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A novel porphyrin-containing polyimide for memory devices†

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We design a novel solution-processable polyimide ZnPor-t-DSDA with porphyrin moiety (electron donor) and sulfone-containing phthalimide (electron acceptor) for polymer memory applications. The resulting memory device can be switched from low-conductivity (OFF) to high-conductivity (ON) by both positive and negative sweeps, exhibiting symmetry biswitching characteristic with a short retention time (30 s). On the basis of the simulation calculation, the coplanar structure between donor and acceptor units results in charge transferring easily back to its original state after being excited by an electric field.

Since the first polymer electronic memory was reported by Sliva *et al.* in 1970,¹ polymeric electronic devices such as solar cells,^{2,3} transistors,^{4,5} light-emitting diodes,^{6,7} and memory devices^{8,9} have attracted significant attention over the years. Among all the studied applications, polymer electronic memory has been developed for the establishment of next generation memory devices. Conventional memory devices based on semiconductor integrated circuits play an important role in the development of information technology. In comparison with inorganic memory devices, polymeric memory devices have the advantages of rich structural flexibility, low-cost, solution processability, three-dimensional stacking capability and ease of miniaturization, and tailored properties through molecular design. The resistive-type memory devices store information based on two bistable states, high current (ON) and low current (OFF) states according to different applied voltages.

In recent years, a large number of memory materials have been developed, such as conjugated polymers,^{10–15} functional polyimides,^{16–20} non-conjugated polymers with electroactive pendant,^{21–24} and polymer hybrids.^{25–28} The electrical be-

haviors of resistive-type memory devices have been illustrated by several different mechanisms,²⁹ including charge transfer (CT), conformation change, filamentary, and charge trapping/detrapping. Furthermore, in order to enhance charge transfer, some of the precedents have reported that the materials containing donor-acceptor (D-A) moieties reveal good charge transfer and bistable electric properties. Polyimides (PIs) have been well known as one of the classical high-performance polymers with an excellent combination of properties such as exceptional mechanical, thermal, electrical, and optical properties along with chemical and solvent resistance. Moreover, PIs have a wide range of applications in engineering industries membranes.^{30–33} The first PI memory material was reported by Kang *et al.* in 2006 which exhibits dynamic random access memory (DRAM) behavior.¹⁶ Furthermore, soluble and air-stable organic semiconductors have received attention due to their ease of processing and large-scale fabrication. Organic semiconductor materials such as porphyrins are given more attention because of their unique properties in photonics and electronics. Porphyrins and their complexes are field responsive materials that can be considered as a building block in producing charge-transporting layer because of their large size, thermal stability, and diversity of their coordination and catalytic chemistry. Moreover, the properties of porphyrins can be custom-made to preferred applications only by a minor alteration of the chemical synthesis by varying the core atoms. Therefore, porphyrins have demonstrated outstanding optoelectronic properties in various organic electric devices, especially in organic solar cells because of their strong absorptions in the visible region and near-IR region.^{34–38} However, only very few porphyrin-containing PIs have been explored for applications in optical materials^{39–41} and membrane sensors.^{42,43}

To the best of our knowledge, porphyrin-containing PIs have never been applied to polymeric memory devices. In this communication, we design a novel donor-acceptor system functional porphyrin-containing PI, **ZnPor-t-DSDA**, derived from **ZnPor-t-diamine** and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) as donor and acceptor moieties, respectively, for resistive type memory applications (Fig. 1).

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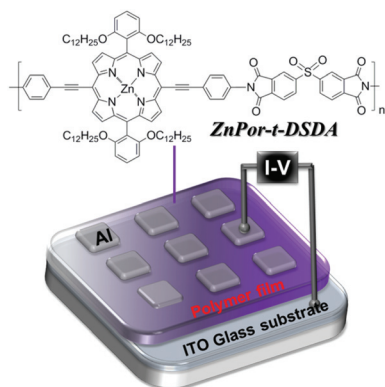


Fig. 1 The chemical structure of ZnPor-t-DSDA and schematic diagram of the resistive memory device.

