$ for PTevTPA, and $7.8 \times 10^3/1.10$ for PBPTPA, respectively. The formation of the C=N$^+$-C bond in the polymer structure has been confirmed by X-ray photoelectron spectroscopy (XPS) (Figure S2). The N1s core-level XPS spectra of these polymers showed two peaks of nitrogen functionalities at 401.69 (the N in C=N$^+$-C bond) and 399.60 eV (the N in C-N bond). Also, the S2p, Se3d, and Te3d core-level XPS spectra of PCVTPA showed S functionalities at 169.23 (2P$_{1/2}$) and 168.02 (2P$_{3/2}$) eV, Se functionalities at 57.51 (3d$_{3/2}$) and 56.57 (3d$_{5/2}$) eV, and Te functionalities at 584.99 (3d$_{3/2}$) and 574.69 (3d$_{5/2}$) eV. These results demonstrated the successful synthesis of both the PCVTPA and PBPTPA polymers.

From Figure 1A, it can be clearly seen that the UV-vis absorption spectrum of the PBPTPA film showed a strong absorption peak at 313 nm, followed by a broad absorption peak centered at 485 nm. The former can be assigned to TPA, whereas the latter corresponded to the typical absorption of bipyridines. Similarly, the PCVTPA film also exhibited the main absorption peaks from the TPA moieties and the chalcogenoviologen moieties. With the changes of chalcogen atoms introduced into viologen scaffolds from S to Se to Te, the absorption band assigned to the viologen moieties were found to be shifted to the longer wavelength (389 nm→415 nm→475 nm) owing to the gradually weakened electron-drawing ability from S to Se to Te. Upon excitation with laser light at 310 nm, all the samples exhibited a strong emission band that is located at 373 nm for PSVTPA, 374 nm for PSeVTPA, 375 nm for PTevTPA, and 378 nm for PBPTPA (Figure S2). The thermal properties of the samples were investigated by thermogravimetric analysis (TGA) (Figure 1B). As a result, the onset decomposition temperature for the thermal bond cleavage of the samples was found to be 178°C for PSVTPA, 322°C for PSeVTPA, 346°C for PTevTPA, and 353°C for PBPTPA, respectively. The thermal stability of PTevTPA is higher than those of PSVTPA and PSeVTPA but smaller than that of PBPTPA without chalcogen atoms.

Redox potentials (versus Ag/Ag$^+$) of the thin film samples, which were measured in deaerated dichloromethane containing recrystallized tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 0.05M) at room temperature, were found to be $E_{\text{red} 1,1/3} = -1.08$ V, $E_{\text{red} 2,1/3} = -0.63$ V, and $E_{\text{red} 3,1/3} = +0.82$ V for PSVTPA; $E_{\text{red} 1,1/3} = -1.03$ V, $E_{\text{red} 2,1/3} = -0.45$ V, and $E_{\text{red} 3,1/3} = +0.75$ V for PSeVTPA; $E_{\text{red} 1,1/3} = -1.04$ V, $E_{\text{red} 2,1/3} = -0.54$ V, and $E_{\text{red} 3,1/3} = +0.79$ V for PTevTPA. Similar to these materials mentioned above, redox potentials
Figure 1. Basic characterization of polymers

