Supporting Information

Effect of single atom substitution in Benzochalcogendiazole Acceptors on the performance of ternary Memory Devices

Zhaojun Liu,[a] Jinghui He,[b] Hao Zhuang, [b] Hua Li,[b*] Najun Li,[b] Dongyun Chen,[b] Qingfeng Xu,[b] Jianmei Lu,*[bc] Keqin Zhang, [a] and Lihua Wang[b]

[1] College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, China

[2] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University,199 Ren'ai Road, Suzhou 215123, China

1. Preparation of PBOP, PBTP and PBSeP.

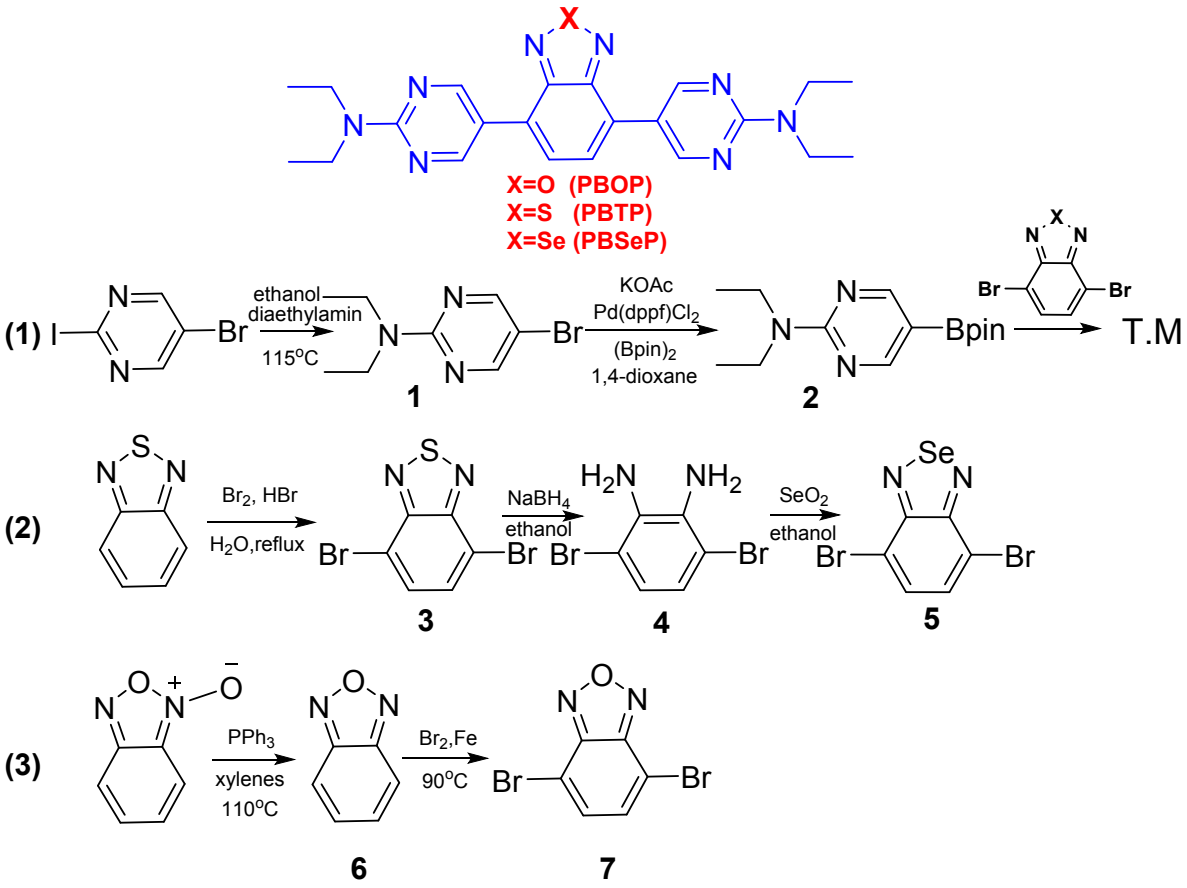


Figure. S1. Synthetic routes of PBOP, PBTP and PBSeP

All reactions were carried out under an air atmosphere unless otherwise stated. The following compounds were synthesized according to the procedures reported in the literature: 1 and 2 [1]; 3, 4 and 5 [2]; 6 [3]; 7 [4]; compounds PBOP, PBTP and PBSeP [5].

