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Improving organic memory performance through mounting conjugated branches on a triphenylamine core

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To study the influence of the number of branches mounting on molecular backbones on the thin-film morphology and performance of their memory devices, we successfully synthesized three conjugated small molecules containing triphenylamine and benzothiazole moieties (TPA-nBBT, n=1, 2, 3) and studied their memory performances. Binary static random access memory (SRAM) characteristics could be achieved for the three compounds-based devices with sandwich-like configuration of ITO/molecule/AI. The device based on TPA-3BBT exhibited best device performance with the lowest threshold voltage and best thermal stability which is related to the temperature insensitive thin-film morphology and film crystallinity. Our results demonstrate that increasing the number of branches in D-A conjugated molecules to adjust film morphology and intermolecular accumulation may be an effective strategy to improve the stability of the device performances.

Introduction

Recently, much attention has been paid to organic molecules and polymers in organic solar cells (OSCs),¹⁻⁴ organic lightemitting diodes (OLEDs),⁵⁻⁸ organic field-effect transistors (OFETs)⁹⁻¹² due to their advantages of low cost, large scalability and designable structure. Organic electronic memory (OEM) also have attracted increasing interest over the past few decades. For instance, Kang,¹³⁻¹⁶ Ree¹⁷⁻¹⁹ and Chen²⁰⁻²³ groups and others' ²⁴⁻²⁹ have studied a variety of materials in OEM in recently years. For the semiconductors materials in microelectronics technology, small organic molecules are more attractive than polymers because of their well-defined molecular structure, light weight, high purity. Our group systematically investigated the influence of molecular structure on multilevel device performances.30-34 Generally, the relatively weaker intermolecular interaction of small organic molecules compared to inorganics often make these organic materials of poor film quality and poor thermal stability, unsuitable working at high temperatures. Particularly, small molecules of conjugated chain structures, which are expected to great potential in OEM applications, often have poor nanoscale film forming abilities suffering from strong aggregation in solid state, affecting the stability of the fabricated devices. Thus preparing organic films with less degree of aggregation and high thermal stability is always necessary during organic device fabrication.³⁵⁻³⁹

Among the various classes of organic materials, triphenylamine (TPA) derivatives have been widely investigated in organic electronics owing to their characteristic of good optical properties and p-type charge transport mobility.⁴⁰⁻⁴² A variety of TPA-based molecules were synthesized through mounting one, two and three linear π conjugated branches on each phenyl rings of TPA. In addition, TPA has special propeller starburst geometrical structure due to the SP3 hybrid orbital of N atom and stereo repulsion between bulky phenyl rings, which lead to amorphous crystallinity but with high hole mobility, isotropic charge transport, well-defined film-forming properties and optical transparency. To date, many TPA-containing chain-like molecules have been designed as organic materials for optoelectronics together with the evaluation on the as-fabricated film quality and thermal stability.43-51 However, a systematical investigation on effect of the branch numbers on the device performance and thermal stability has been scarcely considered.

Herein, we designed and synthesized three conjugated small molecules (**TPA-nBBT**, n=1, 2, 3) containing triphenylamine core attached by one, two and three benzene-linked benzothiazole (BBT) branches as shown in Scheme 1. Benzothiazole is attractive building blocks in organic electronics, such as organic solar cells^{52,53} and sensor,⁵⁴ because of its electron-withdrawing character, high chemical/photophysical stability and multiple reaction sites compared to the other heteroaromatics. In addition, benefitting from the connection

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two aromatics rings, the geometrically rigid structure of BBT facilitates our investigation on the variation of branch number of **TPA** cores. Thermogravimetric analysis (TGA), atomic force microscopy (AFM) and X-ray diffraction (XRD) results demonstrate that the thin-film morphologies and surface roughness of these molecules are improved progressively with increasing attached branches. The performances of the sandwiched memory devices, including on-switching voltages and stability of I-V curves are also developed by increasing BBT branches. Among them, the film crystallinity and device performance of **TPA-3BBT** was almost not affected by annealing at up to 120 °C, indicating an outstanding thermal stability which is very attractive for future organic device application.



Scheme 1. (a) Synthesis Routes for TPA-nBBT (n = 1, 2, 3). (b) scheme of the prototype sandwich device. (c) SEM image of the cross section of a storage cell of TPA-3BBT.

Experimental Section

Materials

4-Bromobenzaldehyde (98%), 4-(diphenylamino)phenylboronic acid (97%), triphenylamine (95%), tris(4-bromophenyl)amine (98%), 2-aminothiophenol (95%), N-Bromosuccinimide (NBS) (99%), bis(pinacolato)diboron (98%), [1,1'bis(diphenylphosphino)ferrocene]dichloropalladium(II) (dppf-PdCl₂) (99%) and tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (98%) were purchased from TCI. Other solvents and chemicals were all purchased from Sinopharm reagent Co., Ltd and used as received without further purification. Synthesis of TPA-nBBT. **2-(4-Bromophenyl)benzo[d]thiazole (5).** Compound 1 (10 g, 54.05 mmol) and 2-aminothiophenol (6.875 g, 55 mmol) were added into DMSO (150 mL) and then the mixture was heated to 160 °C and stirred for 10 h. After being cooled to room temperature, the mixture was poured into ice water to obtain a precipitated gray solid. After filtration, the crude product was purified by column chromatography (dichloromethane: petroleum ether = 1:1) to afford a white solid. Yield: 98%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.10 (d, *J* = 7.90 Hz, 1H), 7.97-7.93 (m, 2H), 7.90-7.88 (m, 1H), 7.63-7.60 (m, 2H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 1H).

