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Synthesis of Nitrogen-Containing Rubicene and Tetrabenzopentacene Derivatives

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Abstract: *Carbon-based materials, such as acenes, fullerenes, and graphene nanoribbons, are viewed as the potential successors to silicon in the next generation of electronics. Although a number of methodologies provide access to these materials' all-carbon variants, relatively fewer strategies readily furnish their nitrogen-doped analogues. Herein, we report the rational design, preparation, and characterization of nitrogen-containing rubicenes and tetrabenzopentacenes, which can be viewed either as acene derivatives or as molecular fragments of fullerenes and graphene nanoribbons. The reported findings may prove valuable for the development of electron transporting organic semiconductors and for the eventual construction of larger carbonaceous systems.*

Carbon-based materials, such as acenes, fullerenes, and graphene nanoribbons (GNRs), have often been touted as the successors to traditional inorganic semiconductors in solar cells and transistors (Figure 1 a).[1–6] Thus, much research effort has focused on the bottom-up preparation of structurally and chemically well-defined variants (and fragments) of such materials via organic chemistry techniques.[7–18] However, a smaller number of studies have reported the solution-phase synthesis of analogous nitrogen-doped constructs.[19–27] Indeed, the rational incorporation of nitrogen heteroatoms, while frequently challenging, is known to be valuable for tuning the properties of graphitic systems,[28–31] as demonstrated by the successful molecular engineering of various N-heteroacenes for improved transistor performance.[32,33] Consequently, the development of new routes to nitrogen-containing acenes, fullerenes, and GNRs remains important for the next generation of semiconductor devices and technologies.

Herein, we report the preparation of previously unknown rubicene[34,35] and tetrabenzopentacene[36,37] variants, which can be viewed either as acene derivatives or as molecular fragments of fullerenes and GNRs. In our strategy, we first synthesize difunctional halogenated building blocks and convert them to derivatized anthracene precursors via the aza-Diels–Alder (Povarov) reaction.[38,39] Subsequently, we use either the Heck coupling[40,41] to form two 5-membered fused rings or base-mediated cyclodehydrohalogenation[42,43] to form two 6-membered fused rings within the anthracene skeletal frameworks, obtaining nitrogen-containing rubicenes or tetrabenzopentacenes, respectively. We in turn characterize these molecules with spectroscopic techniques, electrochemical measurements, and density functional theory calculations. Our general methodology provides facile access to novel materials, which hold promise both as electron transporting organic semiconductors and as model compounds for larger carbonaceous systems.

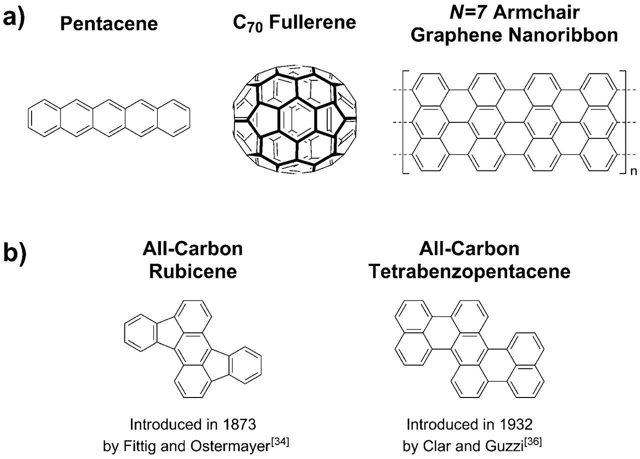

Figure 1. a) Typical carbon-based materials, including pentacene (left), C_{70} fullerene (middle), and an $N=7$ armchair graphene nanoribbon (right). b) The classic all-carbon rubicene and tetrabenzopentacene molecules.

