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Supporting Information: Nonvolatile Ternary Resistive Memory Performance of aBenzothiadiazole-BasedDonor−Acceptor Material on ITO-Coated Glass

Yang Li [1,2,*],Cheng Zhang [1,2],Zhiming Shi [1],Jingni Li [1], Qingyun Qian [1],Songtao Ling [1], Yufen Zhang [1], Xiaolin Zhu [1], Xingzhi Wu [1], Jinlei Zhang [1,*], Run Zhao [1], Yucheng Jiang [1], QijianZhang [3,*], and Chunlan Ma [1,*]

[1] Jiangsu Key Laboratory of Micro and Nano Heat Fluid Flow Technology and Energy Application, School of Physical Science and Technology, Suzhou University of Science and Technology, Suzhou 215009, China; 20164209270@stu.suda.edu.cn (C.Z.); shizhiming2001@163.com (Z.S.); lijingnidw@163.com (J.L.); qianqingyun2000@163.com (Q.Q.); lstzxw0411@163.com (S.L.); zhangyf0015@163.com (Y.Z.); zxlin0909@163.com (X.Z.); wuxingzhi@usts.edu.cn (X.W.); zr@usts.edu.cn (R.Z.); jyc@usts.edu.cn (Y.J.)

[2] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

[3] School of Materials Engineering, Changshu Institute of Technology, Changshu 215500, China

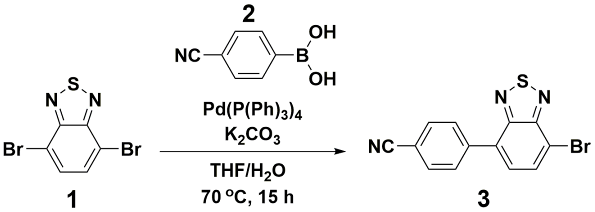
* Correspondence: liyang@usts.edu.cn (Y.L.); zhangjinlei1991@126.com (J.Z.); flashright@163.com (Q.Z.); wlxmcl@mail.usts.edu.cn (C.M.)

1. Experimental section

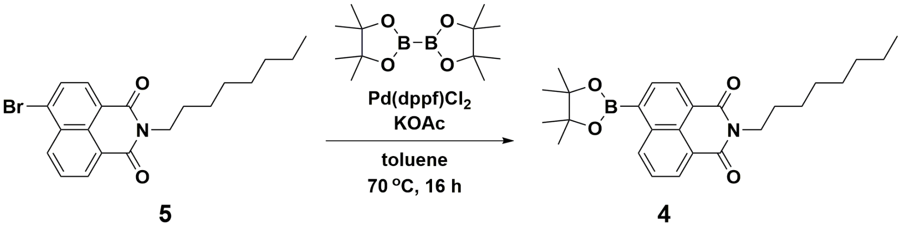
1.1. Materials

2,1,3-benzothiadiazole, 4-cyanobenzeneboronic acid, 4-bromo-1,8-naphthalic anhydride, *n*-octylamine, andbis(pinacolato)diboron (B_2pin_2) were purchased from commercial sources (TCI and Alfa Aesar Ltd.). Compound **5** was synthesized according to the previously reported literature.[1]All other commercially available solvents and reagents were used as received.

