Heteroaromatics

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A Nanoscale Jigsaw-Puzzle Approach to Large π-Conjugated Systems**

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Heteroatom-doped carbon conjugated-materials (CCMs) have evoked considerable interest as functional derivatives of pure CCMs and also as a family of new materials with unique properties and potentials in application.[1–3] These hybrids have distinct stable structural and electronic properties from their pure-carbon counterparts. For example, adjacent pentagons are strictly prohibited in all-carbon, empty fullerenes;[4a,b] in contrast, their existence in N-doped fullerenes (azafullerenes) is believed to be possible.[4c] Unlike carbon nanotubes, which are circular cylinders, carbon nitride nanotubes have bamboo-like shapes with irregular corrugations in the sidewalls.[1] In contrast to graphitic carbons that are sp^2-hybridized, the electronic states of dopant nitrogen atoms vary between sp^2 and sp^3, depending strongly on the local structures where the dopants are situated.[2d,3b] These "conflicting" properties, combined with the huge configuration possibilities, make it particularly difficult to characterize the detailed structures for hybrid CCMs that have been experimentally synthesized before (except the rare cases of azafullerenes[3a] and small N-doped nanographene[2g]) or synthesize new examples with desired structures.

Herein, we develop a simple "jigsaw-puzzle" strategy for the construction of stable CCMs. This strategy unifies the seemingly controversial structural and electronic properties of hybrid and pure CCMs. It provides a generalized rule of thumb to evaluate the stabilities of CCMs, and in particular a systematic way to pre-screen the large number of candidate structures for hybrid CCMs. Our result paves a way to the fascinating world of hybrid CCMs.

Similar to pure CCMs, chemical growths are to date the most popular and even exclusively available methods for the syntheses of hybrid CCMs in laboratory. The bottom-up growth strategy determines that the morphologies of hybrid CCM products depend on the stable morphologies of the intermediates that are transitorily formed during the growth. Therefore, we first explored the structural features for small, stable hybrid CCMs. All geometries and energies were calculated with the B3LYP/6-31G* method. Figure 1 portrays a set of hybrid CCMs that contain nitrogen or oxygen heteroatoms. The calculated HOMO–LUMO gaps, vertical ionization potentials (VIPs), and adiabatic ionization potentials (AIPs) are listed in Table 1. These criteria are those commonly used for chemical viability of molecules.[5] For reference, the corresponding values of a large pure-carbon conjugated molecule $C_{222}H_{42}$, which has been synthesized and characterized experimentally,[6] are also given (for the structure of $C_{222}H_{42}$, see the Supporting Information, part 2). According to Table 1, **1**–**6** have larger HOMO–LUMO gaps,

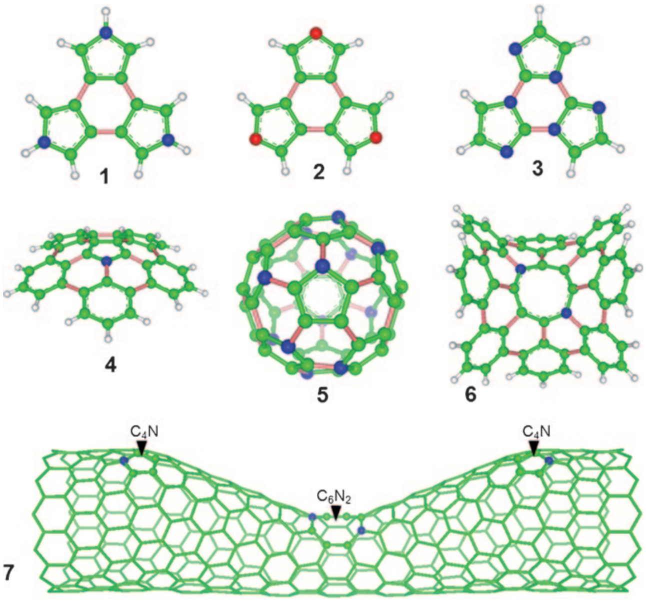

Figure 1. Hybrid carbon conjugated materials (CCMs). C green, N blue, O red, H white; red and green sticks denote single and aromatic bonds, respectively.

