# Synthesis and Morphology of Two Carbazole–Pyrazoline-Containing Polymer Systems and Their Electrical Memory Performance

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A new atom-transfer radical polymerization (ATRP) initiator 4-[1-(2-dodecyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6yl)-3-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-5-yl]phenyl

2-bromo-2-methylpropanoate (IN) as an electron acceptor (A) and a monomer 2-(9*H*-carbazole-9-yl)-ethyl methacrylate (MCz) as an electron donor (D) were simultaneously introduced into two different D–A polymer systems by using the end-functionalizing or blending method. The mass percentage of IN in the end-functionalized polymer PMCz-IN and the mixed polymer composite PMCz+IN were both controlled at approximately 1.0 wt%. The optical, electrochemical, and surface morphology properties of the two polymeric films prepared by means of

spin-coating technology were comparatively investigated. Sandwich devices based on PMCz-IN and PMCz + IN demonstrated nonvolatile write-once-read-many-times memory (WORM) and volatile static random access memory (SRAM) characteristics, respectively, which were further verified by the Kelvin probe force microscopy (KPFM) measurements. The proposed memory mechanism could be attributed to the formation of a stable charge-transfer (CT) complex for PMCz-IN and an unstable CT complex for PMCz + IN. Furthermore, the different distribution of IN in the two polymeric films might be the main reason for the stability of the CT complex.

# Introduction

Over the past few decades, large numbers of resistive-type memory devices based on organic or polymer systems for data storage have been investigated.<sup>[1-10]</sup> In particular, polymer systems have attracted significant scientific interest owing to their unique properties of good mechanical strength, flexibility, and most important of all, ease of processing.<sup>[6-10]</sup> Until now, reported polymer systems have been used for device applications such as static random access memory (SRAM), dynamic random access memory (DRAM), write-once-read-many-times memory (WORM), rewritable (Flash), and negative differential resistance (NDR) memory behavior by means of an external voltage bias or pulse.

Recently, polymer systems containing donor (D) moieties and acceptor (A) moieties have been studied widely for ad-

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vanced memory-device application.<sup>[11-34]</sup> By combining D moieties with A moieties, two direct approaches are provided during the fabrication of devices including incorporating and blending methods. Thus, D-A polymer systems could also be divided into two general groups: non-blended polymers (consisting of conjugated<sup>[11-13]</sup> and non-conjugated<sup>[14-19]</sup> polymers) and blended polymers (including metal nanoparticles,<sup>[20-22]</sup> fullerenes,  $^{\scriptscriptstyle [23-25]}$  carbon nanotubes,  $^{\scriptscriptstyle [26-28]}$  graphene oxide,  $^{\scriptscriptstyle [29-31]}$  and organic dyes<sup>[32-34]</sup>). The incorporating method through the connection of covalent bonds can proceed through various routes, such as copolymerization,<sup>[12-15]</sup> grafting,<sup>[16, 17]</sup> side-chain functionalization,<sup>[18,19]</sup> and end functionalization. Owing to the clear polymer structure of D-A polymers prepared by using the end-functionalization approach, this novel method applied to electrical memory devices has attracted more and more attention recently. For example, Ree et al. covalently incorporated fullerene (A) with carbazole (D) into a single polymer system through living anionic polymerization.<sup>[35]</sup> In addition, in our previous study, we end-functionalized the carbazole-based polymer chain using naphthalimide by means of atom-transfer radical polymerization (ATRP).<sup>[36]</sup> Although using end-functionalizing or blending methods for the development of high-performance memory-device applications has been investigated greatly, to the best of our knowledge the comparison between them has been explored rarely. When we compared the morphologies of polymeric films fabricated by using these two methods, the end-functionalized polymeric film exhibited microphase separation, whereas the blended polymeric film exhibited nanoparticle aggregation phenomena. It has been reported that the morphology of the polymer composite will



affect the electrical memory behavior.<sup>[37–39]</sup> Thus, our current study on the comparison of data storage performance between the end-functionalized polymer system and blended polymer system is necessary.

In this study, we chose a carbazole (MCz) as D and a pyrazoline (IN) as A. To combine MCz and IN into a single polymer system, we utilized the end-functionalizing or blending method, and obtained two polymeric films PMCz-IN and PMCz+IN, respectively. Subsequently, these two electroactive films were fabricated as sandwich memory devices. For comparison purposes, the mass percentage of IN in the two devices was kept at approximately 1.0 wt %. The fabricated indium tin oxide (ITO)/PMCz-IN/AI device shows nonvolatile WORM characteristics, whereas the ITO/PMCz+IN/AI device exhibits volatile SRAM characteristics. It is concluded that the different electrical characteristics of the two devices could be attributed to the formation of a stable or unstable charge-transfer (CT) complex between IN and MCz. Furthermore, the stability of the CT complex might be associated with the distribution of IN in the two films, and the formation of IN nanoparticles in the PMCz+IN film could contribute to the volatile memory characteristics. Therefore, we successfully achieved tunable electrical memory performance by means of two different combined methods based on the same electroactive substances.

