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Bottom-Up Synthesis of Nitrogen-Doped Polycyclic Aromatic Hydrocarbons

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Abstract Bottom-up organic synthesis serves as an efficient method to provide atomically precise heteroatom-doped polycyclic aromatic hydrocarbons (PAHs) with not only well-defined size and edge structures but also specific concentrations and positions of the heteroatoms. We provide a plenary account of the preparation of nitrogen-doped PAHs (N-PAHs) through 1,3-dipolar cycloaddition between different dipolarophiles, as well as pyrazine-type N-doped diaza-hexa-peri-hexabenzocoronene (diaza-HBC). Additionally, we present the synthesis of a class of helical N-charged PAHs, including one charged aza[5]helicene and two charged aza[4]helicenes. Moreover, the bottom-up organic synthesis strategy is further extended to the construction of novel nitrogen-boron-nitrogen (NBN)-containing PAHs. Finally, we discuss the synthesis of four-coordinate boron chromophores containing 6,12,18-tris(alkyl amine)-5,11,17-triazatrinaphthylene derivative ligands.

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Key words polycyclic aromatic hydrocarbons, nanographenes, heteroatoms, nitrogen doping, boron doping

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs), namely, nanographenes (NGs), can be considered as segments of graphene with sp^2 -carbon frameworks.^{1,2} The chemical synthesis of PAHs was pioneered by R. Scholl and E. Clar.^{3,4} Their systematic studies and applications in organic electronics have attracted scientists for decades, especially with the seminal contribution from K. Müllen.^{5,6} The classic synthesis of π -extended PAHs is based on intramolecular cyclodehydrogenation (Scholl reaction), i.e., planarization of the

polyphenylene precursors with three-dimensional dendritic or hyperbranched structures.^{7,8} By utilizing such a synthetic strategy, different types of large PAHs have been successfully achieved with various sizes, edge peripheries, and topological structures in the last two decades.⁹ In particular, hexa-peri-hexabenzocoronene (HBC, with 42 carbon atoms) is a typical case of the most widely investigated PAH.¹⁰⁻¹⁵ Superficially, people may consider that PAHs represent a solitary class of similar molecular structures containing only *sp*² carbons. However, the chemical reactivity and physical properties of PAHs are absolutely different depending on their size and topology, as well as their peripheral substituents.¹⁶⁻²¹ There is no doubt that the electronic properties of PAHs, e.g., the energy gaps, are of great importance for the prospective applications of PAHs in organic or graphene-based nanoelectronics.²² In addition to the size and edge structures, the introduction of heteroatoms into the lattice of *sp*²-carbon frameworks is an effective method for tailoring the intrinsic physical and chemical properties, such as the energy gap, optical properties, and redox behavior, of PAHs.^{23-25,26,27} The initial investigations of heteroatom-doped PAHs date back to studies on natural dyes. For instance, in 1907, R. Scholl elucidated the structure of flavanthrone.²⁸ During the past two decades, research on large polycyclic heteroaromatics has advanced with the development of graphene and its application in molecular and organic electronics.²⁹⁻³¹ Bottom-up organic synthesis can afford atomically precise heteroatom-doped PAHs (N-PAHs) with different sizes and topologies, as well as different concentrations and positions of heteroatoms.²⁹ Furthermore, the introduction of heteroatoms into PAHs can promote the development of stable cationic aromatics, spin-polarized organic compounds, and special redox and supramolecular self-assembly behavior.^{21,32-34} Since the introduction of heteroatom-doped PAHs, nitrogen (N) has always been the key 'dopant' atom because of the feasibility of the synthetic

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methods and the chemical stability of the N-doped PAHs.²⁹ In particular, because of their prospective optical, electronic, and magnetic properties, N-containing PAHs have received much attention for promising applications in electrocatalysts, organic solar cells, sensors, and field-effect transistors.^{35–39} For instance, using electronegative nitrogen atoms to replace C-H units can promote the electron injection and charge-transport properties of PAHs.^{40,41} More importantly, such nitrogen atoms can influence the electronic feature while still maintaining the molecular skeleton of PAHs, and the overall electron-accepting properties can be increased due to the presence of imino nitrogens relative to those of pure hydrocarbons or other heteroatom-doped PAHs. For instance, triphenylenes exhibit p-type charge carrier transport, while hexaazatriphenvlenes, a type of Ndoped triphenylenes, are *n*-type semiconductors.⁴² Moreover, N-PAHs have a significant tendency to pack into 1D