(A) Normalized UV-vis spectra of the thin film samples.
(B) Fluorescence spectra of the samples in DMF (λ<sub>ex</sub> = 310 nm).
(C) TGA curves of the samples.
The effect of film thickness on the current-voltage characteristics of the Al/PTeVTPA/ITO devices has been observed. The film thickness was varied from 37 to 85 nm and to 120 nm. As shown in Figure 3, all the devices showed a pinched hysteretic loop confined to the first and third quadrants of the I-V plane. The main difference between these devices lies in the degree of an increase (or decrease) in the magnitude of the current signal between two sweeps. For example, the device was applied seven consecutive positive voltage sweeps from 0 to 0.5 V and then back to 0 V, the observed device current was found to increase incrementally from 0.27 to 0.67 mA (read at 0.2 V). After that, the device was applied seven consecutive negative voltage sweeps of 0 V → −0.5 V → 0 V, and the device current decreases gradually from −0.89 to −0.42 mA (read at −0.2 V). During the whole voltage sweeping processes, a smoother change of the material conductance or the device current was observed. In contrast to the above observation, for the bistable electrical switching devices reported in the literature, their switching effect usually follows steep conductance or current jumps (Liu et al., 2018; Chen et al., 2012; Lin et al., 2014). Similarly, both the Al/PSVTPA/ITO and Al/PSeVTPA/ITO devices also showed memristive effect (Figures 2B and 2C). Among these three devices, however, the changes in resistance states and the boundary between the pinched hysteretic loops observed in the Al/PTeVTPA/ITO device are much clearer than the other two devices. Unlike PCVTPA-based devices, the PBPTPA-based device displayed unstable memristive behavior (Figure 2D). These results demonstrated that the introduction of chalcogen atoms (S, Se, Te) into viologen scaffolds could greatly improve memristive performance of the resultant materials. Furthermore, by using consecutive multilevel conductance switchings, one can easily realize nonlinear transmission characteristics exhibited by a biological synapse (Figure 5S), and modulation and memory of the synaptic weight, which refers to the conductance of the two-terminal device, or the strength or amplitude of a connection between two nodes in neuroscience.

The absorption peaks of PTeVTPA at different oxidation states are located at 299, 300, and 708 nm for PTEVTPA¹⁺; 299, 357, and 510 nm for PTEVTPA²⁺; and 299, 359 (shoulder peak), 490, and 689 nm for PTEVTPA³⁺, respectively. For better understanding of the absorption spectra measured experimentally, we also used time-dependent density functional theory (TD-DFT) to simulate the above electronic absorption spectra (Figure S3b). All the computational work was carried out by using B3LYP functional and def2-SVP basis set including Grimme's D3 dispersion correction (Becke-Johnson damping) (Frisch et al., 2016; Grimme et al., 2011). As a result, the predicted absorption spectra were in good coincidence with the spectra observed in the thin film sample. Furthermore, it was found that the dipole moments of PTeVTPA at different oxidation states are 12.40 Debye for PTEVTPA³⁺, 14.41 Debye for PTEVTPA²⁺, and 14.41 Debye for PTEVTPA⁺ (Figure S4). In the neutral state (PTEVTPA⁰), the calculated dipole moment is only 0.77 Debye. In general, both the intensive electron delocalization and strong dipole moment of molecule in a D-A polymer system would be able to effectively stabilize the conductive charge-transfer state and consequently produce the non-volatile nature of the high-conductivity state in an electronic memory device.
with increasing film thickness, whereas their turn-on and turn-off voltages almost kept unchanged (Fan et al., 2017). Considering that the oxygen vacancies (oxygen anions) from the ITO electrode will diffuse into the switching layer under external electric field, we replaced the ITO electrode with the Au electrode. As shown in Figure S6, the as-fabricated Al/PTeVTPA/Au device showed almost the same memristive performance as that exhibited by the Al/PTeVTPA/ITO device. This result suggested that the migration of oxygen vacancies from the ITO electrode to the active layer has no obvious influence on the polymer-based device performance.

Resistive switching performance of the polymer memories mainly arise from changes in the intrinsic properties of the switching media. Although several switching mechanisms such as reduction-oxidation interactions, charge transfer, conformation change, and phase change have been proposed (Liu et al., 2018), less direct physical evidence is available to support these proposed mechanisms so far due to the lack of advanced in situ characterization and analysis tools. Therefore, it is still difficult to identify the operation mechanism of the polymer-based memory device and/or memristor at the moment (Jeong et al., 2012). In the present study, a possible operation mechanism might concern the redox process of the as-prepared polymer film under an applied electric field. At the initial stage (no voltage was applied to the device), the polymer backbone is in a positive divalent state (e.g., PTeVTPA$^{2+}$). When a positive sweep voltage was applied to the device, the polymer was gradually oxidized (or partially oxidized) to PTeVTPA$^{3+}$, and consequently the charge carrier concentration in the system increased, giving rise to the increase of the device current, as observed in the first quadrant of the I-V plane. When the device was applied a negative sweep voltage, with increasing the applied voltage, PTeVTPA$^{3+}$ would undergo a one-step or multiple-step electrochemical reduction reaction process (e.g., PTeVTPA$^{3+}$ $\rightarrow$ PTeVTPA$^{2+}$ $\rightarrow$ PTeVTPA$^{1+}$ $\rightarrow$ PTeVTPA$^{0}$). As a result, the charge carrier concentration in the system gradually reduced, followed by the dropping of the device current with increasing the sweep times, as shown in the third quadrant of the I-V plane.

