Donor−Acceptor Effect of Carbazole-Based Conjugated Polymer Electrets on Photoresponsive Flash Organic Field-Effect Transistor Memories

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ABSTRACT: The molecular structure of polymer electrets is crucial for creating diverse functionalities of organic field-effect transistor (OFET) devices. Herein, a conceptual framework has been applied in this study to design the highly photoresponsive carbazole-based copolymer electret materials for the application of photoresponsive OFET memory. As an electret layer, two 1,8-carbazole-based copolymers were utilized; the **copoly(CT)** consisted of carbazole as the donor group and thiophene as the π-spacer, whereas the **copoly(CBT)** was further introduced as an acceptor moiety, benzothiadiazole, for comparison. Both copolymers exhibited efficient visible-light absorption and photoluminescence quenching in the film state, indicating the formation of a considerable number of nonemissive excitons, one of the crucial factors for achieving photoinduced recovery behavior in OFET memories. Compared to **copoly(CT)** with the pure donor system, faster and more effective photoinduced recovery behavior was discovered in the **copoly(CBT)** with the conjugated donor−acceptor structure because of the coexistence of the conjugated donor and acceptor groups. Thus, the dissociation of the generated excitons facilitated the stimulating of the unique ambipolar trapping property, resulting in the high-density data storage devices with multilevel current states. In addition, the nonvolatile and durable characteristics demonstrated the feasibility in application of memory and photorecorders.

KEYWORDS: *polymer electret, organic field-effect transistor memory, photoinduced recovery, donor−acceptor effect, ambipolar*
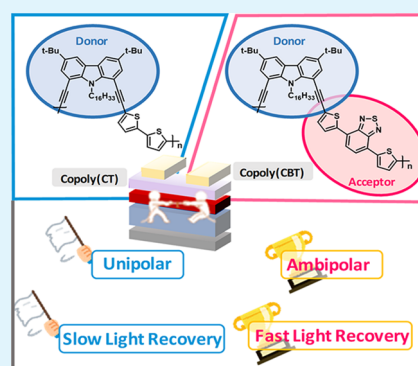
1. INTRODUCTION

Photoresponsive organic field-effect transistor (OFET) memories utilizing the light energy source to erase the recorded memory information have attracted considerable attention because the electrical stress for erasing could be replaced by green energetic light. Additionally, the light-responsive properties of electrets bring out the potential application for a new type of photorecorders. Recently, photoerasing behavior has been reasonably explained by the "photoinduced recovery" mechanism based on the neutralization of the trapped charges with the photogenerated excitons in the photoactive electrets.[1,2] However, the photoactive memories are currently limited to the floating-gate material systems, such as CdSe quantum dots/polymers and C_{60}/polymers. In the floating-gate configuration, homogeneous dispersion of the hybrid materials and precise control of the inorganic materials' particle size are critical issues to demonstrate the excellent memory performances. However, optimization of these parameters is generally difficult.

Very recently, we have reported the photoresponsive OFET memory by using the electret layer based on a carbazoledioxazine polymer.[3] The photoluminescent quenching property of the polymeric electret ensured the formation of excitons under light irradiation. Moreover, the highly π-extended donor−acceptor system of the carbazoledioxazine structure could effectively separate the generated excitons in the electret layer and then neutralize the trapped charges from the semiconductor layer through charge recombination. Although the donor−acceptor structure was included as a structural subunit in the polymer electret, it was not the state-of-the-art donor−acceptor-type conjugated polymer. Therefore, we try to pursue high-performance photoresponsive OFET memories based on donor−acceptor-type conjugated polymer electrets.

To fulfill the photoresponsive properties, conjugated carbazole-based copolymers are promising electret materials because of the unique electroactive behaviors. They have been commonly used for optoelectronic applications, such as OFETs,[4,5] organic solar cells,[6−9] and various types of photonic
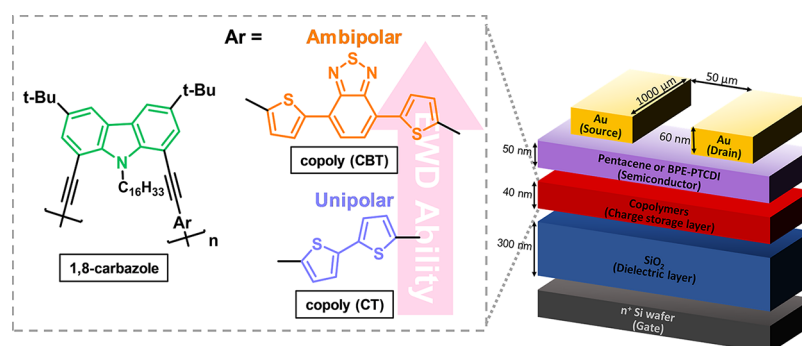
Figure 1. Schematic configuration of OFET memory devices composed of carbazole-based copolymer electrets, **copoly(CT)** or **copoly(CBT)**, having different electron-withdrawing (EWD) abilities.

