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Fjord-edge Graphene Nanoribbons with Site-Specific Nitrogen Substitution

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ABSTRACT: The synthesis of graphene nanoribbons (GNRs) that contain site-specifically substituted backbone heteroatoms is one of the essential goals that must be achieved in order to control the electronic properties of these next generation organic materials. We have exploited our recently reported solid-state topochemical polymerization/cyclization-aromatization strategy to convert the simple 1,4-bis(3-pyridyl)butadiynes **3a,b** into the fjord-edge nitrogen-doped graphene nanoribbon structures **1a,b** (fjord-edge N_2[8]GNRs). Structural assignments are confirmed by CP/MAS ^{13}C NMR, Raman, and XPS spectroscopy. The fjord-edge N_2[8]GNRs **1a,b** are promising precursors for the novel backbone nitrogen-substituted $N_2[8]_A$GNRs **2a,b**. Geometry and band calculations on $N_2[8]_A$GNR **2c** indicate that this class of nanoribbons should have unusual bonding topologies and metallicities.

■ INTRODUCTION

Graphene nanoribbons (GNRs) are expected to usher in the ultimate nanosizing of electronics[1,2,3,4] and sensors[5,6] for next generation devices. The electronic properties of GNRs can be exquisitely tuned by modification of their width, backbone, and edge structure.[1,7,8,9,10] In the last decade, both on-surface and in-solution bottom-up syntheses have achieved precise structural control over these benchmarks.[11,12,13,14,15] Early bottom-up syntheses have focused on GNRs with armchair[16,17,18,19,20] or zigzag[21] edges. More recently, intricate edge or interior configurations, such as chevron,[11,22,23,24] cove,[25,26,27] fjord[28] or holey,[29,30,31] have been obtained. These novel topologies significantly alter the electronic or magnetic properties of GNRs, as do atomically precise[32] substitutions of carbons with heteroatoms such as boron,[33,34] sulfur,[35,36] or nitrogen.[30,37,38] Crucially, site-specific doping at the GNR *backbone* produces a dramatic alteration of its electronics, making such structures the most desirable targets for synthesis.[32,39,40,41] Nitrogen doped GNRs are of particular interest as they produce p-doped materials.[24,37,38,42,43,44,45]

Herein, we describe the synthesis of the first eight-atom wide, fjord-edge nitrogen-doped graphene nanoribbons **1a,b** (fjord-edge N_2[8]GNR; Figure 1). Fjord-edge N_2[8]GNRs **1a,b** were obtained in a facile two-step conversion starting from dipyridyl diynes **3a,b**. Photochemically-induced topochemical polymerization in the crystalline state afforded polydiacetylenes (PDAs) **4a,b**, which were thermally converted to GNRs **1a,b** with no loss of the sidechains. The Hopf cyclization and ensuing aromatization from PDAs **4a,b** to GNRs **1a,b** were monitored by cross-polarization magic angle spinning (CP/MAS) solid state ^{13}C NMR. X-ray photoelectron spectroscopy (XPS) revealed both the pyridinic and amide bonding states of the nitrogen atoms. Raman spectroscopy further confirmed the structural integrity of the fjord-edge N_2[8]GNRs **1a,b**.

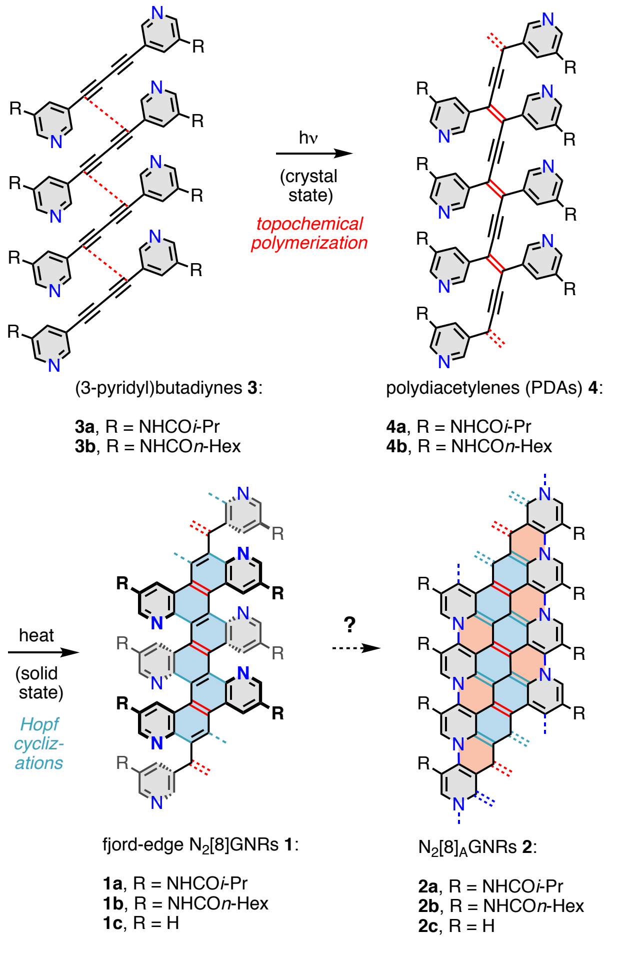
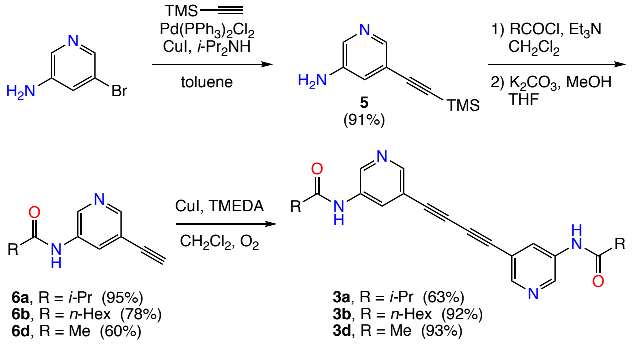