# **Results and Discussion**

## Synthesis and characterization

The monomer, 2-(9*H*-carbazole-9-yl)-ethyl methacrylate (MCz), was synthesized according to previously reported procedures<sup>[40]</sup> and characterized by using the <sup>1</sup>H and <sup>13</sup>C NMR spectra as displayed in Figure S1 in the Supporting Information. Scheme 1 illustrates the synthetic route of the initiator IN, which was characterized by <sup>1</sup>H NMR spectroscopy and LC–MS (see Figures S2 and S3 in the Supporting Information). With the successful preparation of the monomer and the initiator, polymers PMCz and PMCz-IN were prepared by using the ATRP method and their <sup>1</sup>H NMR spectra are shown in Figure S4 in the Supporting Information. The gel permeation chromatography (GPC) analysis (see Figure S5 in the Supporting Information) of PMCz and PMCz-IN indicated a number-average molecular weight ( $M_n$ ) of 12400 and 9200 g mol<sup>-1</sup>, respectively, and a polydispersity index (PDI) of 1.24 and 1.23, respectively.

## **Thermal stabilities**

Figure 1 illustrates the thermal stability of the two polymers evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The 5% weight-loss temperature ( $T_{d5\%}$ ) of PMCz and PMCz-IN were found to be 280 and 290°C, respectively. In addition, polymer PMCz-IN was found to have a glass-transition temperature ( $T_g$ ) of 140°C, which was higher than that of polymer PMCz (124°C). Therefore, the introduction of an end-functionalized initiator led to an increase of  $T_{d5\%}$  and  $T_g$  compared to polymer PMCz. Moreover, the good thermal properties of the two polymers are expected to withstand heat deterioration in the memory devices.<sup>[41]</sup>

## **Optical characteristics**

First, we investigated the content of IN in the obtained polymer PMCz-IN, which was determined as approximately 1.0 wt% by a UV/Vis absorption calibration curve as depicted in Figure 2a. The absorption spectra of PMCz-IN and PMCz + IN in the film state are shown in Figure 2b. The absorption peaks at shorter wavelength (328 and 342 nm), which are consistent with the absorption peaks of pure carbazole-containing poly-



Scheme 1. The synthetic routes to IN, PMCz-IN, PMCz, and the mixed polymer composite PMCz + IN.

mer PMCz (see Figure 2c), are attributed to the  $\pi$ - $\pi$ \* electronic transition of the carbazole moieties.[40] However, the wide absorption band appearing at 350-550 nm is associated with the intermolecular charge-transfer (ICT) character of the initiator IN end-functionalized PMC<sub>7</sub> in (PMCz-IN) or embedded in PMCz (PMCz + IN).<sup>[42, 43]</sup> Furthermore, the similar absorption values of PMCz-IN and PMCz+IN further demonstrate that we have ensured that the two polymeric films have a similar mass percentage of IN.

To further demonstrate the interaction between PMCz and IN, the emission spectra of PMCz-IN and PMCz+IN in the film state were also investigated and are displayed in Figure 2d. With an







Figure 1. a) TGA and b) DSC thermograms of the polymers PMCz and PMCz-IN, recorded under  $N_2$  at a heating rate of 10 and 20 °Cmin<sup>-1</sup>, respectively.



**Figure 2.** a) Calibration curve for determining the mass percentage of IN in PMCz-IN, using IN as standard. b) Normalized absorption spectra of PMCz-IN and PMCz + IN thin films on quartz plate. c) Normalized absorption and emission spectra of PMCz thin film on quartz plate (excitation wavelength: 340 nm). d) Normalized emission spectra of PMCz-IN and PMCz + IN thin films on quartz plate (excitation wavelength: 340 nm).

excitation wavelength of 340 nm, the emission maximum of the carbazole chromophore of PMCz is at 376 nm, as shown in Figure 2c. However, when we use the end-functionalizing or blending method to introduce initiator IN into PMCz, the prepared PMCz-IN or PMCz + IN films exhibit a decrease of the emission peak of the carbazole chromophore and the appearance of a new emission peak at 556 and 567 nm, respectively, whereas the emission maximum of IN is at 626 nm (see Figure S6 in the Supporting Information). This phenomenon might be associated with the occurrence of electron transfer and/or energy transfer,<sup>[24,44]</sup> which is important for their memory characteristics as discussed in the following section. In addition, the different emission peaks of PMCz-IN and PMCz+IN at longer wavelengths must be associated with the phenomenon of molecular aggregation. Compared with PMCz-IN, the prepared PMCz+IN film using the blending method leads more easily to the formation of initiator nanoparticles.<sup>[45]</sup>

