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Efficient Modular Synthesis of Substituted Borazaronaphthalene

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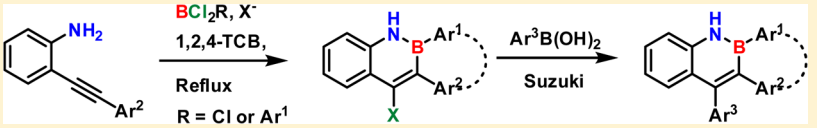
Supporting Information



ABSTRACT: A highly efficient modular synthetic method for BN-fused polycyclic aromatic hydrocarbons (PAHs) composed of a borazaronaphthalene core along with multiple functionalized sites is reported. The halogenated 2,1-borazaronaphthalene cores are constructed through a ring-closing reaction between *o*-ethynylaniline derivatives and boron halides. The controllable halogen substituents make further derivatization of 2,1-borazaronaphthalene cores feasible by using metal-catalyzed cross-coupling reactions. On the basis of the carefully designed precursors, various functional aromatic rings can be fused to the azaborine core via a one-pot nucleophilic tandem reaction, affording previously inaccessible PAHs in moderate yields.

Polycyclic aromatic hydrocarbons (PAHs) have attracted considerable interest, given their wide applications in organic semiconducting materials and electronic devices, such as organic light-emitting diodes (OLEDs),[1a] organic field-effect transistors (OFETs),[1b,c] and organic solar cells (OSCs).[1d,e] In comparison with conventional inorganic materials, they have several advantages, such as light weight, low cost, flexible tailored properties, convenient large-area fabrication, and the great possibility of postfunctionalization.[2] For the past few years, the replacement of a CC unit with its isoelectronic and isostructural BN unit in PAHs has become a promising strategy to tune the molecular geometries, electronic properties, and molecular packing patterns in solid phases,[3] which could decrease the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), lower the reorganization energy in the single crystals, and afford additional intermolecular dipole−dipole interactions.[4] Therefore, the synthesis of novel functionalized BN-PAHs can provide new opportunities for high-performance organic optoelectronic devices.

In particular, 2,1-borazaronaphthalene, which represents one of the smallest BN-PAHs, is a good platform to construct larger functional BN-PAHs. Pioneering efforts by several research groups have demonstrated successful synthesis and post-functionalization of 2,1-borazaronaphthalene. Dewar and his co-workers synthesized 2,1-borazaronaphthalene via an electrophilic substitution, where further functionalization at the B atom could be achieved through nucleophilic substitution and Stille coupling.[5] On the basis of 2,1-borazaronaphthalene, Molander brominated C3 near the B atom to achieve further functionalization through Suzuki−Miyaura cross-coupling reactions with potassium organotrifluoroborates.[6] Paetzold and co-workers also synthesized C4-substituted 2,1-borazaronaphthalene via a three-component reaction.[7] Despite all of the pioneering work above, an efficient construction of 2,1-borazaronaphthalene with all three sites, B atom, C3, and C4, to be modified remains difficult. Herein, we report for the first time the synthesis of halogenated 2,1-borazaronaphthalene and their derivatives through a nucleophilic reaction between *o*-ethynylaniline derivatives and boron halides, which not only provides a feasible way to modify B, C3, and C4 positions effectively but also affords previously inaccessible larger BN-PAHs through a modular synthetic strategy.

To demonstrate our design, we first chose 2-(phenylethynyl)aniline and dichloro(phenyl)borane as the model systems for simplicity. As shown in Scheme 1, the target product, 4-chloro-2,3-diphenyl-2,1-BN-naphthalene (**2a**), can be smoothly prepared in good yield by a one-pot reaction. After examination of several conditions, the solvent, temperature, and reaction time were carefully optimized. It is proved that the best yield of 82% could be achieved in 1,2,4-trichlorobenzene (1,2,4-TCB) at 220 °C for 12 h. The ring-closing and halogenation reactions can be simply completed simultaneously. Triethylamine was added as a weak base to neutralize the HCl generated in the ring-closing reaction. To our delight, the reaction can be easily applied to a wide range of substrates. As shown in Scheme 1, cyclizations with electron-neutral (**2c**), electron-poor (**2d**), and electron-rich (**2e**) 2-(arylethynyl)anilines and even a terminal alkyne (**2b**) proceeded in good yields, and most of them gave more than 80% yields except for **2e**, which is probably due to the instability of the precursor. All of the products were confirmed by HRMS and ^{1}H, ^{13}C and ^{11}B NMR spectra. In addition, the molecular structure of **2a** was further confirmed by a single-