Figure 1. Synthesis of fjord-edge nitrogen-doped graphene nanoribbons (fjord-edge N_2[8]GNRs) **1a,b**).

■ RESULTS AND DISCUSSION

Diyne monomer synthesis: The topochemical polymerization of diynes requires suitable packing of the monomers in the crystal to trigger subsequent chain reactions.[46,47,48] Here, the dipyridyl diyne units of **3a,b,d** (Scheme 1) needed to have their diyne 1,4-carbons within van-der-Waals contact distance (~3.5 Å) to promote the facile formation of intermolecular bonds, a process that often occurs under ambient light.[49,50] Although we synthesized several isomeric dipyridyl diyne systems,[51] only one series, based on 3-amino-5-alkynylpyridine, gave the polymerizable diynes **3a,b**. Accordingly, 3-amino-5-bromopyridine was coupled with trimethylsilylacetylene under Sonogashira conditions, followed by acylation of amine **5** with the corresponding acid chlorides (Scheme 1, R = *i*-Pr, *n*-Hex, Me). Removal of the trimethylsilyl protecting group gave alkynyl amides **6a,b,d** in good to excellent yields. Oxidative coupling under the Hay conditions afforded diyne amides **3a,b,d** in good to high yields.



Scheme 1. Synthesis of the 1,4-bis(3-pyridyl)butadiynes **3a,b,d**.

X-ray structure: Crude diyne **3a** afforded single crystals after slow evaporation from methanol (Figures S28a,b).[51] X-ray diffraction at the Brookhaven Synchroton X-ray source (Figure S29) afforded a 1.0 Å resolution crystal structure of diyne **3a** (Figure 2, Table S1).[51]

The crystal packing geometry for molecules of diyne **3a** validates the desired short, non-bonded C1–C4' distance of 3.45 Å (Figure 2a). The hydrogen bonds between the carbonyl oxygens and amide hydrogens have an optimal distance of 2.00 Å, guiding the assembly of diyne units in **3a** along the unit cell vector *a*. The relative strength of these intermolecular interactions is reflected in the crystal morphology and powder diffraction (Figures S28 and S30). To accommodate the H-bonding motif, the polymer growth axis exhibits a horizontal offset between each molecule, organizing the diynes into an optimal arrangement for topochemical polymerization (Figure 2b). While we were not able to obtain the single crystal structure of **3b**, its powder diffraction displayed a similar packing arrangement to **3a** (Figure S31).

Topochemical polymerization of diynes 3a,b: Both dipyridyl diynes **3a,b** quickly polymerized to dipyridyl PDAs **4a,b** when subjected to UV light, as well as under ambient light, while diyne **3c** was unreactive. The polymerizations were carried out by irradiation of finely pulverized dispersions of the crystals in hexanes using a medium pressure Hanovia lamp (Pyrex filter), typically for 12 h, producing deep purple/black material. Dissolution of unreacted monomer from the polymerized crystals gave the nearly insoluble pristine polydiacetylenes **4a,b** (18 and 4%, respectively) as fibrous powders after filtration. The low polymerization yield for **3b** appears to be inherent to this derivative, since repeated attempts to increase yields by using nanocrystalline material could not raise the conversion yield for this substrate.

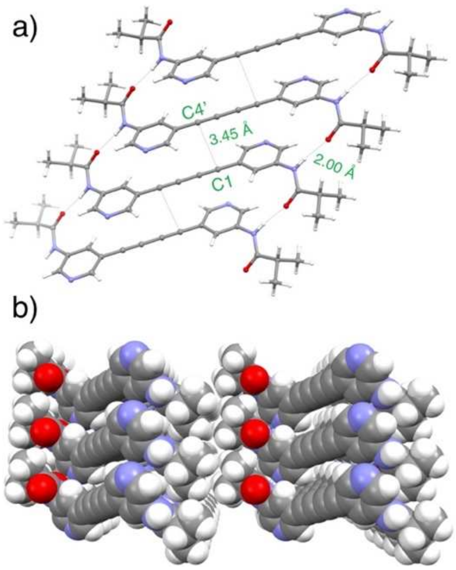


Figure 2. a) Crystal packing structure for diyne **3a** displaying the short C1-C4' distance directed by the C=O···H–N hydrogen-bonded network. b) View of **3a** down the H-bonding axis.