## **Electrochemical characteristics**

The electrochemical characteristics of the polymeric films were investigated by cyclic voltammetry (CV) as shown in Figure 3 and summarized in Table 1. The oxidation and reduction behaviors of PMCz, PMCz-IN, and PMCz+IN on an ITO substrate were measured in 0.1 M TBAPF<sub>6</sub>/acetonitrile solution with Ag/ AgCl as reference electrode and Pt wire as counter electrode. The onset oxidation ( $E_{Ox}^{onset}$ ) estimated from the CV curves for PMCz, PMCz-IN, and PMCz+IN are 1.04, 1.05, and 1.08 V, respectively. In addition, the onset reduction ( $E_{\text{Red}}^{\text{onset}}$ ) estimated from the CV curves for PMCz-IN and PMCz+IN are -0.75 and -1.00 V, respectively. Note that the oxidation half-wave potentials for the external ferrocene/ferrocenium ( $E_{1/2}$ , ferrocene) was measured to be 0.42 V versus Ag/AgCl (see Figure 3a). The HOMO and LUMO energy levels of the prepared polymeric films were calculated from the CV tests with reference to ferrocene (4.80 eV below the vacuum level, which is defined as zero) by applying Equations (1) and (2).[46,47]



**Figure 3.** Cyclic voltammograms of a) ferrocene in solution, b) PMCz, c) PMCz-IN, and d) PMCz + IN films on an ITO substrate in 0.1  $\,$  M TBAPF<sub>6</sub>/acetonitrile solution with Ag/AgCl as reference electrode and Pt wire as counter electrode. A scan rate of 100 mV s<sup>-1</sup> was used.

Table 1. Electrochemical characteristics of the prepared polymeric films.									
Polymeric films	$E_{\rm Ox}^{\rm Onset}$ [V]	$E_{\rm Red}^{\rm Onset}$ [V]	HOMO [eV] <sup>[a]</sup>	LUMO [eV] <sup>[a]</sup>					
PMCz-IN PMCz+IN	1.05 1.08	-0.75 -1.00	-5.43 -5.46	-3.63 -3.38					
[a] The HOMO and LUMO energy levels were calculated from cyclic vol- tammetry with reference to ferrocene (4.80 eV).									



$$E_{\rm HOMO} = -[(E_{\rm Ox}^{\rm onset} - E_{1/2}, {\rm ferrocene}) {\rm versus Ag/AgCl} + 4.80] {\rm eV}$$
(1)

$$E_{\rm LUMO} = -[(E_{\rm Red}^{\rm onset} - E_{\rm 1/2}, \, {\rm ferrocene}) \, \, {\rm versus} \, \, {\rm Ag/AgCI} + 4.80] \, \, {\rm eV} \eqno(2)$$

## Morphology of the thin films

To investigate the morphology of the thin films of PMCz-IN and PMCz+IN, the tapping mode atomic force microscopy (TM-AFM) height and phase images were obtained at room temperature as shown in Figure 4. As shown in Figure 4a, b, we can conclude that both the PMCz-IN and PMCz+IN thin films have a smooth surface with root-mean-square (RMS) roughness values of 1.02 and 1.50 nm, respectively. Hence, the modification of IN using long alkyl chains (such as  $nC_{12}H_{49}$ ) is necessary to achieve homogeneous films. In addition, as shown in Figure 4b, the typical cross-section profile of the TM-AFM height image of the PMCz+IN thin film clearly illustrates the formation of IN nanoparticles (cf. images of PMCz-IN (Figure 4a) and PMCz (Figure S7 in the Supporting Information) thin films). This result is consistent with the emission spectra of the PMCz-IN and PMCz + IN thin films as shown in Figure 2d. Interestingly, when comparing the TM-AFM phase images of PMCz-IN shown in Figure 4c with that of PMCz+IN shown in Figure 4d, the PMCz-IN thin film exhibits microphase separation with a close-packed structure.<sup>[39]</sup>



The electrical and switching characteristics of the ITO/PMCz/Al device have been reported in detail by Kang's group previously.<sup>[48,49]</sup> The device exhibits WORM memory behavior with the switch-on voltage mainly in the range of -1.8 to -2.2 V (with a yield of 56%), as illustrated in Figure S8 in the Supporting Information.

