Synthesis of NBN-Type Zigzag-Edged Polycyclic Aromatic Hydrocarbons: 1,9-Diaza-9a-boraphenalene as a Structural Motif

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Supporting Information

ABSTRACT: A novel class of dibenzo-fused 1,9-diaza-9a-boraphenalenes featuring zigzag edges with a nitrogen—boron—nitrogen bonding pattern named NBN-dibenzophenalenes (NBN-DBPs) has been synthesized. Alternating nitrogen and boron atoms impart high chemical stability to these zigzag-edged polycyclic aromatic hydrocarbons (PAHs), and this motif even allows for postsynthetic modifications, as demonstrated here through electrophilic bromination and subsequent palladium-catalyzed cross-coupling reactions. Upon oxidation, as a typical example, NBN-DBP 5a was nearly quantitatively converted to σ-dimer 5a-2 through an open-shell intermediate, as indicated by UV–vis–NIR absorption spectroscopy and electron paramagnetic resonance spectroscopy corroborated by spectroscopic calculations, as well as 2D NMR spectra analyses. In situ spectroelectrochemistry was used to confirm the formation process of the dimer radical cation 5a-2+. Finally, the developed new synthetic strategy could also be applied to obtain π-extended NBN-dibenzohetapazethrene (NBN-DBHZ), representing an efficient pathway toward NBN-doped zigzag-edged graphene nanoribbons.

INTRODUCTION

Phenalene (1) is the smallest $D_{3h}$-symmetric polycyclic aromatic hydrocarbon (PAH) with 13 carbon atoms and 13 $\pi$ electrons. Thus, one electron remains unpaired, rendering this PAH with an open-shell character (Figure 1). Moreover, this compound is a structural motif of nanographenes and graphene nanoribbons (GNRs) that are terminated exclusively by zigzag-edged peripheries. The neutral form of phenalene is a resonance-stabilized radical that can be generated and observed at room temperature in solution, but the study of its optoelectronic properties remains difficult. Inclusion of heteroatoms in the phenalene backbone can strongly influence the chemical and physical properties, as exemplified by 1-azaphenalene (2) and 9b-boraphenalene (3). Furthermore, the introduction of bilateral benzene rings has been widely used for phenalene derivatives to induce steric shielding of the highly reactive periphery, thus increasing the kinetic stability. We have recently reported that 9a-azaphenalene, which contains a nitrogen atom as a bridgehead within the zigzag-edged periphery, exhibits a stabilized zwitterionic structure similar to that of an azomethine ylide (AMY) with high chemical reactivity.

The implementation of combinations of heteroatoms such as nitrogen and boron, for example, by substituting a C=C unit in an aromatic molecule with an isoelectronic B=N moiety, can significantly affect the electronic structure while leaving the conjugated skeleton unchanged. In addition, in contrast to the nonpolar C=C bond, the B=N bond can also be considered as a zwittieronic double bond in the neutral state, and the oxidation process of the B=N bond has recently received growing interest because of the potential physicochemical properties based on the Lewis acid or base properties of these heteroatoms.

Whereas usually only two carbon atoms are replaced by heteroatoms, more recently the replacement of a full C3 unit of the zigzag edge with heteroatoms raised interest, allowing the synthesis of stable PAHs with extended zigzag edges. For
example, oxygen–boron–oxygen (OBO)-doped double [5]-
helicenes with substantial chemical and thermal stabilities were
synthesized by Hatakeyama’s group and showed excellent
ambipolar conductivity. At the same time, our group
successfully prepared OBO-doped peritetracenes via cyclo-
der hydrogenation of OBO-doped double [5]helicenes,12 of-
fering the possibility to construct novel heteroatom-doped
nanographenes.13
In addition to the incorporation of the OBO-doped
structure, nitrogen–boron–nitrogen (NBN)-containing aro-
matic molecules have also raised interest in molecular
optoelectronic materials, with the NBN units in most cases
restricted to one fused ring.14 During the preparation of this
article, the first example of an NBN-incorporated organic–
inorganic hybrid polymer was reported by Helten’s group, and
its introduction into a PAH with limited \( \pi \)-conjugation across
the NBN unit was proved.15
Here our efforts to understand the effects of heteroatom
doping at the zigzag edges of phenalenyl systems on the stability and optoelectronic properties have focused on
exploring NBN-incorporated heterophenalenes based on a
1,9-diaza-9a-boraphenalene (4) core motif, and in particular,
the NBN-doped benzo-elongated phenalene structures 5–8 are
first reported.16 Besides, one-electron oxidation of the four-\( \pi \)-
electron N–B–N unit could lead to the three-\( \pi \)-electron (N–
B–N)\(^*\) unit, which is isoelectronic to the allylic C–C–C unit,
thereby forming an open-shell odd-electron \( \pi \) system, and can
provide access to isoelectronic derivatives of the unprecedented
full-carbon dibenzophenalene radical.