Synthesis of compound 1 (5-bromo-N,N-diethylpyrimidin-2-amine). N,N-diethylamine (, 10 mL, 97mmol) was added to ethanol solution (30 mL) with 5-Bromo-2- iodopyrimidine (3.0 g, 15.45mmol) in a sealable reaction vessel. After allowing to vent for a few minutes, the vessel was sealed, placed behind a safety shield and heated in a 115°C oil bath for 8 hours. Upon cooling the volatiles were removed in vacuo. The material was dissolved in CH_2Cl_2 (100 mL) and washed with 1M NaOH (50 mL). The aqueous layer was extracted further with CH_2Cl_2 (3x50 mL). The combined organics were dried over $MgSO_4$, The residue was purified by column chromatography using petroleum as eluent to give **1** (3.37 g, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (s, 2H), 3.58 (q, *J* = 4 Hz, 1H), 1.17 (t, *J* = 6.9 Hz, 6H). HRMS: Anal. Calcd. For $C_8H_{12}BrN_3$ $[M + H]^+$ 230.0215, 232.0194 found 230.0235, 232.0210.

Synthesis of compound 2 (N, N-diethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2- yl)pyri midin-2-amine). To a dry 500 mL flask was added compound 1 (2.29 g, 10mmol), potassium acetate (2.94 g, 30mmol), bis(pinacolato)diboron (5.08 g, 20mmol) and dioxane (80 mL). Argon was bubbled through the solution for 15 minutes, at which time 1,1'-bis(diphenylphosphino) ferrocene palladium(II)dichloride (219.5 mg, 0.3mmol) was added. The reaction was refluxed in a 115 °C oil bath for 4 hours under argon. After cooling to room temperature, the volatiles were removed in vacuo and the residue was dissolved in EtOAc (500 mL) and washed with H_2O (3x100 mL), NaCl (sat.), (500 mL), dried over Na_2SO_4, filtered and the solvents were removed in vacuo. Purification by column chromatography on silica gel (ethyl acetate /petroleum 10:1) to give **2** (2.22 g, 80 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 2 H), 3.63 – 3.33 (m, 4 H), 1.19 (s, 12 H), 0.87 (t, *J* = 7.3 Hz, 6H). HRMS: Anal. Calcd. For $C_{14}H_{24}BN_3O_2$ $[M + H]^+$ 278.1962 found 278.1933.

Synthesis of compound 3 (4,7-dibromo−2,1,3−benzothiadiazole). A mixture of 2.72 g (20 mmol) of 2,1,3-benzothiadiazole in 6 mL of 45% hydrobromic acid was heated under reflux with stirring while 9.6 g (60 mmol, 3.0 mL) of bromine was added slowly. After completion of the bromine addition, the reaction mixture became a suspension of solid in hydrobromic acid and 5 mL of hydrobromic acid was added, and the mixture was heated under reflux for another 2.5 h. The mixture was filtered, washed well with water, recrystallized from chloroform, and dried to give **3**

(5.84 g, 90%) as white needle crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (s, 2 H). HRMS: Anal. Calcd. For $C_6H_2Br_2N_2S$ $[M + H]^+$ 292.8305, 296.8265 found 292.8315, 296.8235.

