

Synthesis of BN-Fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation

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S Supporting Information

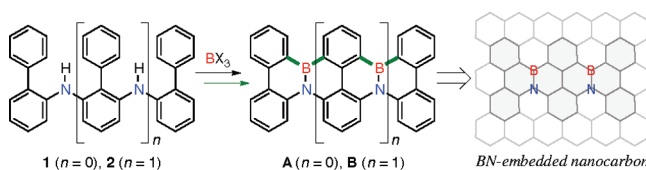
ABSTRACT: A tandem intramolecular electrophilic arene borylation reaction has been developed for the synthesis of BN-fused polycyclic aromatic compounds such as 4b-aza-12b-boradibenzo[*g,p*]chrysene (**A**) and 8b,11b-diaza-19b,22b-diborahexabenzo[*a,c,f,g,j,l,o,p*]tetracene. These compounds adopt a twisted conformation, which results in a tight and offset face-to-face stacking array in the solid state. Time-resolved microwave conductivity measurements prove that the intrinsic hole mobility of **A** is comparable to that of rubrene, one of the most commonly used organic semiconductors, indicating that BN-substituted PAHs are potential candidates for organic electronic materials.

Polycyclic aromatic hydrocarbons (PAHs) are an important class of compounds used to produce organic electronics, dyes, sensors, and liquid crystal displays.¹ Replacement of the C–C units in PAHs by isoelectronic B–N units affords novel hetero- π -conjugated molecules that are structurally similar to their all-carbon analogues but show dramatically different optical and electronic properties because of the local dipole moment or polarized frontier orbitals.² Following the pioneering work of Dewar,³ intensive efforts have been devoted to the synthesis of BN-substituted aromatics. Piers,⁴ Ashe,⁵ and Liu⁶ have carried out extensive research in this direction in recent years.⁷ However, because of the lack of a suitable methodology, construction of polycyclic frameworks with B–N units requires multiple steps;⁴ hence, BN-substituted PAHs have not yet been studied in detail.

We envisioned a tandem electrophilic arene borylation⁸ as an efficient means of constructing extended π -conjugated frameworks with BN ring fusion (Scheme 1). Molecules with such frameworks are not only attractive functional materials but also potential starting compounds for the controlled synthesis of BN-embedded nanocarbons⁹ by surface-assisted coupling¹⁰ or amplification sheet growth.¹¹ Since borylation under conventional conditions did not afford the target compounds, we carefully screened the reaction conditions and identified that a combination of a Lewis acid and a Brønsted base in the appropriate ratio efficiently promotes the tandem electrophilic arene borylation. We report herein the synthesis and physical properties of 4b-aza-12b-boradibenzo[*g,p*]chrysene (**A**, $n = 0$) and 8b,11b-diaza-19b,22b-diborahexabenzo[*a,c,f,g,j,l,o,p*]tetracene (**B**, $n = 1$) to demonstrate potential applications of proposed method and BN-substituted PAHs in material science.

Table 1 summarizes the optimization of the tandem electrophilic arene borylation. Dichloroboraneamine **1'**, prepared *in situ*

Scheme 1. Tandem Intramolecular Electrophilic Arene Borylation To Synthesize BN-Fused PAHs



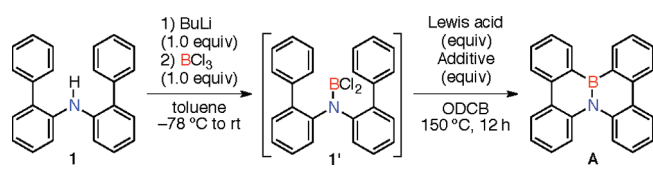
from bis(biphenyl-2-yl)amine¹² **1**, was treated with a variety of Lewis acids and base additives in *o*-dichlorobenzene at 150 °C for 12 h. During the initial screening of Lewis acids such as $AlCl_3$ (entry 1), $AlBr_3$, $GaCl_3$, and $Zn(OTf)_2$, the target compound **A** was not obtained, and the starting amine **1** was recovered. After extensive screening, we found that **A** could be successfully synthesized (yield: 30%) when using a mixture of $AlCl_3$ (4 equiv) and NEt^iPr_2 (1.5 equiv). However, reaction with 0.5, 1.0, and 2.0 equiv of NEt^iPr_2 did not give the desired product (entries 2–5). Screening of the base additives (entries 6–11) indicated that the optimum product yield (67%) was achieved when using 1.5 equiv of 2,2,6,6-tetramethylpiperidine (TMP) (entry 6). Thus, we concluded that the $AlCl_3$ /TMP stoichiometry plays an important role in enhancing the product yield (entries 12–16). The sluggish conversion in the presence of low and high concentrations of the base was possibly due to the decomposition of the product and the deactivation of $AlCl_3$, respectively. The other Lewis acids considered were not as effective as $AlCl_3$ (entries 17–21). It is noteworthy that boron sources other than BCl_3 , such as $BF_3 \cdot Et_2O$, BBr_3 , and $B(OMe)_3$, did not afford the target compound **A** even under the optimized conditions.