2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-

yl)phenyl)benzo[d]thiazole (6). To a toluene solution of compound 5 (3 g, 10.34 mmol) and bis(pinacolato)diboron (3.94 g, 15.51 mmol), dppf-PdCl₂ (0.73 g, 1 mmol) and anhydrous potassium acetate (3.04 g, 31.02 mmol) were added under nitrogen atmosphere and stirred for 9 h at 70 °C. After completion of the reaction, the solvent was removed and the resulting solid was purified via a silica gel column with dichloromethane and petroleum ether (volume ratio = 1:1) to offer a white powder solid. Yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.11-8.09 (m, 3H), 7.94-7.91 (m, 3H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 1H), 1.37 (s, 12H).

4'-(Benzo[d]thiazol-2-yl)-N,N-diphenylbiphenyl-4-amine (TPA-BBT). The mixture of compound 2 (1.1 g, 3.8 mmol), compound 5 (1 g, 3.45 mmol), Pd(PPh₃)₄ (0.12 g, 0.1 mmol) and anhydrous potassium carbonate (1.43 g, 10.4 mmol) were added into a 100 mL two-neck flask, which containing 50 mL toluene, then stirred for 12 h at 80 °C under nitrogen atmosphere. After the reaction was completed, toluene was removed under reduced pressure and the very pale yellow powdered solid was obtained by column chromatography with dichloromethane and petroleum ether (volume ratio = 1 : 6). Yield: 85%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (d, J = 8.4 Hz, 2H), 8.12 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.56-7.49 (m, 3H), 7.43-7.39 (m, 1H), 7.31-7.27 (m, 4H), 7.16-7.14 (m, 6H), 7.08-7.04 (m, 2H). M. P. 208-210 °C. Solubilities: circa 3.0 mg/mL in dichloromethane, 4.0 mg/mL in chlorobenzene at 25 degrees Celsius.

4-bromo-N-(4-bromophenyl)-N-phenylaniline (7). A solution of NBS (7.26 g, 40.8 mmol) in DMF (80 mL) was added dropwise into a solution of compound 3 (5.0 g, 20.35 mmol) in DMF (60 mL), and then stirred at 0 °C for 4 h. After removal of DMF under reduced pressure by oil pump, the residue was chromatographed on a silica gel column with pure petroleum ether to give the transparent viscous liquid. Yield: 90%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.33-7.31 (m, 4H), 7.25-7.22 (m, 2H), 7.08-7.05 (m, 3H), 6.94-6.91 (m, 4H).

4'-(Benzo[d]thiazol-2-yl)-N-(4'-(benzo[d]thiazol-2-yl)biphenyl-4yl)-N-phenylbiphenyl-4-amine (TPA-2BBT). Compound 7 (1 g, 2.48 mmol), compound 6 (2.09 g, 6.2 mmol), Pd(PPh₃)₄ (0.172 g, 0.149 mmol) and anhydrous potassium carbonate (1.03 g, 7.44 mmol) were added together into 100 mL two-neck flask, then added 50 mL 1,4-dioxane to the above mixture. The Published on 02 March 2016. Downloaded by University of California - San Diego on 08/03/2016 05:21:53

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mixture was heated to 80 °C and stirred for 24 h under nitrogen atmosphere. After the reaction was completed, the solvent was removed and the residue was purified by column chromatography (dichloromethane: petroleum ether = 2 : 1) to give a pale yellow powdered solid. Yield: 80%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.16 (d, *J* = 8.3 Hz, 4H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 4H), 7.58 (d, *J* = 8.5 Hz, 4H), 7.52-7.49 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.31 (m, 2H), 7.23-7.20 (m, 6H), 7.13-7.09 (m, 1H). M. P. 273-275 °C. Solubilities: circa 1.3 mg/mL in dichloromethane, 1.0 mg/mL in chlorobenzene at 25 degrees Celsius.

Tris(4'-(benzo[d]thiazol-2-yl)biphenyl-4-yl)amine (TPA-3BBT). Compound 4 (0.7 g, 1.45 mmol), compound 6 (1.72 g, 5.08 mmol), anhydrous potassium carbonate (0.6 g, 4.35 mmol) and Pd(PPh₃)₄ (0.051 g, 0.0435 mmol) were added into 170 mL 1,4dioxane, the mixture was stirred at 80 $^{\circ}$ C for 48 h under N₂ atmosphere. After the reaction was completed, 1,4-dioxane was removed under reduced pressure and the final yellow product was obtained by silica-gel column chromatography (dichloromethane : petroleum ether = 2 : 1). Yield: 60%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.19 (d, J = 8.2 Hz, 6H), 8.11 (d, J = 8.2 Hz, 3H), 7.92 (d, J = 7.9 Hz, 3H), 7.75 (d, J = 8.3 Hz, 6H), 7.63 (d, J = 8.5 Hz, 6H), 7.54-7.50 (m, 3H), 7.42-7.39 (m, 3H), 7.30 (d, J = 8.5 Hz, 6H). M. P. 335-338 ℃. Solubilities: circa 0.3 mg/mL in dichloromethane, 0.7 mg/mL in chlorobenzene at 25 degrees Celsius.