Figure 5c illustrates the electrical and switching characteristics of the ITO/PMCz-IN/AI device. During the first negative voltage from 0 to -3.0 V (Sweep 1), the current density initially remains at a low conductivity (OFF state). At the switch-on voltage around -3.0 V, the current density increases abruptly from  $10^{-8}$  to  $10^{-2}$  A, which indicates the device transition from the initial OFF state to the high-conductivity ON state. The transition from the OFF state to the ON state is equivalent to the "writing" process in a digital memory cell. The current density maintains the ON state for the subsequent negative sweep from 0 to -5.0 V (Sweep 2). Once the device had reached the ON state, it could not return to the OFF state even after turning off the power or upon applying a reverse sweep (not shown). The nonvolatility of the ON state suggests that the ITO/PMCz-IN/AI device exhibits WORM memory behavior with the switch-on voltage around -3.0 V, and the ON/OFF current ratio is up to 10<sup>6</sup>. The cell-to-cell uniformity for the ITO/PMCz-IN/AI device was also investigated. Figure 5b shows the statisti-



**Figure 4.** The TM-AFM height images and typical cross-section profiles of a) PMCz-IN and b) PMCz+IN; c, d) are the corresponding phase images of (a) and (b), respectively. The scan size is  $2 \times 2 \mu m^2$ .



**Figure 5.** a) The schematic diagram of the fabricated memory devices. b) The statistical data of reproducibility of the devices ITO/PMCz-IN/AI. Current density–voltage (*I–V*) characteristics of the c) ITO/PMCz-IN/AI and d) ITO/PMCz+IN/AI devices. Retention times of the ON and OFF states under a continuous readout voltage of -1.0 V for e) ITO/PMCz-IN/AI and f) ITO/PMCz+IN/AI.



cal data obtained from 50 cells, as the switch-on voltage is mainly between -2.6 and -3.0 V (with a yield of 64%).

In the case of the ITO/PMCz+IN/AI device, the electrical and switching characteristics were also investigated, as shown in Figure 5d. Starting with the low-conductivity OFF state of the fabricated device, the current density increases slowly in the range of  $10^{-10}$  to  $10^{-6}$  A with the applied negative voltage. The current remains in the OFF state until the switch-on voltage of about -3.5 V. When the voltage increases further, the current density increases abruptly from  $10^{-6}$  to  $10^{-2}$  A (Sweep 1). The ON/OFF current ratio is up to 10<sup>4</sup>. The ON state was maintained during a subsequent sweep from 0 to -5.0 V (Sweep 2). After reading the ON state in the negative sweep and turning off the power for about five to eight minutes, the device was reprogrammed from the OFF state to the ON state again with a negative biased sweep (Sweep 3) and remains in the ON state (Sweep 4). The ITO/PMCz+IN/AI device exhibited repeated operation from Sweep 5 and Sweep 6, and the ON state could not be maintained after the removal of power and gradually relaxed back to the OFF state. Therefore, the short retention ability based on the electrical switching concludes the volatile nature of the static-random-access-memory (SRAM) on the ITO/PMCz+IN/AI memory device.

The stability of the two memory devices at room temperature under ambient conditions was tested. Figure 5c, d show the retention time tests under a constant stress of -1.0 V for both the ON and OFF states of the ITO/PMCz-IN/AI and ITO/ PMCz+IN/AI memory devices. As shown in Figure 5, an ON/ OFF current ratio of approximately 10<sup>6</sup> (PMCz-IN) and approximately 10<sup>4</sup> (PMCz+IN) can be maintained and no apparent degradation in the current is observed for both the ON and OFF states after periods of at least 10<sup>4</sup> s.

To further verify the electrical bistable phenomenon of these two devices, Kelvin probe force microscopy (KPFM)<sup>[50,51]</sup> was conducted at room temperature as shown in Figure 6. First, a 0.5 × 0.5  $\mu$ m<sup>2</sup> area of the ITO/PMCz-IN and ITO/PMCz+IN thin films was scanned with a tip-applied bias voltage of +6 V, as illustrated in the inset of Figure 6a, d, respectively. Second, a 2 × 2  $\mu$ m<sup>2</sup> area was scanned immediately with a tip-applied bias



**Figure 6.** a–c) Sequence of KPFM images showing the nonvolatile memory characteristics of the PMCz-IN thin film on the ITO substrate; d–f) sequence of KPFM images showing the volatile memory characteristics of the PMCz+IN thin film on the ITO substrate. The scan size with a tip-applied bias voltage of 0 V is  $2 \times 2 \mu m^2$ , whereas the scan size of the area marked in (a) and (d) with a tip-applied bias voltage of + 6 V is  $0.5 \times 0.5 \mu m^2$ .

voltage of 0 V. In Figure 6b, e, the black region corresponds to a decrease of the surface potential after the charge was injected from the scan tip into the films. After waiting for 10 minutes, the same  $2 \times 2 \mu m^2$  areas were scanned at 0 V. As can be seen from Figure 6c, f, compared to the PMCz-IN thin film, the surface potential of the PMCz+IN thin film clearly recovered to the previous level. Consequently, the evident contrast of the KPFM images of the PMCz-IN and PMCz+IN thin films strongly supports the nonvolatile and volatile memory characteristics, respectively, and rule out the metallic filamentary conduction mechanism.

