NBN-Doped Bis-Tetracene and Peri-Tetracene: Synthesis and Characterization

Yubin Fu*, Xiao Chang*, Huan Yang*, Evgenia Dmitrieva, Yixuan Gao, Ji Ma, Li Huang, Junzhi Liu,* Hongliang Lu, Zhihai Cheng, Shixuan Du, Hong-Jun Gao, and Xinliang Feng*

Abstract: Combining solution-based and surface-assisted synthesis, we demonstrate the first synthesis of NBN-doped bis-tetracene (NBN-BT) and peri-tetracene (NBN-PT). The chemical structures are clearly elucidated by high-resolution scanning tunneling microscopy (STM) in combination with noncontact atomic force microscopy (nc-AFM). Scanning tunneling spectroscopy (STS) characterizations reveal that NBN-BT and NBN-PT possess higher energy gaps than bis-tetracene and peri-tetracene. Interestingly, NBN-BT can undergo stepwise one-electron oxidation and convert into its corresponding radical cation and then to its dication. The energy gap of the NBN-BT dication is similar to that of bis-tetracene, indicating their isoelectronic relationship. Moreover, a similar energy gap between the NBN-PT dication and peri-tetracene can be predicted by DFT calculations. This work provides a novel synthesis along with characterizations of multi-NBN-doped zigzag-edged peri-acenes with tunable electronic properties.

Acenes, which can be regarded as laterally fused benzene rings, have drawn great interest in recent decades. From a structural point of view, acenes can be classified as a unique type of polycyclic aromatic hydrocarbon (PAH) with zigzag-edged peripheries (Figure 1a). When two linear acenes are laterally fused at the peri-positions, the resultant PAHs are named peri-acenes. Typical peri-acenes possess two armchair edges and extended zigzag-edged topologies (Figure 1a). As the precursors of peri-acenes, bis-acenes also possess extended zigzag-edged topologies (Figure 1a). The smaller peri-acenes, perylene, and bis-anthene, have been well studied.

Figure 1. a) Chemical structures of acenes, bis-acenes, and peri-acenes; b) chemical structures of bis-tetracene, peri-tetracene, and circum-terracene; c) chemical structures of B-doped bis-anthene, N-doped dibenzopentalene (DBP), NBN-doped DBP, and BNB-doped phenalenyl; and d) this work: NBN-doped bis-tetracene (NBN-BT) and NBN-doped peri-tetracene (NBN-PT). The substituents of all structures are omitted for simplicity.

[+] Dr. Y. Fu, Dr. J. Ma, Prof. X. Feng
Center for Advancing Electronics Dresden (cfaed) & Faculty of Chemistry and Food Chemistry, Technische Universität Dresden
01062 Dresden (Germany)
E-mail: xinliang.feng@tu-dresden.de
X. Chang, Dr. H. Yang, Y. Gao, Dr. L. Huang, Dr. H. Lu, Prof. S. Du, Prof. H. Gao
Institute of Physics and University of Chinese Academy of Sciences, Chinese Academy of Sciences
Beijing 100190 (China)
E-mail: lihuang@iphy.ac.cn
Dr. E. Dmitrieva
Leibniz Institute for Solid State and Materials Research
01069 Dresden (Germany)
Dr. J. Liu
Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong
Pokfulam Road, Hong Kong (China)
E-mail: juliu@hku.hk
Dr. Z. Cheng
Department of Physics and Beijing Key Laboratory of Optoelectronic Functional Materials & Micro-nano Devices, Renmin University of China
Beijing 100872 (China)
[+] These authors contributed equally to this work.
* Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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investigated for several decades.\textsuperscript{[1,6]} Higher peri-acenes, from peri-tetracene up to peri-heptacene, which have been recently synthesized, display open-shell multiradical features at their ground states. Such open-shell character leads to poor ambient stability and high reactivity, which hampers further studies and applications.\textsuperscript{[7]} For instance, peri-tetracene can easily undergo oxidation reactions under ambient conditions, and its bay regions enable its further functionalization through Diels–Alder reactions, yielding the fully zigzag-edged circumanthracene (Figure 1b).\textsuperscript{[7b,8]}