To explore the influence of stimulus frequency and duration on synaptic weights, we successfully emulated the spike-rate dependent plasticity of biological synapses (Markram et al., 1998; Li et al., 2013) by

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**Figure 2. The current-voltage characteristics of the Al/polymer/ITO devices**

(A) PTeVTPA.
(B) PSVTPA.
(C) PSeVTPA.
(D) PBPTPA.
increasing the frequencies of the voltage pulses applied to the Al/PTeVTPA/ITO device (Figures 4A and 4B). During the experiments, the stimulus frequency was changed from 1 to 20 Hz, whereas the numbers of the pulse stimulations was fixed at a constant of 10. As seen from Figure 4A, the more frequently the device acting as biological synapse was being stimulated, the higher the device currents observed in this study became. It was also found that, at the frequency of 1 or 2 Hz, the device current changes with 10 pulse stimulations were very small. With further increasing the frequency, the observed current changes started to become more apparent or remarkable. At a frequency of 20 Hz and the stimulation numbers of 10, the device current changes reached up to 51.99 mA when compared with the stimulation number of 1. These results suggest that the as-prepared memristor can serve as a high-pass filter. Figure 4C shows the device current as a function of the pulse durations at a frequency of 1 Hz and the stimulation numbers of 5, suggesting the good stability of the device. Considering that the sub-threshold potentiation in neurons is associated with both paired pulse facilitation (PPF) and short-term synaptic plasticity (STP), we also established such functionality in our device. From Figure 4D, it can be seen that the PPF shows two

Figure 3. The effect of active layer thickness on device performance
(A–C) The effect of film thickness on the current-voltage characteristics and SEM images of the Al/PTeVTPA/ITO devices with different active layer thicknesses.
(A and D) 37 nm.
(B and E) 85 nm.
(C and F) 120 nm.
characteristic timescales (van de Burgt et al., 2017), with $t_1$ of 71 ms and $t_2$ of 280 ms. These two values are very close to those exhibited by biological synapses (Zucker and Regehr, 2002).

The synaptic potentiation and depression, which are regarded as the neurobiological basis of the brain memory functions, may be realized through action potential spikes. When the device was applied the consecutive negative voltage pulses or positive stimuli, respectively, synaptic weight can be effectively depressed or potentiated (Figure 5A). The synaptic potentiation and relaxation processes are found to compete with each other during the biological stimuli. Figure 5B showed the retention curves for synaptic weight at different numbers of identical voltage pulse stimulations, from which one can see that the synaptic weight undergoes the fast decay at the beginning and then gradually tends to fatten out. This result implies that the numbers of identical voltage pulse stimulations with same amplitude, period, and duration can greatly influence the memory loss or retention performance of the device. Basically, the human memory mainly comes from STP and long-term potentiation/plasticity (LTP). Long-term memory can be sustained for a long time (e.g., several days, several months, even several years), whereas short-term memory only lasts for a very short time (e.g., several seconds or minutes). Even an accidental electrical shock or decay rapidly with time may easily interrupt or destroy short-term memory. As shown in Figure 5C, with increasing the pulse stimulation numbers the relaxation time constant ($\tau$) was changed from 4.51 s@10 pulses to 4.98 s@20 pulses to 6.81 s@30 pulses to 7.40 s@40 pulses to 9.35 s@50 pulses and to 10.36 s@60 pulses. This finding makes the transition from short-term memory to long-term memory possible in our device. And more a "learning → forgetting → re-learning" process shown in human daily life has been successfully explored in this study (Figures 5D–5G). When a stimulation of 50 consecutive voltage pulses was applied to the device, the device current was found to increase gradually with the increase of the pulse numbers (Figure 5D). This is similar to a "learning" process observed during the human learning. Once the power was cut off, the device current dropped gradually to an intermediate state within 200 s (Figure 5E). This process can
be regarded as a “forgetting” process. And then we applied a stimulation of 35 consecutive pulses to the device again, and the current returned to its end level from the first learning stage (Figure 5F). Such a “re-learning” process is similar to the transition process from STP to LTP, by which the human memory capability can be significantly strengthened. Afterward, the as-fabricated device went through a “re-forgetting” process again (Figure 5G). By comparison with the device current detected at the end of the first “forgetting” process, which is about 0.36 mA, the device current observed at the end of the “re-forgetting” process reached up to 0.41 mA, much higher than that of the former. This suggests that the “re-forgetting” speed slows down greatly when compared with the first “forgetting” speed. Surprisingly, it only took 15 voltage pulses for the device current to be recovered to the same higher level as that shown at the end level from the first learning stage (Figure 5H). These results demonstrated that the voltage pulses applied to the device would become fewer and fewer with an increasing number of “re-learning” processes.