#### Proposed memory mechanism

The two memory devices ITO/PMCz-IN/AI and ITO/PMCz+IN/AI show WORM and SRAM characteristics, respectively. This can be explained by the formation of a stable or unstable charge-transfer (CT) complex<sup>[32,46]</sup> between the pendent carbazole donor and pyrazoline acceptor moieties under an electric field.

To understand the charge-transfer mechanism, simulation results of the components in the carbazole-pyrazoline system, including one unit of PMCz, one IN, and a representative unit of PMCz-IN (MCz-IN), were carried out by using DFT/B3LYP/6-31G(d) with the Gaussian 03 program, as illustrated in Table S1 in the Supporting Information. Monomer MCz with a lower HOMO energy level (value) than IN indicates that the MCz group has a stronger tendency to donate an electron, whereas the high LUMO energy level of IN indicates its strong electronwithdrawing ability. When these two components are covalently connected, the HOMO of MCz-IN is located on the MCz side, whereas the LUMO of MCz-IN is located on the IN side. The energy band gaps of IN as well as MCz-IN are much lower than that of MCz, which indicates that the introduction of IN can lead to a polymer system that is highly conductive once it is charged under an electric field. Moreover, the total dipole moments of IN and MCz-IN (7.579 and 5.967 D) are much larger than that of MCz (2.240 D), which can result in a high tendency for charge separation in the carbazole-pyrazoline (D-A) system.

Figure 7 depicts the energy-level diagram for the two devices. In the measurements we used ITO as the anode and AI as the cathode. The work functions of the two electrodes were -4.80 and -4.28 eV for ITO and AI, respectively. For ITO/PMCz-IN/AI, the energy barriers of the ITO/PMCz-IN (HOMO) and



Figure 7. Energy-level diagram for the ITO/PMCz-IN/AI and ITO/PMCz+IN/AI devices.

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PMCz-IN (LUMO)/AI interfaces were 0.63 and 0.65 eV, respectively. As for ITO/PMCz + IN/AI, the energy barriers of the ITO/ PMCz + IN (HOMO) and PMCz + IN (LUMO)/AI interfaces were 0.66 and 0.90 eV, respectively. PMCz with a pendent carbazole group has been reported as a p-type material with the holes as the dominant charge carriers.<sup>(48,49]</sup> Thus, due to the high content of the carbazole moiety of these two polymer systems, the conduction processes under an electric field are also dominated by charge injection. The obtained *I–V* characteristics for the two devices were further analyzed by fitting appropriate conductance models, as shown in Figure 8. The *I–V* data for



**Figure 8.** Experimental and fitted *I–V* curves for the ITO/PMCz-IN/AI device and ITO/PMCz + IN/AI device in the OFF and ON states. Panels (a) and (b) are the OFF state with the SCLC model and the ON state with the ohmic current model for the ITO/PMCz-IN/AI device. Panels (c) and (d) are the OFF state with the SCLC model and the ON state with the ohmic current model for the ITO/PMCz + IN/AI device.

the OFF state of the PMCz-IN- and PMCz+IN-based devices can be fitted by a trap-limited space-charge-limited conduction  $(SCLC)^{[13]}$  model, whereas the ON state current can be fitted by the ohmic model.

The proposed operational mechanism of these two devices is depicted in Figure 9. Initially, under a low bias voltage, charge carriers are blocked by the carbazole electron-donor



**Figure 9.** a, b) Operating mechanism of the ITO/PMCz-IN/AI device; c, d) operating mechanism of the ITO/PMCz+IN/AI device.

moieties and pyrazoline electron-acceptor moieties. At this stage, the devices are at low conductivity (OFF state). When the bias voltage reaches the threshold voltage, electrons in the ground state can transition to the various excited states and a charge-transfer (CT) interaction can occur between MCz and IN (illustrated in Figure 9a, c). Along with the increase of the CT interaction, a channel for charge carriers is formed. Subsequently, the devices reach high conductivity (ON state). However, when the power is turned off, the stability of the formed CT complex for these two devices is different. For the ITO/ PMCz-IN/AI device, the initiator IN is connected to the carbazole polymer chain by the covalent bond, which results in the IN molecules being uniformly distributed and having a strong interaction with MCz. Thus, once the polymer layer was conductive in the ON state, the formed CT complex would be stable as shown in Figure 9b.<sup>[19,35,36,46]</sup> As for the ITO/PMCz+ IN/AI device, the initiator in the polymer matrix aggregates to form nanoparticles. In our previous study, we demonstrated that the compound pyrazoline with the linkage -C=N-N- has volatile memory characteristics.<sup>[52]</sup> Therefore, in this system, the charges trapped by the IN nanoparticles probably redistributed among the IN molecules as shown in Figure  $9d,^{\scriptscriptstyle [32,38]}$  which led to the volatile nature of the ITO/PMCz+IN/AI device.