Conversion of PDAs 4a,b to GNRs 1a,b: Thermal conversion experiments were carried out in separate runs on PDAs **4a,b** under increasingly higher temperatures in argon.[51] This transformation could be conveniently monitored by CP/MAS ^{13}C solid state NMR, focusing on the four distinct carbon signal ranges corresponding to the four functional groups of interest (Figure 3b,c): amide carbonyls (160–170 ppm), aromatic carbons (110–150 ppm), alkynyl carbons (~100 ppm), and amide sidechains (10–40 ppm). As the PDAs **4a,b** were heated under increasingly higher temperatures (1h each per run), the distinct ^{13}C NMR signals tracked an initial Hopf cyclization, as evidenced by the disappearance of the alkyne peak at temperatures between 300 and 350 °C (Figure 3b,c). Thus, the Hopf cyclization reactions of PDAs **4a,b** occur more readily, ~100 °C lower than for our phenyl analogs.[50] The Hopf cyclization step is followed by further aromatization reactions that form fjord-edge N_2[8]GNRs **1a** and **1b** at temperatures between 350 and 400 °C (Figure 3b,c), as revealed by the changes in the overall envelope for the aromatic signals between 110–150 ppm, which adopt an underlying intensity ratio of 1:2:1 for both **1a** and **1b** (Figure 3b,c, Table 1a). Curve fitting of the experimental spectrum of **1b** in the 110–150 ppm range with seven Gaussian curves of equal intensity and width, representing the expected number of aromatic ^{13}C signals for fjord-edge N_2[8]GNR **1b**, affords the fitted peaks in Table 1. These values compare rather well with the calculated values for model compound **1e** (Table 1b, top). Furthermore, the clusters of peaks for the aromatic carbons for each of the alternate possible model structures, i.e. **7c** and **8c** (Table 1b, middle and bottom), which are the structural alternatives in the conversion of polydiacetylenes **4a,b** to fjord-edge N_2[8]GNRs **1a,b** (see discussion below and Figure 5), do not fit the experimental curve as well. In particular, structure **7c** has its A,B peaks clustered around 144 ppm, which leaves a large empty void between these peaks and the C–G peaks. This gap is even wider for structure **8c**, which has a ~20 ppm gap between the clusters of A,B and C–G peaks. Thus, the experimental CP/MAS ^{13}C solid state NMR spectrum of fjord-edge N_2[8]GNR **1b** matches best the calculated chemical shifts of model structure **1e**.

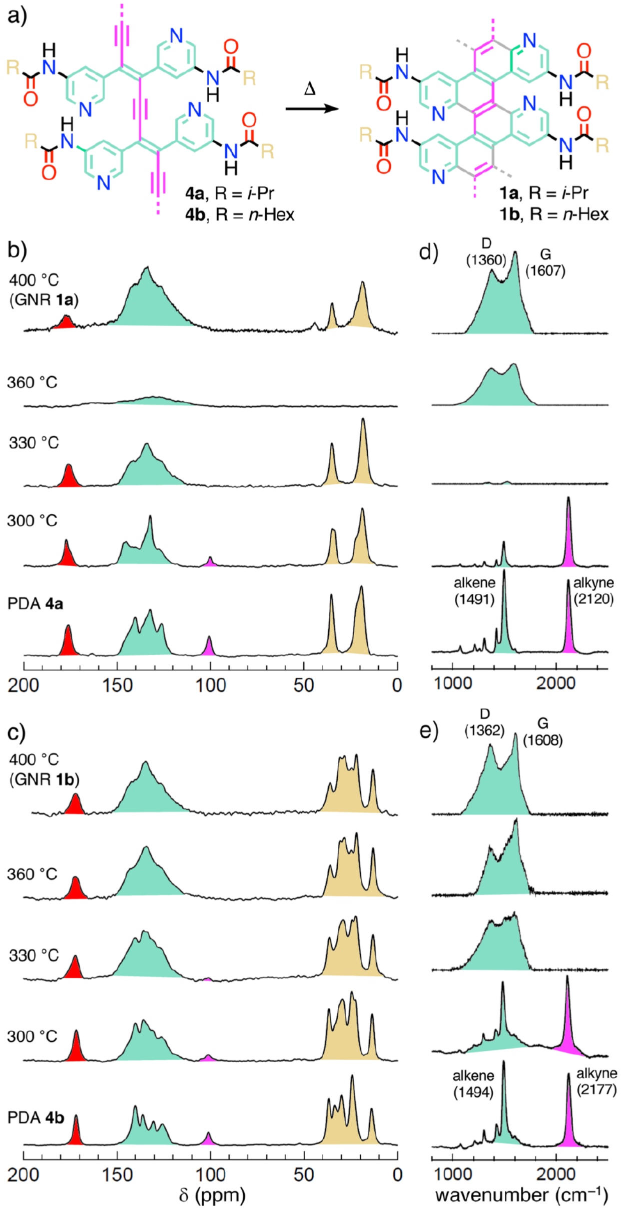
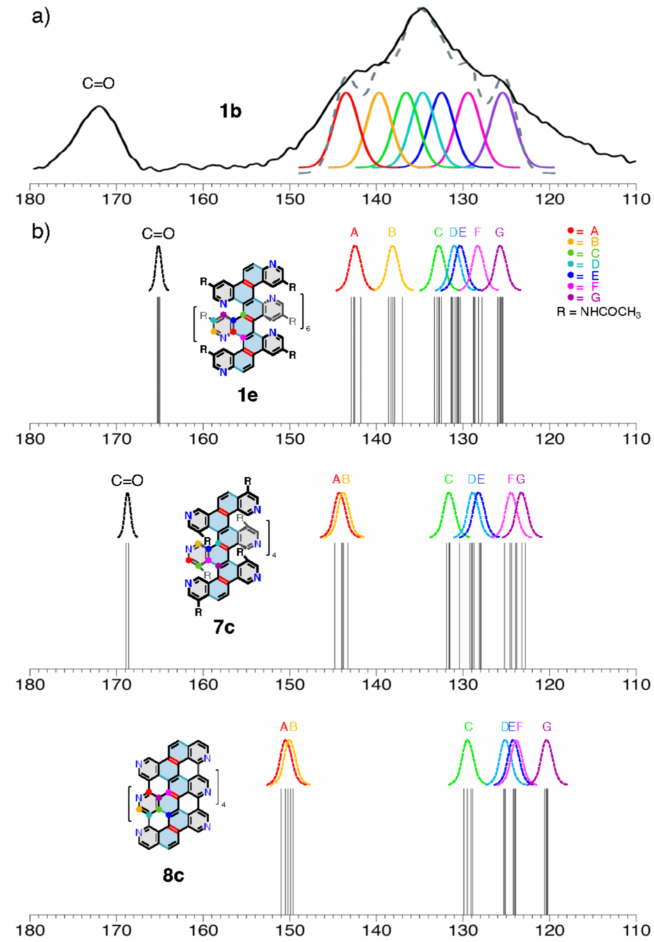