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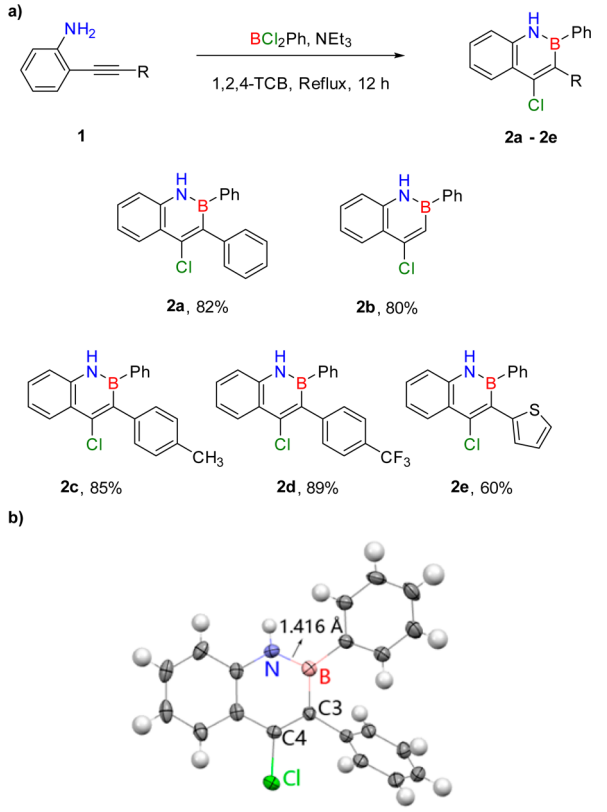
Scheme 1. (a) Synthesis of 4-Chloro-2,1-BN-naphthalenes 2 and (b) Single-Crystal Structure of Compound 2a



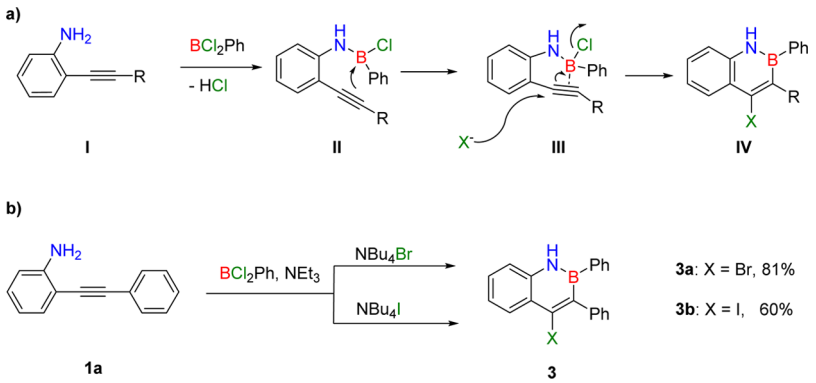
crystal structure, which was obtained in chloroform solution by slow evaporation.[8] The X-ray crystal data associated with the solid-state superstructures are summarized in the Supporting Information and illustrated in Scheme 1b. The X-ray diffraction data of **2a** indicate that the B−N bond length (1.416(4) Å) is shorter than the expected value of a B−N single bond (1.58 Å),[9a] yet a little longer than the localized B═N double-bond length (1.403(2) Å). In comparison with the pristine BN-naphthalene (1.461(1) Å),[9] compound **2a** has a much shorter B−N bond, implying a stronger localization in this structure. The C-substituted phenyl ring is approximately perpendicular to the central BN ring with a dihedral angle of 68.1(4)°, and between the B-substituted phenyl ring and BN ring, the dihedral angle is smaller (27.2(5)°).

