Heme B-like defects in N-doped carbon nanotubes.

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Abstract – It has been previously determined [1] that pyridine-like defects in carbon nanotubes can act as binding sites of molecules, such as ammonia, and can be associated with the behavior of such tubes as sensors. In this work we study the adsorption of iron atoms onto these nitrogen defects, in a configuration similar to a porphyrin molecule. This defect has a non-zero magnetic moment of $2\mu_b$ which is almost entirely localized on the Fe atom. With a combination of density functional theory and recursive Green's functions calculations we study the transport properties of disordered one-dimensional systems [1] composed of such units.

N-doped carbon nanotubes have been already synthesized by a variety of groups [2]. The pyridine-like defects were theoretically investigated by M. Rossi et al., which have shown that 4 nitrogens surrounding a divacancy – 4N-DV defect – (see Fig. 1 a)) is the most stable configuration. This type of defect shows a great similarity to Porphyrin molecules, as show in Fig. 1 b). It is well known that such molecules can bind transition metal atoms, such as iron in the case of the Heme B molecule shown in Fig. 1 c), as found in Hemoglobin and Myoglobin.

We have thus investigated how an iron atom will bond to the 4N-DV defect using Density Functional Theory total energy calculation (Fig. 2). We obtained a formation energy of -1.6 eV (bulk Fe as reference), and a binding energy of -6.3 eV (free atom as reference), with a N-Fe bond distance of approximately 1.95 Å. The local magnetization $m(r) = \rho_\uparrow - \rho_\downarrow$ shows that there is a highly localized magnetization on the iron atom. Moreover, studies considering two such defects separated by approximately 22 Å indicate that they do not interact at such distances.

Using a combination of density functional theory and recursive Green's functions calculations, we investigated the charge transport properties of such a defect (Fig. 3). One can see that at the Fermi energy the minority spin is slightly more scattered than the majority spin, giving a polarization of approximately 0.1, as defined by Eq. 1 below.

$$P = \frac{T^{up} - T^{down}}{T^{up} + T^{down}} \qquad \text{Eq. 1}$$

We will also present charge transport calculations for large nanotubes with randomly distributed Fe-4N-DV. In particular, we will report results for configurations with all the localized magnetic moments pointing in the same direction compared with configurations with 50% of the Fe with spin up and 50% with spin down. Results for both the polarization as well as the magnetoresistance for such systems will be presented.
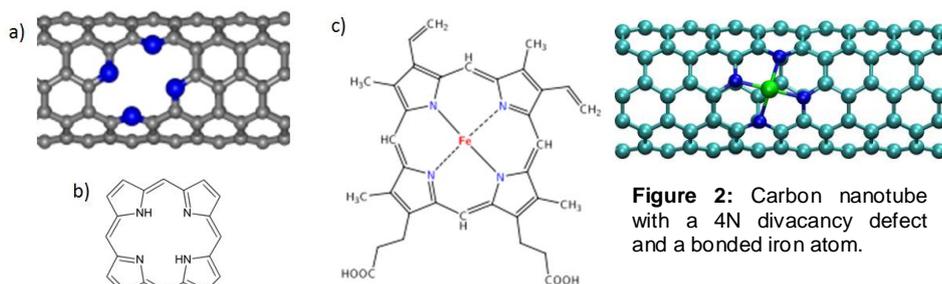

Fig. 1: a) 4N divacancy defect on a carbon nanotube b) Porphyrin molecule c) Heme B molecule.
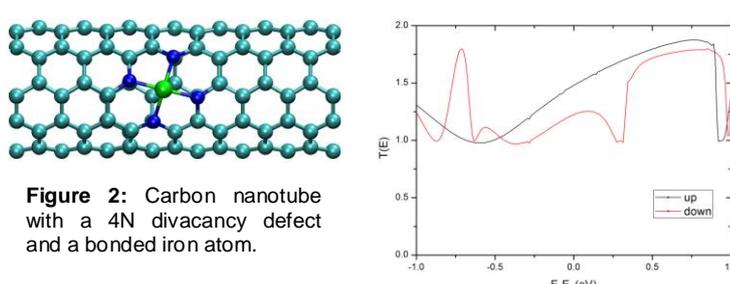

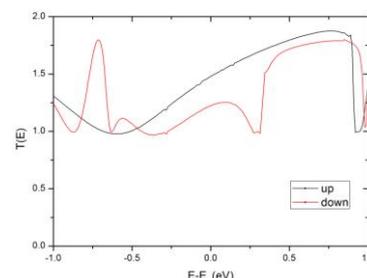**Figure 2:** Carbon nanotube with a 4N divacancy defect and a bonded iron atom.

Figure 3: Transmittance for a Fe-4N-DV defect.

[1] A. R. Rocha, M. Rossi, A. Fazzio and A. J. R. da Silva, Phys. Rev. Lett. **100**, 176803 (2008).
[2] P. Ayala, et al. and references therein, J. Phys. Chem. C, **111**, 7, 2879–2884 (2007).