

Spin manipulation of organometallics by strain engineering of defected graphene

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In organic nanospintronics, one of the objectives is to manipulate the spin states of organic molecules [1] with a d-electron center, by suitable external means, e.g., temperature pressure, light etc. In organometallics, the central atom with unpaired d-electrons can have several spin states available, e.g., low, intermediate and high spin states. If the external agent is able to overcome the energy barrier, one may move from one spin-state to other. For example, in iron porphyrin (FeP) molecule in the gas phase, the ground state has a S=1 spin state with another higher energy minimum at S=2 spin state, which is reachable by crossing an energy barrier of around 0.8 eV. Very recently, we have demonstrated [2] by first principles density functional calculations that a strain induced change of the spin state, from S=1 to S=2, takes place for an iron porphyrin (FeP) molecule deposited at a divacancy site in a graphene lattice. The process is reversible in the sense that the application of tensile or compressive strains in the graphene lattice can stabilize FeP in different spin states, each with a unique saturation moment and easy axis orientation.

The effect is demonstrated in Fig. 1, where the molecular energy diagrams are shown for two spin states along with the magnetization densities for the highest occupied molecular orbital (HOMO). Two situations are shown (0% and 1% strain of the graphene lattice). When graphene is strained, the divacancy site on which FeP is situated affects the bond length between Fe and N in FeP. As a result, the occupancies in the molecular level changes and gives rise to a spin state change from S=1 to S=2. The magnetization densities clearly show the nature of d_{z^2} and $d_{x^2-y^2}$ orbitals of Fe in FeP for S=1 and S=2 spin states respectively.

We also predict that the spin state change may be detected in x-ray magnetic circular dichroism (XMCD) experiments. Our calculated values for the spin-dipole contribution $\langle T_z \rangle$ is quite large ($7\langle T_z \rangle = -1.89 \mu_B$ and $1.32 \mu_B$) for 0% strained (S=1) and 1% strained (S=2) graphene lattice, respectively. Therefore, the measured effective moments (sum of spin moment and spin-dipole moment) will be quite different for the two spin states. The other detection method is the magnetic anisotropy in XMCD experiment. The magnetic anisotropy energy (MAE) and hence, the easy axis of magnetization can be calculated by adding the spin-orbit coupling term in the Hamiltonian. We have used second-order perturbation theory and a 4-level model with HOMO, HOMO-1, LUMO and LUMO+1 states, (HOMO and LUMO being highest occupied molecular orbital and lowest unoccupied molecular orbital respectively) to calculate MAE. We predict that for the S=1 state, Fe will have an out of plane easy axis of magnetization with a MAE of 0.4 meV whereas, S=2 spin state yields an in-plane magnetization with a MAE of 2 meV. Considering these two prominent effects, it is expected that the change in the spin state should be easily detectable in experiments.

References

[1] H. Wende et al., Nat. Mater. **6**, 516 (2007).

[2] S. Bhandary, S. Ghosh, H. Herper, H. Wende, O. Eriksson and B. Sanyal, Phys. Rev. Lett. **107**, 257202 (2011).

Figures

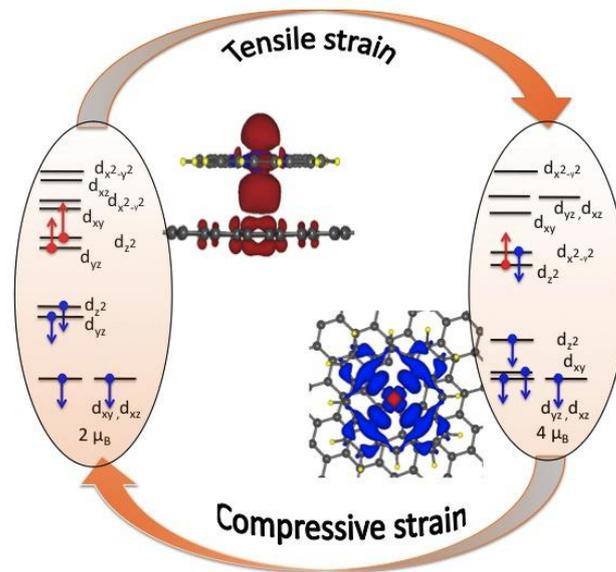


Fig. 1. Magnetization density isosurfaces for FeP on (left) 0% and (right) 1% strained graphene. The isosurfaces have been plotted for an energy window of 0.4 eV below the Fermi levels in both cases. The spin densities shown in the left up (side view) and right down (top view) parts correspond to spin-up and spin-down channels, respectively. The energy levels with the d-orbital character of FeP are shown in the extreme left and right for 0% and 1% strained graphene, respectively.