devices. These diverse applications have been partially achieved by the electron-rich carbazole unit, which has the shallow excited triplet state suitable for both electrical and photonic devices. Thus, both electrical and photophysical properties of the carbazole-based polymers could be manipulated by increasing the conjugated length and introduction of acceptor moieties.[10−13]

Carbazole has several connectivity patterns for functionalization and polymerization, that is, 3,6-, 2,7-, and 1,8-positions.[14,15] Among these three connectivity patterns, the 1,8-connected carbazole polymers are less planar than the copolymers with the linkage on 3,6- and 2,7-positions.[16] Therefore, the 1,8-carbazole-based copolymers are much more suitable for the electrets of OFET memory application because of the unconventional linear conjugation, which could effectively capture and localize the trapped charges in the molecular structure. Based on these promising properties of 1,8-carbazole-based copolymers, the photoresponsive OFET memories by using 1,8-carbazole-based copolymers as electrets were fabricated to investigate the memory behaviors of the resulted OFET devices. In particular, regarding the donor−acceptor effects on photoresponsive memory, two 1,8-carbazole-based conjugated copolymers, carbazole/bithiophene copolymer (**copoly(CT)**) and carbazole/thiophene-benzothiadiazole-thiophene copolymer (**copoly(CBT)**) classified as donor−π-spacer system and donor−π-spacer−acceptor−π-spacer system, respectively,[17] were synthesized and applied to the electrets of OFET memories for comparison. The effects of the donor−acceptor-type conjugated copolymer of **copoly(CBT)** on the photoresponsive ambipolar behaviors were comprehensively investigated in this study.

2. EXPERIMENTAL SECTION

2.1. Materials. The carbazole copolymers, **copoly(CT)** and **copoly(CBT)**, were synthesized according to previously reported methods.[17] The number-average molecular weight (M_n) and polydispersity (M_w/M_n), estimated by gel permeation chromatography using a tetrahydrofuran eluent at the flow rate of 1.0 mL min^{-1}, were 7700 and 1.3 for **copoly(CT)** and 5600 and 1.4 for **copoly(CBT)**. Other reagents were used as received.

2.2. Thin Film Preparation, Device Fabrication. The OFET memory devices in this study were fabricated in the bottom-gate/top-contact type configuration. The heavily n-doped Si wafer with a 300 nm thick SiO$_2$ dielectric layer was precleaned by oxygen plasma treatment for 5 min before coating. The solutions of **copoly(CT)** and **copoly(CBT)**, prepared in chlorobenzene at the concentration of 10 and 6.7 mg mL^{-1}, respectively, were filtered with a polytetrafluoroethylene membrane syringe filters (pore size, 0.22 μm) for film coating. The electret films with the thickness of 40 nm were fabricated

by a spin-coating method at the rotation speed of 3000 rpm for 1 min and the solvent was removed at 100 °C for 1 h. After that, the semiconductor layer of pentacene or BPE-PDCDI layer (50 nm) was deposited on the electret by vacuum deposition at the growth rate of 0.3 Å s^{-1} under 10^{-7} Torr at room temperature. The gold electrodes were successively deposited on the semiconductor layer at the deposition rate of 0.5 Å s^{-1} through a shadow mask with the channel length (L), width, and thickness of 50 μm, 1000 μm, and 60 nm, respectively.

