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Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions**

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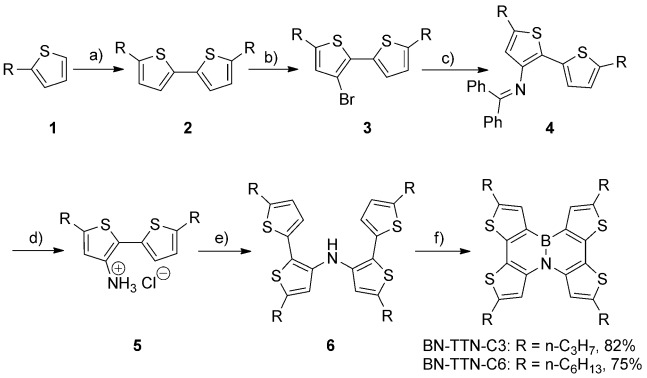
Organic semiconductors have attracted great attention during the past few decades for the development of next-generation electronics.[1] The incorporation of a B–N unit, which is isoelectronic to the C=C moiety, into π systems provides a novel approach in the molecular engineering of organic semiconductors.[2] BN substitution can change the electronic properties of π systems,[3] and afford additional intermolecular dipole–dipole interactions.[4] Therefore, BN-incorporated semiconductors provide new opportunities for organic electronics. Although significant progress has been made in azaborine chemistry,[5,6] the construction of azaborine rings in large π scaffolds remains challenging.[7] Moreover, azaborine compounds are usually susceptible to moisture and oxygen, and their thermal decomposition temperatures are around 200 °C, thus limiting their promising applications as organic materials.[7] As a result, the charge-transport properties of azaborine compounds have rarely been investigated up to now. Only recently, Nakamura and co-workers reported a BN-fused polycyclic aromatic compound which exhibited higher intrinsic hole mobility than its carbon analog by time-resolved microwave conductivity measurements,[7f] implying that BN-substituted aromatics might outperform their carbon analogs in organic electronics. Nonetheless, electronic devices based on azaborine compounds have not yet been demonstrated.

Herein, we synthesize two novel BN-substituted tetrathienonaphthalene derivatives BN-TTN-C3 and BN-TTN-C6 through an efficient one-pot electrophilic borylation method (Scheme 1). Four thiophene rings are fused onto a BN-substituted naphthalene core to extend the π conjugated plane for intermolecular π–π stacking and charge-carrier transport.[8] Alkyl chains are attached to ensure good solubility and to tune the intermolecular interactions.[9] Our investigations indicate that the introduction of the fused thiophene rings effectively improves the aromaticity of the skeleton, and both molecules show excellent chemical and thermal stability. Importantly, organic field-effect transistors (OFETs) based on these two compounds are successfully fabricated, and high hole mobilities up to 0.15 $cm^2V^{-1}s^{-1}$ and on/off ratios over 10^5 are obtained from BN-TTN-C3, which represents the first example of applying azaborine compounds in organic electronic devices.



Scheme 1. Synthetic route to BN-TTN-C3 and BN-TTN-C6. Reagents and conditions: a) Ag_2CO_3, $Pd(OAc)_2$, 2,2′-bipyridine, dioxane, reflux, 24 h; b) *N*-bromosuccinimide (NBS), $CHCl_3$, HOAc, RT, 1 h; c) $Ph_2C{=}NH_2Cl$, Pd_2dba_3, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), *t*BuONa, toluene, 80 °C, 15 h; d) HCl (aq. 6 M), tetrahydrofuran (THF), RT, 10 minutes; e) **3**, $Pd(OAc)_2$, $P(tBu)_3$, *t*BuONa, *o*-xylene, 120 °C, 12 h; f) BBr_3, NEt_3, *ortho*-dichlorobenzene (*o*-DCB), 180 °C, 12 h.

Scheme 1 illustrates the synthetic route to BN-TTN-C3 and BN-TTN-C6. Commercially available 2-alkylthiophenes (**1**) were dimerized through an oxidative coupling reaction.[10] Monobromination of **2** gave compound **3**, which was applied for the Buchwald–Hartwig coupling reaction. Ketimine **4** was hydrolyzed with aqueous HCl in THF to afford ammonium species **5**,[11] which is more stable in air than its amino counterpart. This route is the most efficient one among various attempts to introduce amino groups onto thiophene derivatives. Subsequently, another Buchwald–Hartwig amination between **3** and **5** produced compound **6**. The electrophilic borylation approach was chosen to finish the final

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cyclization step.[7e,f] Compound **6** was simply heated with BBr_3 and NEt_3 in *o*-dichlorobenzene (*o*-DCB) to afford BN-TTN-C3 and BN-TTN-C6. Purification by column chromatography on silica gel and recrystallization from $CHCl_3$/MeOH gave pure products as white solids in around 80% yields. The highly efficient one-pot cyclization step involved an electrophilic borylation of the amino group and subsequent electrophilic substitutions of the two adjacent thiophene rings. Note that using BCl_3 failed to produce the target compounds, probably because of its lower reactivity.