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column supermolecular structures, which can serve as a favorable charge carrier transport pathway.^{43,44} The N atom can be positioned at the edge, leading to pyridine-type nanographenes (such as 1, Figure 1), or at the inner plane of sp²-carbon frameworks, resulting in 'graphitic'-type Ndoped molecules (such as 2). For externally N-derived molecules, arylation, alkylation, or protonation at the N atom can result in a positive charge (such as 3). Furthermore, a positive charge on the nitrogen atoms can also be achieved by doping at a ring junction (such as 4). The chemical features of N-dopants, i.e., pyridinic, pyrrolic, and 'graphitic' N atoms, are consistent with those of various types of Ndoped 6π -aromatic rings instead of benzene rings. Among these, graphitic-type nitrogen is known as one of the most active sites for carbon-based electrocatalysis.⁴⁵⁻⁴⁹ In this Account, we will mainly describe our recent endeavors in the development of nitrogen-doped PAHs in the past few years.

Biographical Sketches





Dr. Junzhi Liu received his Bachelor's degree in materials chemistry in 2008 and Master's degree in materials science in 2011. Then he joined the Max Planck Institute for Polymer Research in Prof. Klaus Müllen's group for PhD thesis and obtained his PhD degree in synthetic chemistry in January 2016. In July 2015, he joined Prof. Xinliang Feng's group as a postdoc at Technische Universität Dresden (TU Dresden). Since

Prof. Feng received his Bachelor's degree in analytic chemistry in 2001 and Master's degree in organic chemistry in 2004. Then he joined the Max Planck Institute for Polymer Research for PhD thesis, where he obtained his PhD degree in April 2008. In December 2007, he was appointed as a group leader at the Max-Planck Institute for Polymer Research, and in 2012 he became a distinguished group leader. Since August 2014, Prof. Feng was the head of the Chair of Molecular Functional Materials at Technische July 2017, he was a research group leader at the Chair for Molecular Functional Materials at TU Dresden. In August 2019, Dr. Liu started his independent research group at the Department of Chemistry at The University of Hong Kong. His current scientific interests include bottom-up organic synthesis of topological carbon nanostructures and their applications for organic electronics. He is an Early Career Advisory

Universität Dresden. His current scientific interests include organic synthetic methodology, organic synthesis and supramolecular chemistry of π -conjugated system, bottom-up synthesis and top-down fabrication of graphene and graphene nanoribbons, 2D polymers and supramolecular polymers, 2D carbon-rich conjugated polymers for optoelectronic applications, energy storage and conversion, new energy devices and technologies. Prof. Feng has been awarded several prestigious prizes such as IUPAC Prize

Board for Chemistry – An Asian Journal (2020). Dr. Liu has been awarded several prizes such as International Union of Pure and Applied Chemistry (IUPAC) International Award for Young Chemists - Honorable Mention Award (2017), 'Chinese Government Award for Outstanding Self-financed Students Abroad' in 2015, 'Marie-Curie' fellowship in 2011–2014.

for Young Chemists (2009), European Research Council (ERC) Starting Grant Award (2012), Journal of Materials Chemistry Lectureship Award (2013), Fellow of the Royal Society of Chemistry (FRSC, 2014), Highly Cited Researcher (Thomson Reuters. 2014-2019), Small Young Innovator Award (2017), Hamburg Science Award (2017), EU-40 Materials Prize (2018), and Member of the European Academy of Sciences (2019).

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Figure 1 PAHs with different types of nitrogen atoms

2 Nitrogen-Doped PAHs Based on Dibenzo-9a-azaphenalene (DBAP)

Azomethine ylides (AMY 1, Figure 2) are classic cases of 1,3-dipolar molecules.^{50,51} Because the negative charge of the allyl anion can be equally distributed on the two adiacent carbon atoms, AMY 1 features isoelectronic properties (see Figure 2). In addition to exhibiting two ionic structures (1a and 1b), AMY 1 also exhibited diradical (1c) character in the ground state (Figure 2).⁵²⁻⁵⁵ Moreover, the diradical character of AMYs has been quantified by theoretical calculations, and their chemical reactivity has also been correlated to the 1,3-dipolar cycloaddition.56,57 Normally, AMYs are extremely reactive; thus far, only a few cases of stable AMYs have been achieved.^{58–63} The extreme reactivity of AMYs enables the facile synthesis of heterocycles containing five-membered rings, and different kinds of approaches, including desilylation and deprotonation of derivative precursors, have been explored.⁶⁴ Recently, the fabrication of AMY conjugated with aromatic rings (PAMY) was first achieved by our group,^{65,66} providing an unprecedented building block for the construction of PAHs containing nitrogen atoms (N-PAHs, see Scheme 1).