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Table 1: Symmetry, energies, and aromatic-ring constituents for species **1**–**6**.[a]

Species	Symm.	Gap	VIP	AIP	Constituent
$C_{222}H_{42}$[b]	D_{6h}	1.77	5.04	5.02	$37\,C_6$
1	D_{3h}	5.45	6.22	6.09	$3\,C_4N$
2	D_{3h}	5.28	7.46	7.41	$3\,C_4O$
3	D_{3h}	5.66	8.02	7.87	$3\,C_3N_2$
4	C_s	3.29	6.05	5.99	$5\,C_6+1\,C_4N$
5	S_6	2.75	6.15	6.03	$12\,C_4N$
6	C_2	2.37	5.27	5.25	$8\,C_6+1\,C_6N_2$

[a] Symm = symmetry, gap = HOMO–LUMO gap [eV], VIP = vertical ionization potential [eV], AIP = adiabatic ionization potential [eV]; calculated at the B3LYP/6-31G* level of theory. [b] Used as a reference; corresponds to experimental compound **9** of Ref. [6].

VIPs, and AIPs than $C_{222}H_{42}$, suggesting their high stability. Reportedly, azafullerene $C_{48}N_{12}$ has been synthesized as the core of nano-onions of carbon nitride,[7] the structure of which has been theoretically characterized as **5** (Figure 1).[8,9]

Why are the seemingly unrelated hybrid species in Figure 1 all stable? Table 1 shows the structural components of compounds **1**–**6**. Despite their different constitutions, all of the six compounds have the same structural feature: If ignoring the peripheral hydrogen atoms that saturate dangling σ bonds, they consist entirely of benzenoid aromatic rings (that is, C_6) and/or heteroaromatic rings (C_4N, C_4O, C_3N_2, and C_6N_2). Taking **5** as an example, its structure can be regarded as 12 C_4N rings joined with single bonds. C_4N has 6 π electrons and enjoys a similar π conjugation with the benzenoid ring (Figure 2a), according to Hückel's rule. Similarly, the other five compounds are also fully made up of aromatic rings (Figure 1 and Table 1). Therefore, their uniform structural feature may be responsible for their high stabilities.

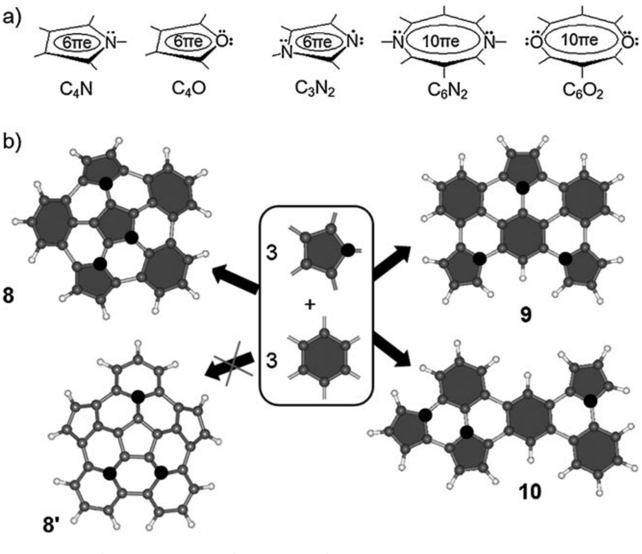

Figure 2. The jigsaw-puzzle approach. a) Heteroaromatic rings as puzzle pieces. b) Construction of fully aromatic CCMs **8**, **9**, and **10** with aromatic-ring puzzle pieces ($3\,C_4N$ and $3\,C_6$). Peripheral dangling bonds are saturated with H atoms; C gray, N black, H white. **8′** is an isomer of **8** that cannot be constructed by the jigsaw-puzzle approach. Though it has a higher symmetry than **8** (C_s versus C_1), it is less stable than **8** by 72.1 kcal mol^{-1} and has a small HOMO–LUMO gap (1.61 eV) at the B3LYP/6-31G* level of theory.