Fabrication and Characterization of the Memory Device

The memory device was fabricated on indium tin oxide (ITO) glass substrate with the configuration ITO/organic compound/Al. Before the vacuum deposition of the organic layer, the ITO glass was precleaned by ultrasonication with water, acetone, and alcohol successively, each for 20 minutes. The active organic film was deposited under high vacuum (about 10⁻⁶ Torr) and the film thickness was circa 100 nm. Then an array of 100-nm-thick Al electrodes with 0.5 mm in diameter, was thermally evaporated and deposited onto the organic surface at about 1×10^{-6} Torr through a shadow mask. The electrical characteristics of memory device were measured with an HP 4145B semiconductor parameter analyzer equipped with a TTPX low and variable temperature probe station. A schematic diagram of sandwiched structure memory devices and SEM cross section image were shown in Scheme 1b and 1c.

Measurement

¹H NMR spectra were recorded on an Inova FT-NMR spectrometer of 400 MHz with deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane as the reference. Thermal properties were estimated from a thermogravimetric analysis system (TGA) and a TA Instruments Dynamic TGA 2950 under a nitrogen atmosphere flow rate of 50 mL•min⁻¹ at a heating rate of 10 °C•min⁻¹, respectively. UV-Vis absorption spectra were measured with a PerkinElmer Lambda-17 spectrophotometer in the 250-700 nm spectral region at room temperature. Cyclic voltammetry was performed with the use of a three-electrode cell in which platinum-wire was used as a

working electrode, at a sweep rate of 100 mV•s⁻¹ on a CorrTest CS Electrochemical Workstation analyzer. A platinum sheet was used as an auxiliary electrode. All cell potentials were taken with the use of an Ag/AgCl reference electrode. A 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane was used. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4700 scanning electron microscope. Atomic force microscopy (AFM) measurements were obtained with a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument to measure the surface morphology of films at room temperature. X-ray diffraction (XRD) patterns were obtained by an X'Pert-Pro MPD X-ray diffractometer.

Results and Discussion

Electrical Switching Effects and Memory Performance.

In order to rule out the possibility that TPA may have storage performance, we first investigated the current-voltage (I-V) characteristics of TPA under different film thicknesses. As seen in Fig. 1, the device fabricated with TPA as the active layer all showed no storage performance. The device showed only a single moderately high conductance state without any switching behavior with a thickness around 100 nm (Fig. 1a). When the film thickness gradually increased to 200 and 300 nm, the current maintained in a low state (Fig. 1c) without any abrupt jump. In short, TPA itself does not have any memory performance, which suggests that the organic memory is mainly determined by the intrinsic properties of the molecule and not influenced by the film thickness. Therefore It is necessary to modify TPA molecule in order to achieve memory performance .



Fig. 1 I–V curve for the device fabricated with TPA film in the different thicknesses a) 100 nm; b) 200 nm; c) 300 nm. The test temperature was R. T.

The SRAM behavior of **TPA-3BBT** based device is shown in Fig. 2g. In the first sweep from 0 to -4 V, the device was initially in a lowconductivity (OFF) state and the current increased slowly in the range of 10^{-11} - 10^{-7} A. With the increase of the scanning voltage, a sharp transition from the initial low-conductivity state to highconductivity state was observed at about -1.5 V. The device remained in this ON state during a subsequent scan followed by the first scan from 0 to -4 V (sweep 2). However, about 90 seconds after the second scan, the current level dropped to original low-current status (10^{-11} - 10^{-7} A) and the device returned to the OFF state when the negative bias was from 0 to -1.5 V (sweep 3). When the negative bias increased to about -1.5 V, the current increase from 10^{-7} to 10^{-2} A could be observed again and the device subsequently

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reached a high-conductivity state. The transition from the OFF- to ON-state could serve as a "writing" process in practical data storage applications. Compared to the TPA-based device without any memory behaviours at the same film thickness, it is clear that the introduction of benzothiazole as electron acceptor is crucial to achieve the memory performance through donor-acceptor structure, which we will discussed in the section of theoretical interpretation.

Similar to TPA-3BBT, the device based on TPA-2BBT and TPA-BBT also showed SRAM memory characteristics as shown in Fig. 2d and Fig. 2a. However, number of branches has nontrivial influence on the devices. For example, the device based on TPA-2BBT showed a switching voltage of about -1.65 V, which is slightly higher than that of TPA-3BBT, implying relatively high power consumption. On the other aspect, the retention time of these SRAM devices is also different (210 seconds for TPA-BBT and 120 seconds for TPA-2BBT). For this result, the retention time decreases with increase of benzothiazole units. The main reason could be that the stacking of molecules greatly changed. The critical performance of the devices based on organic electronic materials is closely related to their film morphology and molecular packing. The details of the microstructure are important because the local packing of neighboring molecules determines the intermolecular electronic orbital overlap, and because the connectivity of the domains determine the paths taken by charge carriers through the film.⁵⁵ For example, TPA-BBT film with the largest root-mean-square (RMS) roughness of 28.61 nm (see below), which might be owing to the strong aggregation of molecules, thus the larger domain is very unfavourable to the rapid transport of charge carriers which led to higher operation voltage and longer retention time. Additionally, the molecule TPA-3BBT formed neat film and the smallest RMS roughness (2.86 nm), which may lead to more efficient charge transport and shorter retention time. The conclusion that the lowconductivity state of TPA-3BBT is more stable than that of TPA-2BBT is summarized via comparing Fig. 2d and Fig. 2g. For the TPA-BBT-based device, the threshold voltage was observed at about -3.5 V and the I-V curves were very unstable.