Thus far, two main strategies, sterically blocking the most reactive position (kinetic stabilization) and heteroatom doping (thermodynamic stabilization), have been established to synthesize stable zigzag-edged acenes.\textsuperscript{[3b,9]} Specifically, the introduction of heteroatoms such as boron (B) or nitrogen (N) on the zigzag edges, not only provides access to stable heteroatom-doped acenes but also offers the possibility to tune their electronic structures.\textsuperscript{[3,10]} For instance, bis-anthene is reactive toward oxygen due to its radicaloid character at its zigzag edges, while B-doped bis-anthene is quite stable under ambient conditions and emits intense fluorescence (Figure 1c).\textsuperscript{[10b,11]} Apart from B-doped bis-anthene, zwitterionic N-doped dibenzophalenenes (DBPs) also demonstrate higher stability than open-shell DBPs (Figure 1c).\textsuperscript{[12]} In addition to mono- or double B/N-doped zigzag-edged PAHs, recent efforts have been mainly paid to substitute a fullerene unit at the zigzag edge with an NBN or NBN-BT motif, such as NBN-doped DBPs or BN-B-doped phenalenyl (Figure 1c), which possess stable zigzag edges.\textsuperscript{[13–15]} Moreover, owing to the BN/CC isosterism,\textsuperscript{[14]} further oxidation or reduction of these NBN-doped DBPs or BN-B-doped phenalenyl generated interesting characteristics, such as comparable electronic structures to their open-shell all-carbon analogs.\textsuperscript{[13–15]} Nonetheless, the multi-NBN-doped zigzag-edged acene-type system remains less explored due to the lack of a suitable molecular design and synthesis strategy.

Herein, we demonstrate the novel synthesis of NBN-doped bis-tetracene (NBN-BT) and peri-tetracene (NBN-PT) by combining both in-solution and on-surface synthesis (Figure 1d). First, NBN-BT can be achieved via a tandem twofold electrophilic borylation approach based on a tetra(aminophenyl)-phenyl precursor (compound 5 in Scheme 1). Subsequently, NBN-PT can be achieved based on NBN-BT through in-solution photocyclization (I\textsubscript{2}, propylene oxide) and surface-assisted intramolecular cyclodehydrogenation reactions. According to the high-resolution scanning tunneling microscopy (STM) characterization, NBN-BT adopts a double-helical structure, while NBN-PT displays planar geometry. The chemical structure of NBN-BT can be further elucidated by noncontact atomic force microscopy (nc-AFM) at the molecular level. The optical energy gaps of NBN-BT and NBN-PT are determined to be 2.48 eV and 2.45 eV, respectively, from the onset of their UV-vis absorption spectra, which are substantially higher than those of their carbon-based analogs bis-tetracene (1.56 eV) and peri-tetracene (1.11 eV). Interestingly, upon chemical or electrochemical oxidation, NBN-BT can be converted into its corresponding radical cation with a near-infrared (NIR) absorption band and an electron paramagnetic resonance (EPR) signal, and further oxidized into its dication instead of its diradical dication according to the absent EPR signal. The optical energy gaps of the NBN-BT radical cation and dication are derived to be 0.88 eV and 1.24 eV, respectively, the latter being similar to its corresponding isoelectronic structure bis-tetracene (1.56 eV). Likewise, DFT calculations reveal a similar energy gap between the NBN-PT dication (1.21 eV) and peri-tetracene (1.11 eV), demonstrating their isoelectronic relationship.

The synthesis routes toward NBN-BT and NBN-PT are illustrated in Scheme 1. First, Suzuki coupling was performed between 2,5-diiodo-1,4-di(trimethylsilyl)-phenyl (1) and nitrophenyl boronic ester, which provided 2,5-dinitrophenyl boronic ester, which provided 2,5-dinitrophenyl boronic ester (compound 3 in Scheme 1). Compound 2 was converted into 2,5-di(di(aminophenyl)-1,4-diodo-phenyl) (3) in an 85% yield. Subsequently, twofold Suzuki coupling of 3 with aminophenyl boronic ester afforded 2,5-di(di(aminophenyl)-1,4-di(aminophenyl)-phenyl (4) in a 78% yield. Afterward, compound 4 was reduced in hydrogen gas with Pt/C at room temperature to provide 1,2,4,5-tetra(aminophenyl)-phenyl (5) in 78% yield. Finally, NBN-BT was successfully achieved in a 20% yield through a tandem twofold electrophilic borylation approach based on compound 5 in the presence of boron triiodide (BI\textsubscript{3}), triphenylborane (BPH\textsubscript{3}), and dichlorobenzene (o-DCB) at 200°C.\textsuperscript{[16]} To obtain NBN-PT, solution-phase synthesis was first performed through a Scholl-type cyclization of NBN-BT under 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or iron(III) chloride (FeCl\textsubscript{3}) condition. However, all attempts failed, probably due to the formation of stable NBN-BT radical cation or dication under the oxidative conditions that prevent further cyclization reaction. Nevertheless, NBN-PT could be synthesized by a photocyclization reaction of NBN-BT in the presence of propylene oxide and iodine (I\textsubscript{2}).