\section*{RESULTS AND DISCUSSION}

In this work, the syntheses of benzo-elongated zigzag-edged
8H,9H-8,9-diaza-8a-borabenzo[\( \text{fg} \)]-tetracene (5a) and its alky-
lated derivative 8,9-dihexyl-8H,9H-8,9-diaza-8a-borabenzo[\( \text{fg} \)]-
tetracene (5b) (also termed dibenzo-fused 1,9-diaza-9a-
diboraphenalenes, denoted as NBN-DBPs) were established.
and further extended to 10,11-dihydro-10,11-diaza-10a-boratribenzo[a,fg,lm]tetracene (6). The high chemical stability of the zigzag-edged NBN-DBPs allows for an electrophilic bromination process and subsequent derivatization by palladium-catalyzed cross-couplings, as exemplified by 8,9-dihexyl-5,12-diphenyl-8H,9H-8,9-diaza-8a-borabenzo[fg]tetracene (7a) and 8,9-dihexyl-5,12-(2-thienyl)-8H,9H-8,9-diaza-8a-borabenzo[fg]tetracene (7b). Moreover, 8,9,18,19-tetrahexyl-8H,9H,18H,19H-8,9,18,19-tetraaza-8a,18a-diboradibenzo[a,b,lm]heptacene (8), which is the next homologue and a diazabora derivative of dibenzoheptazethrene (denoted as NBN-DBHZ), was synthesized to highlight the scope of this solution-based approach toward elongated NBN-edged PAHs.

Single-crystal X-ray analyses of compounds 5b, 6, and 7a demonstrated that the B–N bonds have double-bond character. Theoretical, spectroscopic, and electrochemical studies revealed the aromaticity and optoelectronic properties of these unprecedented NBN-edged PAHs. Upon chemical oxidation, as an example, NBN-DBP 5a was nearly quantitatively converted to the σ-dimer 5a-2 through an open-shell intermediate, as indicated by UV–vis–NIR absorption spectroscopy and electron paramagnetic resonance (EPR) spectroscopy corroborated by spectroscopic calculations. The chemical structure of 5a-2 was unambiguously confirmed by two-dimensional (2D) NMR analysis and MALDI-TOF mass spectrometry as the N-para C–C coupling dimer. To gain insight into the radical cations of the NBN-DBPs after single-electron oxidation, we performed in situ spectroelectrochemical...
First, 1,3-dibromobenzene (5a) was selectively lithiated during cyclic voltammetry of 7a at its first oxidation peak. The vertex potential was 0.74 V vs Fc/Fc'. The asterisk at 1180 nm denotes an artifact of the spectrometer due to the change of detector channels. (b) EPR spectrum of radical cation 7a** measured in situ during electrochemical oxidation of 7a at a potential of 0.59 V. (c) DFT-computed spin density distribution in 7a** (red “+”, green “−”; alkyl chains have been abridged for clarity).

CHCl₃/MeOH to furnish 5a and 5b as colorless crystalline solids in 90% and 87% yield, respectively. Recrystallization from THF/MeOH afforded π-extended derivative 6 as a light-green powder in 80% yield.

The stability of the NBN-DBP adds further modifications of the skeleton that extend the π conjugation and tune the optoelectronic properties of these heteroacenes. Thus, compound 5b was successfully brominated with 2 equiv of N-bromosuccinimide (NBS) to furnish 5,12-dibromo-8,9-dihexyl-8H,9H-8,9-diaza-8a-borabenz[f]tetracene (13) as a white solid in 87% yield, allowing for further functionalization through palladium-catalyzed cross-coupling reactions. For instance, Suzuki and Stille coupling reactions were performed with 13 to produce π-extended compounds substituted with
phenyl and 2-thienyl moieties (7a in 77% yield and 7b in 85% yield, respectively) as colorless solids.

