



# Achieving tunable memory performance from nonvolatile to volatile by altering the trap depth of charge trapping sites in functional imides containing carbazole moieties



Nanfang Jia<sup>a</sup>, Jiacong Guo<sup>a</sup>, Guofeng Tian<sup>a, b</sup>, Shengli Qi<sup>a, b, \*</sup>, Xiaodong Wang<sup>a, b</sup>,  
Dezhen Wu<sup>a, b</sup>

<sup>a</sup> State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup> Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou 213164, Jiangsu, China

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## ABSTRACT

In this work, two functional imides were designed and synthesized to elucidate the influence of charge trap depth on the memory behavior. Two dianhydrides, 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride were selected as the electron acceptor considering their functional moieties of different charge-trapping depth and electron-withdrawing ability. Electrical characterization indicated that the memory devices based on the two imides exhibited nonvolatile write once read many times (WORM) memory behavior and volatile static random access memory (SRAM) behavior. Mechanisms associated with the distinct memory effect were demonstrated based on the molecular simulation. Analysis results indicated that charge trapping process is responsible for the electrical bistability and the different depth of charge-trapping sites in the two imides accounts for the distinct memory behavior of corresponding memory devices. Meanwhile, the two memory devices both show excellent long term operation stability. This paper not only reports two novel memory materials but also provided some guiding principle to the design of organic based memory devices.

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## 1. Introduction

Organic materials showing electrical bistable memory behavior have drawn widespread interests in recent years due to their potential to be applied as next-generation data storage material with the characteristics of ultra-fast access speed, large capacity, low power consumption and flexibility [1]. Among them, organic donor-acceptor (D-A) type molecules are regarded as the most promising choice because of their tailorability in molecular design and memory behavior [2–4]. Over the last couple of decades tremendous attention has been focused on the preparation of organic memory materials and different memory behavior, such as dynamic random access memory (DRAM), static random access memory (SRAM), Flash memory, and write once read many times memory (WORM), have been demonstrated [5–8].

Correspondingly, researchers have proposed several mechanisms related to the electrical switching behavior for organic resistive memories. Among them, charge transfer (CT) theory and local filamentary conduction [9,10] are the most widely-reported mechanisms. The CT process mainly occurs in conjugated systems. To vary the memory behavior of the organic materials, previous reports mainly focused their attention on the design and modification of new electron donors, including triphenylamine [11–13], ferrocene [14], carbazole [15–18], porphyrin [19,20], thiophene [21], selenophene [22] and triphenylethylene [23], into organic molecules. However, the present donor molecules are limited and the design and synthesis of new donors is difficult. As an alternative, we consider to study the unconjugated memory materials with D-A structure, in which, the CT process through conjugated chain is restricted and the electrons mainly transit by a hopping process [9] between adjacent sites. Hence, the properties of charge-trapping sites have considerable effects on the memory performance [24–26].

Upon this consideration, two imides (compound **4** and **5**) with

\* Corresponding author. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

E-mail address: [qisl@mail.buct.edu.cn](mailto:qisl@mail.buct.edu.cn) (S. Qi).

the same electron donor (carbazole) and different acceptors, i.e., 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (compound **1**) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (compound **2**), were synthesized (Scheme 1). The existence of saturated aliphatic chain not only hindered the charge transfer process through the conjugated molecular chain but also endowed the two imides with good solubility in common organic solvents and essential film forming property. In addition, the twisted structures of compounds **1** and **2**, together with the trifluoromethyl group, also contributed to the good solubility of the target imides. More importantly, the two common used acceptors were selected because their functional group (i.e., sulfone and carbonyl group in compound **1**, and carbonyl group in compound **2**) possess different charge-trapping abilities. Thus, it was expected that the charge-trapping process would be greatly altered, leading to varied electrical memory behavior. Current-voltage (I-V) characteristics of the imides based memory devices with the configuration of ITO/Imide/Al indicated that the compound **4** exhibited nonvolatile WORM behavior, while a volatile SRAM behavior for compound **5** was observed. Optical and electrochemical measurements and molecular simulation were performed to clarify the electronic transition process inside the device and molecules. The results obtained here provide theoretical guidance and two potential candidates for next-generation memory application.