3. RESULTS AND DISCUSSION

3.1. OFET Memory Employing Carbazole-Based Copolymers as Electrets. The OFET memory devices were fabricated in a bottom-gate/top-contact configuration by employing **copoly(CT)** or **copoly(CBT)** as the electrets, shown in Figure 1. The measurements of atomic force microscopy (AFM) were used to exhibit the surface morphology of the coated electret films on the SiO$_2$ substrates and the subsequent deposited semiconductors. In Figure S1, the thin films of **copoly(CT)** and **copoly(CBT)** display smooth and uniform surface with low root-mean-square roughness values of 0.28 and 0.30 nm, respectively. Additionally, the pure water contact angles of the **copoly(CT)** and **copoly(CBT)** films were 97 and 94°, respectively, indicating the hydrophobic characteristics and good wettability of organic semiconductors with low surface energy.[18,19] As a result, both pentacene (p-type semiconductor) and *N,N'*-bis(2-phenylethyl)perylene-3,4,9,10-bis(dicarboximide) (BPE-PTCDI) as n-type semiconductor could be deposited smoothly to produce thin films with grain- and nanorod-like morphologies, respectively, as depicted in Figure S2.

3.2. p-Type OFET Memory with copoly(CT) and copoly(CBT) as Electrets. The electrical hysteresis curves of the p-type OFET memories with the carbazole-based copolymer electrets of **copoly(CT)** and **copoly(CBT)** are summarized in Figure S3, and the output curves of the devices are shown in Figure S4. All the measurements were conducted in a truly dark environment within a glove box. In the forward sweep process, the threshold voltages of both devices were around 0 V. However, in the reverse scans, the curves revealed large hysteresis windows located in the negative voltage region because of the strong hole-trapping capability of the carbazole-based copolymers.

In order to utilize the large hysteresis windows related to the memory behavior in detail, different degrees of gate pulses (V_g) for the programming process were applied on the p-type OFET memory devices with the carbazole-based copolymer electrets, and the results are shown in Figure S5. Here, all the

Table 1. Summary of p-Type Copolymer-Based OFET Memory Characteristic

		initial	−30 V, 1 s	−50 V, 1 s	−70 V, 1 s	−90 V, 1 s
copoly(CT)	threshold voltage (V)	−6	−19	−40	−50	−59
	memory window (V)		13	34	44	53
copoly(CBT)	threshold voltage (V)	−7	−21	−35	−43	−56
	memory window (V)		14	28	36	49

transfer curves were measured at the fixed drain voltage of −60 V in a dark inert environment. The threshold voltages were obtained from the tangent lines to the curves of square of drain currents, and the value of memory windows was defined as the difference in the threshold voltages between the initial curve and programmed one, as summarized in Table 1. As a result, the larger the programming voltages applied, larger memory windows could be obtained. As the hole-trapping capability was related to the donor moieties of the electret polymers, the memory window values of these two devices were similar.

For further investigating the memory behavior and photo-induced recovery characteristics of the p-type OFET memories, sequential operations were carried out as depicted in Figure 2. After an initial scanning, a positive gate bias (V_g =
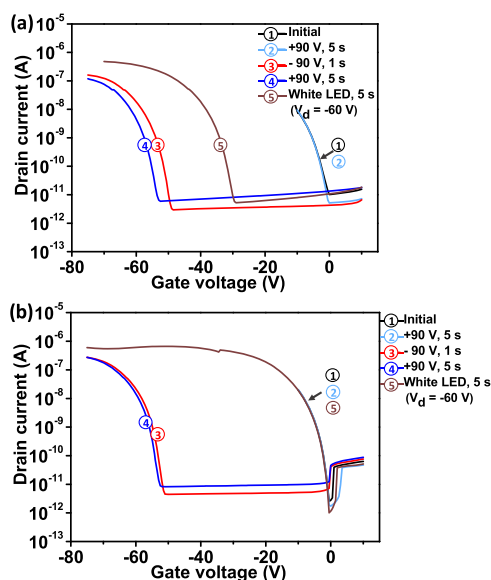

Figure 2. Memory characteristics of the p-type OFET memory devices with (a) **copoly(CT)** and (b) **copoly(CBT)** in the electrical and optical operation mode by irradiating white LED light (25 mW). All currents were measured at the fixed drain voltage (V_d = −60 V) in the dark.

