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Enhancing the coplanarity of the donor moiety in a donor-acceptor molecule to improve the efficiency of switching phenomenon for flash memory devices

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ABSTRACT

Two conjugated small molecules were synthesized by Heck coupling reaction, wherein 1,8-naphthalimide acted as an electron acceptor, while either carbazole or triphenylamine, which contributed the different coplanarity, acted as electron donors, respectively. The devices based on both materials show non-volatile flash memory characteristics, and the effect of molecular coplanarity of the donor groups on the device performance was precisely studied. The results indicated that the reproducibility of the switching phenomenon for the memory device based on the carbazole containing naphthalimide derivative was much better than that based on the triphenylamino based naphthalimide due to the rigid carbazole moiety which improved the surface morphology as revealed by atomic force microscopy measurement. Therefore, the significance of the coplanarity of the donor moiety on improving reproducibility of switching phenomenon for memory device applications was revealed.

1. Introduction

Organic materials have been widely investigated for data storage devices due to scalability, structural flexibility, low cost, and three-dimensional stacking capability [1–8]. A large number of organic compounds, including conjugated polymers [9–15], oligomers [16,17], blends of nanoparticles [18–20] and small organic molecules [21–25], have been reported for electrical switching and memory devices. Especially, organic donor-acceptor (D–A) molecules, due to their ability to exhibit electrical bistability and versatility in molecular design, have received considerable attention [26–29]. Currently, many groups use donor (D) – acceptor (A) switching materials to meet the requirements of high-density data storage. However, the research had been mainly focused on the exploration of different D–A molecules with better electrical properties for data storage. The coplanarity of the terminal donor moiety which changes the surface morphology of the thin film formed by vacuum evaporation affecting the reproducibility of the switching phenomenon for the memory devices, had rarely been precisely studied. A better understanding of the effect of terminal moiety coplanarity on device performance is essential to help design new D–A molecules for memory devices.

Herein, we designed and synthesized two novel D–A molecules (NI-Cz and NI-TPA) with the same electron-accepting 1,8-naphthalimide (NI) moiety which was an attractive deficient electron moiety and had been widely utilized in both small molecule and polymer based memory devices [30,31]. Triphenylamine (TPA) derivatives have good optical properties and hole-transporting ability, but their morphology was amorphous with rougher surface due to the twisted triphenylamine moiety [32–35]. The carbazole (Cz) molecule, also a well-known electron-donor and hole-transporting group, and its substituted analogues have been widely used in the photovoltaic devices and memory devices due to its unique electronic and photochemical properties [36–39]. Compared to the triphenylamine derivatives, the surface morphology of carbazole derivatives was more coplanar due to the rigid carbazole moiety. The study showed that the coplanarity of the terminal group played a key role for the reproducibility of switching phenomenon of the memory devices. For the device based NI-Cz, the turn-on voltage was mainly between −2.2 V and −2.6 V (with yield of 80%), and turn-off voltage was mainly between 2.6 V and 3 V (with yield of 56%). For NI-TPA, the turn-on voltage varied from −0.4 V to −2.0 V, and the turn-off voltage was from 2.4 V to 4.0 V, and it showed no obvious distributed areas.

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This work takes an important step towards rational design of new organic D–A molecules with suitable structures for better reproducibility of switching phenomenon for the memory devices.

2. Experimental

2.1. Materials

4-Bromo-1,8-naphthalic anhydride, 2-ethylhexan-1-amine, palladium diacetate, tri-*o*-tolylphosphine, methyltriphenylphosphonium bromide, potassium *tert*-butanolate, triphenylamine and carbazole were all purchased from Energy Chemical as analytical regents and used without further purification. N,N-Dimethylformamide (DMF) was dried by distillation over CaH_2. Other reagents were used as received without any further purification.

2.2. Instruments

All electrical measurements of the device were characterized under ambient conditions without any encapsulation using an HP 4145B semiconductor parameter analyzer equipped with an HP 8110A pulse generator. NMR spectra were obtained from an Inova 400 FT-NMR spectrometer. High-resolution mass spectra (HRMS) were determined on Micromass GCT-TOF mass spectrometer with an ESI source. Elemental analysis was performed using a Carlo-Erba EA-1110 instrument. UV–Vis absorption spectra were measured at room temperature by using a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry was performed at room temperature using an ITO working electrode, a reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 100 mV/s (CorrTest CS Electrochemical Workstation analyzer). A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous DMF was used. SEM images were taken on a Hitachi S-4700 scanning electron microscope. Atomic force microscopy (AFM) measurements were performed by using an MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument.