Inspired by the efficient cyclization protocol, we aimed to synthesize 8, an NBN-DBHZ containing two 1,9-diaza-9a-boraphenalene motifs (Scheme 2). Because of the decreasing solubility of these larger conjugated systems, we explored the synthesis of NBN-DBHZ 8 from the N-alkyl-substituted quinquephenyl precursor N,N,N’,N”-tetrahexyl-[1,1’:3’,1”:4’,1”’:3”:1””–quinquephenyl]-2,2”’-tetraamine (17). Compound 9 was reacted with 0.5 equiv of boronic acid ester 3b to furnish the monofunctionalized coupling product 3′-bromo-N-hexyl-[1,1’-biphenyl]-2-amine (14). This compound was then converted into the corresponding boronic acid ester, N-hexyl-3’-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1’-biphenyl]-2-amine (15), using Pd(dppf)Cl2 as a catalyst. The crude product was purified by flash column chromatography and used immediately for the next palladium-catalyzed reaction. Excess 15 was reacted with 2,5-dibromo-N,N’-dihexylbenzene-1,4-diamine (16) to obtain 17 as a yellow oil in 73% yield. Finally, product 17 was treated with BCl3 and triethylamine at 180 °C to afford pure NBN-DBHZ 8 as a yellow crystalline solid in 35% yield after purification by column chromatography on silica gel and recrystallization from toluene/MeOH.

The intermediates and targeted compounds of NBN-DBPs and NBN-DBHZ were analyzed by 1H, 13C, and 11B NMR spectroscopy as well as high-resolution mass spectrometry (HRMS). Notably, the broad peak of the amino hydrogen located at around 3.7 ppm in the 1H NMR spectrum (CDCl3) of intermediate 12a disappeared after cyclization to target molecule 5a. For NBN-DBP 5a, pronounced chemical shifts of protons at the nitrogen sites appeared at about 6.3 ppm, suggesting the aromatic character of BN-fused rings.19 In the 1H NMR spectrum (CDCl3) of NBN-DBHZ 8, there are two groups of triplet resonance peaks at 4.2 and 4.1 ppm which are typically from the methylene protons neighboring the nitrogen, demonstrating the distinction of BN-fused rings in the higher homologue skeleton. In the 11B NMR spectra, all of the NBN-edged PAHs show one broad resonance around 26.7–30.6 ppm, which appears at significantly higher field compared with those of the reported heteroacenes with only BN-embedded structures (35–40 ppm).20 These NBN-edged PAHs are stable toward ambient oxygen and moisture as solids. They also exhibit good thermal stability with a weight loss of 5% in the range of 250–350 °C based on thermogravimetric analyses (Figure S1 in the Supporting Information (SI)).

**X-ray Crystallographic Analysis.** Single crystals of compounds 5b and 7a suitable for X-ray structure analysis were obtained by slow evaporation of their chloroform solutions. For compound 6 with poorer solubility, suitable crystals were grown by slow evaporation of its THF solution. All of the crystal structures unambiguously reveal the structure of the defined N–B–N zigzag-edged periphery. Compound 5b shows two types of slightly twisted conformations in one unit cell; the largest dihedral angle of 17.6° is probably due to steric repulsion between the two alkyl chains (Figure 2a). Compound 5b forms slipped stacks in a herringbone fashion through the many C–H···π interactions formed by the long alkyl chains, but

![Figure 8.](image-url)
According to the structural analysis. Notably, the neighboring distance of 3.58 Å, which is below the sum of the van der Waals radius, suggests effective π-π stacking interactions. The peripheral benzene ring has a relatively negative dipole moment (0.83 D) than smaller homologues. The B–N bond lengths in 5b range from 1.42 to 1.44 Å, which are shorter than the analogous bonds in typical BN-embedded PAHs (1.45–1.47 Å); these data indicate the presence of localized BN double-bond character. Compound 6 exhibits C₂, symmetry with an essentially planar backbone; the largest dihedral angle among the fused rings is 2.9°. The two B–N bond lengths in 6 are approximately equivalent to each other at 1.42 Å. The packing diagram of compound 6 reveals a dimeric herringbone motif with intermolecular B–N dipole–dipole interactions at a distance of 3.58 Å, which is below the sum of the van der Waals radii (3.60 Å) (Figure 2b). For compound 7a (Figure S2), the central core shows a slightly twisted conformation with the largest dihedral angles of 14.4°, similar to the structural characteristics of compound 5b.

