Electronic Supplementary Information

Strain-induced spin crossover and spin-polarized currents in a prototype graphene nanoribbon

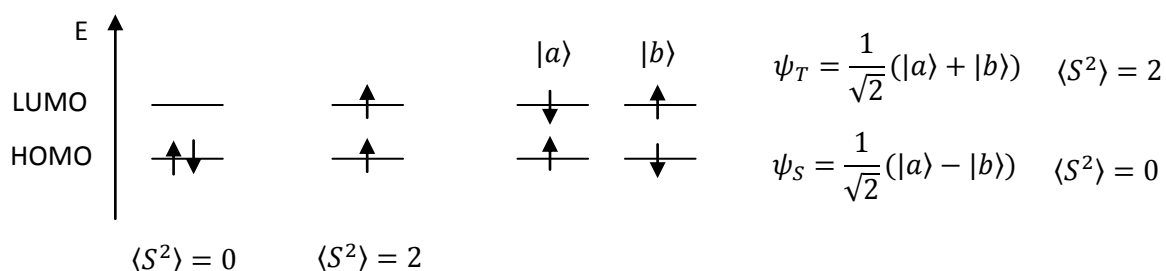Rodrigo Castellanos Caro [a,b] and Maria Cristina dos Santos[a, †]

[a] *Instituto de Física, Universidade de São Paulo, 05508-090 São Paulo SP, Brazil.*

[b] *Departamento de Física, Universidad Nacional de Colombia, A.A. 5997, Bogotá, Colombia.*

† email: mcsantos@if.usp.br

1- Singlet x Triplet states of 13-acene

The molecule 13-acene, as other long n-acenes (n>10), has nearly degenerate HOMO and LUMO levels. It has also an even number of electrons. The natural way of populating the one-particle states is by assuming double occupation of the states until the highest energy HOMO level is occupied, as in the leftmost diagram of Scheme 1.

$$\psi_T = \frac{1}{\sqrt{2}}(|a\rangle + |b\rangle) \quad \langle S^2 \rangle = 2$$

$$\psi_S = \frac{1}{\sqrt{2}}(|a\rangle - |b\rangle) \quad \langle S^2 \rangle = 0$$

Scheme 1. One-particle states occupation in the closed shell singlet (left, $\langle S^2 \rangle = 0$), triplet (middle, $\langle S^2 \rangle = 2$) and the combinations of states $|a\rangle$ and $|b\rangle$ leading to the $S_z=0$ component of the triplet, ψ_T, and the open shell singlet, ψ_S. The arrows represent "spin up" and "spin down" orientations of the electronic spin.

Whether the triplet state, as in the middle diagram of Scheme 1, has lower energy than the closed shell singlet, will depend on details of the electronic interactions and on the HOMO-LUMO energy gap. Density functional theory (DFT) based on B3LYP functional predicts, for 13-acene, that the triplet state is lower in energy than the closed shell singlet. There is still another possibility for the states occupation, illustrated in the rightmost diagram of Scheme 1. Note that states $|a\rangle$ and $|b\rangle$, defined according to the one-particle states occupation given in the diagram, are not eigenstates of the total spin operator S^2. The Kohn-Sham procedure assumed in DFT calculations uses a given occupation of the one-particle states, as in the closed shell singlet, or in the triplet, or even the occupations of states $|a\rangle$ and $|b\rangle$. As states $|a\rangle$ and $|b\rangle$ are not eigenstates of S^2, the expectation value $\langle S^2 \rangle$ obtained for these occupations of one-particle states is usually different from the values given in Scheme 1 for the true eigenstates of the spin operator. This is referred to in the literature as spin contamination. The only electronic configuration that is free from spin contamination in DFT is the closed shell singlet. All other electronic

configurations will lead to electronic densities having some degree of spin contamination. For 13-acene, for instance, the B3LYP/6-31(d,p) calculation of the triplet state results in $\langle S^2 \rangle = 2.05$, instead of 2, representing a deviation of (2.05 - 2)/2 = 2.5%. The problem with spin contamination is that the total energy, calculated with such contaminated states, is a linear combination of the true energies of the eigenstates of S^2. In the present work, total energies where accepted when the spin contamination was smaller than 20%. For a comprehensive discussion of spin contamination of DFT results for oligoacenes, see Ref.1.