Figure 3. CP/MAS solid-state ^{13}C NMR and Raman spectra for the products obtained by heating PDAs **4a,b**. Each heating experiment was carried out for 1 h using a fresh sample of PDA. a) PDAs **4a,b** and GNRs **1a,b** are color-coded by chemical shift region to reflect spectral changes in b) and c). b) PDA **4a** conversion to fjord-edge N_2[8]GNR **1a,** and c) PDA **4b** conversion to fjord-edge N_2[8]GNR **1b**. The very broad, weak signal for the sample heated at 360 °C in b) is due to an air-stable π-radical intermediate formed during heating.[52] Baseline-corrected Raman spectra for the conversion of d) PDA **4a** to fjord-edge N_2[8]GNR **1a**, and e) PDA **4b** to fjord-edge N_2[8]GNR **1b**. The very weak Raman signal for the sample heated at 330 °C in d) is due to the strong background fluorescence of this sample, which was smoothed out through baseline correction.

Furthermore, the convergence of both PDAs **4a** and **4b** to identical aromatic peak shapes after heating indicates that they both likely undergo similar processes to form the same fjord-edge N_2[8]GNR core. Subsequent heating of **4a** and **4b** to temperatures as high as 400 °C shows no change in the ^{13}C CP/MAS spectra, suggesting that the fjord-edge N_2[8]GNRs **1a,b** have fully formed at 330 °C and 360 °C. These lower conversion temperatures prevent sidechain fragmentation, unlike in our previous work on [8]GNR, which required temperatures as high as 500 °C for full conversion.[50]

Table 1. Comparison of a) the Curve-Fitted Experimental Spectrum of fjord-edge N_2[8]GNR 1b, and b) Calculated ^{13}C NMR Chemical Shifts for Model Structures 1e, 7c, and 8c.[51]



Carbon	A	B	C	D	E	F	G
Fitted δ	143.5	139.7	136.5	134.5	132.5	129.4	125.4
1e, calc δ [b,c]	142.6	138.0	132.9	131.3	130.6	128.5	125.7
7c, calc δ [b,c]	144.0	143.6	131.6	129.4	128.2	124.4	123.6
8c, calc δ [b,c]	150.3	150.0	129.4	125.2	124.1	124.0	120.4

[a] The experimental CP/MAS ^{13}C NMR spectrum is plotted as a solid black line, while the sum of curve fits is a grey dashed line. [b] Average of the DFT calculated chemical shifts (GIAO/B3LYP//6-31G(d)) for each of the seven distinct, non-symmetrically related carbons defined in b). Gaussian curves of arbitrary but constant width and height are displayed for better visualization of the groups of chemical shifts belonging to each of the seven types of non-symmetrically related carbons for each structure. [c] See Figures S39–S41.