For the design of our nitrogen-doped compounds, we sought inspiration from the classic all-carbon rubicene[34,35] and tetrabenzopentacene[36,37] motifs (Figure 1 b). Although these molecules were synthesized > 60 years ago, their nitrogen-containing analogues have never been reported (to the best of our knowledge), and tetrabenzopentacene is even still prepared via a relatively limited and harsh method.[44] Moreover, variants of these polycyclic aromatic hydrocarbons (PAHs) have exhibited promising functionality in organic electronic devices, including light emitting diodes, photovoltaics, and transistors.[44–46] Consequently, we regarded nitrogen-containing rubicenes and tetrabenzopentacenes as challenging and exciting synthetic targets.

We began our studies by synthesizing rubicene **3** and tetrabenzopentacene **5** via the Povarov reaction,[38,39] as illustrated in Scheme 1 a. To prepare compounds **3** and **5**,

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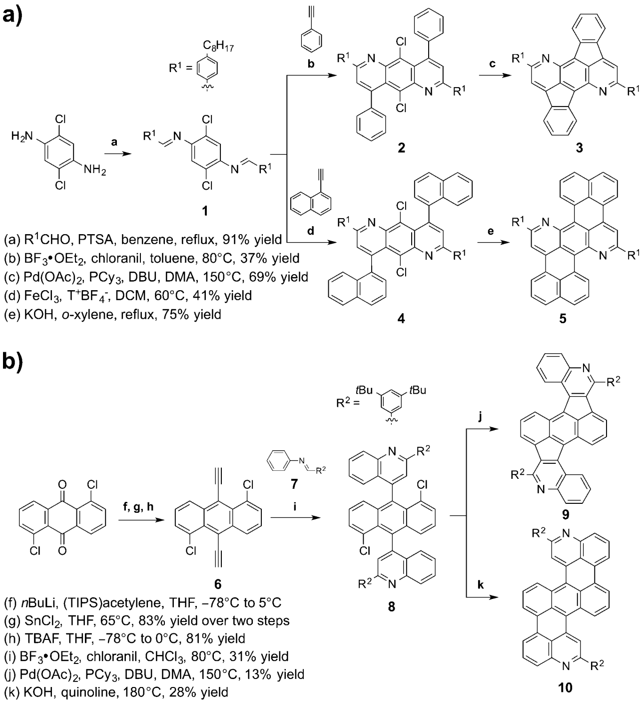

(a) R^{1}CHO, PTSA, benzene, reflux, 91% yield
(b) BF_3•OEt_2, chloranil, toluene, 80°C, 37% yield
(c) $Pd(OAc)_2$, PCy_3, DBU, DMA, 150°C, 69% yield
(d) $FeCl_3$, $T^+BF_4^-$, DCM, 60°C, 41% yield
(e) KOH, *o*-xylene, reflux, 75% yield

(f) *n*BuLi, (TIPS)acetylene, THF, –78°C to 5°C
(g) $SnCl_2$, THF, 65°C, 83% yield over two steps
(h) TBAF, THF, –78°C to 0°C, 81% yield
(i) BF_3•OEt_2, chloranil, $CHCl_3$, 80°C, 31% yield
(j) $Pd(OAc)_2$, PCy_3, DBU, DMA, 150°C, 13% yield
(k) KOH, quinoline, 180°C, 28% yield

Scheme 1. a) Synthesis of rubicene **3** and tetrabenzopentacene **5**. b) Synthesis of rubicene **9** and tetrabenzopentacene **10**.

we first formed bis(aldimine) **1** through a known literature procedure.[22,47,48] Subsequently, we obtained **2** by reacting **1** with phenylacetylene in the presence of $BF_3{\cdot}OEt_2$ as a Lewis acid mediator and chloranil as an oxidant.[22,47,48] Similarly, we obtained **4** by reacting **1** with 1-ethynylnaphthalene in the presence of $FeCl_3$ as a Lewis acid and a TEMPO oxonium salt as an oxidant (the alternative milder conditions improved the stability of the ethynyl precursor, increasing the yield).[49] Next, we synthesized **3** by using the palladium-catalyzed Heck coupling reaction[40,41] to form intramolecular C–C bonds between the acene core and pendant phenyls of **2**. In a parallel approach, we synthesized **5** by using base-mediated cyclodehydrohalogenation[42,43] to form intramolecular C–C bonds between the acene core and pendant napthyls of **4**. These pathways furnished desired products **3** and **5** in moderate yields.

