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Bis-N-Annulated Quaterrylene: An Approach to Processable Graphene Nanoribbons

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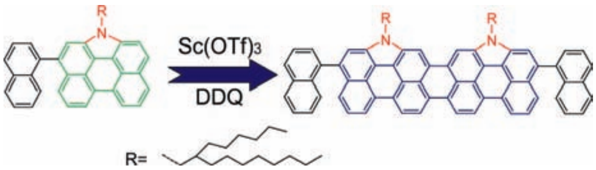
ABSTRACT



A new efficient synthetic method toward processable bis-N-annulated quaterrylene from easily available N-annulated perylene derivatives, which is conducted by DDQ/$Sc(OTf)_3$ oxidative coupling and ring fusion, is reported. In light of the good processability and the strong electron-donating ability, which is evidenced from the low oxidative potentials, bis-N-annulated quaterrylene is very promising for use as functional components in molecular devices.

Graphene nanoribbons (GNRs), for which the width of the sheet is confined to a finite size while the length is considered infinitely long, have attracted considerable interest due to high potentiality in GNR-based nanoelectronics.[1] The bottom-up organic synthetic approach is believed to be the most promising way to construct well-defined functionalized graphene nanoribbons (F-GNRs),[2] while lithographic patterning of graphene sheets has led to the fabrication of GNRs down to widths of ∼20 nm thus far;[3] however, there are difficulties in obtaining smooth edges and reaching true nanometer-scale ribbon width.

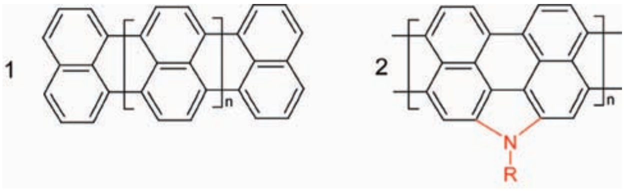


Figure 1. PPNs (**1**) and N-annulated PPNs (**2**).

Poly(*peri*-naphthalene) (PPN, Figure 1), which can be regarded as structurally perfect GNR, is expected to have a very small band gap and thus to be an intrinsic electrical conductor, rendering it a potentially extremely interesting polymer.[4] Whereas the intriguing structural and electro-optical properties of PPN have led to the pursuit of its rational synthesis, to date, the physical properties of perylene (**1**, $n = 0$), the first member in the series of the oligomers of PPN,

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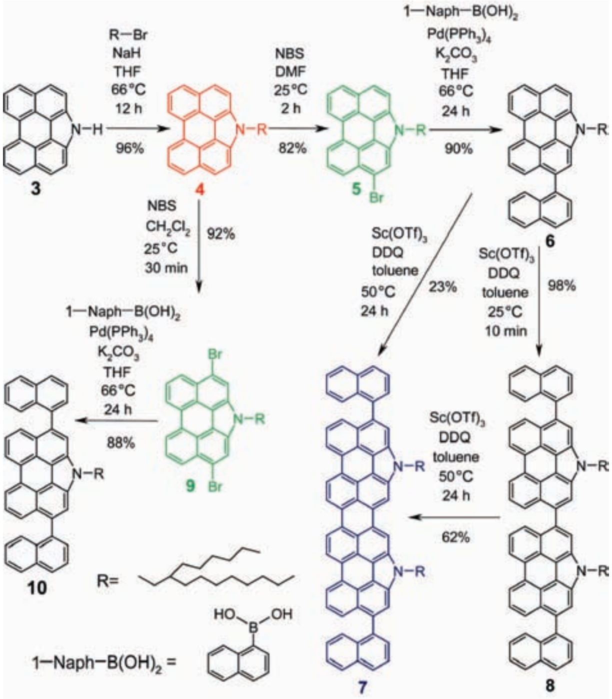
have been extensively studied.[5] Müllen also reported important intermediates with large rylene units,[6] and the higher homologues are still rarely explored due to the lack of selective synthesis of these compounds as well as their improcessability caused by their poor solubility and high melting points.