**NICS Calculations.** To understand how the NBN substitution influences the aromaticity of the dibenzophenalenenes, we performed nucleus-independent chemical shift (NICS) calculations at the B3LYP/6-311+G(2d,p) level. As illustrated in Figure 3, the symmetrical NBN-DBP 5a has a weakly aromatic phenalenone core with a small negative NICS(1) value of −1.7 ppm for both BN rings and moderately aromatic features for the fused benzene rings. Similarly, the NICS(1) values for compound 6 are axisymmetric at −1.4 ppm for the BN rings. The peripheral benzene ring has a relatively negative NICS(1) value of −9.8 ppm, revealing more aromaticity than the rings adjacent to the BN core (−8.6 and −8.9 ppm). In contrast, compound 5b has different NICS(1) values, which may be caused by the steric repulsion between the alkyl chains according to the structural analysis. Notably, the neighboring BN rings in 5b have stronger aromaticity (−2.7 and −3.3 ppm, respectively) than those of 5a, which could be explained by the strengthened electron-donating ability of the alkyl chains derived from the polarity of the B–N bonds. The NICS(1) calculation results for the other NBN-edged PAHs 7 and 8 are shown in Figure S3.

**Absorption and Emission Spectra.** The UV–vis absorption spectra of the as-prepared NBN-edged PAHs are presented in Figure 4a. For NBN-DBPs 5a and 5b, two main absorption features are recorded in the wavelength regions of 250–300 and 300–400 nm, with the absorption maxima for the latter at λ = 351 and 359 nm (log ε = 4.21 and 4.12), respectively, which are the wavelengths assigned to the π–π* transitions. The intensities of the peaks in the high-energy regions and the red shift (30 nm) of the absorption maximum at λ = 381 nm (log ε = 4.35) for 6 exceeded those of 5a; these enhancements originate from the extended aromatic skeleton with the additional terminally fused benzene rings. Compounds 7a and 7b both exhibit a red-shifted absorption onset and stronger absorption intensity at approximately 300–400 nm compared with 5b. These results are attributed to the extended π conjugation for 7a and 7b, while the absorption maxima are blue-shifted to 342 and 346 nm (log ε = 4.28 and 4.57), respectively. For NBN-DBHZ 8, the absorption maximum is shifted further to 435 nm (log ε = 3.90). This large bathochromic shift is consistent with the extended conjugation in the higher homologue 8 with its repeated structural motif. The fluorescence of these compounds was also investigated (Figure 4b). Distinct red shifts were found in the emission maxima of the as-prepared NBN-edged PAHs in the following sequence: 5a (369 nm) < 5b (380 nm) < 6 (393 nm) < 7a (394 nm) < 7b (406 nm) < 8 (448 nm). Notably, NBN-DBHZ 8 exhibits split emission bands at longer wavelengths, and it has a much higher fluorescence quantum yield (ΦFL) (0.83) than smaller homologues 5a–7b.