To confirm the above assumption and to verify whether it is a general tendency that CCMs consisting entirely of aromatic rings are stable, we comparatively studied N-doping of **11** and **12** (Figure 3a–c). The doping of **11** at inner carbons, for example at position a, is energetically unfavorable (doping energy $E_d = 49.0$ kcal mol^{-1}; Figure 3c), giving rise to **11a**, which obviously deviates from a plane (Figure 3a). Therefore, the nitrogen atom in **11a** is more sp^3-hybridized. In contrast, the selective doping of **12** at the pentagonal carbon atoms, for example a, is energetically favorable ($E_d = -16.4$ kcal mol^{-1}; Figure 3c), rending **12a** planar and N sp^2-hybrized (Figure 3b). Similar opposite doping effects were found for the doubly doped species **11b** and **13a** (Figure 3d; see also the Supporting Information, part 3). Structures **11**, **12a**, and **13a** are completely made up of aromatic rings ($4\,C_6$, $3\,C_6+1\,C_4N$, and $2\,C_6+2\,C_4N$), whereas **11a**, **11b**, **12**, and **13** are not. Therefore, such opposite doping effects of **11** to **11a** versus **12** to **12a** and **11** to **11b** versus **13** to **13a** suggest that keeping a π-electron topology consisting entirely of aromatic rings is a tenet dominating the chemical behaviors of CCMs. It is worth noting that N-doping of **11** at outer carbons, for example c and d, prefer the pattern in which nitrogen substitutes C–H to form a pyridine-like aromatic ring, which also obeys the above rule. It is also noteworthy that when referring to pure CCMs of hexagonal rings, the above rule becomes Clar's aromatic sextet rule.[10] Therefore, our rule provides a generalized stability model for both pure and hybrid CCMs.

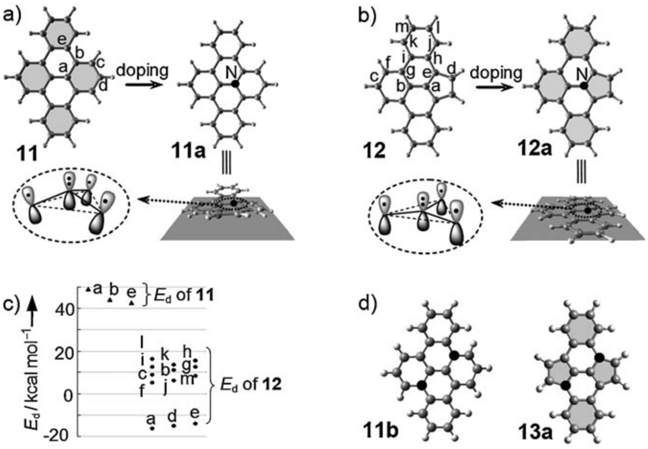

Figure 3. N-doping of CCMs. a) Singly doped **11**. b) Singly doped **12**. c) Doping energies (E_d) of **11** at positions a, b, and e and of **12** at positions a–m. d) Doubly doped **11** (i.e., **11b**) and **13** (i.e., **13a**). C gray, N black, and H white. The orbitals near the nitrogen atom and their occupations are denoted in the side-view blowups of (a) and (b). Rings filled with gray denote aromatic rings. For the calculation of E_d, see the Supporting Information, part 1.

The above rule renders a straightforward "jigsaw-puzzle" approach to construct stable hybrid CCMs bottom-up or from existing hybrid CCMs. Some heteroaromatic rings are shown in Figure 2a.[11] Using for example aromatic rings C_6 and/or heteroaromatic rings as the puzzle pieces, stable CCMs can be easily designed. Figure 2b shows how to construct such compounds using 3 C_6 and 3 C_4N aromatic rings. Arranging one C_4N to be surrounded by others and connecting each pair of the neighboring dangling bonds into a single bond, **8** is obtained. By different arrangements of the six rings, **9** and **10** are obtained. Structures **8**–**10** are also more stable than the reference molecule $C_{222}H_{42}$ (Supporting Information, part 4, Table S1). In sharp contrast, isomers that can not be constructed by the jigsaw-puzzle approach are relatively much more unstable. For example, **8′** is an isomer of **8**; although it has a higher symmetry than **8** (C_s versus C_1), it has a smaller HOMO–LUMO gap (1.61 eV) than the reference molecule and is less stable than **8** by 72.1 kcal mol^{-1} (Figure 2b).