The synthesis of **PAMY** involves the following three steps (Scheme 1). First, compound **3** was obtained through



Figure 2 The isoelectronic structure of AMY 1 with two ionic structures (1a and 1b) and one diradical structure (1c)

Suzuki coupling of 2,6-dibromo-4-(*tert*-butyl) aniline (**2**) and 1-hydroxy-3*H*-2,1-benzoxaborole. Second, precursor **4** was generated using HCl-induced cyclization of **3** under microwave conditions. Then, the key compound **PAMY** was achieved by treatment of **4** with a base. We found that dimethyl-8-(*tert*-butyl)-2a,13b-dihydrobenzo[7,8]indoliz-

ino[6,5,4,3-def]phenanthridine-1,2-dicarboxylate (5) could be directly formed via a selective 1.3-dipolar cycloaddition treating bv 2-(tert-butyl)-8H-isoquinolino[4,3,2*de*]phenanthridin-9-ium chloride (**4a**) with triethyl amine and dimethoxy acetylene dicarboxylate (7a, DMAD, see Figure 3). The resultant 5 with polycyclic aromatics strongly indicates that such 1,3-dipolar cycloaddition can be further developed to synthesize an extended N-PAH. Subsequently, 8-(tert-butyl)-benzo[7,8]indolizino[6,5,4,3-def]phenanthridine-1,2-dicarboxylate (6) with a planar π -extended geometry was achieved in 82% yield through the oxidative dehydrogenation of 5 using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as the oxidant. By this means, unprecedented nitrogen-containing N-PAHs 12-16 could be accessed using different dipolarophiles (Figure 3), such as tilted (8), pentacyclic (9), and hexacyclic (naphthalene-1,4dione **10** and benzoquinone **11**) ethylenes.

Compound **11** can be regarded as a 'double-dipolarophile' and offers a two-sided 1,3-dipolar cycloaddition reaction with the **PAMY** precursor. Accordingly, π -extended N-PAHs **17a** and **17b** (Figure 3) were obtained as red powders. Importantly, compound **17** with 48 π -electrons includes two pyrrolic-type N atoms in the inner planar skeleton of PAH, in which the electrons are delocalized throughout the





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molecular skeleton. In general, from a synthetic point of view, the preparation of such interior N-doped PAHs is more challenging than the synthesis of PAHs in which nitrogen is doped at the corresponding peripheries. Thus, this efficient synthetic route paves the way to develop novel N-PAHs containing central nitrogen atoms.⁶⁷

As mentioned above, compound **5** can be achieved through the [3+2] cycloaddition of **PAMY** and **DMAD**. Interestingly, dimerized compound **18** was also generated in the solution of **PAMY** without **DMAD** in only 3% yield (Scheme 2). Actually, for other **AMYs**, such dimerization has also been observed. Importantly, the yield of **18** (51%) can be improved by heating the solutions of precursor **4** in a highboiling base, such as tributylamine (Scheme 2). Oxidation of **18a** with excess DDQ in dry $C_2D_2Cl_4$ afforded pyrazine-incorporated hexabenzoperylene (HBP) derivative **19**. Diaza-HBP **19** was highly unstable, probably as a result of its antiaromatic pyrazine-type core.⁶⁸

Notably, through the on-surface coupling of dibenzo-9a-azaphenalene (DBAP) salt **4f**, N-doped diaza-HBC **20** was achieved by the subsequent thermally induced cyclodehydrogenation (Scheme 2).⁶⁸ The chemical structure of diaza-HBC **20** was clearly elucidated by high-resolution scanning tunneling microscopy (STM) and frequency-modulated atomic force microscopy (FM-AFM; Figure 4). First, compound **4f** was deposited on Ag(111) through molecular beam evaporation. Then, a small amount of **20** was observed upon annealing at 270 °C (Figure 4, a). In contrast to the results of solution synthesis (Scheme 2), intermediate **18c** was not detected after annealing the deposited **4f** in



Scheme 2 In-solution synthesis of diaza-HBP **19** and surface-assisted synthesis of N-doped diaza-HBC **20**. *Reagents and conditions*: (a) Tributylamine, dimethyl sulfoxide (DMSO), 190 °C; (b) DDQ, $C_2D_2Cl_4$, 100 °C; (c) on the Ag(111) surface in vacuo. Blue: nucleus-independent chemical shifts (NICS) values (unit: ppm) from calculations; in parentheses: NICS(1) value.

