Negative effect on molecular planarity to achieve organic ternary memory: triphenylamine as the spacer

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Adjusting the spacers between the electron-acceptor and the elector-donor is important to design organic ternary memory material but rarely reported. In this paper, two small molecules, ZIPGA and ZIPCAD with benzene ring or triphenylamine as the spacers, were designed and synthesized to fabricate memory devices. The Al/ZIPGA/indium-tin oxide (ITO) device showed ternary characteristics, whereas Al/ZIPCAD/ITO had no obvious memory characteristics. Density functional theory calculation, X-ray diffraction (XRD) and atomic force microscopy (AFM) were employed to interpret the different memory properties. ZIPGA thin film has the closer intermolecular packing and flatter surface morphology than ZIPCAD film, which was favorable to the electron migration. This work demonstrates the importance of spacers and reveals that triphenylamine may be not a good spacer in design of new memory material.

**small molecules, different spacers, ternary memory device, molecular stacking**


1 Introduction

As the era of information explosion emerges, currently used memory devices have almost reached their limitation due to the difficulty in downscaling to further increase the data-storage density [1–4]. Thus, novel data-storage materials with super-high density have attracted intensive attention of scientists in the last two decades. Recently, small molecules are widely applied as electronic materials due to their tunable structure, low cost, good scalability, facile purification and reproducible performance [5–9]. After years of research, small molecule-based materials were successfully introduced into the fabrication of binary memory devices, which largely increased the data-storage density [10]. Compared to downscaling techniques, multilevel (e.g. ternary) storage can increase the information density dramatically from 2^n to 3^n or higher. After the report about a ternary memory device fabricated with a small molecule, many excellent ternary data-storage devices were successfully designed through tailoring molecular conjugation length, changing the side-chains, introducing different terminal acceptors, or tuning the bridging spacers. On the whole, all these methods will result in the modulation of molecular planarity and molecular stacking in film state, which is an important factor to affect the memory behaviors [11–13]. Among them, adjusting the spacers between the electron-acceptor and the elector-donor is reported to improve monomolecular electronic effect [14,15].

In this paper, we investigated the effects of triphenylamine and benzene as the spacers on the memory performance. Tri-
penylamine has been widely employed as an electron donor in organic devices, such as solar cells, optoelectronics, and transistors [16,17], but not employed as a spacer in molecular backbone. TPA as the electron donor in the design of organic memory device has been widely reported. Where there are sufficient electron donors in a molecule, the electron donating properties could be partially omitted. We designed two small molecules, ZIPGA and ZIPCAD (Scheme 1), consisting of a carbazole unit as the electron-donor, while nitro group and benzothiazole serve as two electron-acceptors [18]. The spacer between the nitro and carbazole moieties of ZIPGA is a benzene ring, while for ZIPCAD, the bridge is a triphenylamine (TPA) unit. However, TPA as a spacer, namely a link bridged electron-donating moiety and electron-withdrawing unit will mainly cause changes to geometric property such as planarity, and thus influence the data-storage performance.

The ZIPGA-based memory device exhibited the ternary memory behavior whereas ZIPCAD-based device showed no obvious memory performance. Simulation suggests that the dihedral angles between the spacers and the carbazole moieties showed large difference. Thus, the planarity of these two molecules is different and leads to distinct molecular stacking in film state as confirmed by X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements. This work shows that the spacers in a conjugated molecular backbone plays a crucial role on molecular stacking and thus affects the storage property.

2 Experimental

2.1 Materials

Triphenylamine (98%) and 3-formyl-N-ethylcarbazole (98%) were purchased from J&K, China; N-bromosuccinimide (98%), carbon tetrachloride (97%), acetic anhydride (98%), copper nitrate trihydrate (97%), bis(pinacolato) diboron (97%), 2-aminothiophenol (97%), potassium acetate (97%), methylbenzene (97%) were purchased from TCI, Japan; 1-bromo-4-nitrobenzene (98%) was purchased from Alfa Aesar, USA; all solvents were purchased from commercial companies without further purification. Compounds 1 to 8 were synthesized according to the methods described in the literature [19–23].