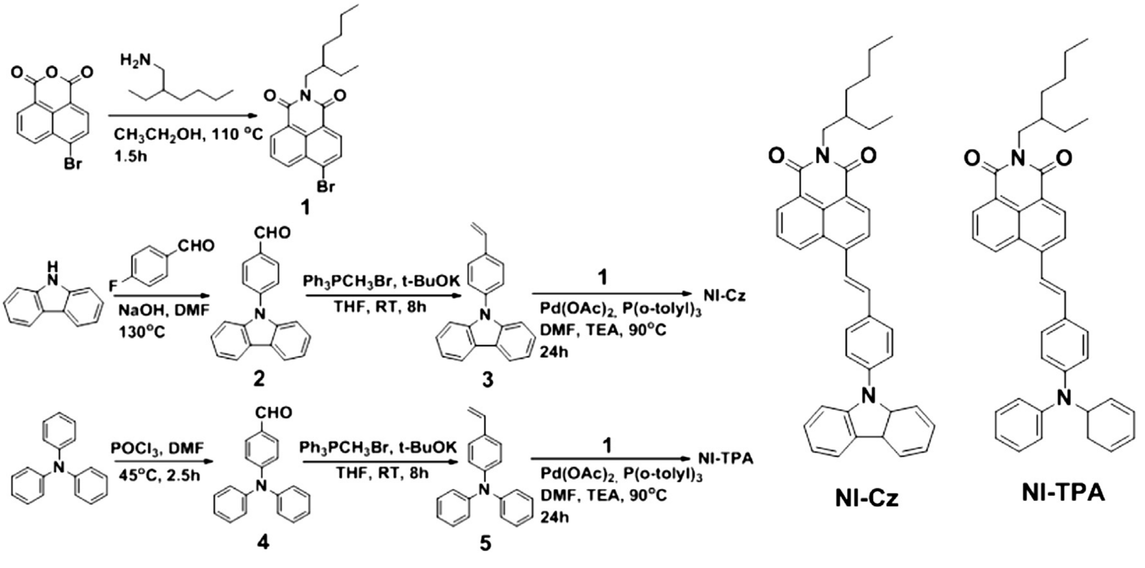
2.3. Synthesis of NI–Cz and NI–TPA

The two molecules were synthesized by Heck coupling reaction in good yields as shown in Scheme 1.

4-Bromo-N-(2-ethylhexyl)-1,8-naphthalimide (**1**). A solution of 4-bromo-1,8-naphtalic anhydride (5 g, 18.05 mmol) in ethanol (100 mL) was added to a 250 mL three-neck round bottom equipped with a reflux condenser and a magnetic stirrer. Then 2-ethylhexan-1-amine (2.33 g, 18.05 mmol) was added drop-wise and the reaction mixture was heated up to 110 °C and stirred under nitrogen overnight. The mixture was cooled to room temperature, and it was filtered. The filtrate was purified by silica gel column chromatography using a mixture of petroleum and dichloromethane (vol. ratio 5:1) as an eluent. After recystallization from the eluent mixture of solvents, yellow crystals were obtained with a yield of 95.01%. Mp = 82–83 °C. IR (in KBr), cm^{-1}: 3071, 2959, 2926, 2871, 2855, 1702, 1653, 1615, 1590, 1571, 1504, 1460,1435, 1404, 1344, 1278, 1231, 1182, 1150, 1102, 1083, 1044, 1024, 949, 897, 855, 782, 749, 730, 716, 664. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 7.3 Hz, 1H), 8.56 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.85 (t, J = 7.9 Hz, 1H), 4.18–4.04 (m, 2H), 2.01–1.85 (m, 1H), 1.43–1.27 (m, 8H), 0.93 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{20}H_{22}BrNO_2$: C, 61.86; H, 5.71; N, 3.61. Found: C, 61.82; H, 5.75; N, 3.57.

4-(9H-carbazol-9-yl)benzaldehyde (**2**). A mixture of 9H-Carbazole (5 g, 0.03 mol), and sodium hydroxide (1.2 g, 0.03 mol) in dry dimethylformamide (DMF) was heated with stirring. Then 4-fluorobenzaldehyde (3.72 g, 0.03 mol) was added, and the reaction mixture was stirred at 130 °C for 6 h. After cooling to room temperature, the mixture was poured into distilled water and extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate and concentrated by vacuum evaporation. The crude product was purified by column chromatography using the mixture of petroleum and dichloromethane (vol. ratio 3:1) as an eluent to get the desired compound as a yellow solid (6.43 g) with a yield of 79.08%. Mp = 156–157 °C. IR (in KBr), cm^{-1}: 2733, 1910, 1702, 1597, 1566, 1510, 1478, 1451, 1389, 1361, 1336, 1316, 1300, 1226, 1208, 1181, 1161, 1123, 1103, 1023, 1000, 914, 829, 750, 720, 633, 619, 566. ^1H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.20–8.10 (m, 4H), 7.80 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H). Anal. Calcd. for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.07; H, 4.87; N, 5.15.

9-(4-Vinylphenyl)-9H-carbazole (**3**). A mixture of **2** (2.71 g, 10 mmol), potassium *tert*-butylate (1.68 g, 15 mmol), and CH_3PPh_3Br (4.28 g, 12 mmol) in dry THF (100 mL) under nitrogen was stirred for 24 h the mixture was poured into distilled water and



Scheme 1. Synthetic routes and molecular structures of NI–Cz and NI–TPA.