different ultrahigh vacuum (UHV) conditions on Ag(100), Ag(111), and Cu(111), nor was the incorporation of boron nitride (BN) on Cu(111), indicating that the homocoupling of **4f** and dehydrogenation of **20** occurred simultaneously at this deposition temperature. Finally, the structure of **20** was confirmed by high-resolution STM (Figure 4, b) and FM-AFM (Figure 4, c and d). Interestingly, a slightly distorted



Figure 4 Surface-assisted coupling of **4f** provides diaza-HBC **20** on Ag(111). (a) Overview scanning tunneling microscopy (STM) image on Ag(111); Vs = 30 mV, It = 10 pA; (b) constant-height STM image of diaza-HBC **20** with partially superposed molecular model; Vs = 5 mV; (c) frequency-modulated atomic force microscopy (FM-AFM) image of **20**; (d) Laplace-filtered FM-AFM image of diaza-HBC **20**; apparent C=C distance of 1.0 Å (black), and N–C distance of 1.8 Å (blue).

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central pyrazine-ring in 20 is observed in the FM-AFM results on Ag(111) (Figure 4, d). Furthermore, nucleus-independent chemical shift (NICS) calculations were performed for **19** and **20**, in which the central pyrazine cores possess high positive values, revealing their antiaromaticity (Scheme 2). These results demonstrate the antiaromatic feature of pyrazine-containing PAHs and offer the possibility of on-surface synthesis of N-doped graphene nanostructures.

Apart from benzene, phenalene is the smallest graphene molecule with full zigzag edge structures.^{69,70} Therefore, the zigzag-edged nanographenes or graphene nanoribbons (GNRs) can be realized by repeating this phenalene unit. This suggests that the N-doped zigzag GNRs can be synthesized by extending the corresponding compound 4 with zigzag edges, which is exemplified by the next-generation 24-1,66,71 a fused dimer with two PAMY units. The synthetic route towards 24-1 is described in Scheme 3. First, one-sided Suzuki coupling was carried out between 1-hydroxy-3H-2,1-benzoxaborole and 2,6-dibromo-4-(*tert*-butyl) aniline (1) to provide 21. Then, twofold Suzuki coupling of 1.5-dibora-2.6-dioxa-sym-hydrindacene-l,5-diol and 21 resulted in the synthesis of 22.

Subsequently, HCl-induced cyclization of 22 under microwave conditions afforded compound 23. Finally, under inert conditions, the dimer 24-1 was generated through the deprotonation of 23 using anhydrous triethylamine. Compared to that of the monomer **PAMY a** (λ_{max} = 580 nm; Scheme 1), the maximum UV/Vis absorption of dimer 24-1 was observed at λ = 751 nm. This large redshift of the UV/Vis absorption of dimer **24-1** is due to the extended π conjugation in the two resonance structures 24-1 and 24-2 (Scheme 3), as well as by an additional quinoid resonance structure in 24-3. In addition, this dimeric PAMY 24 can also be considered a potential building block for the synthesis of large N-doped PAHs or corresponding N-doped GNRs through 1,3-dipolar cycloaddition reactions or surface-assisted homocoupling. In addition to the aforementioned work reported by our group, Ito and Nozaki et al. presented the synthesis of the same isoquinolino[4,3,2-de]phenanthridine (PAMY) core, which was used for 1,3-dipolar cycloadditions with different kinds of alkynes and alkenes to synthesize the corresponding 2,5-dihydropyrroles, pyrrolidines, and pyrroles.⁷² Moreover, this **PAMY** was also utilized as a model segment to generate benzene-fused azacorannulene,73 pyrrole-fused corannulene,74 and a corannulene/azacorannulene hybrid nitrogen-containing buckybowl.75

3 Cationic Nitrogen-Doped Helical PAHs

From a molecular perspective, graphitic-type N doping can be defined as the substitution of one quaternary carbon atom by an N atom. Therefore, this N-doped motif results in a cationic nitrogen species, which alters the electron densitv at the Fermi level and has a tremendous influence on tailoring the optical and electronic structures of graphene.⁷⁶⁻⁸⁴ Cationic N-doped nanographenes (CNDNs) with planar structures have been synthesized as mentioned in section 2, such as PAMY, 4 and 23, which possess interesting chemical and physical properties. However, CNDNs possessing a





Scheme 3 Synthetic route towards the next higher homologue 23 and PAMY dimer 24-1. Reagents and conditions: (a) Pd(PPh₃)₄, 1-hydroxy-3H-2,1benzoxaborole, K₂CO₃, ethanol, toluene; (b) Pd(PPh₃)₄, I,5-dibora-2,6-dioxa-sym-hydrindacene-I,5-diol, K₂CO₃, ethanol, toluene; (c) 1) HCl, dioxane, O₂, microwave; 2) trityl BF4, toluene, acetonitrile; (d) triethylamine. Resonance structures of 24-1, 24-2, and 24-3, in which the Clar sextets are highlighted in gray.