+90 V, 5 s) was applied on the devices. However, the transfer curves of these two devices based on **copoly(CT)** and **copoly(CBT)** electrets did not significantly shift, suggesting that the p-type OFET memories could not effectively capture the electrons despite the presence of the carbazole-based copolymer electrets. Afterward, the application of the negative voltage (V_g = −90 V, 1 s) for the programming process resulted in the apparent shift toward the negative direction, indicating that a great quantity of the holes flew from pentacene and were trapped in the electret layers. Subsequently, a reverse (V_g = +90 V, 5 s) bias was applied to the programmed devices for electrically erasing purposes. However, the transfer curves of the devices almost stay at the same position as the programmed curves, representing the electri-

cally inerasable properties. In Figure S3, the initial and programmed hysteresis curves were used to compare with those of the electrical bias applied devices in order to verify the electrically inerasable property of p-type OFET memory devices with the carbazole-based copolymer electrets. For the programmed hysteresis curves and those scanned after the reverse bias, weak hysteresis windows were obtained, implying that no sufficient electrons could be produced to neutralize the trapped holes or no trapped holes were released.[20,21] Accordingly, this led to the electrically inerasable characteristic.[22] Intriguingly, the photorecovery behavior could be observed in both the p-type OFET memories based on the **copoly(CT)** and **copoly(CBT)** electrets when the white light-emitting diode (LED) light was irradiated. Both of the devices were exposed to white LED light for 5 s with the same light intensity (25 mW) as described in Figure 2, but the device based on the **copoly(CT)** electret showed a lower sensitivity than that based on the **copoly(CBT)** electret. The different light responses between **copoly(CT)** and **copoly(CBT)** may be caused by the absorption efficiency of visible light and the structural factors related to optical behaviors.

3.3. n-Type OFET Memory with copoly(CT) and copoly(CBT) as Electrets. To clarify the structural design based on conjugated donor−acceptor systems for the photo-recovery behavior and memory properties, n-type OFET memory devices with the carbazole-based copolymer electrets were fabricated by using BPE-PTCDI as an n-type semi-conductor. Similar to the p-type OFET memories, the electrical and photonic erasability was examined. The memory characteristics and photoinduced recovery behavior of the n-type OFET memory devices based on the **copoly(CT)** electret are shown in Figure S6. The application of the positive voltage (V_g = +90 V, 1 s) to the freshly prepared device (the blue line with number 2 in Figure S6a) did not inject electrons to the electret layer, which is consistent with the results of the p-type devices. The memory characteristics of both p-type and n-type OFET memory devices based on the **copoly(CT)** electret suggested that the futile effect of electron-trapping could be attributed to the absence of the acceptor groups, resulting in the energy level mismatch [namely, lowest occupied molecular orbital (LUMO) barrier] between semiconductors (pentacene and BPE-PTCDI) and **copoly(CT)**, as shown in Figure 3. Afterward, the negative pulse exerted on the devices could
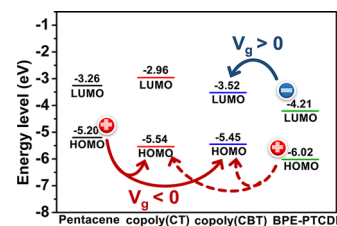

Figure 3. Energy-level diagram of organic semiconductors and carbazole-based copolymers.

cause the shift of the transfer curve toward the negative region, exhibiting the hole-trapping characteristic. Because of the small difference in the highest occupied molecular orbital (HOMO) energy levels between semiconductors (pentacene and BPE-PTCDI) and **copoly(CT)**, the hole-trapping characteristic could be found in both p-type and n-type devices. However, the applications of reverse bias (V_g = +30 to +90 V, 1 s) could not effectively erase the recorded information, as summarized in Figure S6b.