The structure of **A** has been determined by X-ray crystallography (Figure 1a). The B–N bond length (1.426(3) Å) is shorter than in typical BN aromatics (1.45–1.47 Å),^{3–5} thus confirming the double bond character.¹³ On the other hand, the B–C1, B–C2, N–C3, and N–C4 lengths in **A** are 1.535(3), 1.534(3), 1.442(3), and 1.448(3) Å, respectively, indicating that these are single bonds. The aforementioned observations reveal the low aromaticity of BNC₄ rings and are consistent with the results of nucleus-independent chemical shift (NICS) analysis (*vide infra*). Because of steric repulsion between the hydrogen atoms at the *ortho* position and the heteroatoms (dihedral angle C5–C7–C6–C8, 38.87°), **A** adopts a twisted conformation and

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Table 1. Screening of Lewis Acids and Brønsted Bases



entry ^a	Lewis acid (equiv)	additive (equiv)	yield ^b (%) of A
1	AlCl ₃ (4.0)	none	0
2	AlCl ₃ (4.0)	NEt ₃ Pr ₂ (0.5)	0
3	AlCl ₃ (4.0)	NEt ₃ Pr ₂ (1.0)	0
4	AlCl ₃ (4.0)	NEt ₃ Pr ₂ (1.5)	30
5	AlCl ₃ (4.0)	NEt ₃ Pr ₂ (2.0)	0
6 ^c	AlCl ₃ (4.0)	2,2,6,6-tetramethylpiperidine (1.5)	67 ^d
7	AlCl ₃ (4.0)	1,2,2,6,6-pentamethylpiperidine (1.5)	27
8	AlCl ₃ (4.0)	2,4,6-collidine (1.5)	27
9	AlCl ₃ (4.0)	Proton Sponge (1.5)	<1
10	AlCl ₃ (4.0)	NCy ₂ Me (1.5)	15
11	AlCl ₃ (4.0)	^t Bu ₃ N (1.5)	16
12	AlCl ₃ (4.0)	2,2,6,6-tetramethylpiperidine (1.0)	0
13	AlCl ₃ (4.0)	2,2,6,6-tetramethylpiperidine (2.0)	42
14	AlCl ₃ (3.0)	2,2,6,6-tetramethylpiperidine (1.5)	0
15	AlCl ₃ (5.0)	2,2,6,6-tetramethylpiperidine (1.5)	34
16	AlCl ₃ (6.0)	2,2,6,6-tetramethylpiperidine (2.25)	28
17	AlBr ₃ (4.0)	NEt ₃ Pr ₂ (1.5)	30
18	AlBr ₃ (4.0)	2,2,6,6-tetramethylpiperidine (1.5)	36
19	GaCl ₃ (4.0)	NEt ₃ Pr ₂ (1.5)	38
20	GaCl ₃ (4.0)	2,2,6,6-tetramethylpiperidine (1.5)	6
21	Zn(OTf) ₂ (4.0)	NEt ₃ Pr ₂ (1.5)	0

^a Reactions were carried out on a 0.6 mmol scale. ^b The yield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as internal standard. ^c The reaction was carried out on a 15 mmol scale. ^d Isolated yield.

hence has a unique packing structure (Figure 1b). That is, the molecules are arranged in an offset face-to-face stacking array with a π - π distance of 3.3–3.6 Å; in this arrangement, the local dipole moments of the B–N bonds also offset each other. Each array includes an enantiomer with a left- or right-handed helical structure (*M*-helix (shown in pink) or *P*-helix (shown in blue), respectively) with CH- π interaction (3.0–3.4 Å). To understand the isoelectronic relationship between B–N and C–C units, the structure of the isoelectronic carbon analogue, dibenzo[*g,p*]chrysene, was determined by X-ray crystallography (Figure 1c,d). The central C1–C2 bond is highly olefinic (1.3882(16) Å) and much shorter than the four radial C–C bonds (1.4608(19)–1.4657(18) Å), indicating small degree of bond alternation and low aromaticity of the central rings, as observed in **A**. The molecular arrangement in this analogue is the same as that in **A**, and surprisingly, the lattice constants, too, are nearly equal to those of **A**. Further, BN substitution does not cause any notable change in the melting point (**A**, 227 °C; dibenzo[*g,p*]chrysene, 229 °C) but significantly improves the organic solubility (solubility in Et₂O and AcOEt: **A**, 4.4 and 7.7 mg/mL; dibenzo[*g,p*]chrysene, 2.5 and 5.0 mg/mL), probably owing to its dipole moment.

