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Volatile static random access memory behavior of an aromatic polyimide bearing carbazole-tethered triphenylamine moieties

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ABSTRACT

A functional polyimide (6F/CzTPA PI), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)/ 4,4′-diamino-4″-N-carbazolyltriphenylamine (DACzTPA), was synthesized in our present work for electrical resistive memory device applications. Semiconductor parameter analysis on the polyimide memory devices indicates that the synthesized polyimide possesses a volatile static random access memory (SRAM) characteristic with an ON/OFF current ratio of about 10^5 at the threshold voltage of around 1.5 V and −1.8 V. In addition, the device using the 6F/CzTPA PI as the active layer reveals excellent long-term operation stability with the endurance of reading cycles up to 10^8 under a voltage pulse and retention times for at least 8 h under constant voltage stress (−1 V). The charge transfer mechanisms and the roles of the donor and acceptor components in the PI macromolecules associated with the electrical switching effect are elucidated on the basis of the experimental and quantum simulation results.

1. Introduction

In recent years, increasing attention has been paid to applications in memory devices based on polymeric materials possessing bistable electrical resistive switching effects [1–7]. As one of the most promising candidates for the next-generation memory devices characterized by the high data storage density, fast write/read speed, low power consumption and multilevel designs, such kind of polymer electronic materials possesses unique advantages, such as structural simplicity, good scalability, high mechanical flexibility, low fabrication cost, ease of processability, and three-dimensional (3D) multi-stacking capability for achieving high density data storage [8,9]. And completely different from that of the traditional silicon-based memory cells, which stores data by encoding each device as “0” or “1”, polymer memory achieves information storage based on the bistability of the materials, for instance, the high and low electrical conductivity response to an applied voltage [10].

Many polymeric materials have been explored and some of them have been demonstrated to exhibit excellent electrical resistive switching effects with potentials to be applied in memory devices, including conjugated polymers such as poly(9,9-bis(4-diphenylaminophenyl)-2,7-fluorene) (PDPAF) [11], vinyl polymers with specific pendent groups such as poly(N-vinylcarbazole) (PVK) [12–15], functional polyimides (PIs) [16–19], and polymer nanocomposites embedded with metal nanoparticles (NPs) [20–22], fullerenes [23–25], carbon nanotubes (CNTs) [26,27], grapheme [28], and graphene oxide (GO) [29]. Among them, aromatic PIs have gained most widespread attentions in recent years due to their excellent thermal and mechanical properties, high-temperature dimensional stability, chemical inertness, and good processability [30]. These functional electroactive PIs were usually designed to contain both electron-donating and electron-accepting groups within a repeating unit, which can contribute to electronic transitions between the ground and excited states through the induced charge transfer between the electron donor (D) and acceptor (A) moieties under applied electric fields, and therefore exhibit electrical memory behaviors [31–33]. By introducing different electron donor and acceptor moieties into the polymer chain or by designing different molecular structures, PIs have been demonstrated to be able to exhibit non-volatile or volatile memory effect [30,34–37]. This makes us believe that by combining suitable functional groups into the polyimide chain through elaborate molecular design, it is possible to finely tune the highest occupied molecular orbital (HOMO) energy level, the lowest unoccupied molecular orbital (LUMO) energy level, the dipole moment as well as the charge transport ability of the synthesized polyimides and consequently lead to novel electrical memory effect [38–40].

Herein, we report our works on the synthesis and electrical characterization of an aromatic polyimide, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride/4,4′-diamino-4″-N-carbazolyltriphenylamine (6F/CzTPA PI), with structures in which the carbazole-tethered triphenylamine units (CzTPA) function as the

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electron-donating moieties and the hexafluoroisopropylidene phthalimide units (6FDA) serve as the electron-accepting species. Both triphenylamine (TPA) and carbazole (Cz) are typical electron-donating groups, and previous researches by combining them individually with electron acceptor groups have revealed soluble electroactive polyimides showing different memory behaviors such as dynamic random access memory (DRAM) [5,8,36,41–46] and static random access memory (SRAM) [35,36,45] behaviors. Here, the integration of the TPA unit and the Cz unit to form the CzTPA moiety and its subsequent utilization as the electron-donating species is supposed to be able to enhance the electron donating and charge transport capabilities of the resulting polyimide, and correspondingly endow the synthesized material with stronger potential to form electron donor–acceptor couples and consequently novel memory effect. Electrical characterization results suggest that the polymer possesses electrical bistability and the memory devices using the synthesized polyimide as the active layer (ITO|Thin 6F/CzTPA PI Layer|Au) exhibit volatile electrical switching effect, which could be swept both positively and negatively from the low-conductivity (OFF) state to the high-conductivity (ON) state with an ON/OFF current ratio of about 10^5 and a switching time less than 20 ns, and could be applied as static random access memory (SRAM) in digital information storage. Theoretical model analysis was carried out to elucidate the electrical conducting process occurring in the synthesized polyimide. Molecular simulation of the 6F/CzTPA model compound was conducted to clarify the carrier transport process and memory mechanisms in the electroactive polyimide.

2. Experimental

2.1. Materials

4-Fluoronitrobenzene, carbazole, hydrazine monohydrate, 10% palladium on activated carbon (10% Pd/C), isoquinoline, and cesium fluoride were purchased from J&K Scientific Co. Ltd. Anhydrous potassium carbonate, anhydrous magnesium sulfate, sodium hydroxide (NaOH), tin(II) chloride dihydrate, 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), tetrahydrofuran (THF), ethyl acetate, toluene, chloroform, acetone, isopropanol, methanol and ethanol were purchased from Beijing Chemical Works, and they were all used as received. m-Cresol was also bought from Beijing Chemical Works, and it was purified by distillation over zinc powder and stored over 4 Å molecular sieves prior to use. The 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was obtained from Sigma–Aldrich (Shanghai) Trading Co. and sublimated before use.