Fig. 2. (a, d, g) Current-voltage (I-V) characteristics of the ITO/compound/Al device (Unannealed) for TPA-BBT, TPA-2BBT and TPA-3BBT. The test temperature was R. T. The corresponding

stability (b, e, h) and stimulus effect of read cycles (c, f, i) of the three compounds based devices in two states under a constant read voltage of -1 V.

The long-term and stimulus stability of the ITO/compound/AI device were evaluated from the retention time and stress tests of both the ON and OFF states of the three compounds as shown in Fig. 2. Under a constant voltage of -1 V, no significant degradation was observed in the OFF and ON states for at least 100 min for TPA-2BBT and TPA-3BBT during the readout test, as shown in Fig. 2e and Fig. 2h. But significant degradation or transition could be observed for TPA-BBT, indicating the unstable storage performance as shown in Fig. 2b. The effect of continuous read pulses of -1 V on the ON and OFF state was also investigated for the long time test as shown in Fig. 2c. The pulse period and width are 2 and 1 μ s, respectively. Fig. 2f and 2i show cycles of a pulse voltage stress without significant change in ON state and OFF state current for at least 10⁸ times for TPA-2BBT and TPA-3BBT under the effect of continuous read pulses of -1 V. On the other hand, the obvious fluctuations could be observed for ON state and OFF state after more than 10⁸ continuous read cycles for TPA-BBT as shown in Fig. 2c, further indicating instability of device. In short, the branch plays a crucial role in memory performance. With the increase of branches on the molecular skeleton, the stability and reproducibility of the device improved and the operation voltage could also be lowered sequentially.

Optical and electrochemical Properties.

To reveal the effect of benzothiazole branches, we conducted optical and electrochemical measurement. The UV-Vis absorption was measured both in dilute dichloromethane solution and in solid films for the three compounds as shown in Fig. 3a. The UV-Vis absorption spectrum of each compound shows two distinct absorption peaks located at around 300 nm and 400 nm in solution, which could be assigned to the π - π * transition of the triphenylamine moieties. Compared with the absorption spectra in solution state, both absorption peaks in the film state showed a red-shift (from 387 nm to 394 nm in TPA-3BBT film) or significant broadening (in TPA-2BBT film and TPA-BBT film). Optical absorption of both molecules in film state red-shifted and broadened compared with their solution state, which arises from molecular aggregation in the film state.⁵⁶ In addition, the absorption onset correspondingly red-shifted from 436 nm in TPA-BBT film to 450 nm in TPA-2BBT film to 464 nm in TPA-3BBT film due to the greater degree of conjugation attributed to the increase of the BBT units, indicating a reduction in the optical band gap of the D-A molecules. The band gap (Eg) of TPA-BBT, TPA-2BBT and TPA-3BBT can be calculated from the absorption edge to be 2.94 eV, 2.84 eV and 2.76 eV, respectively.

To understand the electrochemical properties we conducted cyclic voltammetry measurements on the three compounds. The onset oxidation potential of ferrocene is 0.48 eV from the CV measurement as shown in Figure S5. The energy level of the HOMO was determined from the onset oxidation (Eox(onset)), which is obtained as shown in Fig. 3b. The HOMO levels of **TPA-BBT**, **TPA-2BBT** and **TPA-3BBT** are calculated to be -5.33 eV, -5.31 eV and -5.27 eV, respectively, by the following equation:⁵⁷ $E_{HOMO} = -[E^{ex}_{onset}]$

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+ 4.80 - $E_{\text{Ferrocence}}$, where $E_{\text{Ferrocene}}$ is the external standard potential of the ferrocene/ferricenium ion couple, and 4.80 eV is the reference HOMO level of ferrocene. These results suggest that the HOMO level slightly increased from TPA-BBT to TPA-2BBT to TPA-3BBT and thus leads to better hole transport ability. On the other hand, the LUMO levels of the three compounds are estimated to be -2.39 eV, -2.47 eV and -2.51 eV by the following equation: E_{LUMO} = E_{HOMO} + E_{g} , respectively, where E_{g} is the optical gap determined from the UV-Vis spectra. Thus, we can summarize that the energy barrier between Φ of ITO (-4.80 eV) and the HOMO level of TPA-BBT is 0.53 eV, which is much lower than the energy barrier between Φ of Al (-4.28 eV) and that corresponding LUMO level (1.89 eV). In addition, similar conclusion applies to TPA-2BBT and TPA-3BBT. It indicates that all the three compounds are all hole transport dominating materials (p-type materials). 57-59 Moreover. the energy barrier between Φ of ITO and the HOMO level of **TPA**-3BBT (0.47 eV) is the lowest, which could contribute to the lowest switch-ON voltages among all compounds.