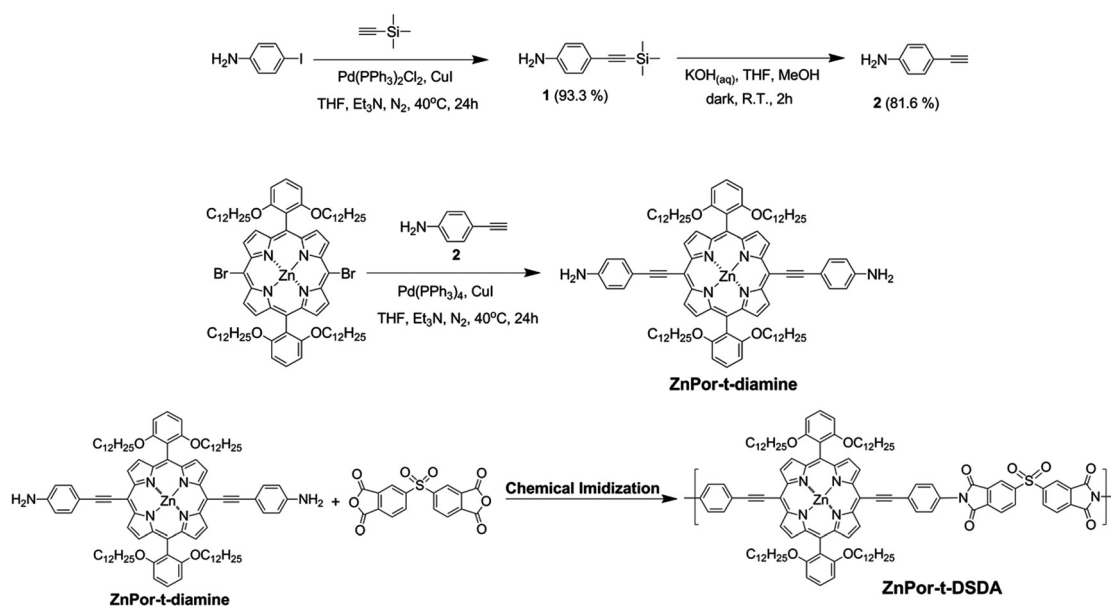
The preparation procedures of ZnPor-t-diamine and the corresponding PI ZnPor-t-DSDA are shown in Scheme 1, and the details of synthesis and basic properties are shown in the ESI.† A novel porphyrin-containing diamine with two triple bonds between the porphyrin moiety and phenylamine functional groups, ZnPor-t-diamine, was employed as a donor moiety to form a PI in this work due to the highly conjugated, electron-rich, planar, and ease of adjusting the chemical structure. The UV-vis absorption spectra of ZnPor-t-diamine and ZnPor-t-DSDA shown in Fig. S5† reveal that the absorption bands of the resulting porphyrin-containing PI blue-shifted from those of the porphyrin monomer possibly due to molecular interactions between the porphyrin units or because of the addition of DSDA moiety. By the donor-acceptor arrangement of chemical structure, a charge-transfer (CT) phenomenon should be

easily induced by applying electric fields. This is a welcome merit of ZnPor-t-DSDA PI in memory applications.

The electrochemical properties of ZnPor-t-DSDA were investigated by cyclic voltammetry (CV). The device for CV measurement is set up by film-casting ZnPor-t-DSDA on the ITO-coated glass substrate as a working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under a nitrogen atmosphere, and the result is summarized in the ESI.†

Two polymer memory devices were fabricated by using Al and Au as anodes, respectively, and the results of the memory properties demonstrated by the current-voltage (I - V) characteristics of the metal (Al or Au)/ZnPor-t-DSDA/ITO sandwich devices are summarized in Fig. 2(a and b). In the case of Al as the anode (Fig. 2a), during the first positive sweep from 0 to 6 V, the current increased abruptly from the initial OFF state (10^{-12} – $10^{-1.3}$ A) to the ON state (10^{-5} A) at 3.9 V (threshold voltage, V_T) defined as “writing” process. Then, the device remained at the ON state when positive (second sweep) and negative (third sweep) voltages were applied, defined as “reading” process in the subsequent scans. Besides, the device exhibits non-erasable properties that cannot be switched to the initial OFF state by applying reverse voltage. After turning off the power for 30 seconds, the device relaxed to the initial OFF state without the erasing process, indicating the volatile behavior of DRAM. The device then could be switched to the ON state again by applying a negative voltage of -3.9 V in the fourth sweep.