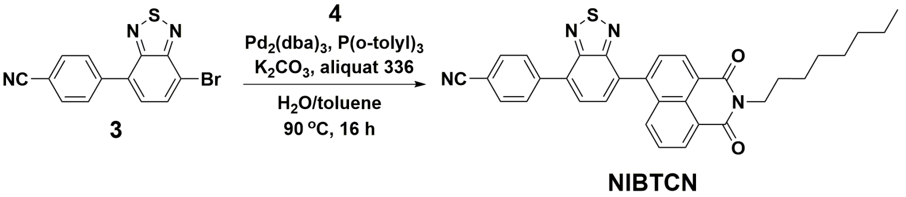
1.2. Synthesis of NIBTCN



4-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)benzonitrile(3):Compound **1** (1.32 g, 4.5 mmol), anhydrous potassium carbonate (2.50 g, 18.1 mmol), tetrakis(triphenylphosphine)palladium ($Pd[P(Ph)_3]_4$) (46.2 mg, 40 μmol), tetrahydrofuran (THF) (30 mL) and distilled water (9 mL) were charged with a 100 mL Schlenk tube under argon protection. The mixture was degassed for 20 min and heated to45 °C for 30 min. A solution of 4-cyanobenzeneboronic acid (compound **2**, 441 mg, 3.0 mmol) in THF (10 mL) was subsequently added dropwise over 1 h, and then the mixture was heated to reflux for 15 h. Then the reaction mixture was cooled down to room temperature, extracted with ethyl acetate and washed with distilled water and brine several times. The organic extract was dried over sodium sulfate and collected by rotary vacuum. Purification of the crude material through column chromatography on silica gel using a mixed mobile phase of dichloromethane and petroleum ether yielded **3** as a kelly solid (1.05 g, 74%). ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 8.08 – 8.01 (m, 2H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.64 (d, *J* = 6.4 Hz,1H).



2-octyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4): Under protection of argon, compound 5 (1.55 g, 4 mmol), bis(pinacolato)diboron (B_2pin_2) (1.52 g, 6 mmol) and anhydrous potassium acetate (1.18 g, 12 mmol) were dissolved into anhydrous toluene (50 mL). The mixture was degassed for 20 min under ambient conditions, then dichloro [1,1'-bis(diphenylphosphino)-ferrocene]palladium(II) (0.29 g, 0.4 mmol) was added quickly and the mixture was degassed for another 10 min. After the reaction mixture was heated at 70 °C for 16 h, it was extracted with dichloromethane and washed with distilled water. The organic extract was dried over sodium sulfate, and solvent was removal under reduced pressure yielded brown viscous oil. Purification by column chromatography on silica gel using dichloromethane-petroleum ether as eluent yielded white solid 4 (1.04 g, 60%). ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 9.10 (d, *J* = 8.5 Hz, 1H), 8.64 – 8.51 (m, 2H), 8.29 (d, *J* = 7.3 Hz, 1H), 7.77 (dd, *J* = 8.4, 7.3 Hz, 1H), 4.25 – 4.08 (m, 2H), 1.80 – 1.67 (m, 2H), 1.48 – 1.40 (m, 12H), 1.34 – 1.20 (m, 10H), 0.89 – 0.84 (m, 3H).



4-(7-(2-octyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)benzonitrile (NIBTCN): Compound**3** (435 mg, 1.0 mmol), compound **4** (316 mg, 1.0 mmol), anhydrous potassium carbonate (552 mg, 4 mmol), toluene (20 mL) and distilled water (4 mL)were charged with a 250 mL three-neck round-bottom flask under argon protection. The mixture was degassed for 15 min before bis(dibenzylideneacetone)palladium (0) ($Pd_2(dba)_3$) (7.32 mg, 8 μmol), tri-o-tolylphosphine ($P(o\text{-}tol)_3$) (9.76 mg, 32 μmol) and 1 drop of aliquot 336 were added quickly. After subsequently degassed again for another 10 min, the mixture was degassed for 20 min and heated to90 °C for 16 h. Then the reaction mixture was cooled down to room temperature, extracted with ethyl acetate and washed with distilled water and brine several times. The organic extract was dried over sodium sulfate and collected by rotary vacuum. Purification of the crude material on silica gel by dichloromethane-petroleum ether as eluent yielded the final product NIBTCN (276 mg, yield 51%).^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 8.75 (d, *J* = 7.5 Hz, 1H), 8.67 (d, *J* = 7.1 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 2H), 8.04 – 7.75 (m, 6H), 7.72 – 7.58 (m, 1H), 4.23 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.44 – 1.25 (m, 10H), 0.88 (t, *J* = 6.3 Hz, 3H);^{13}C NMR (151 MHz, $CDCl_3$, δ): 163.09, 162.87, 153.62, 151.98, 141.76, 140.38, 140.24, 131.73, 131.47, 131.13, 130.94, 130.40, 129.60, 129.45, 129.26, 128.93, 127.98, 127.75, 127.56, 127.29, 126.45, 126.03, 122.07, 117.64, 111.30, 76.32, 76.01, 75.69, 39.56, 30.80, 28.67, 28.33, 27.13, 26.13, 21.62, 13.09; Anal. calcd for$C_{33}H_{28}N_4O_2S$: C, 72.77; H, 5.18; N, 10.29; found: C, 72.42; H, 5.39; N, 10.58.