Moreover, the chlorine substituent in compound **2** can be easily replaced by other halogens simultaneously within the ring-closing reaction, simply by adding the halogen ions as nucleophiles in the reaction (Scheme 2b). Three equivalents of tetrabutylammonium bromide (TBAB) and tetrabutylammonium iodide (TBAI) was added in situ to generate the corresponding Br- and I-substituted products in good yields, respectively. **2a** was also observed in these reactions, which could be separated by means of gel permeation chromatography (GPC). The controllable diverse halogen substitution at BN-PAHs provides possibilities to tune the molecular packing in the solid state toward high-performance organic electronic materials, since halogen substituents could afford additional interactions, such as halogen−halogen interactions and halogen−π interactions.[10] In addition, the intermolecular displacements and distances could also be substantially varied by tuning the substituent halogen substituents.[11] For instance, substitution with large halogens such as bromine and iodine could increase the torsional angle of molecules and reduce their crystallinity, resulting in the performance improvement of OSCs.[12] However, the synthesis of halogenated structures is inconvenient. It is usually required to bring in the halogen substituents in the initial step of the whole synthesis, which would increase the synthetic complexity of target molecules containing different halogens. In this context, our strategy provides an efficient way to construct BN-PAHs with different halogens, and the halogens can be achieved in the final step together with a ring-closing reaction.

According to the experimental results and the literature report,[13] a proposed mechanism is illustrated in Scheme 2a. First, BCl_2Ph combined with an amino group by eliminating HCl to afford the B−N-bonded intermediate **II**. Then the alkyne was activated by coordinating with the empty orbital of B atom. Subsequently, the nucleophile attacked the electron-deficient alkyne, followed by the formation of 2,1-BN-naphthalene backbone **IV**. According to this mechanism, when we use different halide nucleophiles, the substituent at the C4 site can be changed correspondingly.

The different halogen substituents at the C4 site of 2,1-BN-naphthalene could not only tune the electronic properties and change the molecular arrangement but also allow postfunctionalization at the C4 site. We then turned toward examining the metal-catalyzed cross-coupling reactions. Taking compound **3a** for example, its reactivity toward a Suzuki cross-coupling reaction was investigated with different arylboronic acids. As

Scheme 2. (a) Proposed Mechanism of the Ring-Closing Reaction of *o*-Ethynylaniline Derivatives and (b) Halogen-Exchanging Reactions



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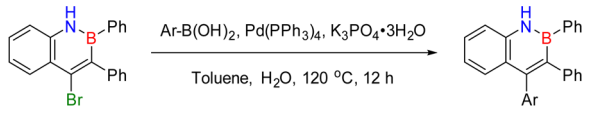
shown in Table 1, the coupling reactions between compound **3a** and electron-neutral and electron-rich arylboronic acids gave

Table 1. Suzuki Cross-Coupling Reactions of Compound 3a



3a **4**

entry	substrate Ar	product	yield (%)
1	phenyl	**4a**	90
2	thienyl	**4b**	91
3	*p*-methoxycarbonylphenyl	**4c**	75

excellent yields of up to 91% (**4a**,**b**). The electron-poor compound **4c** can also be obtained in a satisfying yield of 75%. Such preliminary results suggest a good chemical compatibility of the borazaronaphthalene cores. In comparison with the reported methods, our conditions of cross-coupling reactions on 2,1-borazaronaphthalene do not need expensive catalysts and strict operations. We believe that other cross-coupling reactions such as Stille, Negishi, and Sonagashira reactions could also occur in addition to Suzuki reactions. Thus, our work for the first time realized tunable and effective postfunctionalization at C4 in BN-naphthalene.

The absorption and fluorescence spectra of these compounds were recorded in $CHCl_3$ solution (Figures S1 and S2 in the Supporting Information). All of the compounds exhibited similar absorption maxima and onset, except for **2b**,**e** (Figure 1). The slight difference in absorption may be related to the