The targeted compound NBN-PT was purified by silica column chromatography and then precipitated in acetone/n-hexane. NBN-BT was first characterized by high-resolution
matrix-assisted laser desorption/ionization time of flight mass spectrometry (HR-MALDI-TOF-MS). In Figure 2a, there is only one dominant peak in the mass spectrum of NBN-BT, revealing its defined molecular composition; the isotopic distribution pattern of the mass peak is in good agreement with the calculated pattern (Figure S33). The $^1$H NMR spectrum displays well-resolved peaks (Figure 2b), in which the a-e peaks can be fully assigned by 2D NMR (Figure 2b and S17–20). In addition, there is one sharp resonance at 20.2 ppm in the $^{11}$B NMR spectrum of NBN-BT (Figure S16). In contrast to NBN-BT, the poor solubility of NBN-PT hampers its further purification, leading to its difficult full characterization by NMR and HR-MS. Nonetheless, Figure 2a presents the mass spectrum of NBN-PT with the peak center located at 454.2463, which agrees with the calculated molecular weight. In addition, the isotopic distribution pattern of the mass peak fits well with the calculated pattern (Figure S34).

Due to their poor solubility and crystallinity, single-crystal structures of NBN-BT and NBN-PT cannot be achieved after different crystallization attempts from solvents such as dichloromethane/methanol, acetone/iso-hexane, and tetrahydrofuran/iso-hexane. Through DFT calculations (B3LYP-GD3BJ/6-31G(d,p)), NBN-BT shows a double hetero-[5]helicene geometry with a dihedral angle of 32.7° (Figure 2c), while NBN-PT exhibits a planar structure. The B–N bond lengths in NBN-BT (1.42 Å) and NBN-PT (1.43 Å) are much shorter than a typical B–N single bond (1.58 Å) but slightly longer than a localized B= N double bond (1.40 Å).[17] In addition to the DFT-optimized structure, on-surface characterization of NBN-BT was performed. According to the high-resolution STM characterizations (Figure 2e), when NBN-BT was sublimed onto an Au(111) substrate kept at room temperature under ultrahigh vacuum (UHV) conditions, it demonstrates an “up and down” configuration, clearly revealing a double helical conformation, which is supported by the DFT calculations (Figure 2c). The differential conductance (dI/dV) spectrum in Figure 2f displays that the HOMO and LUMO energy levels locate at -0.82 V and +2.26 V, respectively, which gives an energy gap of 3.08 eV for NBN-BT, comparable with the DFT calculation results (3.07 eV, Figure S25). The dI/dV maps at the HOMO and LUMO energy levels are shown in (g,h) for the same NBN-BT molecule in (e). Scanning parameters: (e) $V_s$ = 1 V, $I_t$ = 100 pA; (f) $V_s$ = 2.5 V, $I_t$ = 300 pA, $V_{mod}$ = 20 mV; and (g,h) $I_t$ = 400 pA, $V_{mod}$ = 10 mV.
LUMO energy levels of NBN-BT are shown in Figure 2g and 2h, respectively, in which the HOMO is mainly located at the planar part of NBN-BT, while the LUMO is delocalized over the entire molecule.

The UV-vis absorption and fluorescence spectra of NBN-BT and the crude product of NBN-PT in anhydrous dichloromethane (DCM) solution are presented in Figure 2d. Due to the rigid conjugated structure of NBN-BT, well-resolved vibronic bands are observed. In particular, the maximum absorption peak at 474 nm can be assigned to the HOMO→LUMO transition based on time-dependent density functional theory (TD-DFT) calculations (Figure S29). The optical energy gap of NBN-BT is estimated to be 2.48 eV from the UV-vis absorption edge (Figure 2d), which is substantially larger than that of the fully carbon-based analog bis-tetracene (1.56 eV).[24] In contrast to the nonfluorescent bis-tetracene, NBN-BT exhibits intense yellow-green fluorescence (quantum yield: 0.31, using fluorescein as the reference) with a maximum emission peak at 491 nm (Figure 2d). Accordingly, the Stokes shift is as small as 17 nm, manifesting the rigid conjugated structure of NBN-BT. Regarding the crude product of NBN-PT, its maximum absorption peak (480 nm) is slightly redshifted compared with that of NBN-BT (474 nm), indicating the extended π-conjugated structures of NBN-PT over NBN-BT. Moreover, the maximum emission peak of NBN-PT (501 nm) is redshifted compared to that of NBN-BT (491 nm).