Surprisingly, the n-type OFET memory devices based on the **copoly(CBT)** electret exhibited ambipolar trapping characteristics as shown in Figure 4, indicating that the n-type OFET
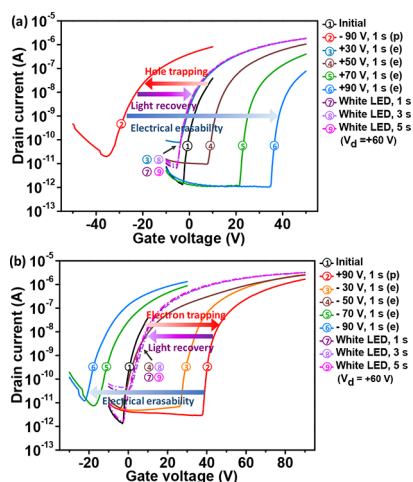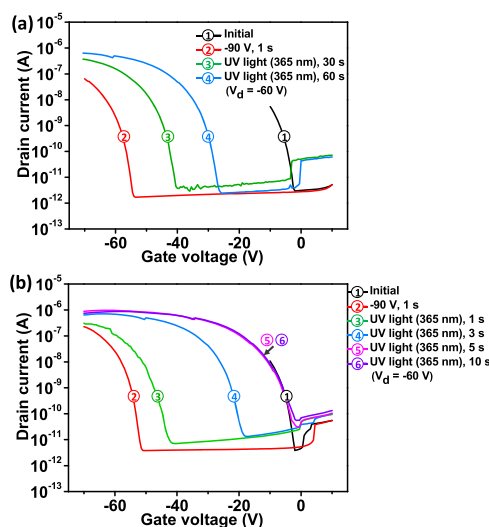

Figure 4. Memory characteristics of the n-type OFET memory devices with the **copoly(CBT)** electret exhibiting ambipolar trapping capability: (a) hole-trapping, electrical and photo-erasable; (b) electron-trapping, electrical and photo-erasable. The optical operation is to irradiate white LED light (25 mW). All currents were measured at the fixed drain voltage (V_d = +60 V) in the dark (noting that every erase scan was performed independently; in other words, every erasing pulse voltage was implemented after initializing and programming).

memory could trap both polarities of carriers.[23,24] In Figure 4a, after application of the negative voltage (V_g = −90 V, 1 s) on the n-type OFET memory devices based on the **copoly(CBT)** electret for the programming operation, the transfer curve significantly shifted toward the negative direction. This result revealed the same hole-trapping ability as the p-type devices, which could be attributed to the carbazole donor groups and the small difference of the HOMO energy levels between organic semiconductors (pentacene and BPE-PTCDI) and **copoly(CBT)**, as illustrated in Figure 3. Interestingly, application of a reverse bias (V_g = +30 to +90 V, 1 s) could effectively revert the transfer curve to the initial state, and then further surpass the initial curve toward the positive direction. This result suggested that the electrons could flow from BPE-PTCDI into the electret layer to neutralize the trapped holes. In addition, the intensely positive external electrical field could further bring on the capture of electrons in the electret layer. This behavior is in sharp contact to that based on **copoly(CT)** and strongly supports that the electron-trapping capability and electrical erasability of **copoly(CBT)** by the applied positive bias could be ascribed to the benzothiadiazole acceptor unit. In other words, a substantial decrease in the LUMO barrier between BPE-PTCDI and the electret occurred (Figure 3), promoting the injection of electrons. The same explanation

could be applied to the small differences in the HOMO and LUMO energy levels between BPE-PTCDI and **copoly(CBT)**. The n-type OFET memories with the **copoly(CBT)** electret could be programmed by the applied negative bias and electrically erased by the positive bias, as shown in Figure 4b. Moreover, the photorecovery behavior was observed for the n-type OFET memories with the **copoly(CBT)** electret.

3.4. Structural Factors in Producing the Photo-induced Recovery Behavior. In order to elucidate the cause of different photoresponses between **copoly(CT)** and **copoly(CBT)**, we should first determine the layer which generates the excitons mainly. Pentacene does not absorb at 365 nm (absorbance of 0.05 for the 50 nm thick film),[3] whereas the carbazole-based copolymers have intense absorption at this wavelength.[17] Therefore, if the illumination of the UV light (365 nm) on the programmed devices realizes the photorecovery behavior, we could conclude that the excitons are generated in the electret layer rather than the pentacene layer.[3] In addition, the absorbance of **copoly(CT)** and **copoly(CBT)** at 365 nm is almost the same,[17] which excludes the possibility of the absorption difference and represents the structural factors. In Figure 5, the photoinduced

Figure 5. Photoinduced recovery characteristics of the p-type OFET memories with (a) **copoly(CT)** and (b) **copoly(CBT)** in UV-irradiated operation (365 nm, 270 μW) modes. The measurements were conducted at the fixed drain voltage (V_d = −60 V) in the dark (noting that every scan after the UV-light illumination was performed independently; in other words, every scan was implemented after initializing and programming).

