European Polymer Journal 95 (2017) 186–194

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Regulating the electrical bistable memory characteristics in functional polyimides by varying the spatial position of the electron-donating species

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ARTICLE INFO

Keywords:
Memory devices
Spatial position
Charge-trapping

ABSTRACT

Four novel functional polyimides (PIs) for electrical memory applications, DATP6Cz-DSDA, DATP2Cz-DSDA, DATP6Cz-NTDA, and DATP2Cz-NTDA, were synthesized through condensation polymerization of two diamines, N,N-bis(4-amino)phenyl-6-(9-carbazol)-hexamine (DATP6Cz) and N,N-bis(4-amino)phenyl-2-(9-carbazol)-ethylamine (DATP2Cz), with two dianhydrides, diphenylsulfone-3,3′,4,4′-tetracarboxylic dianhydride (DSDA) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA). The ethyl and hexyl spacer were intentionally inserted into the diamines to alter the spatial position of the electron donor in the PIs and then to elucidate the effect on the memory behavior. Experimental results show that DATP6Cz-DSDA and DATP2Cz-DSDA exhibit nonvolatile WORM memory behavior, while DATP6Cz-NTDA and DATP2Cz-NTDA exhibit volatile SRAM and DRAM behavior, respectively. Simulation results indicate much stronger charge-trapping effect of the sulphone moiety in DSDA than that of the carbonyl moiety in NTDA, accounting for the nonvolatile feature of the DSDA-based PI memories and the volatile feature of the NTDA-based PI memories. Meanwhile, spatial position effect was observed in the NTDA-based PIs. The spacer of varied length between carbazole group and diphenyl amino group in DATP6Cz and DATP2Cz, i.e., hexyl *vs.* ethyl, has significantly altered the spatial position of the electron donor and the charge transportation path in the PIs, resulting in different retention time and corresponding SRAM and DRAM behavior. The present strategy is expected to be applied in material design in future information technology.

1. Introduction

To meet the exigent need for rapid development of information technology, organic and polymeric materials based memory devices with ultra-high data storage density have attracted tremendous attention in recent years because of their low cost potential, simple structure, 3D stacking capability, and easy processing ability [1-5]. Among various materials, aromatic polyimide (PI) is regarded as one of the most promising candidate considering the demand on dimensional stability and heat-resisting property of the electronic elements [6–10]. Since the first study about the application of PI in memory materials reported by Ling and coworkers [11], numerous efforts have been made to develop PI-based memory devices. Through the introduction of different donor-acceptor pairs into the macromolecular chain, various memory types, including dynamic random access memory (DRAM) behavior, static random access memory (SRAM) behavior, Flash, and write once read many times memory (WORM) behavior, have been realized [1,9,10,12–18]. And, electrical memory mechanisms have been explained by filament formation [19,20], conformation change

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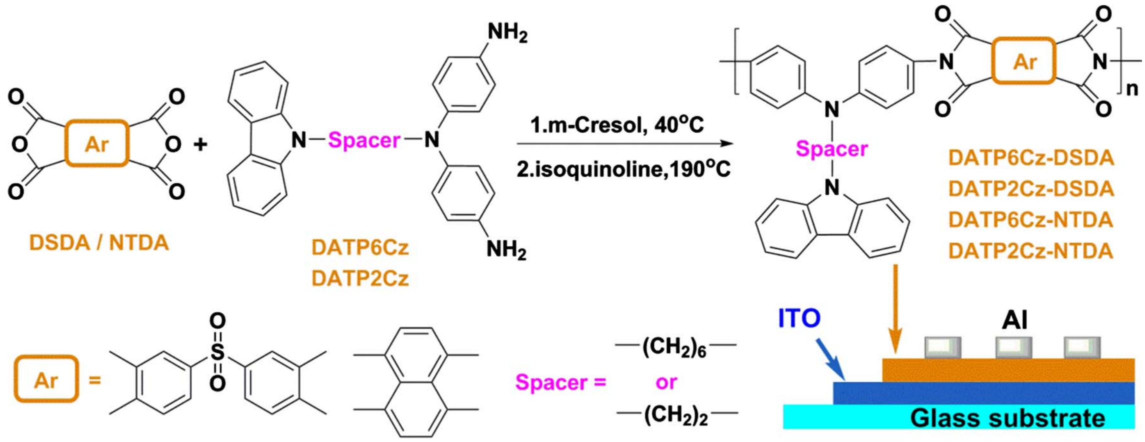
http://dx.doi.org/10.1016/j.eurpolymj.2017.08.012
Received 19 February 2017; Received in revised form 12 July 2017; Accepted 3 August 2017