Fig. 3 (a) UV-Vis absorption spectra of the three compounds in CH_2Cl_2 solution and solid thin films on a quartz substrate. (b) Cyclic voltammetry (CV) curves of the three compounds in anhydrous dichloromethane solution with 0.1 M of $n-Bu_4NPF_6$ as the supporting electrolyte. The scan rate was 100 mV s⁻¹.

Theoretical interpretation

The switching mechanism of the memory devices and the effect of branches could be understood from theoretical calculations. The electronic properties of the three compounds were theoretically explored through density functional theory (DFT). Fig. 4 shows the electrostatic potentials (ESP) surfaces of the three compounds, which were obtained with the B3LYP/6-31G(d) basis set. The continuous red area in the molecular backbone as shown in the ESP surface indicates that charges can migrate through the conjugated backbone along this open channel. However, there is a negative (blue) ESP region (two or three same blue areas) in the molecular backbone, which is generated by the benzothiazolyl moiety, a weak electron-withdrawing group. This negative region can function as a "trap" to block the mobility of the charge carriers,³⁰ leading to charge retention and memory effects. And the traps could be filled almost simultaneously by charge carriers with the increase of applied electric field, leading to the current transition from the OFF state to the ON state. Therefore, the TPA-2BBT and TPA-3BBT based devices exhibited stable binary memory behavior. However, the benzothiazolyl moiety (acceptor) serving as a shallow "trap", cannot hold electrons for long after the power is turned off when

the current is in ON state. Then the trapped electrons can be easily detrapped and the current drops to OFF state level.



Fig. 4 The molecular ESP surfaces of the three compounds from DFT calculations.

Film quality and Thermal stability

To understand the apparent difference in the electrical switching characterization of these three small-molecule-based devices, the microstructure of their thin films was investigated using atomic force microscopy (AFM) and X-ray diffraction (XRD). As shown in Fig. 5, AFM images and height profiles clearly show a wormlike surface for TPA-BBT film, with a large root-mean-square (RMS) roughness of 28.61 nm (Fig. 5a and 5d), which might be owing to the strong aggregation of molecules. It may be not conducive to maintaining the stability of the film. Additionally, the surface of the TPA-2BBT film becomes more continuous compared to TPA-BBT film (Fig. 5b), and the RMS of surface roughness was 6.52 nm as shown in Fig. 5e. Note that the morphology of TPA-3BBT film is distinct from the former two (Fig. 5c), forming two-dimensional grains on substrate with the smallest surface RMS roughness (2.86 nm, Fig. 5f). This uniformly separated small domain and the relatively small surface RMS roughness of film may lead to more efficient charge transport.^{19, 25}



Fig. 5 Tapping-mode height images of AFM topographic images (5x5 μ m) of thin films vacuum-deposited onto ITO at room temperature: (a)**TPA-BBT**; (b) **TPA-2BBT**; (c) **TPA-3BBT**.

Thermal properties of the three compounds were investigated by TGA to assess their thermal stability as shown in Fig. S1. All the compounds displayed good thermal stability, with 5% weight-loss temperatures of 296 °C, 398 °C and 446 °C for **TPA-BBT**, **TPA-2BBT** and **TPA-3BBT**, respectively. These relatively high weight-loss temperatures observed for the three compounds indicated good resistance against high temperature for the devices based on these D-A molecules, especially for **TPA-3BBT**. In addition, it is noteworthy that weight-loss temperature of the three compounds increased rapidly with increasing BBT units in the molecular backbone, indicating a better thermal stability with gradually increased number of branches. This result is consistent with the conclusion obtained above.

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Stability of the three molecular films at room temperature was also traced through taking photographs of films with time. As shown in Fig. S2, the film of **TPA-3BBT** maintained transparent after ten days, while an atomization process occurred for the other two films. Especially, for the **TPA-BBT** film, a strong aggregation occurred as shown in Fig. S2e and it turned white from transparent. This result showed that the stability of the film of the three compounds at room temperature sequentially improved with the increasing of the number of branches and the **TPA-3BBT** film displayed good resistance against moisture or oxygen, which is beneficial to the practical application of device.



Fig. 6 X-ray diffraction spectra of the three films deposited on ITO glass substrates at different temperatures. (a) for the three films at room temperature, (b) **TPA-BBT**, (c) **TPA-2BBT**, (d) **TPA-3BBT**.