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nonplanar geometry, such as helicenes, offer extraordinary graphene nanostructures with unique π – π interactions and π -electron delocalization. In turn, this helical geometry would also affect their physical and chemical properties.^{85–93} For instance, PAHs with chiral centers can be obtained through helicity, which renders helical PAHs promising chiral materials in organic spin filters.^{94–96} Recently, we demonstrated the fabrication of a novel class of helical **CNDNs**, such as singly charged aza[5]helicene and coveedged aza[4]helicenes with two charges (Figure 5).⁹⁷



Scheme 4 Synthesis of N-charged helicenes $27a^+-e^+$. Reagents and conditions: (a) $[Cp^*RhCl_2]_2$, AgO₂CCF₃, MeOH, 120 °C, 20 h; Cp^{*} = C₅Me₅.

First, the synthesis of helical N-charged nanographenes 27a⁺-e⁺ is described in Scheme 4. The desired aza[5]helicenium salt **27a⁺-c⁺**, in which trifluoracetate was incorporated as an anion by using an excess of silver trifluoroacetate, was achieved by a rhodium-induced annulation process.^{98,99} To enhance the solubility of the helical N-charged nanographenes in solution, 1,2-bis[4-(tert-butyl)phenyl]ethyne with a bulky group was employed as the annulation unit. By means of a similar synthetic strategy, a higher-order helicene and larger π -conjugation system was also achieved. Accordingly, the racemic N-doped aza[6]helicenium (27d⁺) and aza[7]helicenium (27e⁺) cations were synthesized as their trifluoroacetate salts in yields of 46% and 70%, respectively. In addition, the successful achievement of singly Ncharged helical nanographenes $(27a^+-e^+)$ led to the synthesis and investigation of larger helical CNDNs, such as those with cove-edged peripheries. Finally, doubly charged Ndoped aza[4]helicenium cations $30a^{2+}-c^{2+}$ were realized through this bottom-up organic synthesis (Scheme 5). The related precursors **29a-c** were obtained by Suzuki coupling of pinacol esters **28a–c** and 2-bromopyridine in one step. N-Charged **30a²⁺-c²⁺** were synthesized through rhodiuminduced annulation as either triflate or trifluoroacetate salts in good vields (83–96%). Moreover, to demonstrate the feasibility of counterions in the synthesis, silver triflate was utilized to present triflate as an anion for **30c²⁺[OTf⁻]**₂.

Compared with all-carbon PAHs, the above N-charged helical PAHs possess energetically low-lying frontier molecular orbitals with a significant stabilization of the lowest unoccupied molecular orbital (LUMO), which leads to a narrower optical energy gap and a higher electron affinity. Moreover, electrochemical or spectroelectrochemical inves-



Scheme 5 Synthesis of double N-charged nanographenes $30a^{2+}-c^{2+}$ with cove-edges. *Reagents and conditions*: (a) Pd(PPh₃)₄, 2-bromopyridine, Na₂CO₃, toluene/H₂O/MeOH, 90 °C, 15 h; (b) [Cp * RhCl₂]₂, 1,2-bis[4-(*tert*-butyl)phenyl]ethyne, AgO₂CCF₃ ($30a^{2+}-b^{2+}$) or AgOTf ($30c^{2+}$), MeOH, 120 °C, 24 h.

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tigations confirmed the *in situ* generation of N-containing neutral or cationic radicals, depending on the number of N atoms. The N-doped aza[4]helicenes with two charges showed stable redox behavior and viologen-like characteristics. Figure 6 (a) displays the UV/Vis/NIR spectra of 27e⁺[CF₃CO₂⁻], which were measured at the reduction step during cyclic voltammetry. Generation of the N-containing neutral radical **[27e]** is followed by loss of the peak at λ = 469 nm for **27e⁺[CF₃CO₂⁻]**, and the new bands appear at λ = 513, 692, and 817 nm (Figure 6, a). A weak NIR absorption was also observed at λ = 1450 nm (Figure 6, a insert). Moreover, the *in situ* EPR measurements verify the generation of the helical radical (Figure 6, b). According to the theoretical calculation, the spin density of this N-containing helical radical is distributed on the skeleton of the azahelicene core (Figure 6, c). Moreover, the hyperfine EPR spectrum could be reproduced very well with the coupling constants of the nitrogen atom and four protons (Figure 6, b). The helical structure of the in situ formed N-containing neutral radical [27e] is described in Figure 6 (d).