2.2. Characterization

Fourier transform infrared (FT-IR) spectra were recorded under ambient conditions on a Bruker Tensor 27 Fourier transform spectrophotometer. KBr was used as a nonabsorbent medium. Proton nuclear magnetic resonance (^{1}H NMR, 400 MHz) spectra were recorded on a Bruker AV400 spectrometer using DMSO-d_6 and $CDCl_3$ as the solvent. Differential scanning calorimetry (DSC) measurements were performed on a TA Q20 system at a heating rate of 10 °C min^{-1} under nitrogen atmospheres. Thermogravimetric analysis (TGA) was undertaken under nitrogen atmospheres using a TA Q50 instrument at a heating rate of 10 °C min^{-1}. Gel permeation chromatography (GPC) analysis was carried out on a Waters 515-2410 system using polystyrene standard as the molecular weight reference and THF as the eluent. Ultraviolet–visible (UV/vis) absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Cyclic voltammetry (CV) measurement was performed on a CHI660D Electrochemical Workstation (Shanghai Chenhua Instruments Inc., China) using a three-electrode cell under nitrogen environment. The polyimide films coated on a platinum square electrode (working electrode) were scanned anodically and cathodically (scan rate: 100 mV s^{-1}) in a solution of tetrabutylammonium tetrafluoroborate (n-Bu_4BF_4) in dry acetonitrile (0.1 M) with Ag/AgCl and a platinum net as the reference electrode and auxiliary electrode, respectively. Ferrocene was used as the external reference for calibration (0.38 V vs. Ag/AgCl). The thickness of the polyimide films coated on the ITO substrate was measured using atomic force microscopy (Digital Instruments Nanoscope IIIa, Veeco Instrument) under contact mode. The current–voltage (*I–V*) characteristics of the sandwich devices were recorded by a Keithley 4200 SCS semiconductor parameter analyzer equipped with a Micromanipulator PW-600 probe station (Advanced Technology Co., limited, Hong Kong) in a clean and metallically shielding box in ambient environment at room temperature. Molecular simulations were carried out on the basic unit of the synthesized polyimide using the Gaussian 09 program package. The molecular orbitals and electronic properties were calculated on theory levels including semi-empirical, ab initio and density functional theory (DFT).

2.3. Monomer synthesis and polyimide synthesis

Scheme 1 shows the synthetic route for the DACzTPA diamine monomer and the final 6F/CzTPA polyimide. Details on their preparation and characterization are given below. The 4,4′-diamino-4″-N-carbazolyltriphenylamine (DACzTPA) was synthesized by the condensation of N-(4-aminophenyl)carbazole (APCB) with 4-fluoronitrobenzene in the presence of cesium fluoride, followed by the hydrazine monohydrate Pd/C-catalyzed reduction of the intermediated dinitro compound (DNCzTPA) according to a similar procedure reported previously [47].

2.3.1. Synthesis of N-(4-nitrophenyl)carbazole (NPCB)

To a solution of 8.36 g (0.05 mol) of carbazole and 5.3 ml (0.05 mol) of 4-fluoronitrobenzene in 100 ml of DMF, 4.14 g (0.03 mol) of anhydrous potassium carbonate was added with stirring at one portion. After heating at 150 °C for 15 h under nitrogen atmosphere, the mixture was poured into 800 ml of distilled water under stirring to obtain a yellow precipitate. The crude product was then collected by filtration and recrystallized with ethyl acetate to afford 11.5 g (80% in yield) of yellow crystals. DSC: m.p. 211 °C and FT-IR (KBr, cm^{-1}): 1594, 1344 (NO_2 stretch). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 8.50 (d, 2H, J = 9.04 Hz), 8.28 (d, 2H, J = 7.53 Hz), 7.98 (d, 2H, J = 9.05 Hz), 7.56 (d, 2H, J = 8.24 Hz), 7.49 (t, 2H, J = 7.70 Hz), 7.36 (t, 2H, J = 7.86 Hz).

2.3.2. Synthesis of N-(4-aminophenyl)carbazole (APCB)

To a solution of 5.76 g (0.02 mol) of NPCB in 40 ml ethanol, 15.8 g (0.07 mol) of $SnCl_2 \cdot 2H_2O$ was added. After refluxing for 24 h, the reaction mixture was condensed under reduced pressure to distill off most of the ethanol followed by neutralization with 40 wt% aqueous NaOH solution until the mixture became alkaline. The resulting mixture was then extracted with toluene, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to get 4.5 g (85% in yield) of yellowish syrup. FT-IR (KBr, cm^{-1}): 3375, 3459 (N–H stretch). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 8.19 (d, 2H, J = 7.67 Hz), 7.40 (t, 2H, J = 7.66 Hz), 7.26 ~ 7.17 (m, 6H), 6.79 (d, 2H, J = 8.61 Hz), 5.43 (s, 2H).

2.3.3. Synthesis of 4,4′-dinitro-4″-N-carbazolyltriphenylamine (DNCzTPA)

To a solution of 2.58 g (10 mmol) of APCB and 2.2 ml (21 mmol) of 4-fluoronitrobenzene in 50 ml of DMF, 1.52 g (10 mmol) of