1.3. Film Deposition and MIM Device Fabrication

The ITO-coated silicate glass substrates were sequentially cleaned with distilled water, acetone, and ethanol via ultrasonication. NIBTCN was thermally deposited onto the substrates under a pressure of ~10^{-6}Torr, with the deposition rate of 1.0 Å/s. Finally, an array of aluminum (Al) electrode with the thickness of about 100 nm was thermally deposited onto the material through a shadow mask of circular patterns. The area of the top electrode for one device cell is 0.0314 mm^2.The electrical switching of the as-fabricated MIM type devices was measured through a Keilthley 4200-SCS (Tektronix UK Ltd, Berkshire, UK) semiconductor characteristic system, wherein the external voltage was applied to the device at the voltage sweeping mode. The detailed sweep parameters of the device testing are shown in Table S1.

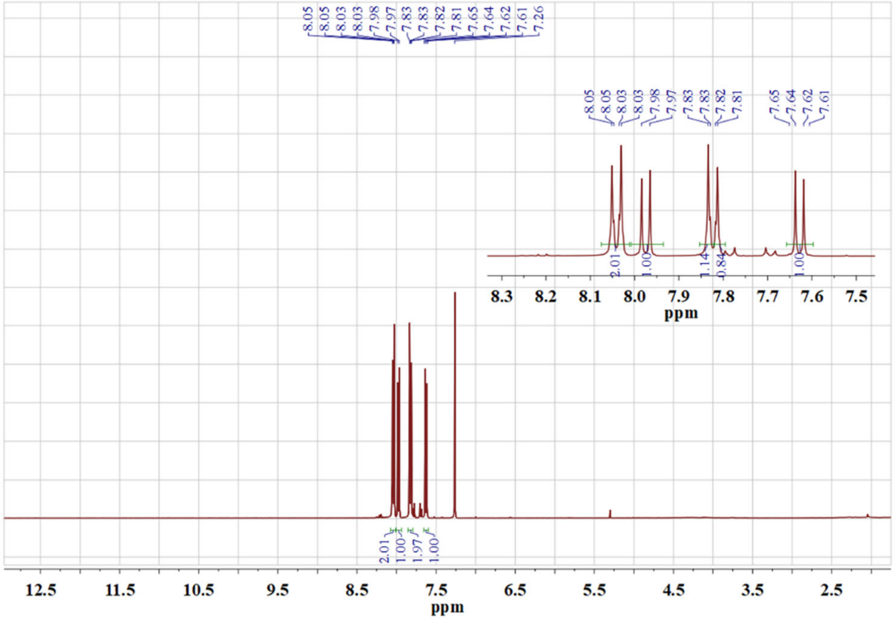


Figure 1. ^{1}H NMR spectrum of compound **3**in CDCl$_3$.