## 2. Materials and methods

### 2.1. Materials

Carbazole (99%) and phthalic anhydride were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. 1,6-Dibromohexane, hexadecyl trimethyl ammonium bromide and tetrabutylammonium bromide were bought from Energy Chemical Reagent Co. Ltd and used without further purification. Hydrazine monohydrate, compound **1** and **2** were bought from Alfa Aesar and used directly. Potassium hydroxide, sodium hydroxide, ethanol, toluene, chloroform, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were bought from Beijing Chemical Works and directly used without further purification.

### 2.2. Instruments and measurements

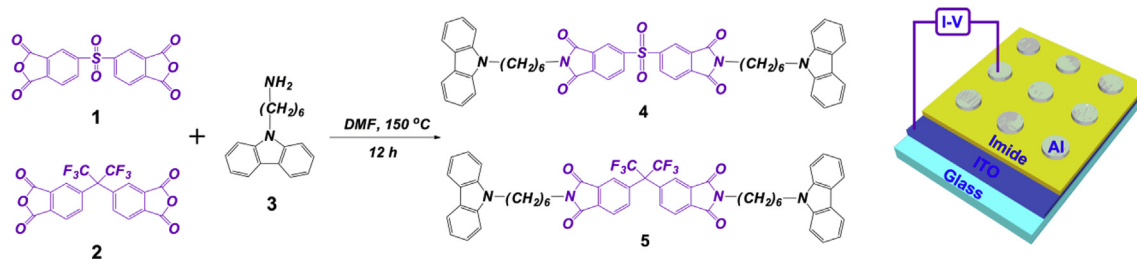
$^1\text{H}$  NMR spectra of the imides were characterized on a Bruker AV400 spectrometer using tetramethylsilane as an internal standard at 400 MHz. FT-IR spectra were measured by a Bruker Tensor 27 infrared spectrophotometer. Elemental analysis was analyzed on a varioELcube elemental analyzer. The thermal properties were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) carried out on a TA Q500 instrument under a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  and  $10\text{ }^\circ\text{C min}^{-1}$ , respectively. The ultraviolet–visible (UV/vis) absorption spectra were recorded

on a Shimadzu UV-2550 spectrophotometer. The electrochemical cyclic voltammetry (CV) sweeps were carried out on a CHI660D electrochemical workstation using a three-electrode system. The thickness, film morphology and surface roughness were characterized by atomic force microscopy (AFM) on a Nanoscope 3D Controller using tapping mode. The X-ray diffraction (XRD) patterns were characterized on an Ultimall X-ray diffractometer. The memory performance, including the current-voltage curves and operation stability, were characterized by a Keithley 4200 SCS semiconductor parameter analyzer on a Micromanipulator PW-600 probe station.