**Electrochemical Properties.** The electrochemical behaviors of NBN-DBPs 5a–7b and NBN-DBHZ 8 were investigated by cyclic voltammetry (CV). The compounds were scanned for their first oxidation potentials in CH₂Cl₂, as shown in Figure 5. NBN-DB 5a showed a quasi-reversible wave at 0.51 V (vs Fc/Fc⁺). The cyclic voltammetry of 5a was also performed in acetonitrile. Notably, besides an irreversible redox wave at a higher potential, a new reversible redox peak appeared at a lower potential upon multicycle scanning, suggesting the formation of possible oligomers or polymers (Figure 6c), and the follow-up experiments proved the π-dimer structure (see below). NBN-DBP 5b, with alkyl substituents on the nitrogen atoms, offered an irreversible peak at 0.60 V. A quasi-reversible peak at 0.25 V was observed for 6, which is much lower than that for 5a as a result of the extended π-conjugated skeleton of 6. Interestingly, 7a terminated with phenyl substituents at the sides showed an one-electron reversible redox peak at 0.49 V, while 7b gave an irreversible wave at 0.47 V, probably because of its thiophene terminal groups with electrochemical activity. The first oxidation potentials of 7a and 7b are remarkably lower than those of 5a and 5b, suggesting that the introduction of aromatic units in the N-para position of such kinds of NBN-DBP enable extension of the π conjugation, the CV profile of NBN-DBHZ 8 exhibits one quasi-reversible oxidation wave at the lowest potential among these molecules, 0.18 V, as a result of its largest π-conjugated backbone. Obviously, the significant differences in the CV profiles of these compounds are highly associated with their intrinsic molecular structures, and even a tiny variation of these molecular structures would cause a significant change in

![Figure 9. (a) Simulated absorption spectra with Gaussian-type line width broadening (σ = 0.1 eV). (b) Simulated excitation energies and the corresponding oscillator strengths. To reduce a systematic offset relative to the experimental data, a polarization shift to account for solvation effects was applied (see the SI).](image-url)
their electrochemical behavior. Accordingly, the highest occupied molecular orbital (HOMO) energy levels of the as-prepared NBN-edged PAHs were evaluated from the onsets of the first oxidation potentials. The low-lying HOMO energy levels of these NBN-DBP’s 5 and 7 (−5.26 to −5.36 eV) suggest that these compounds are promising candidates for air-stable p-type semiconductors. Moreover, the lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the HOMO values and the optical band gaps (Table 1).

Chemical Oxidation of NBN-DBPs. Encouraged by the electrochemical behaviors of the NBN-DBPs, we first examined the chemical oxidation of 5a as a typical example. Given its quasi-reversible redox process with the first oxidation potential of \( E_{ox}^{a} = 0.59 \) V (vs Fc/Fc\(^+\)), an exergonic thermal electron transfer (ET) (\( \Delta G_{ET} < 0 \)) to Cu\(^{2+}\) to form the radical cation can be predicted. Indeed, titration of 5a with Cu(OTf)\(_2\) resulted in a large bathochromic shift, indicating the formation of radical cation species based on the UV–vis–NIR absorption spectra (Figure 6a). With the progressive addition of Cu(OTf)\(_2\), a set of new absorption peaks in the visible and NIR regions of 5a gradually evolved at 404, 620, and 1150 nm with a concomitant decrease of the \( \pi \rightarrow \pi^* \) transition bands at 336 and 352 nm. A well-defined isosbestic point at 367 nm could be clearly identified. Moreover, upon addition of Cu(OTf)\(_2\) in acetonitrile at \( 10^{-3} \) M, the EPR spectrum revealed a strong signal at \( g = 2.0033 \) with a peak-to-peak width of 1 G (Figure 6b), without any hyperfine coupling observed. This result suggests many different couplings from a highly delocalized structure over which the spin density of the unpaired electron is distributed. Meanwhile, the extremely rapid and distinct change from a colorless solution to a deep-green suspension could also be observed by the naked eye. To exclude the EPR-active interference of Cu, we also used the EPR-inactive oxidant NOBF\(_4\) for the oxidation of compound 5a, and under the same conditions we detected a similar but weaker EPR signal (Figure S4).