It also remained in the ON state during the negative sweep (fifth sweep), then the sixth sweep was repeated and reprogrammed at -3.8 V after turning off the power about 30 seconds. In addition, the Au/PI/ITO device (Fig. 2b), which is better for the application because it is more inactive to oxygen than the corresponding Al device, also exhibited the same



Scheme 1 Synthesis route of ZnPor-t-diamine and ZnPor-t-DSDA polyimides.

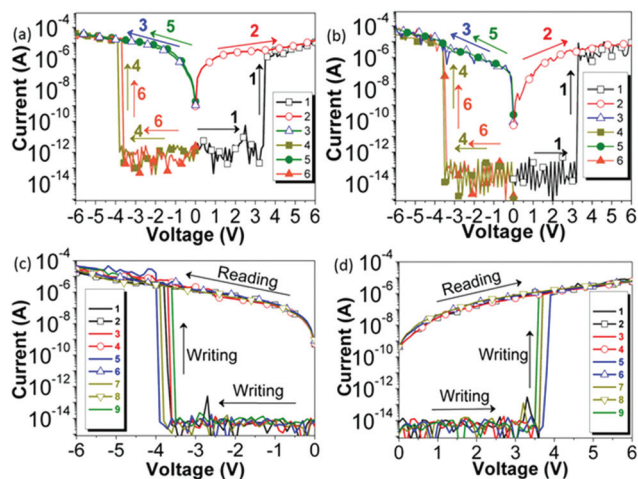


Fig. 2 Current–voltage (I – V) characteristics of (a) ITO/ZnPor-t-DSDA (50 ± 3 nm)/Al memory device, (b) ITO/ZnPor-t-DSDA (50 ± 3 nm)/Au memory device, (c, d) stability test during memory device operation both in negative and positive sweeps.

behavior as in the case of the Al device. Moreover, Au as an electrode is also advantageous in the threshold voltage due to the lower work function of Au (-5.1 eV) than Al (-4.2 eV). Thus, the two different memory devices derived from the novel ZnPor-t-DSDA reveal different symmetric biswitching behaviors compared to our previous study of PIs for Au devices.²⁸ Furthermore, the operation stability of this symmetric biswitching Al/PI/ITO memory device was investigated and is shown in Fig. 2(c and d).

To gain more insight into the memory behavior of ZnPor-t-DSDA, the molecular simulation of the basic unit was carried out by the B3LYP/LanL2DZ Gaussian 09 program. The HOMO and LUMO energy levels of ZnPor-t-DSDA are depicted in Fig. 3 and are in good agreement with the experimental values from electrochemical and optical measurements. According to the previous literature,^{16–20} when the applied electric field reaches the switching-on voltage, some electrons at the HOMO accumulate energy and transit to the LUMO, forming a charge transfer complex (ON state) in different ways. In PI ZnPor-t-DSDA, the HOMO is located mainly at the electron-donating porphyrin moieties, whereas LUMO is located at the electron-withdrawing DSDA units. When the applied electric field reaches the switching-on voltage, some electrons at HOMO accumulate energy and transit to LUMO2 due to the highest possibility/overlapping of electron distribution between HOMO and LUMO2. Nevertheless, electrons at HOMO may also be excited to the other intermediate LUMOs with a lower energy barrier belonging to the acceptor units. Thus, CT occurs through several routes to form the conductive CT complexes, including indirect drop from LUMO2 through intermediate LUMO1 to LUMO, from the intermediate LUMO1 to LUMO, or be directly excited from HOMO to LUMO. When the intra- or intermolecular CT occurs due to the applied electric field, the generated holes can delocalize to the porphyrin moi-