As expected, the presence of sidechains in fjord-edge N_2[8]GNRs **1a,b** increases their solubility to a small extent: sonication in the strong hydrogen-bonding acceptor N-methyl-2-pyrrolidone (NMP), followed by filtration through a 0.2 μm Teflon membrane, gives yellowish solutions of fjord-edge N_2[8]GNRs **1a,b** (UV-vis, see Figure S27).[51]

Raman spectroscopy: The precursor PDAs **4a,b** both exhibit strong alkene peaks at 1494 and 1491 cm^{-1}, respectively, as well as alkyne peaks at 2117 and 2120 cm^{-1}, respectively, which are typical of the enyne backbone (Figure 3d,e, bottom traces). Upon heating, these signals disappear, while the signature D and G peaks of GNRs **1a,b** appear (Figure 3d,e, top traces). The Raman spectra for fjord-edge N_2[8]GNRs **1a,b** show D peaks at 1360 and 1362 cm^{-1}, and G peaks at 1607 and 1608 cm^{-1}, respectively. The G peaks of these GNRs are upshifted by ~30 cm^{-1} from graphene (1580 cm^{-1}), due to the confined, strongly aggregated nature of GNRs **1a,b** (see HR-TEM imaging, Fig. S32).[51] Prior reports on GNRs show similar shifts in the D peak as well.[53] Furthermore, the broad feature of the observed D peaks can be attributed to the fjord edge structure and the high levels of site-specific heteroatom substitutions, as noted below.

Broadening of the D peak is generally caused by defects within the graphene lattice.[54,55,56] The fjord-edge GNRs **1a,b** have two inherent structural features that broaden the D peak beyond previously reported GNR examples. Specifically, fjord-edges represent bond vacancies along the edges of pristine graphene. Broad D and G peaks are characteristic of a large numbers of defects, which can also be seen in the all-carbon fjord edge [8]GNR.[28] Further broadening of the D peaks is caused by distortion of the lattice from the nitrogen dopant. Reports for both nitrogen doped graphene and top-down synthesized doped GNRs have shown this broadening with various levels of dopant atoms.[57,58] The bottom-up approach of our synthesis incorporates higher levels of nitrogen doping, at 12.5%, which likely further accounts for the broad D peak.[59]

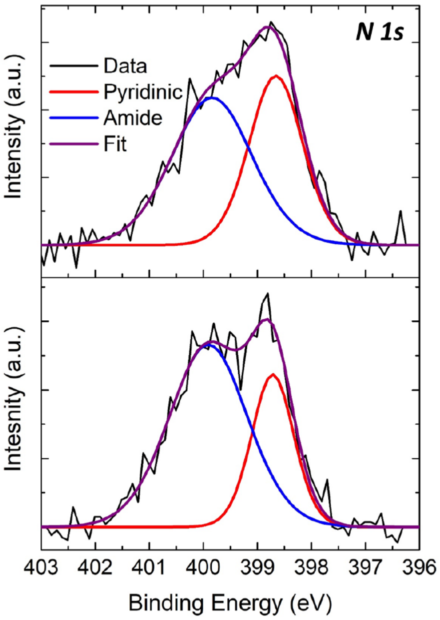


Figure 4. N 1s XPS spectra for fjord-edge N_2[8]GNR **1a** and **1b**, with pyridinic and amide nitrogens centered at 398.7 and 399.7 eV, respectively.

XPS spectra: To confirm the formation of a fjord-edge topology in compounds **1a,b**, we examined the nitrogen bonding environment present in our GNRs using XPS spectroscopy (Figure 4). GNRs **1a,b** should contain solely pyridinic and amide nitrogens if the fjord edge structure is exclusively formed. Examining the XPS spectra for **1a,b**, they show signatures corresponding to the pyridinic[12,13] (398.7 eV) and amide[60] (399.7 eV) bonding, and no other species (Figure 4). Notably, we do not see the presence of internal graphitic (401.7 eV)[61,62,63,64] or pyridinium species (402.5 eV),[65,66] which would indicate further cyclizations have occurred beyond the fjord edge structure (see discussion below and Figure 5). Additionally, the retention of the sidechain substituents indicates that the alternate path of cyclization to an edge-like topology (**8**), via intermediates **7a,b** (Figures 5 and 6), is unlikely to have occurred, in agreement with the calculations (see below), which show this pathway to be highly unfavorable. The increased width of the amide peak relative to the pyridinic peak is consistent with conformational disorder in the side-chains only. Together, these results all indicate that the structure most consistent with the data is that of the fjord-edge N_2[8]GNRs **1a,b**.

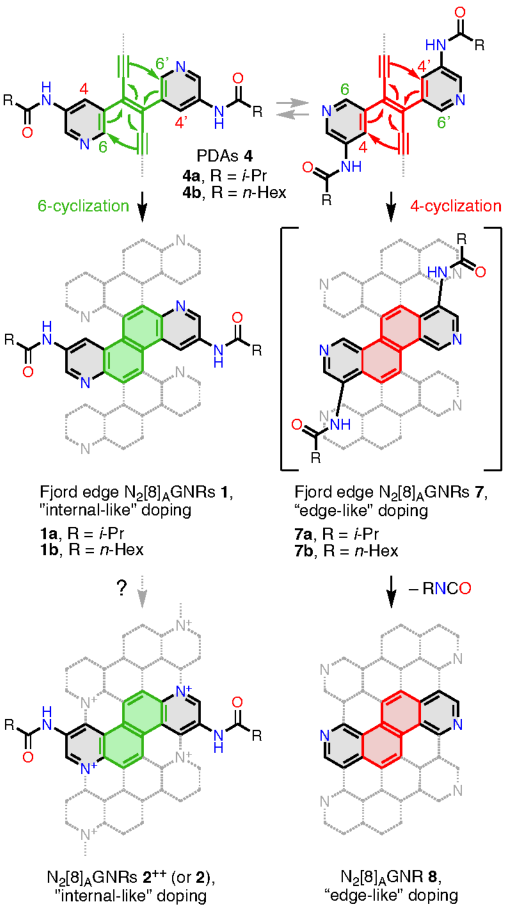


Figure 5. The two Hopf cyclization pathways for PDAs **4a,b**, which can occur at either the 4 or 6-positions of the pyridyl rings, resulting in the nitrogen atoms being located at either internal or edge locations.