The XRD patterns of the three compounds deposited on ITO substrates at room temperature are shown in Fig. 6a. The TPA-BBT film exhibited two sharp diffraction peaks at 21.2° and 21.7° corresponding to d-spacing of 4.2 and 4.1 Å, respectively. This showed that there are two similar type and ordered stacking in the film where. Indexed by the same intensity of ITO characteristic peaks of these three films, the much stronger crystallinity in TPA-BBT compared to the other two. As a result, this strong intermolecular interaction led to severe aggregations in the film of TPA-BBT. However, the diffraction peak located at 21.2° was much sharper and its intensity was stronger than that located at 21.7°, indicating the orientation was packed almost in the way of 21.2 Å in film state. According to the dimension of TPA-BBT molecule (Fig. S6a), the orientation of TPA-BBT is likely out of plane. However, for TPA-2BBT film, a diffraction peak can be observed at 8.3° with dspacing of 16.7 Å, representing a long-range ordered arrangement. The molecular packing of TPA-2BBT is proposed to be in a certain angle with respect to the substrate plane deduced from the molecular dimension in Fig. S6b. Additionally, in the case of TPA-3BBT-based films, the diffraction peak located at 8.3° corresponded to a d-spacing of 10.6 Å. The intensity of this diffraction peak is very weak, indicating that there was no obvious aggregation. The dspacing 10.6 Å is smaller than the primary peak of **TPA-2BBT**, suggesting that **TPA-3BBT** more accumulated closely than **TPA-2BBT** but not aggregate as **TPA-BBT**. Therefore, based on the surface morphologies and crystallinities of these films, **TPA-3BBT** would be of the best for fabrication of organic memory devices among the three molecules.

The XRD patterns of the three films annealed at different temperatures (60, 80, 100 and 120 °C) were investigated (Fig. 6b-d). There were gradual growths of the peak intensities at 21.7° as the annealing temperatures increased for the TPA-BBT and TPA-2BBT films in Figs. 6b and 6c, which indicated that the more serious aggregation occurred. In contrast, for TPA-BBT, the strength of the two sharp diffraction peaks obviously shifted and the peak at 21.2° disappeared at 120 °C, demonstrating that the stacking was completely converted to the denser way indexed by 21.7°. This conversion means that the aggregation became more severe, consistent with the AFM test (Fig. S3a and S3b). However, no significant change in diffraction peaks of TPA-3BBT film at varied temperatures (60, 80, 100 and 120 °C) was observed as shown in Fig. 6d. This indicated that TPA-3BBT film possessed stable crystallinity at high temperatures, suitable for organic devices operated under harsh environments.

The temperature-insensitive crystallinity of TPA-BBT could be further identified via monitoring the morphologies of compounds films by AFM at different temperatures as shown in Fig. S3 and S4. It is obvious that TPA-BBT and TPA-2BBT molecules (Fig. S3) produce server aggregation as the annealing temperature increased. When the annealing temperature reached as high as 120 °C, the roughness of TPA-BBT and TPA-2BBT films exceeded 1 µm, which was no longer suitable for device fabrication. In contrast, TPA-3BBT film (Fig. S4) tended to be smoother with the annealing temperature rising, which would be beneficial to charge transport. Inspired from the best thermal stability, we demonstrate the TPA-**3BBT** as an outstanding organic memory material proper to work under high temperatures. TPA-3BBT-based memory devices show stable binary SRAM behavior annealed at different temperatures (60, 80, 100 and 120 °C) in Fig. 7. The devices at all these temperatures are of almost the same on-switching voltages, which is critical to production of devices in large scale with stable work performance under diverse thermal environments in terms of real application.



Fig. 7 Current-voltage (I-V) characteristics of the ITO/TPA-3BBT/AI device at different temperatures: (a) 60 °C, (b) 80 °C, (c) 100 °C, (d) 120 °C.

Conclusions

summary, three conjugated triphenylamine-based In molecules containing benzothiazole branches have been designed and prepared. The as-fabricated devices based on the three compounds all exhibited binarv SRAM The branch characteristics. number attaching to triphenylamine core has significant impact on the optical, electrochemical properties, thin-film microstructure, thermal stability and performance of the memory devices. However, the stability and reproducibility can be improved and the operation voltage could be lowered sequentially with the increase of branches due to the smaller surface roughness and the higher stability of the corresponding film. In addition, the stability of film and in consequence the memory performances either at room temperature or high temperature increases as the branch number increased. These results obtained here show that increasing the number of branches in the molecular backbone may be a simple and practical approach to further improve the performance as well as thermal stability of the organic devices.

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Notes and references

- 1 X. D. Zhuang, Y. Chen, G. Liu, B. Zhang, K. G. Neoh, E. T. Kang, C. X. Zhu, Y. X. Li and L. J. Niu, Adv. Funct. Mater., 2010, 20, 2916
- 2 M. Ball, Y. Zhong, Y. Wu, C. Schenck, F. Ng, M. Steigerwald, S. Xiao and C. Nuckolls, Acc. Chem. Res., 2014, 48, 267.