The electrochemical behavior of compound NBN-BT in anhydrous acetonitrile (MeCN) was further investigated by means of cyclic voltammetry (CV) measurements (Figure S22). Two oxidation processes are observed with half-wave potentials of 0.23 and 0.47 V vs. Fe/C′/Fe, respectively. Nevertheless, no reduction process is observed. Accordingly, the HOMO energy level of NBN-BT is estimated to be −4.57 eV (Table S1). On the basis of its optical energy gap, the LUMO energy level of NBN-BT is derived to be −2.09 eV (Table S1). The HOMO energy level of NBN-BT is comparable to that of all-carbon-based bis-tetracene, while the LUMO energy level is obviously higher than that of bis-tetracene (Table S1). The CV measurement of NBN-PT cannot be performed due to its poor solubility. Nonetheless, DFT calculations based on NBN-PT reveal its HOMO (−4.68 eV) and LUMO (−1.31 eV) energy level, as well as energy gap (3.37 eV), in contrast to those of the all-carbon-based peri-tetracene (HOMO/LUMO/energy gap: −4.38/−2.62/1.76 eV, Table S1). Therefore, the different electronic properties and stabilities of NBN-BT and NBN-PT from bis-tetracene and peri-tetracene can be attributed to the unique NBN dopant units at the zigzag edges.

In addition to the solution synthesis of NBN-PT, we further carried out the on-surface synthesis of NBN-PT (from the precursor NBN-BT). Planarized NBN-PT was achieved by thermal annealing NBN-BT on Au(111) at 350°C. Figure 3a,b present the STM image in which the NBN-BT molecules separately appear on the Au(111) substrate. To unambiguously clarify the atomically resolved structure of NBN-BT, nc-AFM measurements with a CO-functionalized tip were performed. Figure 3c depicts the resulting constant-height frequency-shift image in which each atom and bond of NBN-PT can be clearly visualized. The d/dV spectra in Figure 3d reveal the HOMO and LUMO energy levels of NBN-BT to be −0.88 eV and 2.40 eV, respectively. Accordingly, the corresponding energy gap is 3.28 eV, which is further supported by DFT calculations (Figure S25, 3.37 eV). Compared to the optical energy gaps of NBN-BT (2.48 eV) and NBN-PT (2.45 eV), the STS measured energy gaps of NBN-BT (3.08 eV) and NBN-PT (3.28 eV) are clearly higher, which can be attributed to their strong interaction with the Au substrate.[18] Moreover, planarized NBN-PT can have a stronger interaction with the Au substrate than the nonplanarized NBN-BT, which leads to larger energy gap change of NBN-PT.[18] The d/dV map at a HOMO energy of −0.88 eV in Figure 3e shows that the armchair edges of NBN-PT have much stronger intensity than the rest of the molecule. On the other hand, regarding the d/dV map at the LUMO energy (2.40 eV) in Figure 3f, both the armchair and zigzag edges possess a stronger state than that at the center of the molecule. Besides, the existence of NBN dopants slightly weaken the HOMO state intensity than that at the carbon periphery, as indicated by the yellow arrows in Figure 3f.

