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Predicting Real Optimized Materials: Novel Nitrogen-Containing Fullerenes and Nanotubes

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DISCLAIMER

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PREDICTING REAL OPTIMIZED MATERIALS:

NOVEL NITROGEN-CONTAINING FULLERENES AND NANOTUBES

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WHITE PAPER

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Summary:

We propose to investigate the possible configurations, electronic, conducting and energetic properties of nitrogen-containing carbon fullerenes and single-walled nanotubes with nitrogen contents up to 30% using first principle density functional theoretical calculations. The proposed research allows for a predictive method to control the electronic properties of fullerenes and nanotubes that could pave the way for controlled fabrication of molecular circuits and nanotube networks.

Background:

Attempts to displace carbon atoms in fullerenes and nanotubes with nitrogen atoms provide an opportunity for a new exciting research field to **fine-tune** the structural, electronic, and conductive properties of these materials, making them promising candidates for building blocks of molecular-scale machines and nanoelectronic devices. So far, the applications of all-carbon forms of these materials have been limited due to the weak interaction from van der Waals bonds. Replacement of some carbon atoms with nitrogen should enhance the chemical reactivity of these materials and alter their electronic properties to suitable applications. Recent experiments, for example, have shown that doped single-wall nanotubes (SWNT) exhibit conductivity enhancement and charge transfer. [1,2] For fullerenes, a recently synthesized onion-structured, nitrogen-substituted fullerene material was demonstrated to have the "soccer ball," $C_{48}N_{12}$ molecule at its core. [3] Nanoindentation tests showed evidence of a highly elastic material, combined with an appreciable resilience, properties that render the nanostructured material ideal for wear-protective applications. Earlier, synthesis of solid $C_{59}N$ was also reported, [4] a highly unstable radical that transforms into the more suitable dimer form $(C_{59}N)_2$. [5] These studies clearly indicate that doping of carbon fullerenes and nanotubes with nitrogen atoms has a profound effect on the electronic and structural properties of these materials. Theoretical investigations through first-principle quantum mechanical calculations serve to predict the stable configurations, electronic and energetic properties of these nanostructured materials as a function of the nitrogen doping

contents in order to optimize their utilities. Such is the purpose of this proposed work.

In a recent theoretical study, we were able to predict the stable structure of the newly synthesized $C_{48}N_{12}$ (shown in Fig.1 with its electron-density cloud). [6] We performed a series of quantum mechanical, density-functional calculations, and showed that the extended aromaticity of an eight all-carbon hexagonal rings plays the stabilizing role for this novel molecule. In this new structure, the nitrogen atoms were distributed as one atom per pentagon, a total of twelve. The top and bottom of the azafullerene each consists of a triphenylene-type unit (has four six-member ring carbon) connected to three nitrogen atoms. The 18 electrons in each unit are distributed to give the outer rings a benzene-like sextet. The six remaining nitrogen atoms lie around the fullerene's equator. The extended region of electron delocalization provided by these two units enhances the molecule stability via resonance energy contribution, while precluding a weaker N-N link. The resulting structure is 0.5 eV more stable than the previously reported structure with only two hexagonal an all-carbon conformation. [7]

Our work on elucidating the molecular structure of $C_{48}N_{12}$ and its infrared spectroscopic signature was very well received by the scientific community and has attracted many attentions. The work was noted in a science concentrate in the American Chemical Society (ACS) national magazine, Chemical &Engineering News, [8] and the published article was selected and listed as a " Hot Article" on the ACS website.

It is the object of this proposal to conduct quantum based computational work to build upon these exciting findings, and predict novel structural and electronic properties of nitrogen containing fullerenes and nanotubes to optimize their applications.

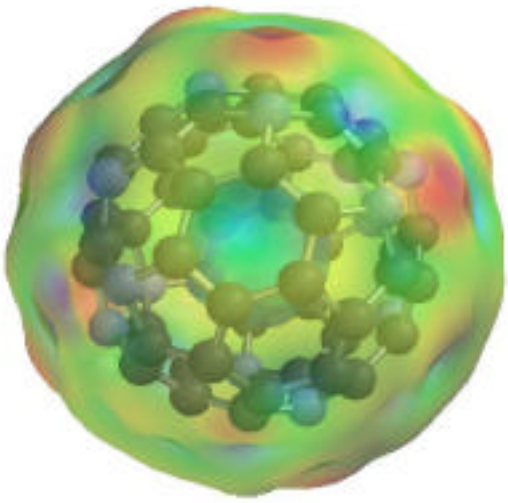

Figure 1. The predicted stable structure of $C_{48}N_{12}$.

Research Proposal:

We propose to systematically study the effect of nitrogen doping on the electronic and structural properties of carbon fullerenes and nanotubes using first principal, quantum density functional calculations in combination with molecular dynamics simulations. Our proposed work will concentrate on the following:

1- The molecular structure of the synthesized $C_{48}N_{12}$ buckyball has now elucidated. Of **urgency** is to determine the crystal and solid-state structure of this material. The crystal structure of C_{60} was shown to be face-centered cube (fcc). We will conduct calculations on several lattices to find the optimum, energetically favorable crystal structure and determine the lattice parameters. Several types of crystal systems will be examined such as cubic, orthorhombic, tetragonal, and hexagonal. Total energies, band structure, local density of states, and cohesive energies will be calculated using density-functional theory (DFT) within the generalized-gradient approximation (GGA), and implementing different exchange-correlation functionals such as Pedrew-Wang (PW91) [9] and Pedrew-Burke-Ernzerhof (PBE) [10]. These calculations will be performed using either of two state-of the art codes: CASTEP and VASPS, well established codes in the

condensed-phase community. These calculations will determine the solid structure of $C_{48}N_{12}$, whether it's a semi-conductor or an insulator, and weather it's prone to form dimmers. These determinations are fundamental and will set the stage for subsequent studies that predict other properties such as bulk and magnetic, and confirm future experimental findings. The stability of $C_{48}N_{12}$ at varied temperature will be established via MD simulations for up to a few pioseconds, implementing DFT based tight-binding computation that we currently use for other applications on chemical reactivity of organic materials.