From the above discussion, we can see that our device shows a consecutive resistive switching effect at any device current levels. This result is very interesting and can be used to implement arithmetic addition, subtraction, multiplication, and division. When a stimulation of consecutive voltage pulses was applied to the device, as shown in Figure 6A, whatever positive sweeping or negative sweeping, the relationship between the pulse numbers and the device currents read at ±0.5 V is perfectly linear. This relationship guarantees the normal operation of the device as a decimal abacus. It was also found that the pinched hysteretic loops shown in Figures 2A–2C are highly symmetric. For calibration, an X-X = 0 operation is carried out in pulse mode to guarantee the calculating accuracy (Figure 6B). After a stimulation of 10 consecutive positive pulses (0.5 V and 10 ms) was applied to the device, the observed device current reached 0.43 mA. As such, when a current of ~0.43 mA is read, the number 10 will be counted in future calculation. By setting the device current of <0.2 mA as the initial state of the device, the decimal numbers of 0–10 can be indexed proportionally. When a subsequent stimulation of 10 consecutive negative pulses was applied, the device current got back to the initial state again. With such an operation, one can easily realize the subtraction...
operation of 10–10 = 0 and calibrate the as-fabricated device for accurate decimal arithmetic operations. In this device, the application of positive voltages, which can result in the increase of the device current, was used to make addition operations, whereas the negative voltages applied to the device correspond to the subtraction function of an “abacus.” By monitoring the current changes with respect to the initial state of the device, the quantity of the input pulse stimuli can be counted.

The application of a succession of six consecutive positive pulses (0.5 V and 10 ms) followed by an extra train of four consecutive positive pulses with the same duration and amplitude as those of the former produces a device current of ~0.43 mA, which exactly confirms 6 + 4 = 10 (Figure 6C). When we reverse the sequence of the two sets of input pulse signals, the device current also reached ~0.43 mA under the same experimental conditions. These results verify such a commutative law that X + Y = Y + X (6 + 4 = 4 + 6 = 10). After the pre-loading of 10 positive pulses (0.5 V and 10 ms), which gives a device current of ~0.43 mA, the sequential application of four consecutive negative pulses and a following train of six consecutive negative pulses

Figure 6. Demonstration of arithmetic computing with the Al/PTEVTPA/ITO memristor
(A) Linear relationship between the device currents read at ± 0.5 V and voltage sweeping numbers.
(B) Calibration of the memristor with the operation of 10–10 = 0 for decimal arithmetic calculations.
(C) Commutative addition conducted with the PTEVTPA device.
(D) Subtraction conducted with the PTEVTPA device.
(E) Multiplication conducted with the PTEVTPA device.
(F) Fractional division conducted with the PTEVTPA device.
resulted in that the device current is down back to the initial state again (Figure 6D). This confirmed $10 - 6 - 4 = 0$. Reversing the loading order of the input signals can also reduce the device current to the value at the initial state ($10 - 4 - 6 = 0$), which confirms that $X - Y - Z = X - Z - Y$ ($10 - 6 - 4 = 10 - 4 - 6 = 0$). These findings demonstrated the commutative subtraction operation. Similarly, the accumulative addition operation-based multiplication also obeys the commutative law (Figure 6E). The result obtained from the application of two sets of five positive pulses is the same as that from the application of five sets of two positive pulses, assuring that $XY = YX = 2 \times 5 = 5 \times 2 = 10$. The fractional division is based on the combination of the subtraction and addition operations. For example, we can carry out the division operation of $6 \div 4$ with our device (Figure 6F). The device was first reset to the initial state, and then was applied six consecutive positive voltage pulses, followed by another series of four negative pulses, to perform $6 - 4$. As a result, a remainder of 2 and an integer quotient of 1 were achieved. Considering the remainder 2 is smaller than the divisor 4, we added two series of 9 positive voltage pulses to the device to replace 2 with “$2 + 2 \times 9$” ($2 \times 10$). Subsequently repeated subtraction of $2$ for five times ($20 - 4 - 4 - 4 - 4 - 4$) made the device current back to the initial state again. The fractional division calculation was then terminated. These results demonstrate that the decimal number of 5 was at the tenths position and the quotient of $6 \div 4 = 1.5 (1 + 0.5)$.