We in turn synthesized rubicene **9** and tetrabenzopentacene **10** via the Povarov reaction,[38,39] as illustrated in Scheme 1 b. To obtain compounds **9** and **10**, we first prepared bis(alkyne) **6** (see the Supporting Information for additional details). We then formed aldimine **7** and reacted it with **6**, again in the presence of a Lewis acid mediator and an oxidant, producing intermediate **8**.[22,47,48] Next, we obtained **9** and **10**, with **8** serving as the sole starting material. Thus, we prepared **9** by using the palladium-catalyzed Heck coupling reaction[40,41] to form intramolecular C–C bonds between the acene core and pendant quinolines of **8**. In a parallel approach, we prepared **10** by using base-mediated cyclodehydrohalogenation[42,43] to form intramolecular C–C bonds between the acene core and pendant quinolines of **8**. These pathways furnished desired products **9** and **10** in modest yields.

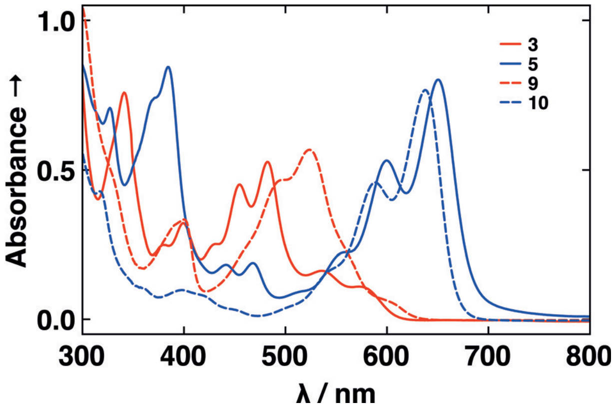

Figure 2. The UV/Vis absorption spectra obtained for rubicene **3** (solid red line), tetrabenzopentacene **5** (solid blue line), rubicene **9** (dashed red line), and tetrabenzopentacene **10** (dashed blue line).

We initially characterized **3**, **5**, **9**, and **10** with ultraviolet-visible (UV/Vis) spectroscopy. For **3** and **9**, we found that the spectra generally resembled those reported for rubicene and its derivatives.[35,45,46,50] For example, the spectrum obtained for **3** featured characteristic clusters of absorption peaks at 341 nm, 399 nm, and 483 nm (Figure 2). By comparison, the spectrum obtained for **9** was broadened and red-shifted (presumably due to the molecule's expanded aromatic system), with prominent absorption peaks at 400 nm and 524 nm (Figure 2). Likewise, we found that the spectra for **5** and **10** were similar to the ones reported for tetrabenzopentacene[36,37,44] and other pentacene derivatives.[7,8,26,27] The spectrum obtained for **5** featured a cluster of three characteristic absorption peaks at 555 nm, 600 nm, and 650 nm (Figure 2). The spectrum obtained for **10** was slightly blue-shifted but comparable to **5**, with absorption peaks at 543 nm, 588 nm, and 638 nm (Figure 2). Overall, these findings indicated that the UV/Vis spectroscopic properties of our nitrogen-doped rubicene and tetrabenzopentacene variants resembled those of their all-carbon parent molecules.

We next investigated the electrochemical behavior of **3**, **5**, **9**, and **10** with cyclic voltammetry (CV) (Figure 3). Here, we found that **3** and **9** were easier to reduce but more difficult to oxidize compared to the all-carbon rubicene (Table 1).[50] For **3**, the voltammogram featured two quasi-reversible redox couples at reductive potentials of −0.83 V vs. Ag/AgCl and −1.24 V vs. Ag/AgCl, but no obvious reversible redox couples at oxidative potentials. For **9**, the voltammogram was similar, with two quasi-reversible redox couples at reductive potentials of −0.73 V vs. Ag/AgCl and −1.04 V vs. Ag/AgCl, and, again, no obvious reversible redox couples at oxidative potentials. Likewise, we found that **5** and **10** were easier to reduce but more difficult to oxidize than previously reported substituted pentacenes.[7] For **5**, the voltammogram featured two quasi-reversible redox couples at reductive potentials of −0.99 V vs. Ag/AgCl and −1.41 V vs. Ag/AgCl, as well as a quasi-reversible redox couple at oxidative potentials of 0.70 V vs. Ag/AgCl. For **10**, the voltammogram was similar, with two quasi-reversible redox couples at reductive potentials of −0.91 V vs. Ag/AgCl and −1.16 V vs. Ag/AgCl, as well as a quasi-reversible redox couple at oxidative potentials of