recovery phenomenon could be observed in both p-type OFET memories with **copoly(CT)** and **copoly(CBT)** after UV light (365 nm, 270 μW) illumination. The results could be interpreted as the electrets produced excitons upon absorbing the photons; then, the excitons were dissociated and separated into positive and negative carriers, which were used to neutralized the trapped opposite charges.[1,2]

The observed difference of recovery between **copoly(CT)** and **copoly(CBT)** would be caused by the generation and dissociation efficiencies of excitons. From the above statement, we could preclude the generated exciton amount as the major factor in producing the different photoresponses, and thus put emphasis on the analysis of dissociation extent of the excitons. Therefore, we focused on the molecular design of polymer

electrets, which determines the photoresponsive properties and distinct trapping ability. The excitons are electron−hole pairs bound together because of Coulombic attraction. Introducing the donor−acceptor systems is a common strategy to overcome the Coulombic force and enhance the charge separation efficiency. Additionally, the π-conjugated polymers could effectively facilitate the dissociation of electron−hole pairs through charge delocalization, especially when the donor and acceptor moieties are highly twisted.[25−28] To go a step further, we connect the molecular design with the energy level of the polymer to explain the behavior of ambipolar and faster photoresponse for **copoly(CBT)**. First, the carbazole-based conjugated polymers by direct conjugation or by alkyne spacer at the 1,8-position could be found in previous literature,[15,17] which obviously indicates that polymers with an alkyne spacer provide a lower energy level of HOMO than those with direct conjugation. Therefore, the carbazole-based conjugated polymers with an alkyne spacer as the electron-donating moiety are chosen for this donor−acceptor system. Herein, regarding the donor−acceptor effect on photoresponsive memory, the different extend of EWD molecules are introduced for comparison, such as thiophene and benzothia-diazole. A strong acceptor can reduce the LUMO energy level to admit an electron-trapping site, whereas the HOMO energy level can be maintained for hole-trapping because of the twisted donor−acceptor structure. In the case of **copoly(CT)**, which is composed of only donor and π-extended thiophene units, the memory devices showed photorecovery behavior at a slow photoresponse time. In contrast to this result, **copoly-(CBT)** possesses the electron-accepting benzothiadiazole group. The requirements for the effective dissociation of electron−hole pairs include a significant difference in the electronegativity between the donor and acceptor moieties and assistance of the charge delocalization. 1,8-Carbazole-based polymers generally adopt nonplanar structures suitable for the charge delocalization. Because of the absence of strong acceptor groups in **copoly(CT)**, inefficient separation of electron−hole pairs occurred, leading to a poor photo-responsive performance. On the other hand, **copoly(CBT)** could effectively stabilize the formed electrons and holes on the LUMO and HOMO, respectively. Consequently, twisted π-conjugated polymer structures with donor−acceptor units for exciton dissociation and charge stabilization are the crucial parameters to influence the performance of the photoinduced recovery behavior.

3.5. Application to a Photorecorder. As for a memory device, the capability of data retention is the critical parameter for storage reliability; in other words, it concerns the retained time of the storage information. Figure 6a,b displays the retention characteristics of the p-type OFET memories with the **copoly(CT)** and **copoly(CBT)** electrets set at a reading voltage of −10 V. Both the p-type OFET memory devices could maintain the off state for more than 10^4 s with the on/off ratio of around 10^3. In addition, we used the extrapolation method to estimate the retention time of each memory device. The data are summarized in Table 2 and show their applicability in photorecorders. Furthermore, it is worth noting that the ambipolar characteristic of n-type OFET memory devices with the **copoly(CBT)** electret was demonstrated. Thus, three-level data storage could be achieved, significantly expanding the storage density as illustrated in Figure 6c.