Both compounds exhibit excellent stability to ambient conditions. In consistence with the complexation behavior of other azaborine derivatives,[7e] no change of the absorption features was observed when acids (trifluoroacetic acid), or bases (iPr_2NH, Et_3N, pyridine, dimethylaminopyridine, OH^-, Cl^-, Br^-, and I^-) were added to a solution of BN-TTN-C3 or BN-TTN-C6 in CH_2Cl_2 (1×10^{-5} M). Surprisingly, our compounds remained intact in the presence of 0.01 M nBu_4NF, whereas other azaborine derivatives exhibited specific binding to F^- ions at a low concentration of F^- ions.[7e] In addition, thermogravimetric analysis (TGA) revealed decomposition temperatures (5% weight loss) as high as 358 °C for BN-TTN-C3, and 400 °C for BN-TTN-C6 (Figure S1), the highest values for azaborine compounds reported to date. Such remarkable thermal stability is crucial for their applications in materials science.

The molecular structures and packing modes of both molecules were unambiguously determined by single-crystal X-ray diffraction (Figure 1).[12] In BN-TTN-C3, the B–N bond length (1.474(6) Å) is shorter than the expected value for a B–N single bond (1.58 Å),[5c] but larger than the localized B=N double bond (1.403(2) Å), and close to the delocalized double bond in aromatic 1,2-azaborines (1.446(2) Å) and the parent BN-naphthalene (1.461(1) Å; Figure 1a).[13] The C–B bond (1.52 Å) is slightly shorter than those reported in literature (1.58 Å), so is the C–N bond (1.42 Å versus 1.48 Å).[13a] The C2–C3 single bond (1.414(6) Å) is also shorter than that in bithiophenes (1.454(4) Å).[14] The lengthening of the B=N double bond and the shortening of the formal single bonds indicate significant π electron delocalization in BN-TTN-C3, as suggested by density functional theory (DFT) calculations. The molecular orbitals of BN-TTN-C3 are fully delocalized over the entire backbone, similar to those of CC-TTN-C3 (Figure 2). The HOMO and LUMO energy levels of BN-TTN-C3 also show little difference to those of CC-TTN-C3, only with a slightly larger band gap (3.89 eV versus 3.80 eV). These observations reveal that the azaborine rings are aromatic, which is further supported by nucleus-independent chemical shift (NICS) calculations (Figure 2).[15] The central C_4BN rings in BN-TTN-C3 show a NICS(1) value of −6.0, revealing a moderate yet greater aromaticity than the reported BN-fused dibenzo[*g*,*p*]chrysene (−2.9).[7f] This increased aromaticity, presumably resulting from the more planar structure and the electron-rich thiophene rings, may be an important reason for the remarkably high chemical and thermal stability.[16]

BN-TTN-C3 and BN-TTN-C6 show different packing structures in single crystals. BN-TTN-C3 exhibits *P*- and *M*-helical structures with BN dipole moments opposite to each other (Figure 1b). There are two sets of enantiomers in a unit cell with different C2-C3-C6-C7 dihedral angles (19.03° for *P1-M1* and 16.60° for *P2-M2*), which are much smaller than that of the BN-fused dibenzo[*g*,*p*]chrysene (38.87°)[7f] because of the incorporation of thiophene rings. Each enantiomer is arranged into a sheet along the *a* axis, which forms slipped π stacks along the *b* axis with alternating head-to-tail orientation of the BN dipole moments (*P1-M1-P2-M2*; Figure 1c). The unique dipole–dipole interactions, along with the intermolecular S···S contacts (3.58 Å) and the close π–π stacking (3.44 Å), dominate the crystal growth of BN-TTN-C3, providing a highly ordered packing mode.[17] As revealed by