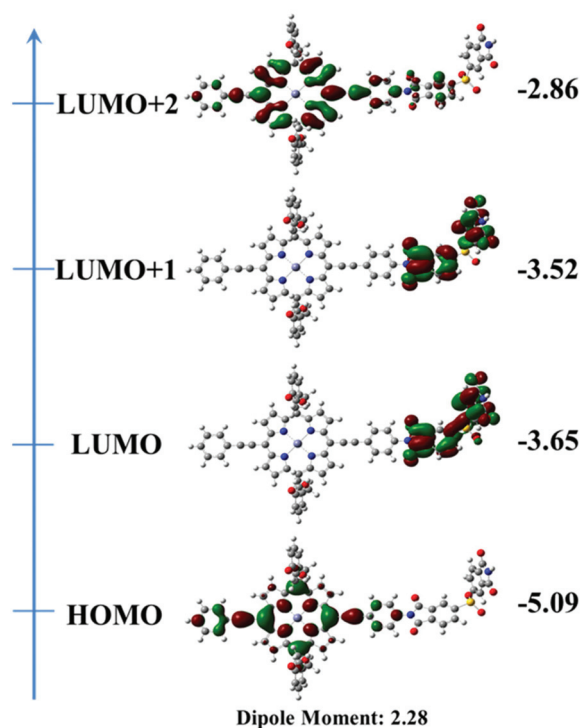


Fig. 3 Calculated molecular orbitals and the corresponding energy levels.

eties forming an open channel in the HOMO for the charge carriers (holes) to migrate through. Therefore, the current increases rapidly and the memory device can be switched to the high conductivity state (ON state).

When the applied external electric field reached the switching-on voltage, the electron density distributed from the Zn-porphyrin to DSDA moiety, and the CT resulted in the ON state of the device. Furthermore, according to the simulation result depicted in Fig. 4, the twist angle between the porphyrin and phthalimide ring is almost coplanar (0.4°) due to the triple bond linkage. Therefore, after turning off the power of the memory device in the ON state, the coplanar structure facilitates the CT go back to the porphyrin moiety, resulting in a short retention time of DRAM characteristic. Furthermore, a transparent memory device was also prepared as shown in

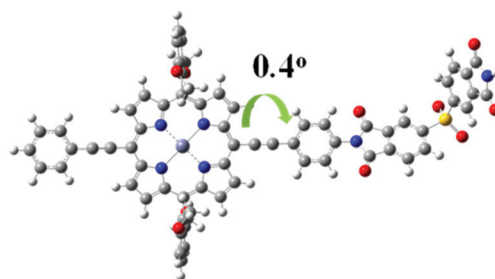


Fig. 4 The twist angle between the porphyrin and phthalimide ring of the basic unit for ZnPor-t-DSDA.

Fig. S6,[†] and the “*in situ*” UV-vis absorption spectroscopy during the switching program before and after the electric field was applied was investigated and is summarized in Fig. S7.[†] When the external electric field applied was 5.5 V and 6 V for 5 seconds, both the red shift behavior and enhanced intensity of the B band absorption peak were observed. After removal of the electric field for 30 seconds, the peak of the B band decreased in intensity and blue shifted to the original state. Thus, the result of short retention time in the B band absorption peak of the transparent memory device mentioned above implies that the DRAM behavior is similar to the metal/PI/ITO devices shown in Fig. 2(a and b).

In summary, a novel solution-processable porphyrin-containing PI **ZnPor-t-DSDA** was synthesized in this study, and the obtained PI used as a memory material exhibited symmetric biswitching and volatile DRAM characteristic in both devices with different metals (Au, Al) as anodes. The coplanar structure resulting in short retention time of the DRAM property was also elucidated by “*in situ*” UV-vis absorption spectroscopy. The reason for symmetric switching behavior is still not clear and is under investigation.

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