Time-resolved microwave conductivity (TRMC) measurements¹⁴ confirm that **A** has high intrinsic hole mobility (0.07 cm² V⁻¹ s⁻¹), rivaling that of rubrene (0.05 cm² V⁻¹ s⁻¹),

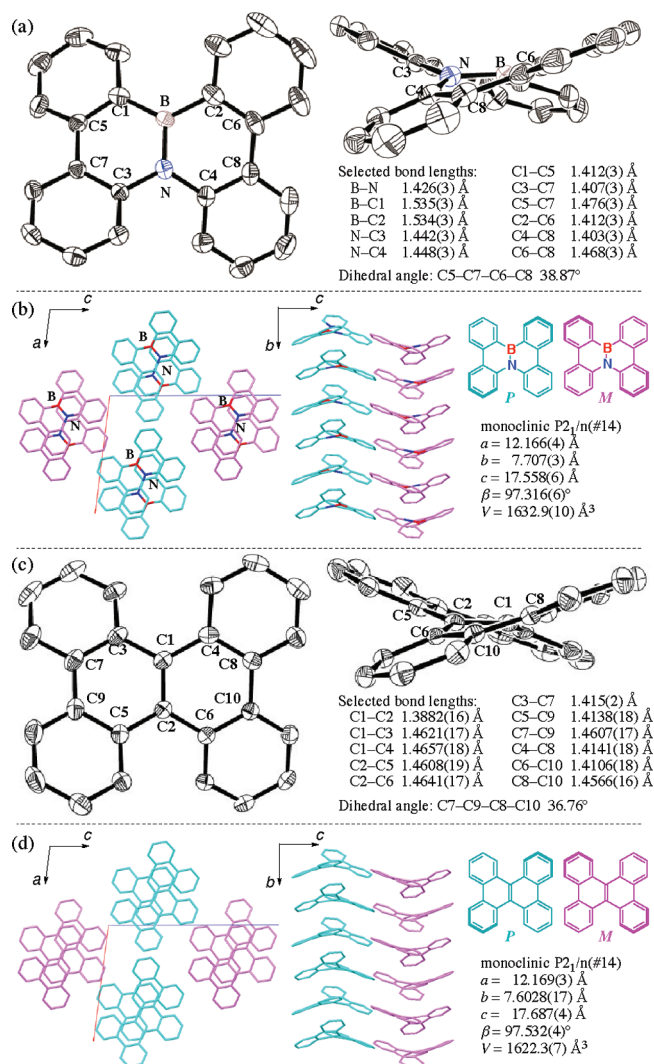


Figure 1. ORTEP drawing and packing structure of **A** (a,b) and dibenzo[*g,p*]chrysene (c,d). Thermal ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity. (*P*)-enantiomer, blue; (*M*)-enantiomer, pink.

one of the most popular organic semiconductors.^{14d} Interestingly, the hole mobility of dibenzo[*g,p*]chrysene is only one-tenth that of **A** (0.007 cm² V⁻¹ s⁻¹). The transient conductivity is not quenched even in a SF₆ environment, suggesting that the major charge carriers in **A** are positive charges (holes). The pseudo-first-order decay kinetics (Figure 2a) also indicate that the mobile holes are trapped rapidly by impurities/structural defects at interfaces, rather than the bulk recombination with negative charges via second-order reactions in the polycrystalline phases.

To gain a deeper insight into the hole mobility, the electronic coupling *V* (meV) between neighboring molecules is calculated from the X-ray crystal structures of **A** and dibenzo[*g,p*]chrysene (Figure 3).^{15,16} Although the molecular packing is virtually the same in these compounds, the electronic coupling varies significantly. The *V* values along the *a*-axis in **A** (6.1 and 2.4 meV, Figure 3a) are 10 times larger than the corresponding values in dibenzo[*g,p*]chrysene (0.6 and 0.3 meV, Figure 3c), while those along the *b*- and *c*-axes are comparable to each other (Figures 3a–d). We suppose that the BN-substitution-induced partial localization of the frontier orbitals (*vide infra*) strengthens the electronic coupling