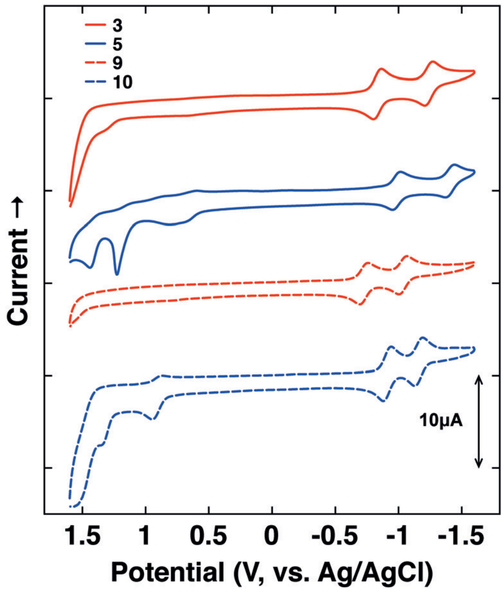

Figure 3. The cyclic voltammograms obtained for rubicene **3** (solid red line), tetrabenzopentacene **5** (solid blue line), rubicene **9** (dashed red line), and tetrabenzopentacene **10** (dashed blue line). The voltammograms have been offset for clarity.

Table 1: Experimental and theoretical frontier molecular orbital energies for the all-carbon rubicene, all-carbon tetrabenzopentacene, rubicene **3**, tetrabenzopentacene **5**, rubicene **9**, and tetrabenzopentacene **10**.

Compound	HOMO [eV]	LUMO [eV]	HOMO[d] [eV]	LUMO[d] [eV]
Rubicene	−5.51[a]	−3.40[a]	−5.54	−2.80
3	−5.71[b]	−3.68[c]	−5.60	−3.01
9	−5.74[b]	−3.77[c]	−5.80	−3.25
Tetrabenzopentacene	–	–	−4.71	−2.71
5	−4.94[c]	−3.50[c]	−4.89	−2.87
10	−5.23[c]	−3.58[c]	−5.13	−3.11

[a] The values were reproduced from reference [50]. [b] The values were calculated from the absorption onset of the UV/Vis spectra and the onset of the redox couples observed with cyclic voltammetry by using ferrocene as an internal standard.[51,52] [c] The values were determined from the onset of the redox couples observed with cyclic voltammetry by using ferrocene as an internal standard.[51,52] [d] The values were determined from the density functional theory calculations.

0.91 V vs. Ag/AgCl. Together, these observations indicated that the incorporation of nitrogen heteroatoms enhanced our molecules' electron accepting properties, in agreement with literature precedent for various *N*-heteroacenes.[26,27,32,33]

To gain further insight into the electronic structure of our compounds, we performed density functional theory (DFT) calculations for **3**, **5**, **9**, and **10** (Figure 4), as well as for their all-carbon analogues (Supporting Figures S23 and S24). From these calculations, we obtained the shapes and energies of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) for all six molecules (Figure 4, Supporting Figures S23 and S24, and Table 1). We were thus able to assign the redox couples observed with cyclic voltammetry for **3**, **5**, **9**, and **10** to their respective frontier molecular orbitals, as appropriate (Table 1).[51,52] The DFT calculations indicated that, regardless of the presence of heteroatoms, the HOMOs and LUMOs were similar in shape and encompassed the aromatic core, both for the three rubicenes and for the three tetrabenzopentacenes. However, we found that the energies of the theoretically-predicted HOMOs and LUMOs for the nitrogen-doped compounds were lowered with respect to the energies of the corresponding frontier orbitals for the all-carbon analogues, as also suggested by some of the electrochemical measurements (Figure 3 and Table 1). Notably, the electronic properties of **3**, **5**, **9**, and **10** appeared to be influenced by the precise location of the nitrogen dopants, with **9** featuring a lower lying LUMO and HOMO than **3**, and **10** featuring a lower lying LUMO and HOMO than **5**, again in agreement with the electrochemical measurements (Figure 3 and Table 1). Overall, the theoretical calculations supported the experimental findings and implied that our molecules may constitute candidate electron transporting organic semiconductor materials.[53,54]