ournal of Materials Chemistry C Accepted Manuscrip

- 3 X. Guo, A. Facchetti and T. J. Marks, Chem. Rev., 2014, 114, 8943.
- C. J. Brabec, S. Gowrisanker, J. J. Halls, D. Laird, S. Jia and S. 4 P. Williams, Adv. Mater., 2010, 22, 3839.
- 5 D. Sun, D. Meng, Y. Cai, B. Fan, Y. Li, W. Jiang, L. Huo, Y. Sun and Z. Wang, J. Am. Chem. Soc., 2015, 137, 11156.
- 6 S. R. Forrest, Nature, 2004, 428, 911.
- S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. 7 Lüssem and K. Leo, Nature, 2009, 459, 234.
- 8 M. Helander, Z. Wang, J. Qiu, M. Greiner, D. Puzzo, Z. Liu and Z. Lu, Science, 2011, 332, 944.
- 9 T. Chiba, Y. J. Pu and J. Kido, Adv. Mater., 2015, 27, 4681.
- 10 M. L. Hammock, O. Knopfmacher, T. N. Ng, J. B. H. Tok and Z. Bao, Adv. Mater., 2014, 26, 6138.
- 11 M. Y. Lee, H. J. Kim, G. Y. Jung, A. Han, S. K. Kwak, B. J. Kim and J. H. Oh, Adv. Mater., 2015, 27, 1540.
- 12 M. L. Tang, A. D. Reichardt, N. Miyaki, R. M. Stoltenberg and Z. Bao, J. Am. Chem. Soc., 2008, 130, 6064.
- 13 H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler and A. Facchetti, Nature, 2009, 457, 679.
- 14 G. Liu, Q.-D. Ling, E. Y. H. Teo, C.-X. Zhu, D. S.-H. Chan, K.-G. Neoh and E.-T. Kang, ACS nano, 2009, 3, 1929.
- 15 Q.-D. Ling, F.-C. Chang, Y. Song, C.-X. Zhu, D.-J. Liaw, D. S.-H. Chan, E.-T. Kang and K.-G. Neoh, J. Am. Chem. Soc., 2006, 128, 8732.
- 16 Q. D. Ling, Y. Song, S. L. Lim, E. Y. H. Teo, Y. P. Tan, C. Zhu, D. S. H. Chan, D. L. Kwong, E. T. Kang and K. G. Neoh, Angew. Chem. Int. Ed., 2006, 118, 3013.
- 17 Y.-G. Ko, D. M. Kim, K. Kim, S. Jung, D. Wi, T. Michinobu and M. Ree, ACS Appl. Mat. Interfaces, 2014, 6, 8415.
- 18 S. Park, K. Kim, D. M. Kim, W. Kwon, J. Choi and M. Ree, ACS Appl. Mat. Interfaces, 2011, 3, 765.
- 19 S. G. Hahm, S. Choi, S. H. Hong, T. J. Lee, S. Park, D. M. Kim, W. S. Kwon, K. Kim, O. Kim and M. Ree, Adv. Funct. Mater., 2008, 18, 3276.
- 20 W.-Y. Lee, T. Kurosawa, S.-T. Lin, T. Higashihara, M. Ueda and W.-C. Chen, Chem. Mater., 2011, 23, 4487.
- 21 S.-L. Lian, C.-L. Liu and W.-C. Chen, ACS Appl. Mat. Interfaces, 2011, 3, 4504.
- 22 A.-D. Yu, T. Kurosawa, Y.-H. Chou, K. Aoyagi, Y. Shoji, T. Higashihara, M. Ueda, C.-L. Liu and W.-C. Chen, ACS Appl. Mat. Interfaces, 2013, 5, 4921.
- 23 H.-C. Wu, A.-D. Yu, W.-Y. Lee, C.-L. Liu and W.-C. Chen, Chem. Commun., 2012, 48, 9135.
- 24 C. Ye, Q. Peng, M. Li, J. Luo, Z. Tang, J. Pei, J. Chen, Z. Shuai, L. Jiang and Y. Song, J. Am. Chem. Soc., 2012, 134, 20053.
- 25 B.-B. Cui, Z. Mao, Y. Chen, Y.-W. Zhong, G. Yu, C. Zhan and J. Yao, Chem. Sci., 2015, 6, 1308.
- 26 H. Wang, F. Meng, Y. Cai, L. Zheng, Y. Li, Y. Liu, Y. Jiang, X. Wang and X. Chen, Adv. Mater., 2013, 25, 5498.
- 27 S. T. Han, Y. Zhou and V. Roy, Adv. Mater., 2013, 25, 5425. 28 G. Wen, Z. Ren, D. Sun, T. Zhang, L. Liu and S. Yan, Adv.
- Funct. Mater., 2014, 24, 3446.
- 29 P.-Z. Jian, Y.-C. Chiu, H.-S. Sun, T.-Y. Chen, W.-C. Chen and S.-H. Tung, ACS Appl. Mat. Interfaces, 2014, 6, 5506.
- 30 H. Li, Q. Xu, N. Li, R. Sun, J. Ge, J. Lu, H. Gu and F. Yan, J. Am. Chem. Soc., 2010, 132, 5542.
- 31 S. Miao, H. Li, Q. Xu, Y. Li, S. Ji, N. Li, L. Wang, J. Zheng and J. Lu, Adv. Mater., 2012, 24, 6210.
- 32 P.-Y. Gu, F. Zhou, J. Gao, G. Li, C. Wang, Q.-F. Xu, Q. Zhang and J.-M. Lu, J. Am. Chem. Soc., 2013, 135, 14086.
- 33 Y. Li, H. Li, H. Chen, Y. Wan, N. Li, Q. Xu, J. He, D. Chen, L. Wang and J. Lu, Adv. Funct. Mater., 2015. 25. 4246.
- 34 Q. F. Gu, J. H. He, D. Y. Chen, H. L. Dong, Y. Y. Li, H. Li, Q. F. Xu and J. M. Lu, Adv. Mater., 2015. 27. 5968.
- X. Yang, J. Loos, S. C. Veenstra, W. J. Verhees, M. M. Wienk, 35 J. M. Kroon, M. A. Michels and R. A. Janssen, Nano Lett., 2005, 5, 579.