Synthesis of compound 5 (4,7-dibromo−2,1,3−benzoselenadiazole). To a suspension of 4,7-dibromo-2,1,3-benzothiadiazole (3) (2.94 g, 10 mmol) in ethanol (100 mL) was added portionwise sodium borohydride (7 g, 0.19 mol) at 0 °C, and the mixture was stirred for 12 h at room temperature. After evaporation of the solvent, 100 mL of water was added, and the mixture was extracted with ether. The extract was washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 3,6-dibromo-1, 2-phenylenediamine (4) (2.3 g) as a pale yellow solid in 87% yield. To a solution of 4 (2.1 g, 8 mmol) in refluxing ethanol (50 mL) was added a solution of selenium dioxide (1.0 g, 9 mmol) in hot water (20 mL). The mixture was heated under reflux for 2 h. Filtration of the yellow precipitates and recrystallization from ethyl acetate gave **5** (2.5 g, 92%) as golden yellow needles. ^{1}H NMR (400 MHz, DMSO) δ = 7.80 (s, 2H). HRMS: Anal. Calcd. For $C_6H_2Br_2N_2Se$ $[M + H]^+$ 340.7750, 344.7709 found 340.7761, 344.7739.

Synthesis of compound 6 (2,1,3−benzooxadiazole). benzofuroxan (1.36 g, 10 mmol) and triphenylphosphine (3.93 g, 15 mmol) are stirred in xylenes (100 mL) at 100˚C for 2h, followed by 120˚C for an additional hour. The mixture is cooled to room temperature, filtered on a short silica gel plug and the plug is rinsed with dichloromethane. Evaporation of the solvents under reduced pressure affords a crude product that is purified by recystallization from EtOH to yield **6** as an off-white solid (720 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J*=100.6 HZ, 4H). HRMS: Anal. Calcd. For $C_6H_4N_2O$ $[M + H]^+$ 121.0324 found 121.0345

Synthesis of compound 7 (4,7-dibromo-2,1,3-benzooxadiazole). Benzofurazan (1.20 g, 10 mmol) and iron powder (115 mg, 2 mmol) were placed in a round bottom flask and the materials heated to 90^{o}C. Elemental bromine (4.8 g, 30 mmol) was added dropwise over an hour, and upon complete addition the reaction mixture was heated at reflux for 2 h. The reaction mixture was allowed to cool, which caused it to solidify. The residue was dissolved in DCM (10 mL) and washed with brine (25 mL). The organic fraction was separated and washed with saturated sodium bicarbonate solution (4 × 30 mL), with brine (3 × 30 mL) and with water (3 × 30 mL).The organic fraction was dried over magnesium sulfate and reduced in vacuo. The brown crude product was chromatographed on silica gel (hexane/ethyl acetate 9:1 eluant) to afford **7** (1.79 g, 65 %) as a

cream powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (s, 2H). HRMS: Anal. Calcd. For $C_6H_2Br_2N_2O$ $[M + H]^+$ 276.8534, 280.8493 found 276.8540, 280.8497.

Synthesis of compound PBOP (5,5'-(benzooxadiazole-4,7-diyl)bis(N,N-diethylpyrimidin-2 -amine). A mixture of 4,7-dibromo-2,1,3-benzooxadi azole (1.38 g, 5 mmol), compound 2 (2.25 g, 15 mmol), potassium carbonate (2.76 g, 20 mmol), $Pd(PPh_3)_4$(47 mg, 0.04 mmol), H_2O (20 mL) and toluene (30 mL) was heated at 90°C for 10 h. After cooling, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and then dried with anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was recrystallized from ethanol to afford **PBOP** (1.29 g, 62%) as a crimson solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.01 (s, 4H), 7.51 (s, 2H), 3.72 (dd, *J* = 13.9, 6.9 Hz, 8H), 1.26 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.53, 156.89, 148.80, 125.35, 123.08, 116.61, 42.25, 13.07. HRMS: Anal. Calcd. For $C_{22}H_{26}N_8O$ $[M + H]^+$ 419.2230 found 419.2241.

Compounds PBTP and PBSeP were synthesized use using a similar procedure for compound PBOP.