Figure 6 (a) UV/Vis/NIR spectra of **27e**⁺ performed at the electrochemical reduction. (b) Simulated and experimental EPR spectra during the electrochemical reduction of **27e**⁺. c) Spin density distribution and main hyperfine coupling constants of neutral radicals **[27e]**⁺ from the calculation (in Gauss; H black, N gray). (d) The proposed chemical structures of the *in situ* produced **[27e]**⁺.

4 Nitrogen–Boron–Nitrogen-Doped PAHs

The chemical and thermal stabilities of polyacenes can be dramatically improved by the introduction of heteroatoms into their carbon skeletons; accordingly, the molecular energy levels (such as HOMO and LUMO) of the resulting heteroacenes can be essentially tailored.^{100–103} In this respect, replacement of one or more *sp*² carbon–carbon (*C*=*C*) units with isoelectronic boron–nitrogen (BN) bonds provides BN-doped PAHs with outstanding alteration in their electronic structures.^{104–107} In particular, the different beDownloaded by: University of Newcastle (UK). Copyrighted material.

havior of the electronegativities of nitrogen and boron atoms in a BN motif results in BN-doped nanographenes with unique polarities.¹⁰⁸⁻¹¹² Therefore, alteration of the locations of nitrogen and boron atoms in BN-doped PAHs strongly influences their dipole moments. Recently, we presented an efficient synthetic method for the fabrication of various ladder-type heteroacenes containing BN units based on the cyclization of aromatic borylation.¹¹³⁻¹¹⁷ In addition to the introduction of BN heteroatoms into PAHs, nanographenes containing nitrogen-boron-nitrogen (NBN) units have also attracted great interest due to their prospective applications in molecular optoelectronic devices.¹¹⁸⁻¹²⁵ Importantly, the NBN unit in PAHs can be selectively oxidized into the corresponding radical cation, which is the isoelectronic structure of its pristine carbon frameworks with open-shell character (Scheme 6, a).



We demonstrated the efficient synthesis of the first case of NBN-doped 1,9-diaza-9a-boraphenalenes with zigzag edges, namely NBN-dibenzophenalenes (NBN-DBPs, **34**, Scheme 6, b).¹¹⁸ Based on a three-step method, the synthesis of **34** is described in Scheme 6 (b). As a key point of this synthetic route, a trimethylsilyl (TMS) group was adopted as a guiding unit to easily generate the N–B–N bond at the periphery of PAHs by electrophilic-induced aromatic borylation. First, compound **32** was synthesized through selective lithiation of **31** using lithium diisopropylamide (LDA), followed by quenching the reactions by trimethylsilyl chloride (TMSCI). Subsequently, compound **33** was obtained

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through the Suzuki coupling of 2-aminoarylboronic acid esters and **32**. Finally, NBN-doped PAHs **34** were achieved in 90% yield through electrophilic aromatic borylation in the treatment of BCl₃ and triethylamine at 180 °C. Following a similar synthetic strategy, π -extended compound **39** was synthesized by further modification of the carbon framework of **34** (Scheme 7), which can serve as the next-generation homologue NBN-edged dibenzoheptazethrene (denoted as **NBN-DBHZ**). This efficient protocol offers the opportunity for the in-solution synthesis of NBN-edged PAHs or GNRs with a stable zigzag periphery.



Scheme 7 Synthetic route towards NBN-edged PAH **39**. *Reagents and conditions*: (a) Pd(PPh₃)₄, CsCO₃, toluene/ethanol, 90 °C; (b) (Bpin)₂, KOAc, DMSO, 100 °C; (c) Pd(PPh₃)₄, CsCO₃, toluene/ethanol, 90 °C; (d) BCl₃, Et₃N, o-DBC, 180 °C.