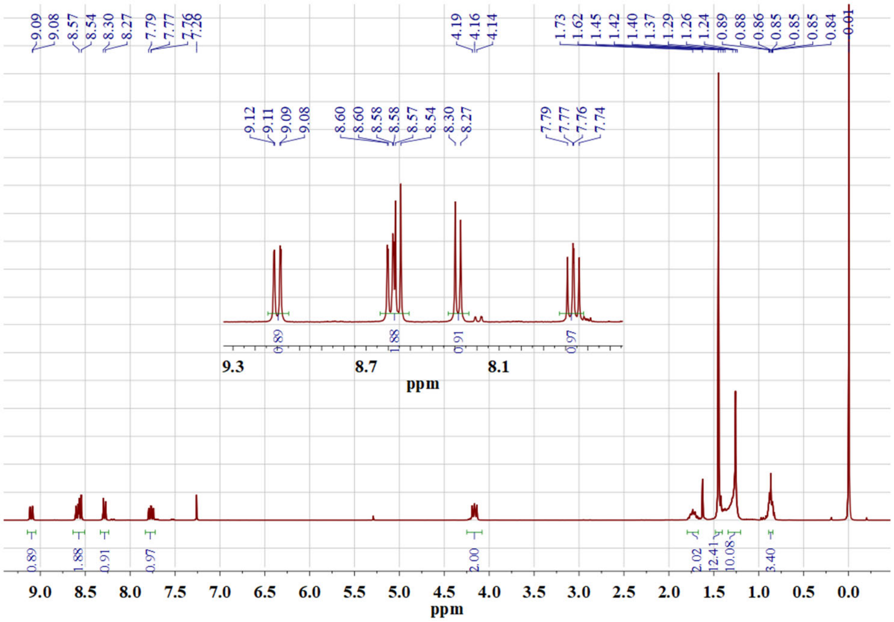


Figure 2. ^{1}H NMR spectrum of compound **4**in CDCl$_3$.

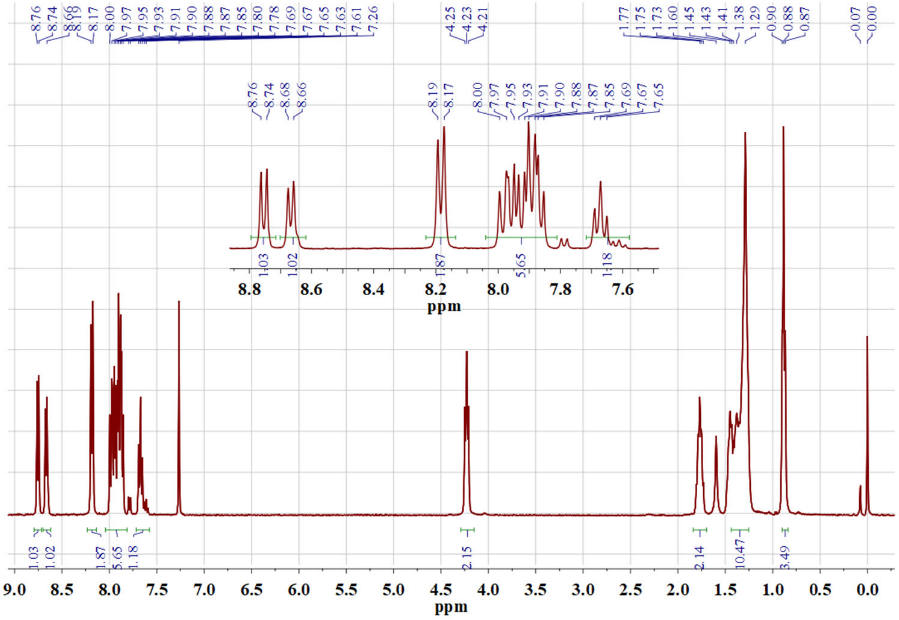


Figure 3. ^{1}H NMR spectrum of NIBTCN in $CDCl_3$.