Synthesis of compound PBTP (5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(N,N-diethyl pyrimidin-2-amine)). 1.63 g, 75%, crimson solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.98 (s, 4H), 7.67 (s, 2H), 3.70 (dd, *J* = 13.3, 6.5 Hz, 8H), 1.24 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.28, 157.55, 153.75, 127.70, 125.53, 118.41, 42.14, 13.09. HRMS: Anal. Calcd. For $C_{22}H_{26}N_8S$ $[M + H]^+$ 435.2001 found 435.2011.

Synthesis of compound PBSeP (5,5'-(benzo[c][1,2,5]selenadiazole-4,7-diyl)bis(N,N-diethyl pyrimidin-2-amine)). 2.00 g, 83%, orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.88 (s, 4H), 7.50 (s, 2H), 3.73 (dd, *J* = 13.5, 6.6 Hz, 8H), 1.27 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.25, 159.47, 157.81, 129.55, 126.04, 119.01, 42.13, 13.10. HRMS: Anal. Calcd. For $C_{22}H_{26}N_8Se$ $[M + H]^+$ 483.1446 found 482.1452.

References

[1] M. T. Burger, M. Knapp, A. Wagman, Z. J. Ni, T. Hendrickson, G. Atallah, Y. C. Zhang and S. Pecchi, *ACS Med. Chem. Lett.* 2011, **2**, 34 –38.

[2] R. Q. Yang; R. Y. Tian, J. G. Yan, Y. Zhang. J. Yang, Q. Hou, W. Yang, C. Zhang and Y. Cao, *Macromolecules,* 2005, **38**, 244-253.

[3] J. H. Boyer; S. E. Ellsey, *J. Org. Chem.* 1961, **26**, 4684–4685.

[4] K. Pilgram; M. Zupan, *J. Heterocycl. Chem.* 1974, **11**, 813-814.

[5] J. M. Raimundo, P. Blanchard, H. Brisset, S. Akoudand and J. Roncali, *Chem. Commun.*, 2000, 939-940.

2. Thermal properties image

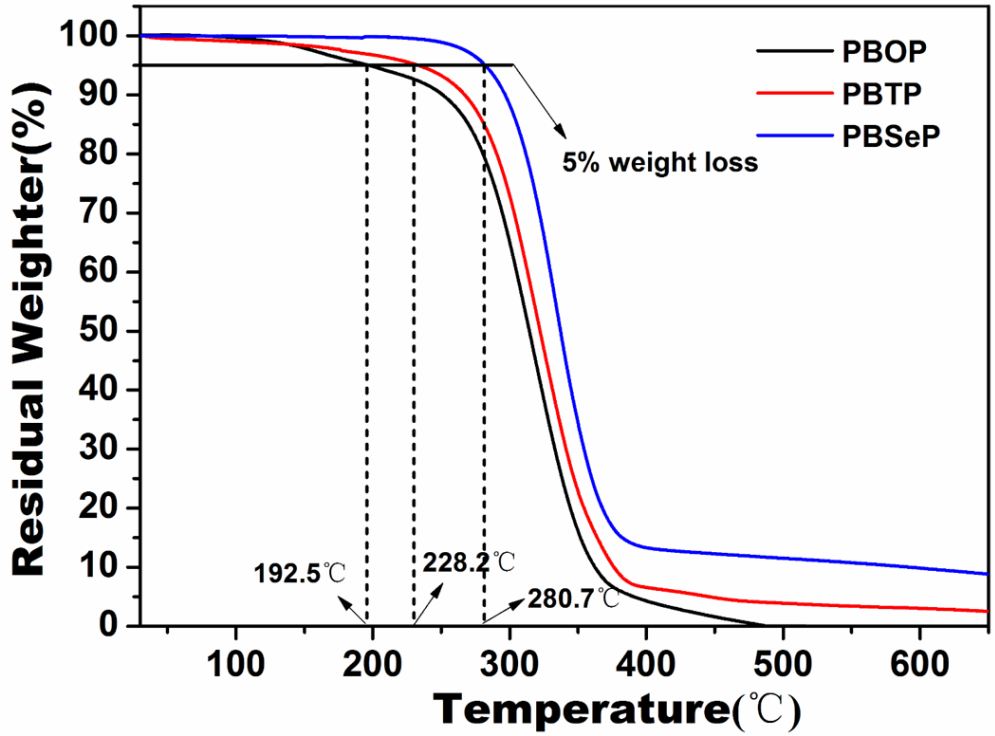


Figure. S2. TGA curves of the three molecules with a heating rate of 20°C min^{-1} under nitrogen