Interestingly, compound 34 was quantitatively transformed into its σ -dimer **34-2** upon chemical oxidation in the treatment of Cu(OTf)₂ (Scheme 6, c). From the UV/Vis spectrum, the maximum absorption peak of 34 is at approximately λ = 351 nm, which is associated with two absorption bands in the range of 250-300 and 300-400 nm. Compared to that of monomer 34, the maximum absorption peak of the NBN-edged **39** is shifted to λ = 435 nm. This redshift of **39** is due to the extended π -conjugation. It is worth noting that compound 39 displays split emission bands and exhibits a much better fluorescence quantum yield (Φ_{PI} = 0.83) than monomer **34** (Φ_{PI} = 0.24). Titration of compound **34** with Cu(OTf)₂ led to the generation of radical cations, which could be detected by UV/Vis/NIR spectroscopy measurements (Figure 7, a). By addition of Cu(OTf)₂, a new absorption band of 34 gradually evolved in the visible/NIR regions at λ = 404, 620, and 1150 nm, accompanying decreased peaks at λ = 336 and 352 nm. Additionally, the EPR analysis demonstrated a significant signal at g =2.0033 (Figure 7, b). This oxidation behavior of 34 clearly revealed the regioselective activity of this kind of NBNdoped PAH with zigzag edges.





Figure 7 a) UV/Vis/NIR absorption spectra of compound **34** upon addition of different concentrations of Cu(OTf)₂ in acetonitrile (10^{-5} M, Cu(Otf)₂: 0, 0.5, 1.0, 1.5, 2.0, 2.5 equiv); b) EPR results of the reaction mixture of **34** + Cu(Otf)₂ in acetonitrile (10^{-3} M); c) cyclic voltammetry (scan rate: 100 mV/s) of compound **34** in acetonitrile (*n*-Bu₄NPF₆, 10^{-1} M).

We recently reported an efficient approach towards the construction of NBN-doped PAHs **43** and **46** containing pentagonal and heptagonal rings in addition to hexagonal rings (Scheme 8).¹²⁶ First, N^2 -(2-bromophenyl)-2'-(trimethylsilyl)-[1,1':3',1''-terphenyl]-2,2''-diamine (**41**) was synthesized by treatment of **40** with 1 equivalent of 1-bromo-2-iodobenzene. Then, 9-(2-bromophenyl)-8H,9H-8,9-diaza-8a-borabenzo[*fg*]tetracene (**42**) was obtained by heating a solution of **41** with BCl₃ and excess triethylamine in *o*-dichlorobenzene (*o*-DCB) at 180 °C. Afterwards, 4b,15b-diaza-4b1-borabenzo[*fg*]indeno[1,2,3-*op*]tetracene (**43**) was



Scheme 8 Synthesis of NBN-doped PAH **43** and **46**. *Reagents and conditions*: (a) 1-bromo-2-iodobenzene, DPEphos, Pd(OAc)₂, NaOtBu, toluene; (b) BCl₃, o-DCB, Et₃N; (c) DPEphos, Pd(OAc)₂, NaOtBu, toluene; (d) Ni(COD)₂, 4,4'-bipyridine, COD, DMF/toluene.

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synthesized through a Buchwald–Hartwig reaction of **42** in 70% yield. Following a similar synthetic method, 8,9-bis(2-bromophenyl)-8H,9H-8,9-diaza-8a-borabenzo-[fg]tetra-

cene (45) could be obtained from the same starting material 40 (Scheme 8). Finally, the Yamamoto intramolecular reaction of 45 afforded 4b,15b-diaza-4b1-borabenzo[fg]dibenzo-[4,5:6,7]cycl-ohepta[1,2,3-op]tetracene (46) in 78% yield. Introduction of five- and seven-membered rings into NBN-doped PAHs can not only tune their optical and electronic properties but also alter the geometry of the molecules. For instance, 43 containing one five-membered ring displays a planar structure: however, compound 46 possesses a double hetero[4]helicene geometry. Interestingly, pentagon-embedded 43 and heptagon-embedded 46 exhibit higher stability under electrochemical oxidative BN-doped conditions than previously reported PAHs.^{113,114,117} Moreover, on the basis of DFT calculations and single-crystal X-ray studies, these nonhexagonal ringembedded 43 and 46 display unique global-aromatic features with antiaromatic NBN rings, indicating that the π electrons are delocalized over the whole skeleton. The single-crystal OFETs of 43 and 46 deliver a p-type mobility of 0.05 cm²V⁻¹s⁻¹ and 0.01 cm²V⁻¹s⁻¹, respectively, indicating the potential application in organic electronics for such NBN-embedded π -conjugated compounds.