In order to gain further insight into these interesting results, the reaction of 5a with Cu(OTf)\(_2\) in acetonitrile was carried out on a preparative scale (Scheme 3). Treatment of 5a with 2 equiv of Cu(OTf)\(_2\) under a nitrogen atmosphere gave a deep-green suspension in the early stage of the reaction, which resembled the UV–vis–NIR and EPR studies of the initial in situ investigation. Afterward, two different workup methods were employed. In the first one, we added excess hydrazine hydrate to the resulting suspension, leading to a color change from deep green to milky white. After filtration, a new compound (denoted as 5a-2) with good purity was collected as a white powder in a yield of 92% and was first characterized by \(^1\)H NMR spectroscopy. In comparison with the observation of only one broad peak at 8.24 ppm with respect to nitrogen protons for 5a, the \(^1\)H NMR spectrum (DMSO-\(d_6\)) of 5a-2 showed two broad peaks at 8.30 and 8.34 ppm assignable to the different nitrogen protons on the phenalenyl scaffold (Figures S5 and S6). On the basis of 2D NMR analyses (pp S35–S49 in the SI), 5a-2 was unambiguously confirmed as the N-para C–C coupling dimer, also in accordance with the results of MALDI-TOF MS analyses. In the other workup method, the deep-green suspension was directly filtered to afford a dark-green powder without the addition of any reductant. The resulting powder was dissolved in DMSO-\(d_6\) as a green solution and was NMR-silent at room temperature, suggesting the existence of an unpaired electron, while after heating for several minutes in air, the green solution was transformed to a colorless one that showed a set of proton signals consistent with that of the neutral dimer 5a-2 (Figure S7). Combined with the well-resolved MALDI-TOF and negative-mode electrospray ionization MS spectra as well as EPR spectra, this confirmed the formation of the radical cation of 5a-2 with an OTf\(^-\) counteranion (5a-2\(^+\)-OTf\(^-\)) (pp S50 and S55 and Figure S8 in the SI). Therefore, oxidative dimerization of 5a via an open-shell intermediate is proposed, as shown in Scheme 3. The conversion between the neutral dimer and the dimer radical cation can be smoothly conducted by a simple redox treatment, as validated by cyclic voltammetry and UV–vis–NIR absorption spectroscopy (Figures S9–S12).

Similarly, N-alkyl NBN-DBP 5b also could be nearly quantitatively converted to the dimer 5b-2 as a white powder upon oxidation treatment. The molecular structure of 5b-2 involving the N-para C–C linkage, similar to 5a-2, was clearly confirmed by \(^1\)H and \(^{13}\)C NMR spectra and HR-MALDI-MS analyses. On the contrary, for compound 7a, the phenyl substituents at the N-para position was expected to block the formation of similar dimers, which indeed was confirmed by MALDI-TOF MS upon chemical oxidation (pp SS1–SS2 in the SI). Such a result is highly consistent with its aforementioned reversible electrochemical behavior and clearly demonstrates the highly regioselective activity of such kinds of NBN-edged PAHs.

In Situ Spectroelectrochemistry of NBN-DBPs. To understand the formation process of radical cation 5a-2\(^+\) in more detail, we further performed in situ spectroelectrochemistry (SEC) on compound 5a in acetonitrile. At a low scan rate of 2.5 mV/s, electrochemical oxidation was followed by a chemical reaction that formed a new compound with an oxidation potential near 0.25 V (Figure S13). In situ EPR–vis–NIR SEC studies showed that oxidation of 5a in acetonitrile caused the appearance of an absorption band at 1100 nm accompanied by a relatively narrow EPR signal at \( g = 2.0027 \) with a line width of 0.7 G. These spectroscopic features are similar to those observed for the solution of the precipitate formed during chemical oxidation of 5a by Cu\(^{2+}\) as discussed in the previous section. In addition, the oxidation potential of the dimer 5a-2 coincides with the oxidation potential of the follow-up products of the electrochemical oxidation of 5a (Figure S14). These results thus enable us to conclude that the precipitate observed in the chemical oxidation of 5a is the radical cation 5a-2\(^+\) (see the detailed structure in Figure S15). The SEC studies also showed that the absorption intensity at 1100 nm increased almost 2-fold at the second voltammetric cycle, and the formation of a film was observed on the electrode after the measurements. Presumably, 5a not only dimerized upon electrochemical oxidation but underwent a further electropolymerization.