Conformation preference, cyclization pathways and reaction barriers: The conformational preference in a model system for the fjord-edge N_2[8]GNR **1**, R = –NHCOMe) was investigated with its two extreme cases, all-zigzag and helical. The fjord edge structure of **1a,b** imparts strong steric repulsion between the pyridine nitrogen lone pairs and the C– H bonds of adjacent diazachrysene units. Thus, the two possible key conformations, all-zigzag (alternating up-down pyridyl units) and helical (all pyridyl units staggered in a non-alternating fashion) were calculated at the semiempirical (PM3) and DFT (B3LYP) levels (see Section S4.8).[51] The differences in energy (35.9 and 60.2 kcal·mol^{-1} for PM3 and B3LYP, respectively) between the two conformers is very high, thus it is likely that only the zigzag conformation exists in the fjord-edge N2[8]GNRs **1a,b** as shown in Figure 1.

There are two possible Hopf cyclization pathways for PDAs **4a,b** (Figure 5), which can afford fjord-edge GNRs with two different topologies. The internal-like topology (**1a,b**) has the nitrogen atoms opposite to C–H bonds of the next "diazachrysene" units, while the edge-like topology has them at the edges of the fjord-edge nanoribbon **7a,b**, or the ensuing N$_2$[8]$_A$GNR **8**, since it can be expected that the amide sidechains should be easily lost from structure **7a,b** under our heating conditions. Unlike our previous work on [8]$_A$GNR,[50] which forms the same structure regardless of the initial cyclization pathway at the 2 or 4-positions of the PDAs' *m*-amidophenyl rings, cyclization at either the similarly related 4 or 6-positions of the pyridyl rings in PDAs **4a,b** could give two different fjord-edge GNRs, or a statistical mixture alternating both pathways along the nanoribbon length. However, cyclization at the 4-position should be strongly disfavored owing to the severe steric clash between the amide groups and adjacent pyridyl units during Hopf cyclization (structures **7a,b**, Figure 5). Furthermore, aromatization to an edge-doped armchair GNR should easily ensue if the edge-like pathway is followed, resulting in total loss of the sidechains. This is not the case, based on our experimental data (CP/MAS solid-state ^{13}C NMR and XPS, Figures 3 and 4). In fact, cyclization appears to favor the 6-position, which produces the lesser strained, internally doped fjord-edge N$_2$[8]GNRs **1a,b** with their amide sidechains pointing away from the series of fused "diazachrysene" units. The transition state calculations reported below lend further strong support for the fact that the Hopf cyclization occurs at the 6-pyridyl positions to yield fjord-edge N$_2$[8]GNRs **1a,b**.

To further understand the energetics and pathway of the Hopf cyclization of PDAs **4a,b**, we base our theoretical considerations on previous results by Prall *et al.*[67] and our own work.[50] The Hopf cyclization mechanism has been calculated to proceed through an initial 6π-electrocyclization, followed by two consecutive [1,2]-H shifts, with the first H-shift as the rate-determining step.[67] As discussed above (Figure 5), the enediyne units of PDAs **4a,b** can undergo cyclization at either the 6-position (*para* to the amide group) or the 4-position (*ortho* to the amide group), the latter of which is intuitively unfavorable due to the large steric bulk of the amide group, compared to only H in **1a,b** (Figure 5).

Using density functional theory (DFT), we computed the geometries of the model system **9** (Figure 6), the transition states for the initial 6π electrocyclizations (**10** and **10'**), the strained allene intermediates **11** and **11'**, and the transition states for the 1,2-shifts (**12** and **12'**). These structures were optimized in the gas-phase using B3LYP/6-31G(d), and single-point energy calculations were performed using M06-2X/6-311+G(d,p) with B3LYP frequencies to obtain free energy values. The potential energy surfaces for the two cyclization pathways are shown in Figure 6.