# Conclusion

In this study, we successfully synthesized the monomer MCz and the initiator IN, and further prepared the two electroactive layers PMCz-IN and PMCz+IN by utilizing the end-functionalizing and blending methods, respectively. The fabricated ITO/ PMCz-IN/AI and ITO/PMCz+IN/AI devices had the same mass percentage of IN, which showed WORM and SRAM memory characteristics, respectively. This switching phenomenon was further supported by KPFM measurements of the PMCz-IN and PMCz+IN thin films. These phenomena were mainly caused by the formation of a stable or unstable charge-transfer (CT) complex between pendent carbazole donor and pyrazoline acceptor moieties under an electric field. Compared to the PMCz-IN thin film with a microphase separation structure, the formation of IN nanoparticles in the PMCz+IN thin film might be the main reason for the unstable CT complex. Finally, we provided a new approach to tune the electrical memory performance using two different carbazole-pyrazoline-containing polymer systems.

## **Experimental Section**

## Materials

Carbazole, chloroethanol, methacryloyl chloride, 4-bromo-1,8-naphthalic anhydride, dodecylamine, hydrazine hydrate (85%), 4-hydroxybenzaldehyde, 4'-nitroacetophenone, and 2-bromo-2-methylpropionyl bromide were used. CuBr (Sinopharm Chemical Reagent Co., Ltd, 98.5%) was purified in acetic acid, washed with methanol, and dried under vacuum to obtain a white powder. Cyclohexanone and N,N,N',N,'N''-pentamethyldiethylenetriamine (PMDETA) were distilled under vacuum. All other reagents and solvents were analytically pure and used as received without further purification.



### Characterization

<sup>1</sup>H NMR spectra were measured using INOVA 400 MHz NMR spectrometers, with CDCl<sub>3</sub> or [D<sub>6</sub>]DMSO as solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Molecular weights and polydispersity indexes (PDIs), relative to PMMA, were measured using Waters 1515 GPC with THF as a mobile phase at a flow rate of 1 mLmin<sup>-1</sup> and with a column temperature of 30°C. SEM images were recorded on a Hitachi S-4700 scanning electron microscope. Thermogravimetric analysis (TGA) was conducted on a TA Instruments Dynamic TGA 2950 at a heating rate of 10 °C min<sup>-1</sup> and under an N<sub>2</sub> flow rate of 50 mLmin<sup>-1</sup>. Differential scanning calorimetry (DSC) analysis was performed on a Shimadzu DSC 860A 85 instrument. UV/Vis absorption spectra were determined on a Shimadzu RF540 spectrophotometer. Room-temperature emission spectra were recorded using an Edinburgh-920 fluorescence spectrophotometer. Atomic force microscopy (AFM) measurements were performed by using a Dimension Icon. Cyclic voltammetry (CV) was performed at room temperature using an ITO working electrode, a reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 100  $\rm mV\,s^{-1}$  (PGSTAT302N Electrochemical Workstation analyzer). All electrical measurements of the devices were characterized under ambient conditions without any encapsulation using an Agilent Technologies B1500A semiconductor device analyzer equipped with a TTPX low and variable temperature probe station.

## **Fabrication of devices**

The schematic diagram of the fabricated memory devices is shown in Figure 5a. The indium tin oxide (ITO)/glass (ITO: approximately 200 nm, see Figure S9a) was precleaned by sonication, with deionized water, acetone, and ethanol for 15 min each. Samples (10 mg mL<sup>-1</sup>) of PMCz, PMCz-IN, and PMCz+IN (PMCz blended with approximately 1.0 wt % IN) shown in Scheme 1 in 1,2-dichloroethane were prepared and filtered through microfilters with a pinhole size of 0.22 µm, after this the solution was spin-coated onto the ITO/glass substrate at a rotational speed of 1500 rpm for 20 s. These films were annealed at 90 °C in a vacuum oven for 12 h; the films had a thickness of about 70-90 nm measured by SEM (shown in Figure S9b-d). Finally, Al was thermally evaporated onto the film surface at  $5 \times 10^{-4}$  Pa through a shadow mask to yield top electrodes with a thickness of approximately 150 nm. The active area of the fabricated device was 0.126 mm<sup>2</sup> (a nummular point with a radius of 0.2 mm). Thus, the three memory devices ITO/PMCz/Al, ITO/PMCz-IN/AI, and ITO/PMCz+IN/AI were fabricated by the above method. Herein, we focused on the investigation of the two devices ITO/PMCz-IN/AI and ITO/PMCz+IN/AI.