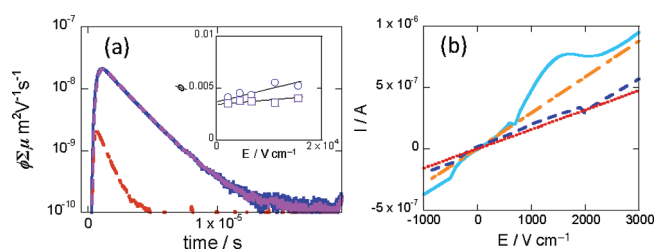


Figure 2. (a) Conductivity transients monitored for the polycrystalline phase of **A** in Ar (blue) and SF₆ (violet) environments. Identical traces were observed for both atmospheres. The kinetic trace for transient conductivity was also observed for dibenzo[*g,p*]chrysene (red). Excitation was carried out at 355 nm using 13 mJ cm^{-2} pulses for all transients. Dependence of ϕ on the applied electric field strength between interdigitated Au electrodes with a $5\text{-}\mu\text{m}$ gap. The values of ϕ were determined by photocurrent integration under illumination of a thin film of **A** (120 nm thick) and dibenzo[*g,p*]chrysene (80 nm thick) at 355 nm, 22 mJ cm^{-2} . The photocurrent under 355-nm illumination was also traced using identical samples; the I – V traces are illustrated in (b). Blue dashed and red dotted lines are the traces of **A** (dark and illuminated, respectively), and turquoise solid and orange dot-dashed lines are the traces of dibenzo[*g,p*]chrysene (dark and illuminated, respectively).

along the *a*-axis in **A**, leading to improvement of the total hole mobility. The reorganization energies of **A** and dibenzo[*g,p*]chrysene are 0.21541 and 0.20413 eV, respectively.^{14,15} Such a small difference is unlikely to be a dominant factor affecting the difference in the hole mobilities of these compounds.

In cyclic voltammetry (CV) experiments, reversible oxidation and reduction waves with peak potentials at +0.76 V (+0.89 V) and –2.77 V (–2.65 V) vs Fc/Fc⁺, respectively,¹⁷ are observed for **A** (dibenzo[*g,p*]chrysene). BN substitution leads to a negative shift in the redox potential, which can partially account for the improved hole mobility.

The aromaticities of the six-membered rings in **A** and dibenzo[*g,p*]chrysene are evaluated by NICS calculations (Figure 4).¹⁸ Interestingly, the BNC₄ rings in **A** have low aromaticity, as suggested by their NICS(1) value of –2.9,¹⁹ whereas the corresponding C₆ rings in dibenzo[*g,p*]chrysene have moderate aromaticity (–6.5). On the other hand, BN substitution does not significantly affect the aromaticity of the surrounding C₆ rings in **A** (cf. benzene: –11.2). Despite the low aromaticity of the central BNC₄ rings, the π -conjugation in **A** is extended over the entire molecule and reasonable polarization¹⁶ is observed, as indicated by molecular orbital calculations. It should be noted that similar trends were observed in extended π -conjugated molecule **B**.²¹

Based on the present synthetic strategy, we state that an extended π -conjugated framework with two fused BN rings can be synthesized in two steps from commercially available sources (Scheme 2). *N,N'*-Bis(biphenyl-2-yl)biphenyl-2,6-diamine (**2**), which was prepared from 2,6-dichlorobiphenyl and 2-aminobiphenyl in 87% yield, was used for the synthesis of 8b,11b-diaza-19b,22b-diborahexabenzo[*a,c,f,g,j,l,o,p*]tetracene (**B**).²² Introduction of boron substituents in **2** and subsequent tandem electrophilic arene borylation afforded **B** in 32% yield.

The results of CV experiments indicate that **B** shows an irreversible oxidation wave and a reversible reduction wave with peak potentials at +0.10 and –1.57 V, respectively (vs Fc/Fc⁺). While the electrochemical HOMO–LUMO gap (1.67 eV) in **B** is smaller than that in pentacene (2.09 eV),²³ no obvious decomposition was observed, even at the melting point (358 °C) under atmospheric conditions. Despite its polycyclic aromatic structure,

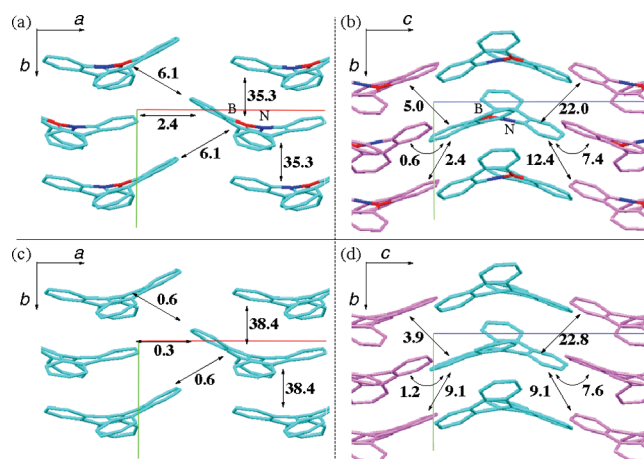


Figure 3. Electronic coupling V (meV) between neighboring molecules in the X-ray crystal structures of **A** (a,b) and dibenzo[*g,p*]chrysene (c,d).