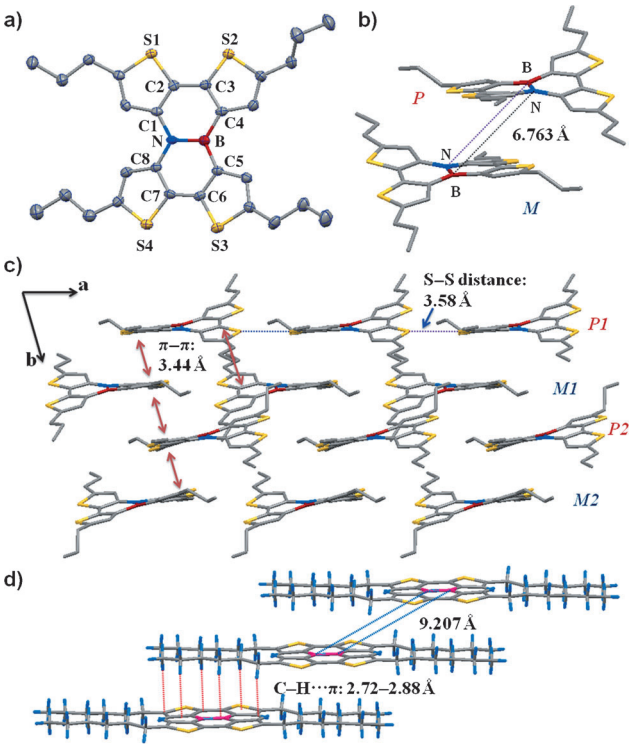

Figure 1. a) ORTEP drawing of BN-TTN-C3 with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. b) *P*-helical and *M*-helical structures of BN-TTN-C3. c) Crystal packing of BN-TTN-C3 viewed along the *c* axis. d) Crystal packing of BN-TTN-C6 with B and N atoms crystallographically undistinguishable.

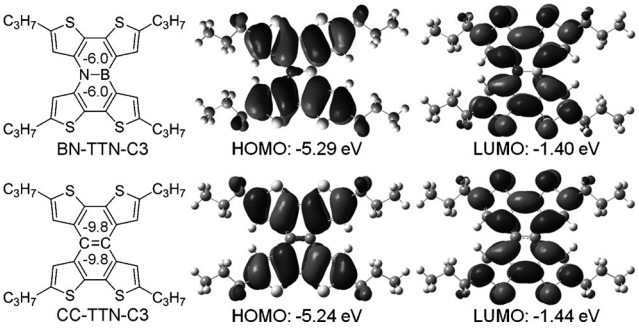

Figure 2. Calculated NICS(1) values, molecular orbitals, and corresponding energy levels of BN-TTN-C3 and its isoelectronic carbon analog CC-TTN-C3.

the calculated electronic couplings (V) based on the single-crystal structure of BN-TTN-C3, the adjacent molecules with good π–π stacking exhibit V values as large as 56.2 meV (Figure S10). In other words, the major charge-transport channel in the solid state is along the π–π stacking direction. In contrast, although BN-TTN-C6 also adopts a layered packing mode with intermolecular S···S contacts of 3.505 Å (Figure S5), B and N atoms are not crystallographically distinguishable, presumably because of the lack of ordered BN dipole interactions (Figure 1d). Scrutiny of the crystal structure reveals that the long alkyl chains formed multiple C–H···π interactions, and the closest intermolecular BN dipole–dipole distance was enlarged to 9.207 Å. Such a long distance may weaken the effect of the intermolecular BN dipole–dipole interactions, resulting in a disordered orientation of BN dipoles.

The different packing structures of BN-TTN-C3 and BN-TTN-C6 in the solid state can also be evidenced from the absorption spectra. The absorption features of BN-TTN-C3 and BN-TTN-C6 in solution are almost identical (λ_{max} = 325 nm), but they are different in solid state (Figure 3).

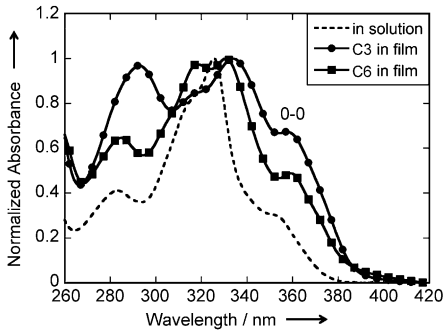

Figure 3. Normalized absorption spectra of BN-TTN-C3 and BN-TTN-C6 in CH_2Cl_2 (dashed line) and in film (solid line). The thin films (50 nm) were prepared by thermal evaporation under 4×10^{-4} Pa.