### 2.3. Synthesis and characterization

Scheme 1 displays the synthetic route to compounds **4** and **5**. The amine, *N*-(6-aminohexyl)carbazole (compound **3**) was synthesized according to the previous literature [27]. The target imides were synthesized through the condensation of the amine with the dianhydrides (compound **1** and **2**). Taking the synthesis of compound **4** as an example, in a solution of DMF (16 mL), compound **3** (532.8 mg, 2 mmol) and compound **1** (358.3 mg, 1 mmol) were dissolved at  $30\text{ }^\circ\text{C}$ . Then the reaction temperature was set at  $150\text{ }^\circ\text{C}$  and the solution was stirred for 12 h. After the solution cooling down to the room temperature, a red brown precipitate appeared, which was subsequently collected by filtration, and washed with water and petroleum ether. After being dried in vacuum oven under  $80\text{ }^\circ\text{C}$ , target product **4** was obtained. Compound **4**, red brown powder, 692.6 mg, yield: 81%, FT-IR (KBr):  $3054, 2929\text{ cm}^{-1}$  (C-H);  $1779, 1720\text{ cm}^{-1}$  (C=O);  $1390\text{ cm}^{-1}$  (C-N);  $1325, 1148\text{ cm}^{-1}$  (O=S=O);  $748\text{ cm}^{-1}$  (imide ring);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz),  $\delta$  (ppm): 8.49 (d, 2H,  $J = 7.82\text{ Hz}$ ), 8.49 (s, 2H), 8.07 (d, 4H,  $J = 7.66\text{ Hz}$ ), 8.04 (d, 2H,  $J = 7.73\text{ Hz}$ ), 7.50 (d, 4H,  $J = 8.25\text{ Hz}$ ), 7.38 (t, 4H,  $J = 8.12\text{ Hz}$ ), 7.14 (t, 4H,  $J = 7.17\text{ Hz}$ ), 4.31 (t, 4H,  $J = 6.94\text{ Hz}$ ), 3.49 (t, 4H,  $J = 6.83\text{ Hz}$ ), 1.70 (t, 4H,  $J = 6.53\text{ Hz}$ ), 1.48 (t, 4H,  $J = 6.76\text{ Hz}$ ), 1.27 (m, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 166.2, 166.1, 146.0, 140.3, 136.1, 133.5, 133.2, 125.5, 124.4, 122.7, 120.3, 118.7, 108.5, 77.2, 42.8, 38.4, 28.8, 28.2, 26.8, 26.6. HRMS (ESI,  $m/z$ ) calcd. For  $\text{C}_{52}\text{H}_{46}\text{N}_4\text{O}_6\text{S}$  ( $\text{M} + \text{H}^+$ ) 855.3138, found 855.3140.

Compound **5** was synthesized by the same procedure. Compound **5**, light yellow powder, 724.1 mg, yield: 77%, FT-IR (KBr):  $3050, 2935\text{ cm}^{-1}$  (C-H);  $1775, 1718\text{ cm}^{-1}$  (C=O);  $1390\text{ cm}^{-1}$  (C-N);  $1250, 1140\text{ cm}^{-1}$  (C-F);  $750\text{ cm}^{-1}$  (imide ring);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz),  $\delta$  (ppm): 8.14 (d, 4H,  $J = 7.67\text{ Hz}$ ), 8.009 (d, 2H,  $J = 8.06\text{ Hz}$ ), 7.847 (d, 2H,  $J = 8.09\text{ Hz}$ ), 7.638 (s, 2H), 7.586 (d, 4H,  $J = 9.12\text{ Hz}$ ), 7.426 (t, 4H,  $J = 7.16\text{ Hz}$ ), 7.178 (t, 4H,  $J = 7.28\text{ Hz}$ ), 4.373 (t, 4H,  $J = 7.02\text{ Hz}$ ), 3.522 (t, 4H,  $J = 6.82\text{ Hz}$ ), 1.757 (t, 4H,  $J = 6.46\text{ Hz}$ ), 1.523 (t, 4H,  $J = 6.41\text{ Hz}$ ), 1.320 (m, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 167.2, 167.0, 140.3, 138.6, 135.4, 132.9, 132.6, 125.6, 124.7, 123.5, 122.8, 121.9, 120.3, 118.7, 108.6, 77.2, 42.9, 38.2, 28.8, 28.4, 26.9, 26.6. HRMS (ESI,  $m/z$ ) calcd. For  $\text{C}_{55}\text{H}_{46}\text{F}_6\text{N}_4\text{O}_4$  ( $\text{M} + \text{H}^+$ ) 941.3423, found 941.3444. As shown in Fig. S8, the DSC scanning of compound **4** and **5** shows no obvious melting peaks,



**Scheme 1.** Chemical structures of the two imides containing *N*-phenylcarbazole moieties and illustrative configuration of the sandwich memory devices.

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