2- Single walled carbon nanotubes can be either metallic or semi conducting, depending on the chiral vectors (n, m), which specify the wrapping vector from an infinite sheet of graphite with a wrapping angle $0<\varphi<30°$. Figure 2 shows a nanotube with (10,10) wrapping and nitrogen contents of 25%.

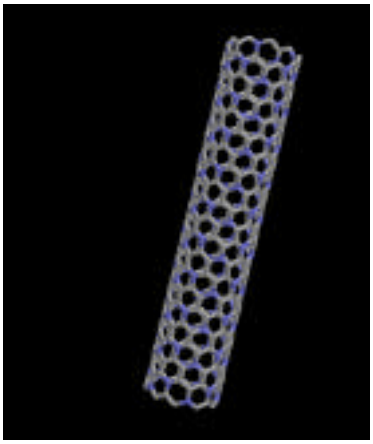

Figure 2. The configuration of (10,10) nanotube with 25% nitrogen (in blue).

We will construct configurations of (n, m) SWNT with n and m in the range 5-10. We will substitute nitrogen atoms for carbon up to 30% in the SWNT with different distributions and calculate the cohesive energy to determine the optimum configuration and nitrogen contents. Thus, the calculations will yield the optimal nitrogen contents for substitution and the geometrical structure of the resulting nanotube. For the resulting, fully relaxed structures, we will calculate the band gap of these configurations and the local density of states around the Fermi level to deduce what correlations exist with respect to substitution and to the reference all-carbon nanotube. Based on the difference in C-N versus C-C bonding, we

expect the electronic and energetic properties to be altered. The results should establish what nitrogen percentage and configurations would alter the band gap property and transitions from semiconductor to metallic regime or vice versa, thus tailoring the material structure to function.

3- The inclusion of nitrogen in the nanotubes will certainly enhance their reactivity at a specific site. We will study the possibility of welding together doped SWNT (figure 3). This study could pave the way for controlled fabrication of molecular circuits and nanotube networks. Density functional based tight binding methodology (DFTB) allow us to construct models with several hundreds atoms. We will use DFTB in conjunction with molecular dynamics in an annealing simulation to examine this possibility of welding two, doped SWNT via thermal heating. A newly developed version of tight-binding allows us to examine the welding possibility under irradiation with a classical electromagnetic field. These studies have never been attempted on nanotubes and should lead computational work in this field. Results will be published in leading scientific journals due to the high visibility of work on nanotubes currently receives and to the ground breaking results we expect to achieve.

Figure 3. Welding SWNTs at different sites

Milestones:

1st year: Determine the stable crystal structure and electronic properties of $C_{48}N_{12}$.
Determine stable configurations and nitrogen concentration of SWNT.
Determine stability to decomposition of $C_{48}N_{12}$ via MD simulations.

2nd year: Determine electronic properties of stable configurations of optimum SWNT.
Determine welding mechanisms of SWNT via ab initio/MD simulations.
Determine stable molecular structures for $C_{60-2n}N_{2n}$ (n=1-5).

Budget:

$200K /yr, for two years to support 0.5 FTE of PI and 1 FTE for two summer students. Graduate students from Paderborn University, Germany, where DFTB methodology is being developed will be working with us for the full summers, and throughout the year.

References:

1 R. S. Lee, H. J. Kim, and e. al., *Nature* **388,** 255 (1997).

2 A. M. Rao, P. C. Eklund, and e. al., *Nature* **388,** 257 (1997).

3 L. Hultman, S. Stafstrom, Z. Czigany, J. Neidhardt, N. Hellgren, I. F. Brunell, K. Suenaga, and C. Colliex, *Phys. Rev. Lett.* **87,** 225503 (2001).

4 J. C. Hummelen, B. Knight, J. Pavlovich, R. Gonzalez, and F. Wudl, *Science* **269,** 1554 (1995).

5 C. M. Brown, E. Beer, C. Bellavia, L. Cristofolini, R. Gonzalez, M. Hanfland, D. Hausermann, M. Keshavarz, K. K. Kordatos, K. Prassides, and F. Wudl, *J. Am. Chem. Soc.* **118,** 8715 (1996).

6 M. R. Manaa, D. W. Sprehn, and H. A. Ichord, *J. Am. Chem. Soc.* **124,** 13990 (2002).

7 S. Stafstrom, L. Hultman, and N. Hellgren, *Chem. Phys. Lett.* **340,** 227 (2001).

8 M. R. Manaa, in *Chemical &Engineering News*, Vol. 80 (2002), pp. 30.

9 J. P. Perdew and Y. Wang, *Phys. Rev. B* **46,** 6671 (1992).

10 J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77,** 3865 (1996).

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