2.2 Molecular synthesis

2.2.1 N,N-diphenyl-4-bromoaniline (1)

Triphenylamine (24 mmol, 5.88 g) and N-bromosuccinimide (NBS, 24 mmol, 4.28 g) were dissolved in CCl₄ (50 mL). The solution was refluxed for 4 h in the darkness. The insoluble substance was filtered, and the solvent was then extracted from the solution with dichloromethane (DCM) and washed thoroughly with saturated saline solution. The solution was dried then the remaining from the solvent was recrystallized with ethanol. The obtained white crystalline powder through the suction filter was dried in a vacuum oven (6.8 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.3–7.13 (m, 6H), 7.06–6.95 (m, 6H), 6.88 (d, J = 8.1 Hz, 2H).

2.2.2 4-Bromo-N-(4-nitrophenyl)-N-phenylalanine (2)

Bromotriphenylamine (6.61 mmol, 2 g) and copper nitrate trihydrate (3.08 mmol, 0.75 g) dissolved in acetic anhydride were stirred for 4 h to get the light yellow product (2.02 g, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.94 (m, 2H), 7.43–7.36 (m, 2H), 7.19 (s, 1H), 7.31 (m, 2H). 7.09 (d, J = 8.2 Hz, 2H), 6.97 (t, J = 8.8 Hz, 2H), 6.92–6.82 (m, 2H).

2.2.3 4-Nitro-N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)alanine (3)

Compound 2 (5.7 mmol, 2 g) and bis(pinacolato)diboron (8.6 mmol, 2.2 g) were dissolved in toluene (50 mL), then dry potassium acetate (17 mmol, 1.67 g) was added quickly. It was important to keep the reaction dry. The catalyst dppcPdCl₂ (0.4 mmol, 0.29 g) was dropped into a flask in nitrogen after ten minutes. The mixture was heated to 70 °C for 20 h, then mixture was extracted with water and ethyl acetate. Finally the product (1.22 g, 51%) was obtained from the upper organic phase after rotary evaporation. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 9.3 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.31–7.27 (m, 2H), 7.16–7.13 (m, 1H), 7.10–7.06 (m, 4H), 6.91 (d, J = 9.3 Hz, 2H), 1.28 (s, 12H).

2.2.4 6-Bromo-9-ethyl-9H-carbazole-3-carbaldehyde (4)

NBS (3.02 g, 16.97 mmol) dissolved in 20 mL of DMF and 9-ethyl-9H-carbazole-3-carbaldehyde (3.79 g, 16.97 mmol) was added dropwise in ice bath. After 12 h, the mixture was poured into water, stirred and filtered. The crude product was purified recrystallization with ethanol to obtain white needle crystals. 4.20 g, 82%. ¹H NMR (400 MHz, DMSO) δ 10.05 (s, 1H), 8.54 (s, 1H), 8.26 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.34 (d, J = 8.6 Hz, 1H), 4.51 (q, J = 7.0 Hz, 2H), 1.33 (t, J = 7.0 Hz, 3H).

2.2.5 2-(6-Bromo-9-ethyl-9H-carbazol-3-yl)benzo[d]thiazole (5)

Compound 4 (4 mmol, 1.21 g) and 2-aminobenzenethiol (6 mmol, 0.75 g) were dissolved in DMSO (30 mL). The solution was refluxed for 3 h at 180 °C. The mixture was poured into water (about 15 mL), stirred and filtered. Yield (1.38 g) 85%, light blue. ¹H NMR (400 MHz, DMSO) δ 9.01 (s, 1H), 8.69 (s, 1H), 8.26 (d, J = 8.1 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.68–7.63 (m, 2H), 7.55–7.52 (m, 1H), 7.46–7.42 (m, 1H), 4.51 (q, J = 6.9 Hz, 2H), 1.33 (t, J = 6.9 Hz, 3H).

2.2.6 4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (6)

1-Bromo-4-nitrobenzene (20 mmol, 4.18 g), bis(pinacolato)diboron (B₂pin) (30 mmol, 7.7 g), potassium acetate...