The energetic trends for this bispyridyl system are similar to the all-carbon system previously studied by us.[50] As expected, the barriers for cyclization at the 4-position are higher than at the 6-

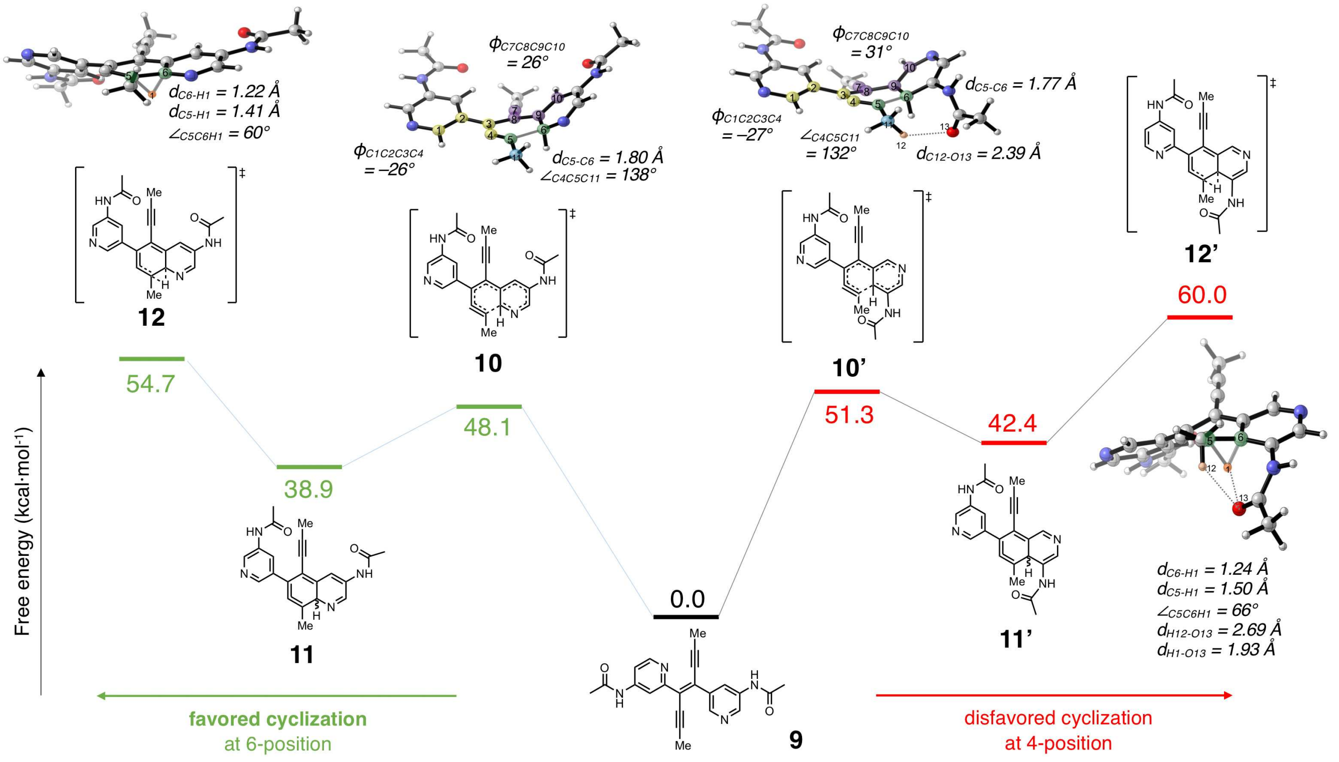


Figure 6. Free energies (in kcal·mol^{-1}) of the intermediates and transition states for both the favored (left) and disfavored (right) Hopf cyclization pathways relative to starting structure **9**.

position. The activation free energies for the more favorable transition states **10** and **12** are 48.1 and 54.7 kcal·mol^{-1}, respectively, while the analogous transition states **10'** and **12'** have higher barriers of 51.3 and 60.0 kcal·mol^{-1}, respectively. Like the all-carbon PDAs previously studied, the 1,2-shift following electrocyclization is the rate-determining step in both pathways, and the preference for the pathway with cyclization at the 6-position is substantial (5.3 kcal·mol^{-1}). This energy difference virtually ensures that the analogous series of cyclizations within PDAs **4a,b** should occur exclusively at the 6-positions (*para* to the amide group) of the pyridyl rings.

The geometries of the transition states **10** and **10'** are similar to each other and to their all-carbon variants. In **10** and **10'**, the π-system of the alkynes is planar, while the flanking pyridyl groups are out-of-plane by approximately 30°. The slightly higher barrier of **10'** is likely due to the close proximity of the amide oxygen and methyl group on the forming C–C bond. More ample differences can be seen between the rate-determining states **12** and **12'**. In **12**, the quinoline intermediate is planar, and the C6–H1 bond stretches to 1.22 Å from its normal C–H bond length of 1.09 Å. However, in the less-favorable transition state **12'**, the bulky amide group forces the quinoline out of plane, largely due to unfavorable steric interactions between the amide oxygen and the shifting hydrogen and adjacent methyl group, which accounts for the intrinsic preference for the 6-position cyclization.

Calculations for the unsubstituted variant (no amide groups) were also computed to probe the intrinsic preference for the 6-position (Figure S35).[51] The barriers of the rate-determining 1,2-shift for the unsubstituted system are 53.7 and 55.7 kcal·mol^{-1} for the 6 and 4-positions, respectively, with less strong of a preference (2.0 kcal·mol^{-1}) for the 6-position. Thus, the increased preference for the 6-position in the substituted system **9** can be wholly attributed to the unfavorable steric interactions between substituents in the rate-determining transition state structure **12'**.