### Synthesis of the monomer (MCz)

2-(9*H*-Carbazole-9-yl)ethanol (Cz): A mixture of carbazole (4.17 g, 25.0 mmol) and potassium hydroxide (2.10 g, 37.5 mmol) in *N*,*N*-dimethylformamide (DMF) (50 mL) was stirred for 1 h and chloroethanol (2.95 g, 37.5 mmol) was added dropwise. After stirring for 12 h at room temperature, the mixture was poured into deionized water (500 mL) and the resultant white precipitate was removed by filtration. The reactant was dissolved in aqueous alcohol (70 vol%, 20 mL) and insoluble matter was removed by filtration. The filtrate was poured into deionized water (100 mL), and the white flocculent precipitate was removed by filtration and dried under vacuum. Yield: 4.01 g, 75.4%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =3.74–3.85 (m, 2H), 4.45 (dd, *J*=4.41, 7.07 Hz, 2H), 5.51 (t, *J*=

5.37 Hz, 1 H), 7.15–7.26 (m, 2 H), 7.40–7.50 (m, 2 H), 7.65 (dd, *J* = 4.70, 10.23 Hz, 2 H), 8.10–8.21 ppm (m, 2 H).

2-(9*H*-Carbazole-9-yl)ethyl methacrylate (MCz): Methacryloyl chloride (7.95 g, 40.0 mmol) was added dropwise to a solution of Cz (4.00 g, 19.0 mmol) in chloroform (50 mL) and triethylamine (Et<sub>3</sub>N) (7.60 g, 75.0 mmol) at 0–5 °C and reacted for 12 h. The crude product was isolated by evaporating the solvent and was purified twice by recrystallization from 95 % alcohol. Yield: 4.34 g, 82.1%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =8.15 (d, *J*=7.7 Hz, 2H), 7.66 (d, *J*=8.2 Hz, 2H), 7.46 (t, *J*=7.7 Hz, 2H), 7.21 (t, *J*=7.5 Hz, 2H), 5.74 (s, 1H), 5.53–5.50 (m, 1H), 4.75 (t, *J*=5.0 Hz, 2H), 4.48 (t, *J*=4.9 Hz, 2H), 1.65 ppm (s, 3H); <sup>13</sup>C NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =167.02, 140.80, 136.03, 126.71, 126.28, 122.83, 120.88, 119.61, 110.08, 63.52, 41.84, 18.45 ppm.

## Synthesis of the initiator (IN)

The synthetic procedure for the initiator IN is detailed in Scheme 1.

6-Bromo-2-dodecyl-1*H*-benzo[*de*]isoquinoline-1,3-(2*H*)-dione (BrDBO): 4-Bromo-1,8-naphthalic anhydride (2.76 g, 10 mmol) and dodecylamine (2.78 g, 15 mmol) were dissolved in ethanol (100 mL). The reaction mixture was stirred and heated at reflux for 24 h. The resulting mixture was filtered and the resulting solid was recrystallized from ethanol. Yield: 2.66 g, 61.4%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 8.53 (dd, *J* = 11.9, 7.9 Hz, 2H), 8.30 (d, *J* = 7.8 Hz, 1 H), 8.19 (d, *J* = 7.8 Hz, 1 H), 7.97 (t, *J* = 7.9 Hz, 1 H), 4.01 (t, *J* = 7.2 Hz, 2 H), 1.62 (dd, *J* = 8.9, 4.6 Hz, 2 H), 1.32–1.17 (m, 18 H), 0.84 ppm (t, *J* = 6.6 Hz, 3 H).

2-Dodecyl-6-hydrazinyl-1*H*-benzo[*de*]isoquinoline-1,3-(2*H*)-dione (DHBO): BrDBO (4.43 g, 10 mmol) and 85% hydrazine hydrate (2.0 mL) were dissolved in 2-methoxyethanol (20 mL). The reaction mixture was stirred and heated at reflux for 4 h. Then, the powder was collected by filtration and washed with chloroform. Yield: 3.08 g, 78.0%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =9.13 (s, 1H), 8.60 (d, *J*=8.4 Hz, 1H), 8.40 (d, *J*=7.3 Hz, 1H), 8.28 (d, *J*=8.6 Hz, 1H), 7.62 (t, *J*=7.9 Hz, 1H), 7.24 (d, *J*=8.6 Hz, 1H), 4.68 (s, 2H), 3.99 (t, *J*=7.2 Hz, 2H), 1.62–1.54 (m, 2H), 1.31–1.19 (m, 18H), 0.84 ppm (t, *J*=6.5 Hz, 3H).