3. Stability tests of the devices

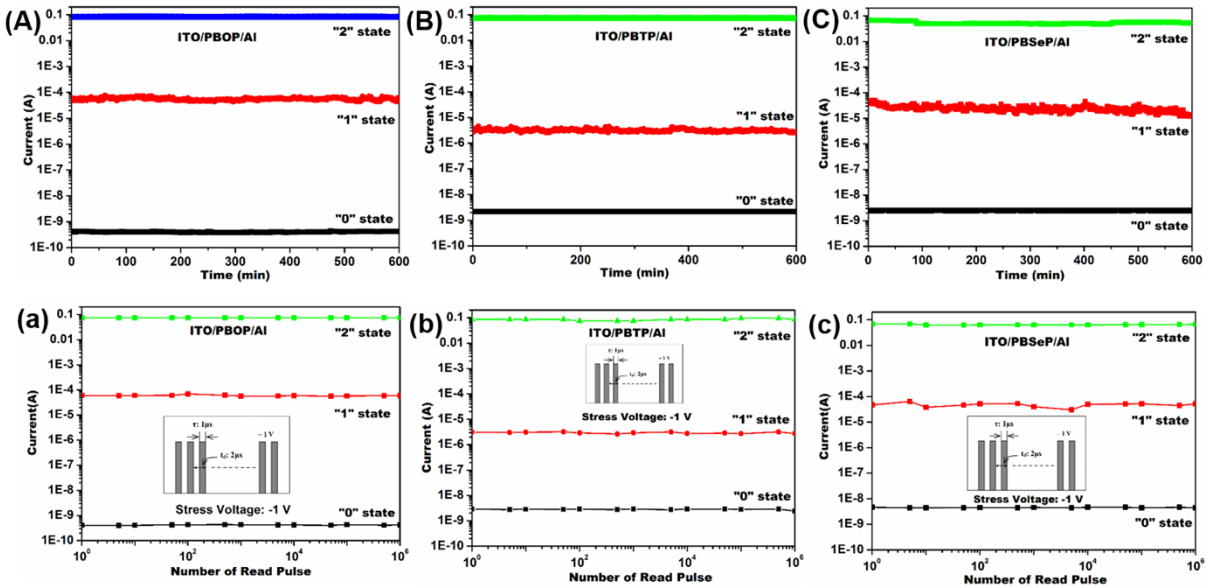


Figure. S3. Stability tests of the fabricated ITO/PBOP (A and a), PBTP (B and b) and PBSeP (C

and c)/Al memory device: (A, B and C) retention time measurement for the ON-, intermediateand-, OFF-states with a constant reading voltage of -1 V; (a, b and c) effect of read pulse of -1 V on the ON-, intermediate- and OFF-states. The inset shows the pulse shape employed