For comparison, we also performed the in situ SEC studies on NBN-DBP 7a. Obviously, the phenyl substitutions at the N-para positions (which are dimerization sites in 5a) prevent dimerization/polymORIZATION of 7a. In situ EPR–vis–NIR measurements during electrochemical oxidation revealed absorption bands of the 7a\(^+\) radical cation at 598 and 1380 nm and a broad EPR signal at \( g = 2.0026 \) with the sign of hyperfine structure (Figures 7a,b and S16). Density functional theory (DFT) computations were then conducted with the ORCA package at the B3LYP level using the de2-TZVP basis set for C and the specially tailored EPR-III basis set for H, N, and B, and we found that the spin density in 7a\(^+\) is delocalized...
over the whole π system (Figure 7c), which results in relatively large hyperfine coupling constants (hfcc’s) for many nuclei. In particular, the largest hfcc values are predicted for B (~13.5 MHz), one of the protons in the CH2 groups next to the atoms of nitrogen (16.0 and 18.0 MHz), N (2 × 9.9 MHz), and two protons at the 4,6-diazaboraphenalene positions (2 × −8.3 MHz). The hfcc values for other protons are less than 3 MHz (Figure S17). A combination of many magnetic nuclei with a broad distribution of hfcc values gives a broad EPR signal with a rich hyperfine structure, which cannot be fully resolved.

Spectroscopic Calculations. We further performed DFT calculations using the Gaussian 09 software package33 at the M06-2X/cc-pVTZ level34 to characterize the electronic structures of all of the NBN-DBPs and their absorption spectra, as shown in Table 1 and Figures 8 and 9 (see the SI for more details). For all of the molecules except compound 6, the HOMO (LUMO) frontier orbital is separated by more than 0.4 eV from the lower (higher) energy levels. For compound 6, the LUMO and LUMO+1 are close, with an energy separation of 0.14 eV. The frontier orbitals of compounds 5a, 5b, 6, 7a, and 7b have similar shapes and exhibit a nodal structure that keeps the boron atom clear of weight (Figure 8). The HOMO is partially localized at the nitrogen atoms, while the LUMOs have no weight at that point. For compound 6 the frontier molecular orbitals are even more strongly delocalized over the entire molecule, leading to a reduced ionization potential (IP), a smaller energy gap, and a further red shift in the absorption spectrum (Figure 9), remaining consistent with the experimental CV and UV–vis results. The dominant absorption peak doublet above 300 nm is caused by the energetic proximity of the LUMO and LUMO+1 levels, which are both involved in the electronic transitions. Frontier MOs with greater π delocalization are observed in NBN-DBHZ, leading to a further decrease in the HOMO–LUMO gap and a red shift in the absorption, in agreement with the UV–vis results. Functionalizing 5b to obtain 7a and 7b increases the absorption intensity, while the IP and electron affinity (EA) values and absorption onsets are almost unchanged, corroborating our experimental observations. In addition, we found that the simulated absorption spectra of 5a-2 in various oxidation forms also showed strong absorption in the NIR region similar to the experimental findings, consistent with the reaction of the 5a monomer to form the 5a-2 dimer structure (Figures S18–20; see the detailed discussion in the SI).

■ CONCLUSIONS

A synthetic route toward unprecedented heteroatom-doped PAHs featuring a nitrogen–boron–nitrogen-type zigzag-edged periphery based on a 1,9-diaza-9a-boraphenalene core structure was introduced. Alternating nitrogen and boron atoms impart high chemical stability to these zigzag-edged PAHs; this motif even allows for postsynthetic modifications. The possibilities for lateral extension were demonstrated by the synthesis of the higher homologue 8, suggesting that NBN-doped zigzag-edged graphene nanoribbons could be synthesized via this route.35 Upon chemical oxidation, as an example, NBN-DBP 5a was nearly quantitatively converted to the N-para C=C-linked dimer 5a-2 through an open-shell intermediate, revealing the highly regioselective activation of NBN-DBPs at their molecular peripheries. The additional phenyl substituents in 7a prevented oligomerization, and the clean single-electron oxidation of the NBN unit into the isoelectronic allyl radical could be performed by means of in situ spectroelectrochemistry, generating radical cation 7a+*, which is isoelectronic to the unprecedented full-carbon dibenzophenalene radical. This work provides a new class of PAH molecules with tunable properties while promoting our strategy to obtain tailor-made complex architectures such as conjugated polymers,66 dendrimers,37 organic framework materials,38 and graphene nanoribbons39 with stable NBN-doped zigzag-edged peripheries.

■ ASSOCIATED CONTENT

3 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04445.

Experimental details, TGA spectra, single-crystal X-ray diffraction data, in situ SEC results, computational details, NMR spectra, and HRMS spectra (PDF)

Crystallographic data for 5b (CIF)
Crystallographic data for 6 (CIF)
Crystallographic data for 7a (CIF)

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