2- HOMO-LUMO gaps in sulfur-substituted 13-acenes: molecules 1,3,5, and 7
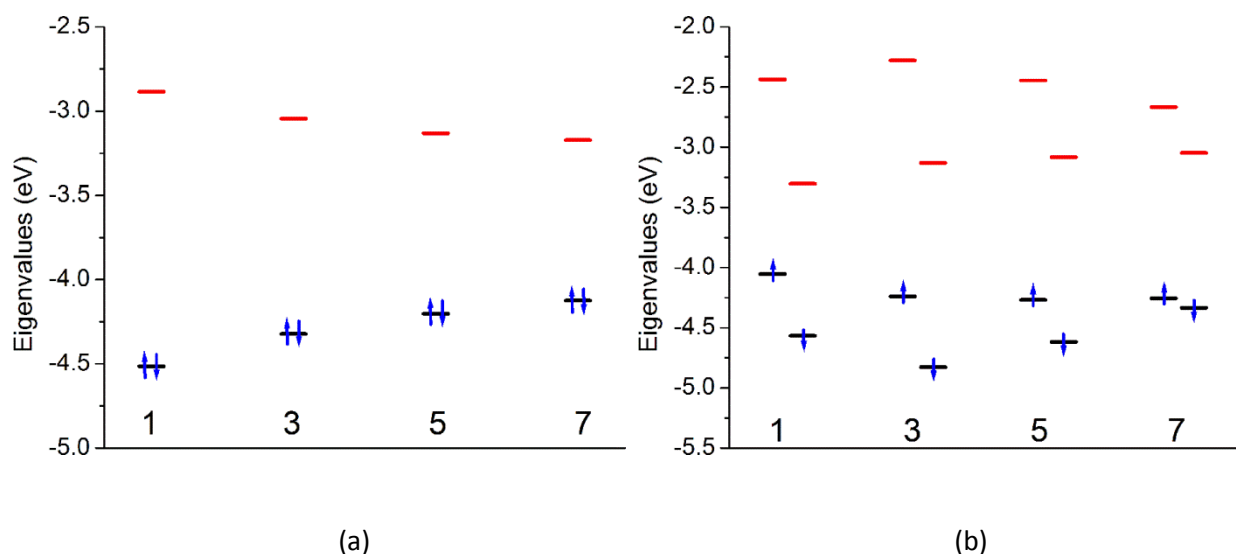

(a) (b)

Figure S1: Energy level diagrams showing HOMO (black bars) and LUMO (red bars) energies of molecules 1,3,5, and 7: (a) closed shell singlet states, where one-particle states are doubly occupied, and (b) triplet states, showing spin polarization effects. Blue arrows indicate spin orientation.

3- Extended molecules for Transport Calculations

The extended molecules built for transport calculations include the organic part, the thiolate (—S—) bridge, and the left and right electrode models. There are three ways of connecting the leads to the organic molecule, as illustrated in Scheme 2. Structure (a) is the *cis*-like, labeled as C in the text, for which the expectation value of the total spin in the triplet state, in our DFT calculation, is $\langle S^2 \rangle$ = 2.14. The other two structures are *trans*-like: (b), labeled as T in the text, resulted in $\langle S^2 \rangle$ = 2.11 , while this value for structure (c) is 3.19, indicating a high degree of spin contamination. The most likely contaminant state should be a quintet state ($\langle S^2 \rangle$ = 6) that is closer in energy to the triplet state in structure (c) due to the interaction of the electrodes with the frontier orbitals of the organic molecule. Note that the Kohn-Sham orbitals shown in Fig. S2 spread along the zigzag line of bonds and away from the substitution sites, so that the interaction with the leads is stronger in structure (c) of Scheme 2, leading to spin contamination.
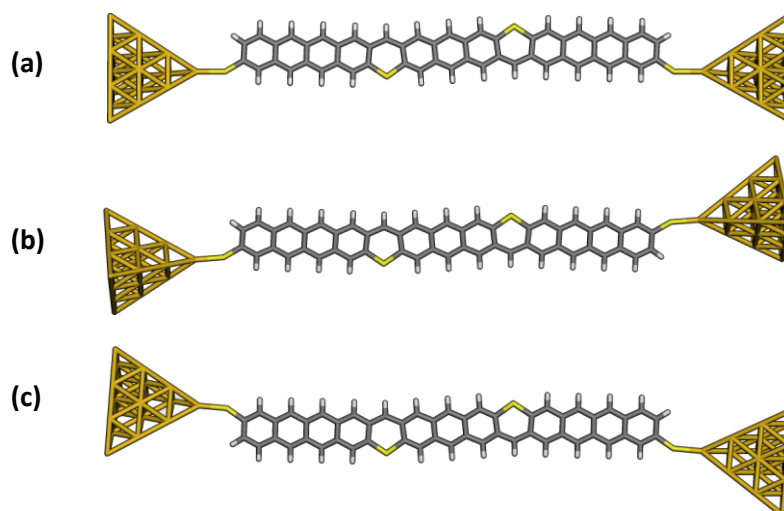
Scheme 2. Binding of the organic molecule to the electrodes: (a) *cis*-like (C), (b) *trans*-like (T), and (c) another *trans*-like structure. Note that in (b) the electrodes are closer to the substituting S atoms than in (c).
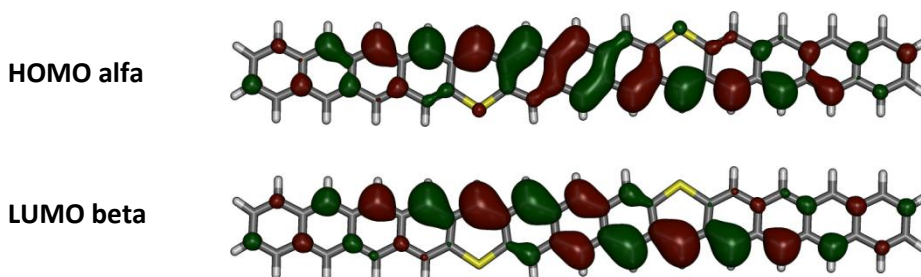
HOMO alfa

LUMO beta

Figure S2. Kohn-Sham orbitals for molecule 3 elongated by 2.0 Å. HOMO alfa is the highest occupied one-particle state of alfa (majority) spin orientation and LUMO beta is the lowest unoccupied state of beta (minority) spin orientation. These are the one-particle states closest to the Fermi energy of the electrodes.

References

D. H. Ess, E. R. Johnson, X. Hu, and W. Yang, *J. Phys. Chem. A*, 2011, **115**, 76.