The above rule paves not only a way towards stable hybrid CCMs, but also an approach to pre-screen the candidate structures and understand the electronic properties for hybrid CCMs that have been synthesized and studied before.[1–3] Based on the rule, if a pentagon is embedded in the basal plane of graphenes or the side-wall of carbon nanotubes, the selective single doping of the pentagonal carbons with nitrogen atoms is an inevitable step to retain a fully aromatic ring structure and thus is favorable. Such selectivity has indeed been shown in our calculations (Figure 3b,c), which is in good agreement with experiment that the concentration of nitrogen atoms in N-doped nano-onions is proportional to that of pentagons therein.[7] Such pentagons are responsible for positive curvatures of carbon conjugated surfaces.[12–14] Consequently, this result also agrees with the observation that nitrogen atoms induce corrugation[1f] and closure[1i] of carbon systems during growth. Thus, it rationalizes well the findings that the 12 N atoms are exactly situated in the 12 pentagons of **5** to give the lowest-energy isomer.[7–9] On the other hand, the substitution of any inner carbon in defect-free graphenes or carbon nanotubes by nitrogen inevitably causes deviations from fully aromatic ring structures, which is unfavorable to conjugation and stability and leads to an sp^3 hybrid state of the nitrogen (Figure 3a,c). The sp^3 hybridization explains the donor states on N-doped carbon nanotube sidewalls, which have been predicted before.[1g,15] Thus, it is also easy to understand why adjacent pentagons are prohibited in fullerenes,[4a,b] whereas they are permitted in azafullerenes.[4c] Adjacent pentagons are 10-π-electron antiaromatic systems, which bear large strains when embedded in fullerenes.[16] However, after doped by nitrogen atoms, the instability pertaining to them is relieved as C_5 becomes a C_4N heteroaromatic ring or as sp^2 C is replaced by sp^3 N, which releases the strain. The introduction of octagons into graphene surfaces causes surface expansion, which is opposite to that of pentagons. Therefore, a simultaneous inclusion of the pentagons and octagons will give a reasonable explanation to the growth mechanism of bamboo-like carbon-nitride nanotubes.[1] As mentioned above, pentagonal-ring C_4N and octagonal-ring C_6N_2 are aromatic. Structure **7** thus represents an ideal model for bamboo-like carbon nitride nanotubes.

In conclusion, we show that keeping a π-electron topology consisting entirely of aromatic rings is a general tenet to stable CCMs. Based on this rule, a simple jigsaw-puzzle strategy towards the design of a family of highly viable hybrid CCMs has been developed. It provides a systematic way to prescreen among an overwhelming number of candidate structures. Unlike the Clar's sextet rule for pure hexagonal carbon, our rule works for both pure and hybrid carbon systems formed of aromatic rings of any size and shape. Not only is our rule is supported by experiments, but it also rationalizes the properties of the hybrid CCMs that have been experimentally synthesized. In the past several decades, pure CCMs have been studied often. Although the study of the hybrid systems is still in its infancy, the time is ripe. Our proposal should not only stimulate further experimental and theoretical studies in the fascinating world of hybrid CCMs but also pave the way for rationalizing the findings.

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[1] For nitride-doped carbon nanotubes, see for example: a) K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* **2009**, *323*, 760; b) Y. Tang, B. L. Allen, D. R. Kauffman, A. Star, *J. Am. Chem. Soc.* **2009**, *131*, 13200; c) X. Ma, E. G. Wang, *Appl. Phys. Lett.* **2001**, *78*, 978; d) C. J. Lee, S. C. Lyu, H.-W. Kim, J. H. Lee, K. I. Cho, *Chem. Phys. Lett.* **2002**, *359*, 115; e) W. Xu, T. Kyotani, B. K. Pradhan, T. Nakajima, A. Tomita, *Adv. Mater.* **2003**, *15*, 1087; f) J. W. Jang, C. E. Lee, S. C. Lyu, T. J. Lee, C. J. Lee, *Appl. Phys. Lett.* **2004**, *84*, 2877; g) H. J. Choi, J. Ihm, S. G. Louie, M. L. Cohen, *Phys. Rev. Lett.* **2000**, *84*, 2917; h) S. H. Yang, W. H. Shin, J. K. Kang, *Small* **2008**, *4*, 437; i) B. G. Sumpter, V. Meunier, J. M. Romo-Herrera, E. Cruz-Silva, D. A. Cullen, *ACS Nano* **2007**, *1*, 369.