Conclusions
A proof-of-concept PCVTPA-based polymer memristor with a configuration of Al/PCVTPA/ITO exhibited excellent history-dependent memristive switching and multilevel storage performance. Associated with the unique memristive behavior, the as-fabricated device can be used to not only emulate the human’s learning and memorizing functions but also execute decimal arithmetic operations of addition, subtraction, multiplication, and division. These results demonstrated that the PCVTPA polymer showed a great potential in constructing high-performance intelligent computing system in the near future.

Limitations of the study
This work is mainly focused on the design and synthesis of new chalcogenoviologen and triphenylamine-based alternative copolymer for constructing high-performance synaptic biomimicking and neuromorphic computing system. This material shows excellent history-dependent memristive switching and multilevel storage performance. The memristive performance of the polymers mainly arises from changes in the intrinsic properties of the switching media. In contrast to the inorganic materials-based memory and memristor, the proposed main switching mechanisms of the polymer-based devices are reduction-oxidation interactions, charge transfer, conformation change, and phase change. However, less direct physical evidence is available to support these proposed mechanisms so far owing to the lack of advanced in situ characterization and analysis tools. Therefore, it is still difficult to identify the operation mechanism of the polymer-based memristors at the moment. Future work should be focused on the design of new high-performance conjugated polymer functional materials for memristors, exploration of the operation mechanism, and determination of the relationship between the structural parameters and the memristive response while seeking to optimally combine materials and devices.

STAR+METHODS
Detailed methods are provided in the online version of this paper and include the following:

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Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.103640.

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AUTHOR CONTRIBUTIONS
Y.C., Z.Z., and B.Z. conceived the idea. Z.Z., Q.C., K.W., and J.L. synthesized and characterized all the materials. Y.F. simulated the electronic absorption spectra of the samples. Y.C. wrote the manuscript. All authors discussed the experimental results.

DECLARATION OF INTERESTS
The authors declare no competing interests.
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STAR★METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| **Chemicals, peptides, and recombinant proteins** | | |
| 3-Benzopyridine (AR) | Aladdin | CAS.626-55-1 |
| 4,4'-bipyridine (98%, AR) | Aladdin | CAS.553-26-4 |
| Diisopropylamine (>99%, GC) | Aladdin | CAS.108-18-9 |
| Phosphorus tribromide (99%, AR) | Aladdin | CAS.7789-60-8 |
| Phosphorus oxychloride (98%, AR) | Aladdin | CAS.10025-87-3 |
| Copper chloride (98%, AR) | Aladdin | CAS.7447-39-4 |
| Triphenylamine (98%, AR) | Aladdin | CAS.603-34-9 |
| Selenium powder (99.999% (metals basis), 200mesh) | Adamas-beta | CAS.7782-49-2 |
| Sulfuryl chloride (98%, RG) | Adamas-beta | CAS.7791-25-5 |
| Trifluoromethanesulfonic acid (99%, AR) | J&K | CAS.1493-13-6 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Prof. Yu Chen (chentangyu@yahoo.com; yuchenavh@ecust.edu.cn).

Materials availability
All materials generated in this study are available from the lead contact.

Data and code availability
This study does not generate data sets/code.

EXPERIMENTAL MODEL AND SUBJECT DETAILS
This study does not use experimental models typical in the life sciences.