Both compounds display obvious red-shifts of λ_{max} and enhanced 0–0 transitions compared to those in solution, indicating strong intermolecular interactions in solid state. However, these two compounds show distinct absorption fine structures in the films. These observations indicate great differences of the intermolecular interactions and molecular packings caused by the different length of the alkyl chains. Cyclic voltammetry (CV) experiments were performed to determine the energy levels of BN-TTN-C3 and BN-TTN-C6. These two compounds show almost the same oxidative waves. The HOMO energy level estimated from the onset value is about −5.38 eV, which is in good agreement with the theoretical calculations. The LUMO level, calculated from the HOMO level and the optical band gap (3.31 eV), is about −2.07 eV. The low-lying HOMO energy level suggests that BN-TTN-C3 and BN-TTN-C6 are good candidates as air-stable p-type semiconductors.[18]

OFET devices were successfully fabricated in a bottom-gate/top-contact (BG/TC) configuration. CYTOP (Asahi Glass Co., Ltd.) was spin-coated onto Si/SiO_2 substrates, providing a 230 nm thick film. The organic layer was vacuum-deposited onto the substrates and gold was patterned through a shadow mask as the source/drain electrodes. All devices were measured in ambient conditions, exhibiting p-channel FET characteristics. Devices based on BN-TTN-C3 reveal the highest hole mobility up to 0.15 $cm^2V^{-1}s^{-1}$, with a threshold voltage of −52 V and a current on/off ratio of 5×10^5. Typical transfer and output characteristics are shown in Figure 4.

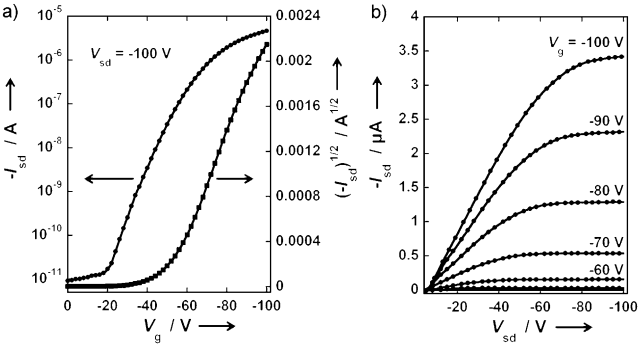

Figure 4. a) Transfer and b) output characteristics of the OFET of BN-TTN-C3 with a hole mobility of 0.15 $cm^2V^{-1}s^{-1}$ (V_{sd} = source-drain voltage, I_{sd} = source-drain current, and V_g = gate voltage).

More than 20 devices were measured with an average carrier mobility of 0.12 $cm^2V^{-1}s^{-1}$. This performance is even better than the carbon analogs with a larger π conjugated plane,[19] which can partly be attributed to the low reorganization energy (λ) of 162 meV, the smallest one among reported polycyclic azaborine compounds (270 and 215 meV).[7e,f] However, BN-TTN-C6 only shows the highest mobility of 0.03 $cm^2V^{-1}s^{-1}$ and an averaged mobility of 0.01 $cm^2V^{-1}s^{-1}$ (20 devices) under optimized conditions (Figure S6). To understand the different device performances, atomic force microscopy (AFM) and X-ray diffraction (XRD) of the thin films deposited on CYTOP™-treated Si/SiO_2 substrates were performed. Both thin films showed similar morphologies with highly crystalline domains in AFM images (Figure S7), which could not be a key factor determining the difference in carrier mobilities. However, further XRD analysis indicated distinct packing modes in the films. Both compounds showed (001) and higher-order diffraction peaks, which indicates lamellar packing structures (Figure S8).[20] The interlayer distance (d-spacing) in BN-TTN-C3 is calculated to be 16.3 Å, which is in good agreement with the molecular length, indicating an edge-on orientation. The d-spacing in BN-TTN-C6 is 17.9 Å, much smaller than the molecular length (about 23 Å), which may result from the packing of hexyl chains with π-moieties due to multiple C–H···π interactions. The significant difference in solid-state packing modes may account for the different device performances.

In conclusion, two BN-substituted tetrathienonaphthalene derivatives, BN-TTN-C3 and BN-TTN-C6, have been synthesized through a highly efficient one-pot electrophilic borylation strategy. The chemical stability of azaborine compounds to F^- is reported for the first time. The molecules exhibit the highest decomposition temperatures up to 400 °C and the smallest reorganization energy of 162 meV among

reported azaborine compounds. Single crystal analysis and DFT calculations reveal improved aromaticity, which may contribute to the remarkable stability. The first organic electronic devices based on azaborine compounds have been demonstrated with the highest FET mobility of $0.15\ cm^2V^{-1}s^{-1}$. Interestingly, different alkyl chains are observed to affect the crystal packing structures and result in different device performances. This work opens the gate of applying the rapidly developing azaborine chemistry in electronic science, and demonstrates a novel molecular engineering concept of organic semiconductors with BN substitutions, providing a broad class of promising BN-substituted semiconductors for future organic electronics.

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