We are particularly interested in the bottom-up synthesis of well-defined GNRs with tunable electro-optical properties. Quite recently, we reported an experimental study encompassing synthesis and characterization of *n*-type fully conjugated tri(perylene bisimide) nanoribbons.[7] Herein, we present the facile one-pot synthesis of bis-N-annulated quaterrylene (BNQ) from the easily available N-annulated perylene (NP) derivative,[8] which represents the first step toward processable *p*-type graphene nanoribbons. The introduction of nitrogen bridges into the edge of GNRs is expected to not only have a substantial influence on the electro-optical properties but also provide the active sites for chemistry modification.

Bis-N-annulated quaterrylene was synthesized as shown in Scheme 1. The key starting material was NP with dovetailed alkyl substituents (**4**), which was obtained in 96% yield by deprotonation of NP (**3**) with NaH and subsequent alkylation with branched alkyl bromide. Regioselective NBS bromination of **4** provided versatile building blocks, named monobrominated alkylated NP (**5**) and dibrominated alkylated NP (**9**), for the construction of processable GNRs.

Scheme 1. Synthesis of Bis-N-Annulated Quaterrylene **7**



The reaction of **5** with commercially available 1-naphthaleneboronic acid under Suzuki conditions gave **6** in 90% yield. Oxidative fusion of **6** to N-annulated terrylene (**1**, *n* = 1) was attempted both using $FeCl_3$ and $AlCl_3$/CuCl conditions, but in both cases the desired product was not detected. However, when **6** was treated with 5 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and scandium trifluoromethanesulfonate [Sc(OTf)$_3$] in toluene at 50 °C for 24 h, bis-N-annulated quaterrylene (**7**) was separated after column chromatography in 23% yield, while DDQ or Sc(OTf)$_3$ alone did not effect any change of **6**. The structure of **7** was unambiguously verified by ^{1}H NMR and HRMS. Although the system of DDQ/Sc(OTf)$_3$ has been proven to be powerful in electron-rich systems to prepare triply linked oligoporphyrins,[9] there are only a few examples of the more accessible polycyclic aromatics.[10] It is remarkable that under this simple condition the expansion of the π system was successfully achieved along the long molecular axis, which is probably due to the introduction of electron-donating N-bridges resulting in region-selective activitation of **6**.

The reactivity of the precursor, the amount of DDQ/Sc(OTf)$_3$, as well as the reaction temperatures are presumed to be key factors to oxidative coupling and further ring fusion of NP units. While the NP itself under the same condition was found only to afford a mixture of oligomers without ring-fusion, it was conjectured that controllable oxidative homocoupling of **6** may allow the preparation of the key precursor **8** due to the blocking of one active *peri*-position by the less reactive naphthalene unit.

Accordingly, we treated **6** with 1 equiv of DDQ/Sc(OTf)$_3$ at room temperature for 10 min and observed that **6** was quantitatively converted to **8**. Moreover, the ring fusion of **8** with 5 equiv of DDQ/Sc(OTf)$_3$ afforded BNQ **7** in 62% yield. For comparison, Suzuki coupling of dibrominated NP (**9**) with 1-naphthaleneboronic acid afforded **10**, on which the DDQ/Sc(OTf)$_3$ system did not effect any change.

The key feature of the implemented space-demanding alkyl chains in BNQ **7** is the close proximity of the branching site to the aromatic core, which is expected to dramatically influence the processablities. Accordingly, **7** is well soluble in common organic solvents, such as $CHCl_3$, THF, and toluene, which guaranteed the investigations of its electro-optical properties.

According to thermogravimetric analysis (TGA), the degradation temperature (T_{deg}) of **7** corresponding to 5% weight loss under nitrogen flow is 370 °C. The compounds show melting points at 304 °C indicating good processability.