Scheme 1. Synthetic route of the target polyimides and illustrative configuration of the sandwich memory devices.

[21–25], and charge transfer (CT) theory [11,26-29].

However, previous works are mainly focused on the design and synthesis of novel electron-donating species to explore their influence on the memory behaviors. So far, many different electron-donating units, either typical or atypical, including triphenylamine (TPA) [11,14], ferrocene [30], carbazole (Cz) [12], porphyrin [31], thiophene, selenophene [32], and triphenylethylene [28], have been explored. However, few attentions have been paid on the spatial position effect of the electron donor on the memory performance of the PIs. On this point, tethering an aliphatic spacer with different lengths to the electron-donating species might be one of the simplest ways to alter the spatial position of the electron donor in a functional PI.

Based on this consideration, two new electron-donating diamines, DATP6Cz and DATP2Cz, which contain in respective a hexyl and an ethyl spacer between the carbazole and the diphenyl amino part, were designed and synthesized. Four PIs, DATP6Cz-DSDA, DATP6Cz-NTDA, DATP2Cz-DSDA, and DATP2Cz-NTDA were prepared through their polycondensation with the two dianhydrides, DSDA and NTDA, as shown in Scheme 1. The different aliphatic spacer, i.e., hexyl *vs.* ethyl, in DATP6Cz and DATP2Cz is considered to be able to change the spatial position of the electron donor species in the synthesized PIs, which might probably lead to distinctive electronic structure and different electrical behavior. DSDA and NTDA are selected because they are typical electron acceptors and bear different charge-trapping ability. Memory behaviors are characterized by current-voltage (I − V) measurements on the ITO/PI/Al sandwich devices and distinct performances were observed. Quantum simulation on B3LYP/6-31G(d) level, optical and electrochemical measurements were conducted to clarify the intramolecular charge transition process, the switching mechanism, and the spatial position effect. This study suggests that the electrical memory performance could be tuned via the careful alteration of the spatial position of the electron donor in functional PIs.

2. Experiments

2.1. Materials

Carbazole, cetyl trimethyl ammonium bromide, phthalic anhydride, 1,2-dibromoethane, and 1,6-dibromohexane were obtained from J & K Scientific Co. Ltd and applied without further purification. 1-Fluoro-4-nitrobenzene, hydrazinium hydroxide, palladium 10% on carbon (wetted with ca.55% water), and isoquinoline were purchased from TCI (Shanghai) Co. Ltd. Anhydrous potassium carbonate and the organic solvent such as chloroform, methanol, acetone, ethanol, m-cresol, dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and tetrahydrofuran (THF) were bought from Beijing Chemical Works. Among them, DMF, DMAc, and THF were purified before use. 6FDA was bought from J & K Scientific Co. LTD and purified by vacuum sublimation prior to use.

2.2. Synthesis of the polyimides

Scheme S1 and Scheme 1 show the synthetic route of target diamines and target PIs. The detailed synthetic procedures and characterization results of DATP2Cz and DATP6Cz were given in the supporting information. The target PIs were synthesized by typical two steps condensation polymerization of the diamines and dianhydrides, DSDA and NTDA. Details of the preparation and structural characterization results are also given in the supporting information.

2.3. Device fabrication

The synthesized PIs were elaborately fabricated to sandwich devices. The structure was shown in Scheme 1. The ITO on glass substrate was beforehand cleaned by ultrasonication with toluene, acetone, and ethanol each for 15 min. Afterwards, a solution of