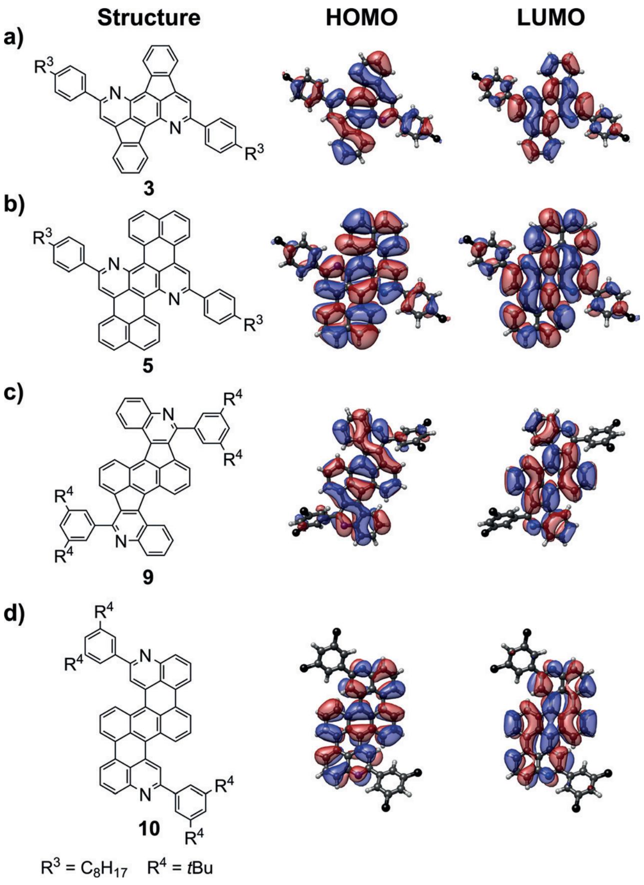

Figure 4. The chemical structure (left), HOMO (middle), and LUMO (right) for a) rubicene **3**, b) tetrabenzopentacene **5**, c) rubicene **9**, and d) tetrabenzopentacene **10**. Note that the side chains have been partially omitted for the isosurface plots.

In summary, we have prepared nitrogen-containing rubicenes and tetrabenzopentacenes, and our study holds significance for a number of reasons. First, the described modular approach encompasses two distinct yet complementary synthetic pathways, which require few steps, straightforward conditions, and commercially available precursors, facilitating both the incorporation of nitrogen heteroatoms at distinct positions and the installation of varying alkyl substituents. Second, our general methodology leverages accessible and established chemical transformations, including the aza-

Diels–Alder (Povarov) reaction,[38,39] the Heck coupling,[40,41] and base-mediated cyclodehydrohalogenation,[42,43] making it potentially useful for a broad range of researchers. Third, given the difficulties inherent to designing n-type and ambipolar organic semiconductors[53,54] and the known utility of nitrogen substitution for coaxing such behavior from acenes,[32,33] the reported rubicenes and tetrabenzopentacenes hold particular promise as organic electronic functional materials. Finally, nitrogen-containing fullerenes and graphene nanoribbons remain relatively rare and challenging to prepare,[19–25] and as such, we envision that our approach could eventually prove valuable for the design and construction of extended doped carbonaceous frameworks. Altogether, our findings may open new research avenues and provide unique opportunities for the solution-phase synthesis of novel carbon-based materials.

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