In contrast, the introduction of four-coordinate boron units into various sp²-carbon skeletons leads to the synthesis of boron-containing chromophores, which have achieved significant progress.¹²⁷⁻¹³¹ In this Account, both the weak B,N-coordinated bond and the strong B,N-covalent bond are considered NBN systems. Interestingly, this four-coordinate NBN system not only possesses a shapepersistent molecular skeleton but also has a great influence on controlling molecular packing and optical and electronic properties.^{132,133} Moreover, the position and number of the B.N-coordinated unit in π -expanded PAHs also affect the geometric and electronic structures.¹³⁴⁻¹³⁶ Recently, we presented the synthesis of unique chromophores with triple B.N-coordinated units (Scheme 9).¹³⁷ Through a typical three-step reaction followed by the Buchwald-Hartwig reaction, hydrolysis, and cyclization, the key building block of 6,12,18-trichloro-5,11,17-triazatrinaphthylene (50) was obtained from 1,3,5-tribromobenzene. Then, 6,12,18tris(hexylamine)-5,11,17-triazatrinaphthylene **51a** and 6,12,18-tris(dodecylamine)-5,11,17-triazatrinaphthylene 51b were synthesized by the reaction of 50 with different kinds of alkylamines at 135 °C. Compounds 52a and 52b were obtained with yields of 69% and 66%, respectively, upon treatment of ligands 51a and 51b with boron trifluoride etherate (BF₃·OEt₂) at 80 °C in toluene. 53a and 53b were obtained with yields of 60% and 64%, respectively, by using triphenylboron under similar reaction conditions.

Interestingly, the lengths of the covalent and coordination B–N bonds in **52** and **53** are similar (1.53 Å and 1.56 Å for **52a**; 1.56 Å and 1.61 Å for **53a**), indicating that the elec-



Scheme 9 Synthesis of triple B,N-coordinated chromophores. *Reagents and conditions*: (a) Pd(OAc)₂, Cs₂CO₃, toluene, reflux; (b) 5% NaOH, acetone, reflux; (c) POCl₃, reflux; (d) R–NH₂, reflux; (e) Et₃N, BF₃·OEt₂, 90 °C, toluene; (f) B(Ph)₃, toluene, 120 °C.

trons in 52 and 53 are likely delocalized over the N-B-N system. However, the lengths of the B-N bonds in 52 and 53 are longer than those of the aforementioned NBN-embedded PAHs. For instance, the B-N bond lengths in 34 are approximately 1.42-1.44 Å. Notably, in comparison to the maximum absorption of **52a** (λ_{max} = 428 nm), the maximum absorption of **53a** (λ_{max} = 454 nm) is exceedingly bathochromically shifted by 26 nm, indicating that the optical properties of the B.N-coordinated system can be influenced by the substituents on the boron centers. This bathochromic shift for **53a** can be caused by the electron-donating effect of the phenyl groups. Moreover, among the B,N-coordinated chromophores, 52a and 53a display the highest Stokes shifts of 106 nm and 157 nm, respectively. In addition, upon irradiation with white and UV light, 52a can become cross-linked both in the solid state and in solution and is thus employed as a negative photoresist.¹³⁸

5 Conclusion and Outlook

In recent decades, the synthesis of PAHs containing heteroatoms has received increasing attention because of their promising electronic and magnetic properties, with promising applications in organic electronics, sensing, and metal-free catalysis. The bottom-up organic synthetic method provides the opportunity to access the precise control of different heteroatoms and doping positions at the molecu-

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lar level. In the past decade, different groups have explored the synthesis and device applications of N- or NBN-embedded PAHs.^{72,111,139-143} However, efficient synthetic protocols are highly demanded to enhance the chemical diversity of such heteroatom-doped PAHs. In this Account, we have highlighted our recent efforts towards efficient synthesis. For instance, we have demonstrated synthetic access to PAMYs, which can serve as flexible building blocks for the fabrication of large N-containing nanographenes. Moreover, the solution chemistry of PAMYs can be employed for the surface-assisted synthesis, yielding pyrazine-type diaza-HBC through on-surface homocoupling and concomitant cyclodehydrogenation. Instead of solely N-doped NGs, replacement of one or more carbon-carbon (C=C) bonds with isoelectronic B-N units provides BN-doped PAHs with exceptional variation in their electronic structures. The feasible synthesis of NBN-embedded PAHs containing pentagonal and heptagonal rings has also been achieved using metal-catalyzed cyclization. The successful synthesis of heteroatom-doped nanographenes at the molecular level provides substantial opportunities not only for the investigation of their electronic structures but also for their application in organic electronics, such as in OLEDs and OFETs. Moreover, the exploration of heteroatom-doped, structurally defined GNRs^{144,145} is a future goal in this area.

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