Figure 2 shows the comparison of the absorption spectra of **7**, **8**, and **10** in THF. In sharp contrast, the spectrum of **7** displays a drastical bathochromic shift (222 nm, 230 nm) compared with **8** and **10**, respectively, which reflects the ladder-type conjugated structure leading to a great degree of planarity and corresponding large delocalization of electron wave functions like reported quaterrylenes. In comparison with *tert*-butyl substituted quaterrylene, **7** exhibits a bathochromic shifted (13 nm) absorption band probably due to the electron-donating effect of nitrogen bridges. The small Stoke's shift between the absorption and emission bands of **7** is probably due to the rigid structure;

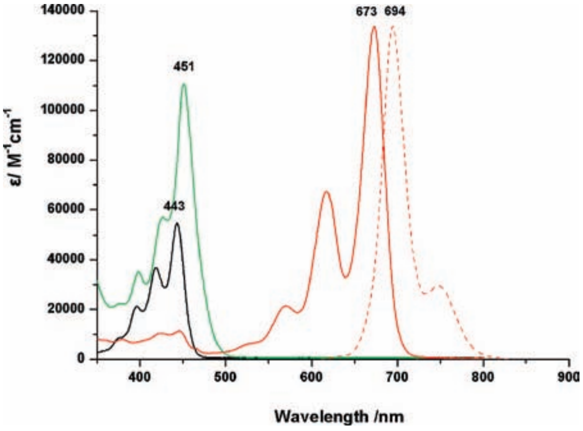
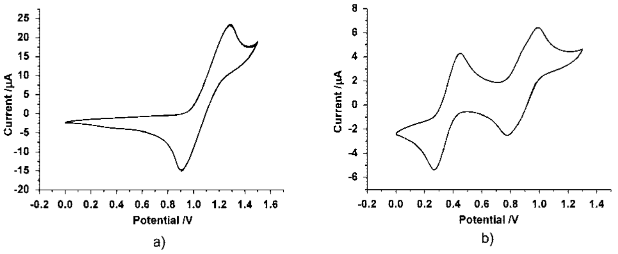


Figure 2. UV/vis absorption spectra of **8** (green) and **10** (black) and UV/vis absorption (solid line) and emission (dash line) of **7** (red) in THF.

moreover, the fluorescence quantum yield of **7** is 0.26, while the *tert*-butyl-substituted quaterrylene shows only weak emission.[6a]

Cyclic voltammetry (Figure 3) on **7** and **10** in THF, using a Ag/AgCl as the quasi-reference electrode and ferrocene as an internal potential marker, has been investigated. The cyclic voltammogram of **7** exhibits two well-defined, reversible oxidative waves, while only one oxidative wave is found in that of **10**. The half-wave oxidative potentials vs Fc/Fc$^+$ are −0.04 and 0.48 for **7** and 0.69 for **10**, respectively, while the first half-wave oxidative potentials of *tert*-butyl-substituted perylene and quaterrylene vs Fc/Fc$^+$ are 0.47 and −0.08,[6a] thus revealing the extremely strong electron-donating ability of BNQ.



a)

b)

Figure 3. Oxidative cyclic voltammogram of 1.2 mM **10** (a) and **7** (b) in THF. Scan rate: 0.1 V/s (electrolyte: 0.1 M $TBAPF_6$).

In summary, we report a new efficient synthetic method toward processable bis-N-annulated quaterrylene from easily available N-annulated perylene derivatives, which is conducted by DDQ/$Sc(OTf)_3$ oxidative coupling and ring fusion. In light of the good processability and the strong electron-donating ability, which is evidenced from the low oxidative potentials, bis-N-annulated quaterrylene is very promising for use as functional components in molecular devices. Extension of this synthetic strategy to higher oligomeric graphene nanoribbons as well as further investigation of the structure/property relationship is a fascinating next project that is currently underway.

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Supporting Information Available: Experimental details and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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