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- 36 K. Sivula, C. K. Luscombe, B. C. Thompson and J. M. Fréchet, J. Am. Chem. Soc., 2006, **128**, 13988.
- 37 B. J. Kim, Y. Miyamoto, B. Ma and J. M. Frechet, Adv. Funct. Mater., 2009, 19, 2273.
- 38 J. Jang, S. Nam, D. S. Chung, S. H. Kim, W. M. Yun and C. E. Park, Adv. Funct. Mater., 2010, 20, 2611.
- 39 G. Griffini, J. D. Douglas, C. Piliego, T. W. Holcombe, S. Turri, J. M. Fréchet and J. L. Mynar, Adv. Mater., 2011, 23, 1660.
- 40 Y. Shirota, J. Mater. Chem., 2000, 10, 1.
- 41 Y. Shirota, J. Mater. Chem., 2005, 15, 75.
- 42 A. Cravino, S. Roquet, O. Alévêque, P. Leriche, P. Frere and J. Roncali, *Chem. Mater.*, 2006, **18**, 2584.
- 43 S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frere and J. Roncali, J. Am. Chem. Soc., 2006, **128**, 3459.
- 44 J. Zhang, Y. Yang, C. He, Y. He, G. Zhao and Y. Li, *Macromolecules*, 2009, **42**, 7619.
- 45 G. Zhao, G. Wu, C. He, F.-Q. Bai, H. Xi, H.-X. Zhang and Y. Li, J. Phys. Chem. C, 2009, **113**, 2636.
- 46 J.-Y. Pan, L.-J. Zuo, X.-L. Hu, W.-F. Fu, M.-R. Chen, L. Fu, X. Gu, H.-Q. Shi, M.-M. Shi and H.-Y. Li, ACS Appl. Mat. Interfaces, 2013, 5, 972.
- 47 M. I. Mangione, R. A. Spanevello, A. Rumbero, D. Heredia, G. Marzari, L. Fernandez, L. Otero and F. Fungo, *Macromolecules*, 2013, 46, 4754.
- 48 P. Wei, X. Bi, Z. Wu and Z. Xu, Org. Lett., 2005, 7, 3199.
- 49 P. Hrobárik, V. Hrobáriková, I. Sigmundová, P. Zahradník, M. Fakis, I. Polyzos and P. Persephonis, J. Org. Chem., 2011, 76, 8726.
- 50 D. Gudeika, A. Michaleviciute, J. V. Grazulevicius, R. Lygaitis, S. Grigalevicius, V. Jankauskas, A. Miasojedovas, S. Jursenas and G. Sini, *J. Phys. Chem. C*, 2012, **116**, 14811.
- 51 L. Shi, C. He, D. Zhu, Q. He, Y. Li, Y. Chen, Y. Sun, Y. Fu, D. Wen and H. Cao, *J. Mater. Chem.*, 2012, **22**, 11629.
- 52 N. Saeed, A. Fahdan, A. M. Asiri, A. Irfan, S. A. Basaif and R. M. Shishtawy, *J. Mol. Model.*, 2014, **20**, 2517.
- 53 C. Siua, C. Ho, J. He, T. Chen, X. Cui, J. Zhao and W. Wong, J. Organomet. Chem., 2013, **748**, 75.
- 54 F. Wanga, S. Nama, Z. Guoa, S. Parka and J. Yoon, Sensor Actuat B-Chem., 2012, 161, 948.
- 55 D. M. DeLongchamp, R. J. Kline, D. A. Fischer, L. J. Richter, and M. F. Toney, *Adv. Mater.*, 2011. 23. 319.
- 56 K. H. Kim, S. Y. Bae, Y. S. Kim, J. A. Hur, M. H. Hoang, T. W. Lee, M. J. Cho, Y. Kim, M. Kim and J. I. Jin, *Adv. Mater.*, 2011, 23, 3095.
- 57 G. Liu, B. Zhang, Y. Chen, C.-X. Zhu, L. Zeng, D. S.-H. Chan, K.-G. Neoh, J. Chen and E.-T. Kang, J. Mater. Chem., 2011, 21, 6027.
- 58 A. Bandyopadhyay, S. Sahu and M. Higuchi, J. Am. Chem. Soc., 2011, 133, 1168.
- 59 X. D. Zhuang, Y. Chen, G. Liu, B. Zhang, K. G. Neoh, E. T. Kang, C. X. Zhu, Y. X. Li and L. J. Niu, *Adv. Funct. Mater.*, 2010, **20**, 2916.
- 60 J. A. Marsden, J. J. Miller, L. D. Shirtcliff and M. M. Haley, J. Am. Chem. Soc., 2005, 127, 2464.

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Improving organic memory performance through mounting

conjugated branches on a triphenylamine core

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The devices based on TPA-nBBT all exhibited binary SRAM characteristics, however, the stability and reproducibility can be improved and the operation voltage could be lowered sequentially with the increase of branches due to the smaller surface roughness and the higher stability of the corresponding film.