METHOD DETAILS
All reactions were carried out under dry nitrogen atmosphere by using standard Schlenk techniques. 3-Benzopyridine and diisopropylamine were redistilled before use. Copper chloride was dried under vacuum overnight at 200°C before use. The other analytically pure chemicals were used without further purification. Organic solvents were purchased from purified, dried, and distilled under dry argon. About the synthetic procedure, measurements, instruments, device fabrication and characterization, and structural modeling are listed as follows.

Measurements and instrument
Ultraviolet/visible (UV/Vis) absorption spectra were measured on a Shimadzu UV-2540 spectrophotometer. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer (HORIBA Scientific, France) was used to record the steady-State fluorescence spectra. Thermogravimetric analyses (TGA) of all samples were measured using a Perkin-Elmer Pyris1 thermogravimetric analyzer with a heating rate of 20°C min⁻¹ under N₂ atmosphere. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 spectrometer at a resonance frequency of 400 MHz for ¹H in deuterated solution with a tetramethylsilane (TMS) as a reference for the chemical shifts. Cyclic voltammetry (CV) measurements were performed on a model CHI 650D electrochemical workstation using tetrabutylammonium hexafluorophosphate (0.05M) in DCM as the supporting electrolyte, a platinum disk as working electrode, an Ag/AgCl electrode as reference, and a Pt wire as counter electrode. Fourier transform infrared (FT-IR) spectra were recorded using Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a
constant dwell time of 100 ms and pass energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA, respectively. The pressure in the analysis chamber was maintained at 5 x 10⁻⁸ Torr or lower during each measurement. The number-average (Mn) and weight-average (Mw) molecular weights of the polymers were determined with a Gel Permeation Chromatograph PL-GPC50 using a polystyrene standards eluting with DMF. Field emission scanning electron microscopy (FE-SEM) images were tested on 500-300000/GeminiSEM 500.

Synthetic procedure

Synthesis of 3,3’-dibromo-4,4’-bipyridine(1). To a stirred solution of the newly synthesized lithium disopropylamide (LDA, 2 M in THF, 30 mmol) in THF was added dropwise 3-bromopyridine (9.8 g, 73 mmol) added. After stirring overnight at the same temperature, the reaction mixture was allowed to warm to the room temperature. The solution was removed under reduced pressure. The residual brown solid was taken up in H₂O (30 mL), NH₄OH (25 %, 30 mL) and NH₄Cl (sat., 30 mL). The mixture was extracted several times with CHCl₃ (50 mL each time), the combined organic phases were dried over anhydrous Na₂SO₄ and concentrated to give a brown oil, which was purified by column chromatography (SiO₂, petroleum ether/ethyl acetate, 5:1) to give 2.03 g (43 %) of white powder. ¹H-NMR (400 MHz, CDCl₃): δ/ppm=8.88 (s, 2H), 8.65 (d, 2H), 7.18 (d, 2H).

Synthesis of thieno[2,3-c:5,4-c’]bipyridine(2a). To a stirred solution of 3,3’-dibromo-4,4’-bipyridine (628 mg, 2.0 mmol) in dry THF (60 mL) was added dropwise a solution of n-BuLi (2.5 M in hexanes, 1.68 mL, 4.2 mmol) via syringe at -94 °C. After stirring for 1 hour at the same temperature, S₂Cl₂ (284 mg, 2.1 mmol) was added dropwise to the above solution. The reaction mixture was then allowed to warm to the room temperature and stirring was continued overnight. After evaporation of the solvent under reduced pressure, the residue was taken up in H₂O (30 mL), NH₄OH (25 %, 30 mL) and NH₄Cl (sat., 30 mL). The mixture was extracted several times with CHCl₃ (50 mL each time), the combined organic phases were dried over anhydrous Na₂SO₄ and concentrated to give a brown oil, which was purified by column chromatography (SiO₂, petroleum ether/ethyl acetate, 2:1) to give 150 mg (40 %) of light yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ/ppm=9.30 (s, 2H), 8.76 (d, 2H), 8.14 (d, 2H).