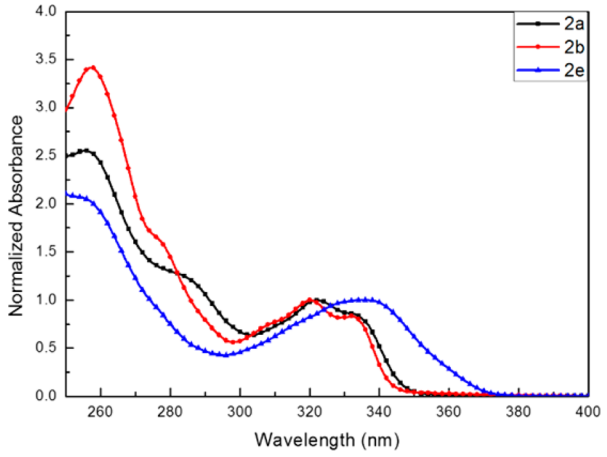
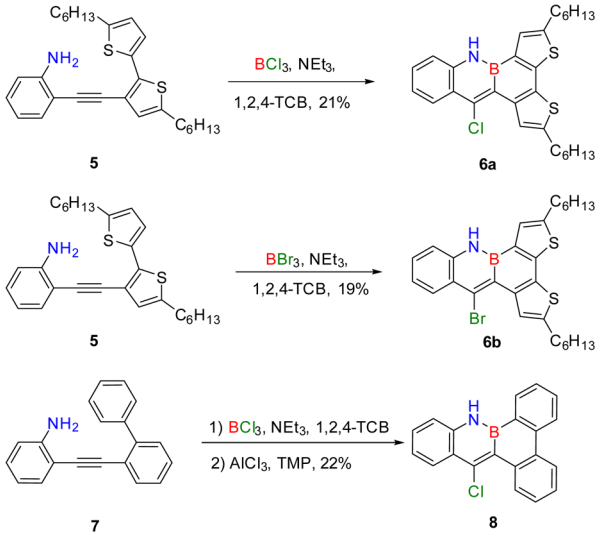


Figure 1. UV−vis absorption (1×10^{-5} M) of compounds **2a**,**b**,**e** in chloroform.

bulky aryl group, which restricts the rotation of the substituent groups at the C3, C4, and B atom, and influences the $\pi-\pi$ interaction between the substituent aryl group and BN ring.

Interestingly, larger BN-fused conjugated backones could be constructed through a tandem synthetic strategy derived from the above synthetic method, which closed two six-membered rings in one step (Scheme 3). Boron trichloride and boron tribromide were used to introduce the chlorine and bromine atoms in the final products, respectively. The formation of compounds **6a**,**b** and **8** involved two steps. First, the nucleophile attacked the alkyne, closing the first ring, which is identical with the mechanism described in Scheme 2a.

Scheme 3. Synthesis of Larger Conjugated Systems through the One-Pot Nucleophilic Tandem Reaction



Second, a Friedel−Crafts-like electrophilic substitution reaction occurred to close the second ring, after elimination of the third halide anion. For compounds **6a**,**b**, these two steps of the reaction can be completed in one pot because of the electron-rich properties of the bithiophene fragment.[14] However, for compound **8**, adding $AlCl_3$ is necessary in the second step for the electrophilic substitution, because the biphenyl group is less electron rich than the bithiophenyl group.[15]

The absorption and emission spectra of compounds **6** and **8** were investigated, as shown in Figure S3 in the Supporting Information. Compounds **6** show a broad absorption band peak at 428 nm which might be ascribed to intramolecular charge transfer.[16] In the emission spectra, compounds **6** show a substantial red shift of the emission maxima in comparison to compound **8** (from λ 436 to 522 nm). The results indicate that the photophysical properties of these BN-fused PAHs could be easily adjusted by changing the cyclization precursor, providing a convenient way to synthesize BN-fused PAHs with different properties.

From these examples, we believe that this method could be used in more fused rings, which would enable the synthesis of more complicated and functional BN-fused PAHs. Further research on the application of these BN-fused PAHs in electronic devices is ongoing.

In summary, we have developed an efficient method to synthesize 2,1-borazaronaphthalene-based PAHs. Starting from *o*-ethynylaniline derivatives, we obtained the 2,1-BN-naphthalene cores in one step and different halogen anions could be attached to the C4 site. The halogen at the C4 position could be easily functionalized by a Suzuki cross-coupling reaction. Larger BN-fused PAHs were also constructed through one-pot nucleophilic tandem reactions. Taking advantage of the chemical flexibility and extensibility, more BN-PAH-based materials with diversiform structures can be synthesized through such a modular one-pot tandem synthetic protocol. Application of this chemistry to functional optical and electronic materials is currently being explored in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00811.

Experimental details, photophysical properties, crystallographic data, and NMR spectra (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(8) CCDC 1491582 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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