The photoresponsive characteristic of these electrets in memory devices allowed the extra application to a photo-
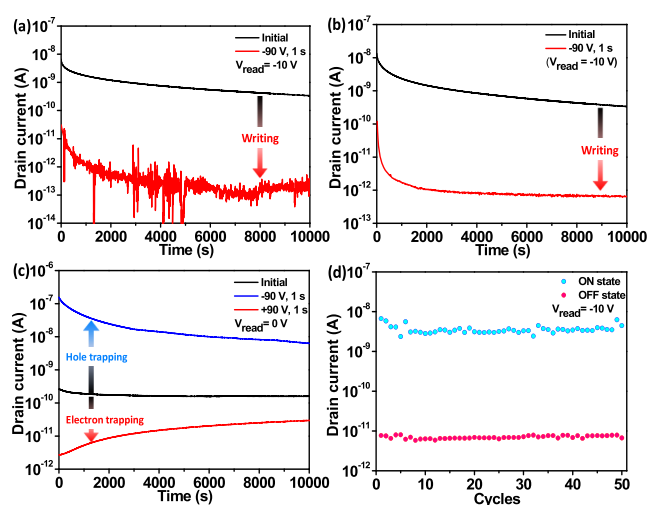
Figure 6. Retention characteristics of (a) p-type OFET memory devices with **copoly(CT)** electrets and (b) p-type OFET memory devices with **copoly(CBT)** electrets before and after writing (V_g = −90 V) operation. The gate voltage was set at V_g = −10 V for reading. (c) Multilevel retention characteristics of the n-type OFET memories with **copoly(CBT)** electrets. The gate voltage was set at V_g = 0 V for reading (noting that the blue and red lines were obtained independently). (d) 50 switching cycles' durability test for photo-recorder application of the p-type OFET memory devices with **copoly(CBT)** electrets.

Table 2. Summary of the Estimated Retention Time for Each Memory Device

	copoly(CT)		copoly(CBT)	
	p-type	n-type	p-type	n-type
retention time	$\sim10^9$	$\sim10^5$	$\sim10^5$	$\sim10^6$

recorder. To quantize the photoresponsive characteristic, the white LED light source was modulated by the light exposure time (with constant intensity) and light intensity (with constant exposure time) as summarized in Figures S7 and S8, respectively. These results suggested that the devices based on **copoly(CBT)** exhibited much more sensitive and prompt photoresponsive characteristics than those based on **copoly-(CT)**.

Based on the excellent photorecovery performances of the device based on the **copoly(CBT)** electret, we further demonstrated the stability for photorecorder application. The 50-cyclic switching durability test of the p-type OFET memory with the **copoly(CBT)** electret was performed as shown in Figure 6d. During the test, every point for the on state represented the average value in the period of 30 reading seconds, detected after white LED light (25 mW) illumination for 2 s (except for the first point, which is the initial state). The currents in the off state were measured after programming, and the points represented the average values in the period of 30nreading seconds. The on/off ratio could be retained even after the 50-cycle switching, indicating the high durability of the device.

4. CONCLUSIONS

In this study, we verified the mechanism of photorecovery behavior. Through the structure−property relationship study of the 1,8-carbazole-based copolymers, we demonstrated the significance and the effect of the donor−acceptor system on

the performance of photoresponsive OFET memory devices. In the series of experiments, **copoly(CBT)** with the donor–acceptor structure exhibited superb photosensitivity and photorecovery responses to the counter **copoly(CT)**, implying that **copoly(CBT)** is an emerging electret material suitable for the application of photorecorders. Moreover, we established the rational design strategy of polymer electrets from the viewpoint of chemical structures and elucidated the major factors influencing the performances of the photoresponses. The donor–acceptor-type conjugated polymers based on the 1,8-carbazole unit could facilitate the separation of the excitons (electron–hole pairs) by charge stabilization. Thus, the generated excitons at the twisted donor–acceptor moieties could be efficiently dissociated into free charges. Furthermore, the donor–acceptor structure allowed the electret to capture both the electron and hole, providing ambipolar trapping behavior. For the practical application as electronic storage devices, the memories based on both the **copoly(CT)** and **copoly(CBT)** electrets showed nonvolatile characteristics. Notably, because of the ambipolar property of the n-type OFET memory with the **copoly(CBT)** electret, the multiple-level data storage based on the three different states could be substantiated. As for a photorecorder, the photoinduced recovery behavior has been determined by modulating the white LED light intensity and exposure time. Last but not least, **copoly(CBT)**-based devices passed the durability test with 50 times switching cycles and could be stably operated without any obvious degradation. To sum up, a conceptual framework to design the high-performance photoresponsive polymers was provided and demonstrated the excellent operation of not only OFET memories but also photorecorders.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b20960.

AFM topography images; electrical hysteresis curves, output characteristic, and transfer curves of **copoly(CT)** and **copoly(CBT)** for n-type and p-type OFET memory devices (PDF)

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Notes

The authors declare no competing financial interest.

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