Synthesis of selenopheno[2,3-c:5,4-c’]bipyridine(2b). To a stirred solution of 3,3’-dibromo-4,4’-bipyridine (628 mg, 2.0 mmol) in dry THF (60 mL) was added dropwise a solution of n-BuLi (2.5 M in hexanes, 1.68 mL, 4.2 mmol) via syringe at -94 °C. After stirring for 1 hour at the same temperature, SeCl₂ (315 mg, 2.1 mmol) in THF (5 mL) was added dropwise to the above solution. The reaction mixture was then allowed to warm to the room temperature and stirring was continued overnight. After evaporation of the solvent under reduced pressure, the residue was taken up in H₂O (30 mL), NH₄OH (25 %, 30 mL) and NH₄Cl (sat., 30 mL). The mixture was extracted several times with CHCl₃ (50 mL each time), the combined organic phases were dried over anhydrous Na₂SO₄ and concentrated to give a brown oil, which was purified by column chromatography (SiO₂, petroleum ether/ethyl acetate, 1:1) to give 89 mg (20 %) of light yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ/ppm=9.19 (s, 2H), 8.70 (d, 2H), 8.07 (d, 2H).

Synthesis of telluropheno[2,3-c:5,4-c’]bipyridine(2c). To a stirred solution of 3,3’-dibromo-4,4’-bipyridine (628 mg, 2.0 mmol) in dry THF (60 mL) was added dropwise a solution of n-BuLi (2.5 M in hexanes, 1.68 mL, 4.2 mmol) via syringe at -94 °C. After stirring for 1 hour at the same temperature, TeCl₄ (566 mg, 2.1 mmol) in THF (5 mL) was added dropwise to the above solution. The reaction mixture was then allowed to warm to the room temperature and stirring was continued overnight. After evaporation of the solvent under reduced pressure, the residue was taken up in CH₂Cl₂ (40 mL) and then added saturated Na₂S solution (20 mL). The reaction mixture was vigorous stirred at room temperature until the solution was clarified. The mixture was extracted several times with CH₂Cl₂ (40 mL each time), the combined organic phases were dried over anhydrous Na₂SO₄ and concentrated to give a brown oil, which was purified by column chromatography (SiO₂, petroleum ether/ethyl acetate, 1:1) to give 188 mg (33 %) of brown solid. ¹H-NMR (400 MHz, CDCl₃): δ/ppm=9.19 (s, 2H), 8.70 (d, 2H), 8.07 (d, 2H).
Synthesis of 4-(bromomethyl)-N-(4-(bromomethyl) phenyl)-N-phenylaniline (3). A mixture of 4,4’-(Phenylazanediyl)dibenzaldehyde (1.36g, 4.5mmol) and sodium borohydride (0.378 g, 10.0 mmol) in 120 mL of a mixed solvent of dry CH₂Cl₂ and ethanol (1:1) was stirred in the dark at room temperature overnight. 120 mL of water was then added to the above reaction mixture. The obtained mixture was extracted several times with CHCl₃ (120 mL each time), the combined organic phases were dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, the residual white powder was directly suspended in 50 mL of dry diethyl ether without further purification. Then a solution of phosphorus tribromide (514 mL, 5.4 mmol) in 10 mL of dry diethyl ether was added dropwise to the above suspension within 5 minutes at 0°C. The reaction mixture was allowed to warm to the room temperature, followed by overnight stirring in the dark. A mixture of ice water (60 mL) and saturated NaHCO₃ solution (30 mL) was added to the above reaction system. The reaction mixture was extracted several times with CH₂Cl₂ (60 mL each time), the combined organic phases were dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, a sticky light green solid (1.88 g, 96%) was obtained. ¹H NMR (400 MHz, CD₂Cl₂): δ/ppm= 7.31-7.26 (m, 6H), 7.11-7.09 (m, 3H), 7.03-7.01 (d, 4H), 4.52 (s, 4H). EI: calcd for C₂₀H₁₇Br₂N: 430.97; found: m/z=430.97 (M+, 100%).

Synthesis of PCVTPA(5). A stirred mixture of 2 (1.0 mmol) and 3 (1.0 mmol) in DMF (30 mL) was heated at 60°C for 5 days. The precipitate was isolated via vacuum filtration and washed with CH₂Cl₂ for several times (30 mL each time). The product was collected and dried under high vacuum at 65°C to give the polymer 4.

To 4 (0.5 mmol) dispersed in acetonitrile (30 mL) was added an excessive of methyl triflate at room temperature, followed by an overnight stirring. After reaction was finished, a 500 mL of ice methanol was added slowly to the above reaction system. The precipitate was isolated via vacuum filtration and washed with methanol for several times (50 mL each time). The product was collected and dried under high vacuum at 65°C to give the polymer 5.