We note that the barrier of the rate-determining step in pyridyl system **9** is ~3 kcal·mol^{-1} lower than that of the all-carbon system, which correlates well with the ~100 °C lower conversion temperature for this N-based system.

Electronic properties of fully cyclized N$_2$[8]$_A$GNR: In order to better understand the electronic properties of the fully cyclized (graphitic) N$_2$[8]$_A$GNR system **2c**, we calculated the electronic Density of States (DOS) for the parent systems **1c** and **2c** by means of periodic DFT (Figures 1 and 7).[51] The DOS of **1c** and **2c**, obtained from the HSE06 functional on the basis of PBE geometries,[68,69] are depicted in Figure 7. As we can see, fjord-edge GNR **1c** is expected to be a semiconductor, with a bandgap of 2.04 eV (Figure 7a). On the other hand, fully cyclized N$_2$[8]$_A$GNR **2c** clearly displays metallic behavior, as indicated by the continuous DOS landscape at the Fermi level depicted in Figure 7b. Notice that the HSE06 results are in agreement with the results at the PBE level of theory (Figure S37).[51] Namely, both predict **2c** to be metallic and **1c** to be a semiconductor, although the band gap predicted by PBE is smaller than by HSE06 (1.43 eV *vs* 2.04 eV, respectively), as expected from the DFT delocalization error.[70] Furthermore, bond-equalization of many of the carbon-carbon bonds within the structure of fully fused N$_2$[8]$_A$GNR **2c**, unlike those in fjord edge structure **1c** (Figure S38),[51] indicates that N$_2$[8]$_A$GNR **2c** has quinoid character, which incites its metallic nature. This fact is in agreement with the charge density at the Fermi level, which exhibits a delocalized π-character (Figure 7b, inset).

These calculations indicate that experimental isolation of the fully cyclized, metallic N$_2$[8]$_A$GNRs **2a,b** could be challenging, and despite our best efforts so far, this step is awaiting further work. Formation and characterization of these novel, exciting graphene nanoribbons is currently under investigation.

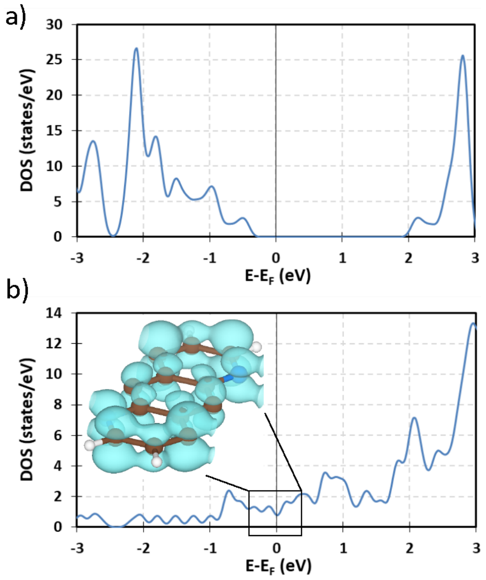


Figure 7. DOS plots calculated at the HSE06 level for a) fjord-edge GNR **1c**, and b) fully cyclized N$_2$[8]$_A$GNR **2c**. The inset shows a 3D representation of the partial charge density at the Fermi level in the [−0.2, 0.2] eV range for **2c**.

■ CONCLUSION

In summary, we have demonstrated the synthesis of a novel fjord-edge N$_2$[8]GNR system with site-specific nitrogen substitution. The stepwise conversion from dipyridyl diynes **3a,b** to the nitrogen doped, fjord edge N$_2$[8]GNRs **1a,b** via topochemical polymerization of PDAs **4a,b**, followed by Hopf cyclizations to the GNRs, proceeded at relatively moderate temperatures of 330-360 °C. The formation of the fjord-edge structure in the GNRs **1a,b** was confirmed via CP/MAS ^{13}C NMR, XPS, and Raman spectroscopy. The success of our bottom-up method demonstrates the versatility of the crystalline state topochemical polymerization method to incorporate heteroatom substitution and structural diversity into GNR structures.

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge at: https://pubs.acs.org/doi/10.1021/jacs.XXXXX.

Experimental procedures and spectroscopic characterization data, crystallization procedures, HR-TEM imaging, and details of the DFT and Molecular Mechanics calculations (PDF).
Crystallographic data (CIF)

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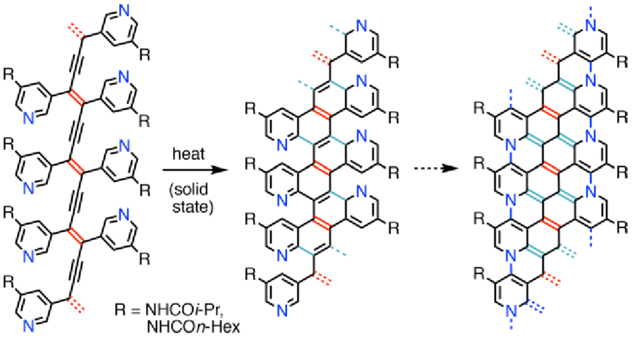
heat
(solid state)
R = NHCO*i*-Pr, NHCO*n*-Hex