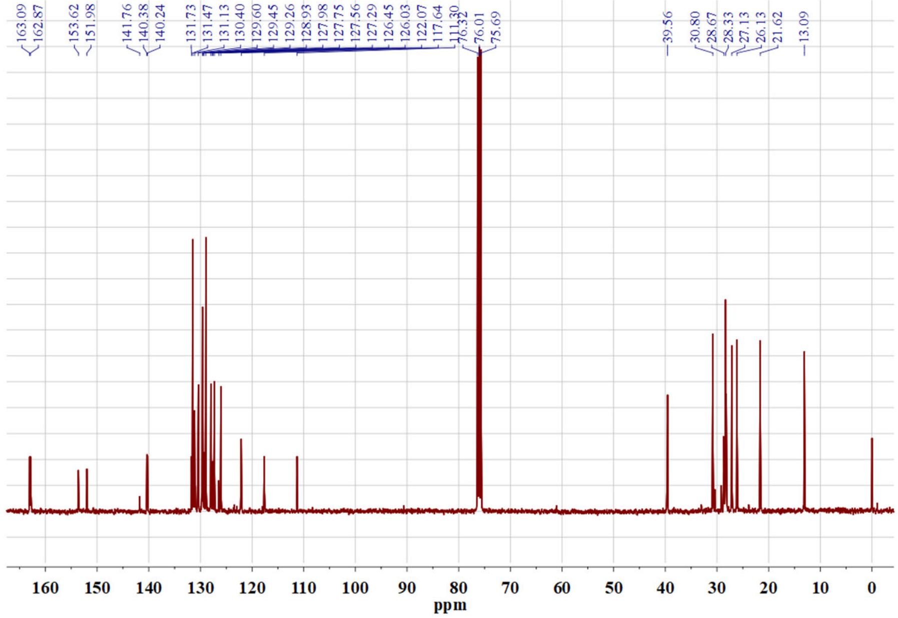


Figure 4. ^{13}C NMR spectrum of NIBTCN in $CDCl_3$.

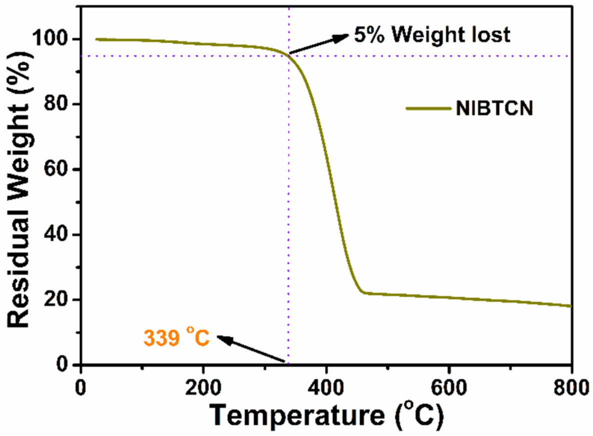


Figure 5. TGA curve of NIBTCN at a heating rate of 10 ºC min^{-1}under a nitrogen atmosphere.

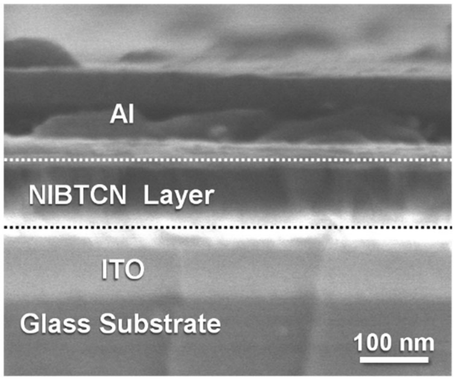


Figure 6. The cross-sectional SEM image of ITO/NIBTCN/Al device.

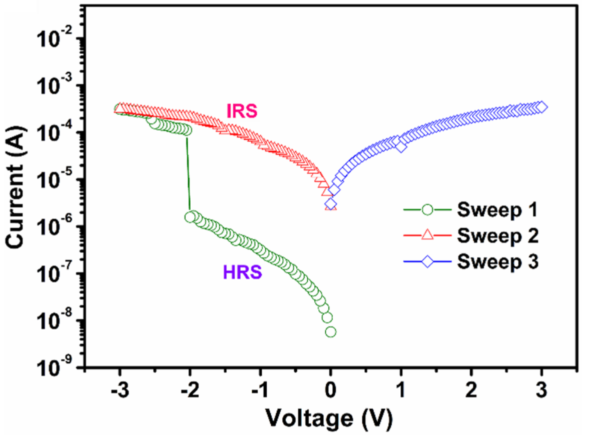


Figure 7. *I*–*V* sweep curves of IRS for the ITO/NIBTCN/Al device.