3-(4-Hydroxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one (HNPE): 4-Hydroxybenzaldehyde (2.44 g, 20 mmol), 4'-nitroacetophenone (3.30 g, 20 mmol), and sulfuric acid (2 mL) were dissolved in acetic acid (60 mL). The reaction mixture was stirred and heated at reflux for 24 h. The resulting mixture was poured into a water/ice bath. The white solid was obtained after filtering and was dried under vacuum. Yield: 4.57 g, 85.0%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 10.20 (s, 1 H), 8.35 (q, *J*=8.7 Hz, 4 H), 7.80–7.73 (m, 4 H), 6.86 ppm (d, *J*=8.3 Hz, 2 H).

2-Dodecyl-6-[5-(4-hydroxyphenyl)-3-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]-1*H*-benzo[*de*]isoquinoline-1,3-(2*H*)-dione (DHHB): HNPE (1.35 g, 5 mmol), DHBO (1.97 g, 5 mmol), and hydrochloric acid (2.00 mL) were dissolved in ethanol (45 mL). The reaction mixture was stirred and heated at reflux for 24 h. Then, the powder was collected by filtration and washed with cooled ethanol. Yield: 2.65 g, 82.0%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 9.51 (d, *J* = 8.6 Hz, 1H), 9.45 (s, 1H), 8.49 (d, *J* = 7.2 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.83 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 2H), 6.03–5.95 (m, 1H), 4.07–3.99 (m, 1H), 3.96 (d, *J* = 8.0 Hz, 2H), 3.30 (d, *J* = 7.5 Hz, 1H), 1.57 (s, 2H), 1.23 (d, *J* = 27.1 Hz, 18H), 0.83 ppm (t, *J* = 6.4 Hz, 3H).



4-[1-(2-Dodecyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6yl)-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-5-yl]phenyl 2-bromo-2methylpropanoate (IN): DHHB (1.62 g, 2.5 mmol) and Et<sub>3</sub>N (1.26 g, 12.5 mmol) were added into freshly distilled tetrahydrofuran (THF) (40 mL) and stirred vigorously at 0 °C under a nitrogen atmosphere. The 2-bromo-2-methylpropionyl bromide (1.73 g, 7.5 mmol) solution in THF (20 mL) was added dropwise to the mixture. After 1 h, the ice/water bath was removed and the reaction was allowed to continue for 12 h at room temperature. The solution was filtered and poured into a large amount of water (200 mL). The precipitated product was washed with ethanol to give a red powder. Yield: 1.49 g, 75.0%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta = 9.53$  (d, J = 8.8 Hz, 1 H), 8.49 (d, J = 7.0 Hz, 1 H), 8.31 (d, J = 8.1 Hz, 2 H), 8.21 (d, J =8.0 Hz, 1 H), 8.04 (d, J=8.0 Hz, 2 H), 7.84 (t, J=7.7 Hz, 1 H), 7.53 (d, J=8.0 Hz, 2H), 7.13 (d, J=7.5 Hz, 3H), 6.15 (t, J=10.1 Hz, 1H), 4.14-4.01 (m, 1 H), 3.95 (t, J=6.5 Hz, 2 H), 3.41 (dd, J=16.7, 7.4 Hz, 1 H), 1.97 (s, 6 H), 1.56 (s, 2 H), 1.27–1.17 (m, 18 H), 0.82 ppm (t, J =6.0 Hz, 3 H); LC–MS: *m/z* calcd. for C<sub>43</sub>H<sub>48</sub>BrN<sub>4</sub>O<sub>6</sub><sup>+</sup>: 795.2752; found: 795.2752.

#### Synthesis of the polymers PMCz and PMCz-IN

PMCz was synthesized by the ATRP method, using MCz (8 mmol) as monomer, *tert*-butyl 2-bromoisobutyrate (0.02 mmol) as an initiator, CuBr (0.04 mmol) as a catalyst, and PMDETA (0.08 mmol) as a ligand. PMCz-IN was also synthesized by ATRP, using MCz (4 mmol) as monomer, IN (0.02 mmol) as a macroinitiator, CuBr (0.04 mmol) as a catalyst, and PMDETA (0.08 mmol) as a ligand. The polymerization was both carried out at 80 °C in cyclohexanone (6 mL) under a nitrogen atmosphere for 24 h and was stopped by quenching the reaction mixture in a flask in ice/water. After being diluted with THF, the diluted solution was passed through an alumina column to remove the copper catalyst. The crude polymers were precipitated in methanol (200 mL) under vigorous stirring. The crude polymers were purified using a Soxhlet extractor with ethanol to remove excess amounts of monomer to obtain PMCz (yield: 800 mg, 35.8%) and PMCz-IN (yield: 360 mg, 32.2%).

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