5a PSVTPA: ¹H-NMR (400 MHz, CD₃CN): δ/ppm = 9.80 (s, 2H), 9.17-9.14 (m, 2H), 9.00-8.99 (m,2H), 7.52-7.07 (m, 13H, PhH), 5.95(s, 4H); ¹F NMR (400 MHz, CD₃CN): δ/ppm = -79.25 (s, CF₃); GPC: Mw =4.7 × 10³, Mn=6.7 × 10², PD=1.00.

5b PSeVTPA: ¹H-NMR (400 MHz, CD₃CN): δ/ppm = 9.75 (s, 2H), 9.12-9.08 (m, 2H), 9.02-8.99 (m,2H), 7.52-7.10 (m, 13H, PhH), 5.91(s, 4H); ¹F NMR (400 MHz, CD₃CN): δ/ppm = -79.25 (s, CF₃); GPC: Mw =6.4 × 10³, Mn=6.1 × 10², PD=1.05.

5c PTeVTPA: ¹H-NMR (400 MHz, CD₃CN): δ/ppm = 9.69-9.65 (m, 2H), 8.45-8.43 (m,4H), 7.45-7.07 (m, 13H, PhH), 5.82(s, 4H); ¹F NMR (400 MHz, CD₃CN): δ/ppm = -79.17 (s, CF₃); GPC: Mw=5.9 × 10³, Mn=4.9 × 10², PD=1.21.

Synthesis of PBPTPA. A stirred mixture of 4,4’-bipyridine (1.0 mmol) and 3 (1.0 mmol) in DMF (30 mL) was heated at 60°C for 5 days. The precipitate was isolated via vacuum filtration and washed with CH₂Cl₂ for several times (30 mL each time). The product was collected and dried under high vacuum at 65°C to give the polymer 6.

To 6 (0.5 mmol) dispersed in acetonitrile (30 mL) was added an excessive of methyl triflate at room temperature, followed by an overnight stirring. After reaction was finished, a 500 mL of ice methanol was added slowly to the above reaction system. The precipitate was isolated via vacuum filtration and washed with methanol for several times (50 mL each time). The product was collected and dried under high vacuum at 65°C to give the polymer PBPTPA. ¹H-NMR (400 MHz, CD₃CN): δ/ppm = 9.01-8.98 (m, 4H), 8.45-8.43 (m,4H), 7.45-7.07 (m, 13H, PhH), 5.79 (s, 4H); ¹F NMR (400 MHz, CD₃CN): δ/ppm = -79.25 (s, CF₃); GPC: Mw=7.8 × 10³, Mn=8.0 × 10², PD=1.10.

The synthetic routes of the monomers and polymers are shown in Figure S8.

Device fabrication and characterization
The ITO glass substrate was carefully precleaned sequentially with deionized water, acetone, and 2-propanol in an ultrasonic bath for 15 min, and then treated with oxygen plasma. A 100 µL of the sample solution (10 mg·mL⁻¹) in acetonitrile was spin-coated on the pre-cleaned ITO sheet at a spinning speed of 800 rpm for 20 s and then 1500 rpm for 45 s, followed by the removal of the solvent under vacuum at 60°C overnight.
Al top electrodes were deposited on the surface of active layer through a shadow mask at 10^{-7} Torr via E-beam evaporation. All electrical measurements were performed on a Keithley 4200 semiconductor parameter analyzer in ambient condition without any device encapsulation.

**Structural modeling**

All density functional theory (DFT) calculation was performed using the Gaussian 16 program. The B3LYP functional with D3 correction (Becke–Johnson damping) was used for geometry optimization in the ground state. The def2-SVP basis set was used. All geometry optimization was done in the gas phase. In order to simulate the UV/Vis spectra of the samples, TD-DFT calculations were carried out by using B3LYP functional and def2-SVP basis set. For better comparison to the experimental absorption spectra, the polarity of dichloromethane as solvent was added.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

This study does not include statistical analysis or quantification.

**ADDITIONAL RESOURCES**

Additional resources containing the, NMR, XPS spectra, structural modeling UV-Vis spectra, ESP modeling images, cyclic voltammogram, can be found in the supplemental information.