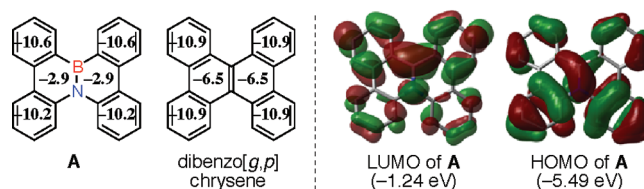
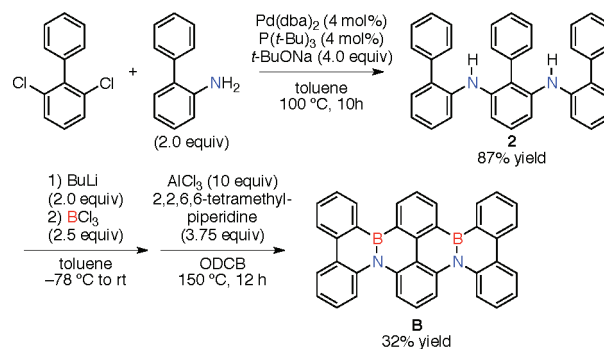


Figure 4. NICS(1) values of **A** and dibenzo[*g,p*]chrysene, and the Kohn–Sham LUMO and HOMO of **A** at the B3LYP/6-31G* level.

Scheme 2. Two-Step Synthesis of **B**



B is moderately soluble in organic solvents such as chlorobenzene (6.7 mg/mL) and 1,2-dichlorobenzene (8.6 mg/mL), probably owing to its flexible molecular framework and dipole moment. These advantageous physical properties of **B** make it suitable for use in organic electronics.

In summary, we have developed a tandem intramolecular electrophilic arene borylation to synthesize BN-fused polycyclic aromatic compounds that adopt twisted geometries. TRMC measurements confirm that substitution of the C–C units in dibenzo[*g,p*]chrysene with isoelectronic B–N units dramatically enhances hole mobility, owing to the strong electronic coupling between neighboring molecules in the solid state. Our strategy is simple and practical, and it can be employed for the extension of π -conjugated frameworks, thus forming the basis for pioneering research in material science and spurring the development of bottom-up approaches toward BN-embedded nanocarbons.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details, characterization data, and computations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Bis(biphenyl-2-yl)amine **1** was prepared in 98% yield from commercially available 2-bromobiphenyl and 2-aminobiphenyl.
- (13) The typical length of the B=N bond is 1.37–1.40 Å. On the basis of the atomic radii of B and N, the length of the B–N bond is expected to be 1.58 Å. See ref 2b and citations therein.
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- (16) Electronic coupling (V) and reorganization energy (λ) calculations were performed using the PW91 or B3LYP hybrid functional with the DZP basis set of the ADF2010 program. The electronic hopping rate (W) is proportional to V^2 based on the Marcus–Hush equation. See ref 14c and citations therein.
- (17) Redox potentials were determined by cyclic voltammetry measurements in THF (E_{red}) or CH_2Cl_2 (E_{ox}) with 0.10 M $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ or $n\text{-Bu}_4\text{N}^+\text{BPh}_4^-$. See the Supporting Information for details.
- (18) DFT calculations, including NICS analysis, were performed using the B3LYP hybrid functional with the 6-31G(d) basis set implemented in the Gaussian 03 or 09 program. See the Supporting Information for details.
- (19) Reported NICS(1) values for the BNC₄ rings in BN-substituted aromatics are –4.5 (ref 4d) and –9.5 (ref 4e).
- (20) Moran, D.; Stahl, F.; Bettinger, H. F.; Schaefer, H. F., III; Schleyer, P. V. R. *J. Am. Chem. Soc.* **2003**, *125*, 6746.
- (21) NICS(1) values for the four BNC₄ rings in **B** are –2.2 to –2.6, while those for the six C₆ rings are –10.1 to –11.2. See the Supporting Information for details.
- (22) Isoelectronic carbon analogue: Mochida, K.; Kawasumi, K.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 10716.
- (23) $E_{\text{ox}} = 0.22$ V, $E_{\text{red}} = -1.87$ V: Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukui, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.