[2] For nitrogen-doped graphenes, see for example: a) X. Li, H. Wang, J. T. Robinson, H. Sanchez, G. Diankov, H. Dai, *J. Am. Chem. Soc.* **2009**, *131*, 15939; b) D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang, G. Yu, *Nano Lett.* **2009**, *9*, 1752; c) L. S. Panchakarla, K. S. Subrahmanyam, S. K. Saha, A. Govindaraj, H. R. Krishnamurthy, U. V. Waghmare, C. N. R. Rao, *Adv. Mater.* **2009**, *21*, 4726; d) Y. Li, Z. Zhou, P. Shen, Z. Chen, *ACS Nano* **2009**, *3*, 1952; e) A. Lherbier, X. Blase, Y.-M. Niquet, F. Triozon, S. Roche, *Phys. Rev. Lett.* **2008**, *101*, 036808; f) X. Wang, X. Li, L. Zhang, Y. Yoon, P. K. Weber, H. Wang, J. Guo, H. Dai, *Science* **2009**, *324*, 768; g) M. Takase, V. Enkelmann, D. Sebastiani, M. Baumgarten, K. Müllen, *Angew. Chem.* **2007**, *119*, 5620; *Angew. Chem. Int. Ed.* **2007**, *46*, 5524.

[3] For nitrogen-doped fullerenes, see for example: a) J. C. Hummelen, B. Knight, J. Pavlovich, R. González, F. Wudl, *Science* **1995**, *269*, 1554; b) Z. Chen, R. B. King, *Chem. Rev.* **2005**, *105*, 3613, and references therein; c) V. López, G. R. Pérez, A. Arregui, E. Mateo-Marti, L. Bañares, J. A. Martín-Gago, J. M. Soler, J. Gómez-Herrero, F. Zamora, *ACS Nano* **2009**, *3*, 3352; d) D. Schultz, R. Droppa, Jr., F. Alvarez, M. C. dos Santos, *Phys. Rev. Lett.* **2003**, *90*, 015501; e) S. Sun, Y. Cao, Z. Sun, Z. Tang, L. Zheng, *J. Phys. Chem. A* **2006**, *110*, 8064.

[4] a) H. W. Kroto, *Nature* **1987**, *329*, 529; b) T. G. Schmalz, W. A. Seitz, D. J. Klein, G. E. Hite, *J. Am. Chem. Soc.* **1988**, *110*, 1113; c) P. E. Christopher, *Nano Lett.* **2006**, *6*, 890.

[5] See for example, R. Hoffmann, P. von R. Schleyer, H. F. Schaefer III, *Angew. Chem.* **2008**, *120*, 7276; *Angew. Chem. Int. Ed.* **2008**, *47*, 7164.

[6] K. Müllen, J. P. Rabe, *Acc. Chem. Res.* **2008**, *41*, 511, and references therein.

[7] L. Hultman, S. Stafström, Z. Czigány, J. Neidhardt, N. Hellgren, I. F. Brunell, K. Suenaga, C. Colliex, *Phys. Rev. Lett.* **2001**, *87*, 225503.

[8] M. R. Manaa, D. W. Sprehn, H. A. Ichord, *J. Am. Chem. Soc.* **2002**, *124*, 13990.

[9] Z. Chen, H. Jiao, D. Moran, A. Hirsch, W. Thiel, P. von R. Schleyer, *J. Phys. Org. Chem.* **2003**, *16*, 726.

[10] E. Clar, *The Aromatic Sextet*, Wiley, London, **1972**.

[11] For the electronic structure of C_6O_2, see: X. Gao, L. Wang, Y. Ohtsuka, D. Jiang, Y. Zhao, S. Nagase, Z. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 9663.

[12] S. Iijima, T. Ichihashi, Y. Ando, *Nature* **1992**, *356*, 776.

[13] G. K. Gueorguiev, J. Neidhardt, S. Stafström, L. Hultman, *Chem. Phys. Lett.* **2005**, *410*, 228.

[14] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*; Oxford University Press, Oxford, **1995**.

[15] J. Robertson, C. A. Davis, *Diamond Relat. Mater.* **1995**, *4*, 441.

[16] X. Gao, Y. Zhao, *J. Comput. Chem.* **2007**, *28*, 795.