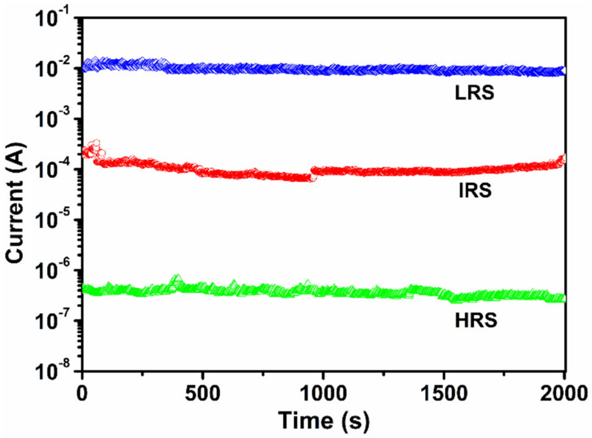


Figure 8. Retention stability of ITO/NIBTCN/Al device at HRS, IRS and LRS under a constant "read" voltage of −0.1 V; the current states were well separated with narrow fluctuations within 1 order of magnitude.

Table 1. Detailed sweep profile and parameters of the device testing.

Test Name	**reIV#1@1**	
Mode	Sweeping	
Speed	Normal	
Sweep Delay	0	
Hold Time	0	
Site Coordinate	0,0	
KTEI Version	V9.0 SP1	
Interlock	High Voltage Enabled	
Device Terminal	A	B
Instrument	SMU1	SMU2
Name	AV	BV
Forcing Function	Voltage Sweep	Voltage Bias
Master/Slave	Master	N/A
Start/Level	0	0
Stop	-5 V or 5 V	N/A
Step	0.05 V	N/A
Number of Points	101	0
Compliance	0.1 A	0.1 A
Measure I	Measured	No
Measure V	Programmed	No
Range I	Limited Auto	Limited Auto
Range V	Best Fixed	Best Fixed
Range C	N/A	N/A
AC Voltage	N/A	N/A
Over Voltage Setting	OFF	OFF
Formulas	RES = AVG(AV/AI)	

Table 2. Optical and electrochemical properties of **NIBTCN.**

Absorption λ_{max} (nm)		**λ_{onset}(nm)**	**E_g[c]**	**HOMO[d]**	**LUMO[e]**	**Injection Barrier**	
Solution[a]	**Film[b]**	**film[b]**	**(eV)**	**(eV)**	**(eV)**	**Hole[f] (eV)**	**Electron[g] (eV)**
360	370	445	2.79	–6.31	–3.51	1.51	0.79

[a] In CH_2Cl_2 solution at 10^{-4} M. [b] Thin film. [c] Estimated from the absorption onset of thin film: $E_g = 1240/\lambda_{onset}$. [d] Determined by the onset of the oxidation peak of CV. [e] Determined by the onset of the reduction peak of CV, as reported in ref.2 and 3. [f] The difference between the work function of ITO and the HOMO energy level. [g] The difference between the work function of Al and the LUMO energy level.

References

1. Li, Y.; Li, H.; He, J.; Xu, Q.; Li, N.; Chen, D.; Lu, J. Inserting thienyl linkers into conjugated molecules for efficient multilevel electronic memory: A new understanding of charge-trapping in organic materials. *Chem. Asian J.***2016**, *11*, 906–914.
2. Li, W.; Roelofs, W.S.; Turbiez, M.; Wienk, M.M.; Janssen, R.A. Polymer solar cells with diketopyrrolopyrrole conjugated polymers as the electron donor and electron acceptor. *Adv. Mater.* **2014**, *26*, 3304–3309.
3. Lin, Y.; Cheng, P.; Liu, Y.; Shi, Q.; Hu, W.; Li, Y.; Zhan, X. Small molecules based on bithiazole for solution-processed organic solar cells. *Org. Electron.* **2012**, *13*, 673–680.