The NBN unit not only provides the high stability of NBN-BT but can also be further subjected to oxidation into the corresponding radical cation and dication, which provides the chemical tunability of NBN-doped zigzag-edged PAHs.[13b] Toward this end, the chemical oxidation of NBN-BT was carried out by using Cu(OTf)2. Indeed, the titration of NBN-BT with Cu(OTf)2 results in a mega-large (800 nm) bathochromic shift of the UV-vis absorption bands (Figure 4a). During the progressive addition of Cu(OTf)2, from 0 to 1.0 equivalents, a series of new absorption peaks in the visible and NIR regions gradually appear at 684 and 1239 nm with a concomitant decrease in the absorption bands at 320 and 476 nm. In addition, a distinct isosbestic point at 500 nm can be observed (Figure 4a). The strong NIR absorption band in
product can be the NBN-BT diradical dication ([NBN-BT]$^{2+}$) or NBN-BT dication ([NBN-BT]$^{3+}$, Figure 4e), which can be regarded as the isoelectronic structures of all-carbon-based bis-tetraene (Figure 4e). To determine the reaction species formed during the chemical oxidation process of NBN-BT, in situ spectroelectrochemical (SEC) measurements, a combination of CV, electron paramagnetic resonance (EPR) and UV-vis-NIR absorption spectroscopy, were performed. The EPR spectra show a broad unresolved signal with a g value of 2.0027 during the first oxidation process in the CV curve (Figure 4c). The appearance of a broad signal without hyperfine splitting (see Figure S23) reveals that the spin density in [NBN-BT]$^{2+}$ is distributed over the whole molecular skeleton. The UV-vis-NIR spectra of the charged species generated during the chemical and electrochemical oxidation of NBN-BT are identical (Figure 4a and b). Additionally, the absorption bands and the ESR signal appear simultaneously, and their intensities show the same potential profile (Figure 4d). These absorption bands can be unambiguously attributed to the corresponding monoradical species [NBN-BT]$^{+}$. At the potentials of the second oxidation process in CV, the intensities of the ESR signal and absorption bands of the radical cation (1230 nm as representative band) decrease, and new absorption bands (912 nm as representative band) occur in the UV-vis-NIR spectra (Figure 4d), suggesting that [NBN-BT]$^{2+}$ converts into the diamagnetic species [NBN-BT]$^{3+}$ instead of the diradical dication [NBN-BT]$^{2+}$.

According to the CV results, NBN-BT can undergo two reversible oxidation processes. In the first step, NBN-BT loses one electron to form the NBN-BT monoradical cation ([NBN-BT]$^{+}$, Figure 4e), which possesses an open-shell character. After adding more than 1.0 equivalent of Cu(OTf)$_2$, the second oxidation step occurs, and a possible

![Figure 4](https://example.com/image.png)

Figure 4. a) UV/Vis/NIR absorption spectra of NBN-BT titrated with Cu(OTf)$_2$ (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 equivalents) at a concentration of 10$^{-5}$ M in MeCN (reference spectrum: MeCN solution), inset: photographs of the NBN-BT and NBN-BT radical cation/dication in MeCN; b) UV/Vis/NIR spectra measured during the electrochemical oxidation of NBN-BT in MeCN solution (reference spectrum: NBN-BT solution); c) EPR spectra of NBN-BT recorded in situ at different potentials; d) the potential profiles of absorption bands and the EPR signal intensity (only the representative bands at 1230 and 912 nm are presented); e) the plausible oxidation process of NBN-BT and its corresponding isoelectronic structures; f) Calculated energy diagrams and energy gaps of bis-tetraene, NBN-BT, NBN-BT radical cation and NBN-BT dication (SOMO: single occupied molecular orbital).
DFT calculations of NBN-PT are employed to study its corresponding oxidation behavior. Likewise, the energy gaps of the NBN-PT radical cation ([NBN-PT]$^2^+$), 0.96 eV) and dication ([NBN-PT]$^{2^+}$, 1.21 eV) are significantly lower than that of its neutral compound (3.37 eV, Figure S28). Similar to NBN-BT, [NBN-PT]$^{2^+}$ exhibits a calculated energy gap similar to that of peri-tetracene (1.76 eV, Figure S28), which clearly reveals their isoelectronic relationship (Figure S28).

In summary, we demonstrated the novel synthesis of two double NBN-doped zigzag-edged nanographenes, namely, bis-tetracene (NBN-BT) and peri-tetracene (NBN-PT), through a combination of solution-based and surface-assisted synthesis. Based on the high-resolution STM characterization, NBN-BT adopts a double-helical structure, while NBN-PT displays planar geometry, in which the atomically resolved structure of NBN-PT is further unveiled by nc-AFM characterization. Compared with their carbon-based analogs bis-tetracene (1.56 eV) and peri-tetracene (1.11 eV), the NBN-BT (2.48 eV) and NBN-PT (2.45 eV) exhibit excellent stability under ambient conditions, which is associated with their higher energy gap. Notably, through controlled continuous single-electron chemical or electrochemical oxidation, NBN-BT can be converted into its corresponding radical cation (0.88 eV) and further to dication (1.24 eV), which demonstrates a similar energy gap to its isoelectronic structure bis-tetracene (1.56 eV). This work opens up a new avenue for the synthesis of stable zigzag-edged nanographenes with multi-NBN units and paves the way for investigating the isoelectronic structures of pristine carbon-based zigzag-edged acenes.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** bis-tetracene - isoelectronic - NBN doping - peri-tetracene - zigzag edges

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