4. SEM images

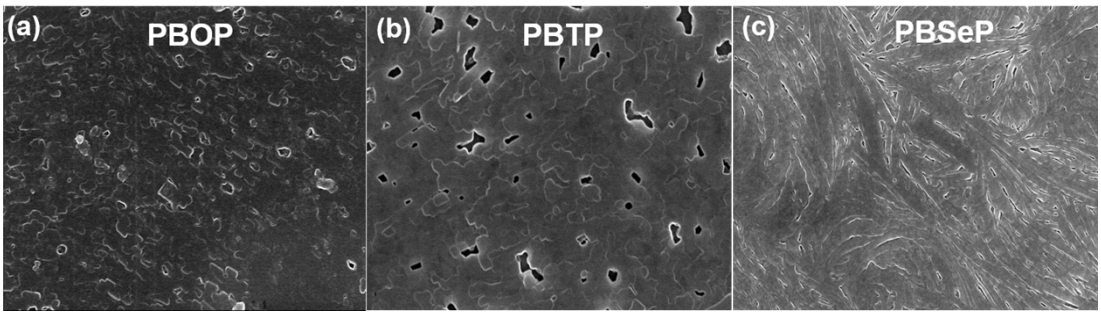


Fig. S4. SEM images of the films of PBOP (a), PBTP (b) and PBSeP (c) (5μm × 5μm).

5. DFT molecular simulation results

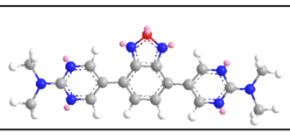
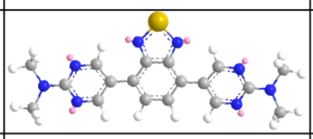
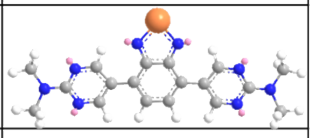
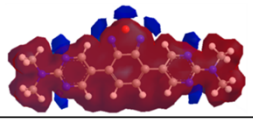
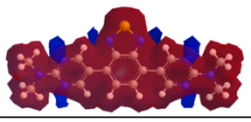
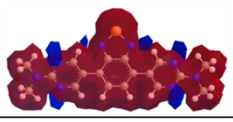
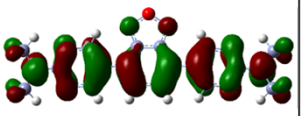
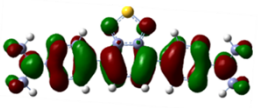
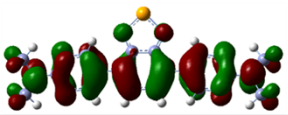
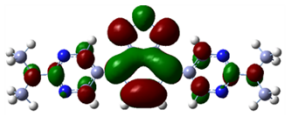
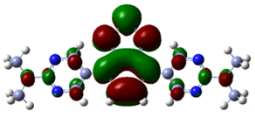
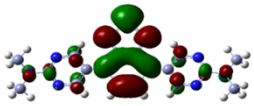
Index	PBOP	PBTP	PBSeP
Optimized Geometry			
ESP			
HOMO			
LUMO			

Figure S5. HOMOs and LUMOs of PBOP, PBTP and PBSeP in their optimized ground-state structures.

6. I-V Curve

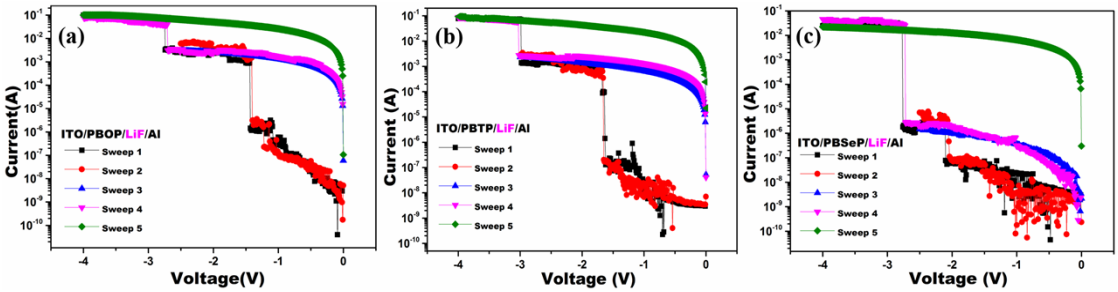


Figure S6. Current-voltage (I-V) characteristics of the memory device with the structure of ITO/compound/LiF (5nm)/Al: (a) PBOP; (b) PBTP; (c) PBSeP.