SUPPORTING INFORMATION

A DFT exploration of the organization of thiols on Au(111): a route to SAM of magnetic molecules

Gopalan Rajaraman[†], Andrea Caneschi, Dante Gatteschi and Federico Totti*

Dipartimento di Chimica, Polo Scientifico, INSTM

Università degli Studi di Firenze, via della Lastruccia 3, 50019 Sesto fiorentino, Italy

EXPERIMENTAL DETAILS

Synthesis

The synthesis of p-benzyl-S-methyl-nitronyl-nitroxide and the preparation of the self-assembled monolayer of this radical on gold surface from a dichloromethane solution are reported elsewhere.[16]

STM

The STM investigation has been done on a freshly prepared sample using a NT-MDT P47-pro system (www.ntmdt.com) equipped with a customized low current head and mechanically cut Pt/Ir 90:10 tip. For this set of analyses best imaging condition was found in constant current-mode using a tunnelling current of 25Ampere and applying a bias voltage of 220mV
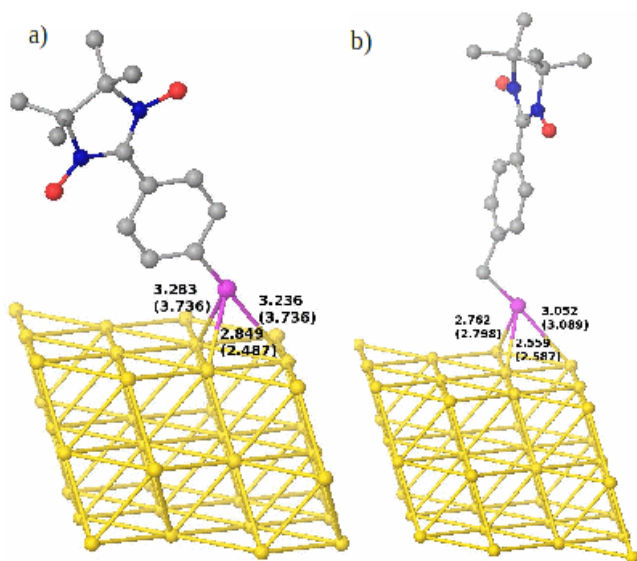

Figure S1. The DFT computed structure of a) [1]NitR-**A**-S• and b) [1]NitR-**B**-S• species

The Broken Symmetry Formalism

The exchange coupling constant J, of the Heisenberg–Dirac–van Vleck spin Hamiltonian (SH), $H = J\mathbf{S}_i\cdot\mathbf{S}_j$, where i and j are the paramagnetic centres bearing spins S_i and S_j, respectively, is computed using the broken symmetry (BS) approach developed by Noodleman *et al.*[1] as already described in the literature[2]. This method is based on an one-to-one matching between the computed SCF energy of a suited single determinant, the BS state, which is the eigenstate of $\mathbf{S}_z$, and the diagonal element of the appropriate SH matrix, computed in a product of singlecenter spin functions basis set. The BS determinant is built from spin orbitals appropriately localized onto the two spin centers, each of them being in the high spin state, imposing an opposite spin configuration on the two centers. This yields the state with the lowest value of $\langle\mathbf{S}_z\rangle$. This state is sometimes called the antiferromagnetic state of the system. The energy difference between this state and that corresponding to the parallel alignment of the spins on the two centers (the ferromagnetic state) can be computed and compared to the expression obtained with the SH, allowing the calculations of J. In our case the following equation used is therefore

$$J_{ij} = (E(Smax)-E(BS))/2S_iS_j$$

About the choice of this equation see ref 2.

1 L, Noodleman, J.-G. Norman, Jr. *J. Chem Phys* 1979, **70**; 4903; L. Noodleman, *J Chem Phys* 1981, **74**, 5737.
2 A. Bencini, F. Totti, *Int.* J. Quant.Chem. 2005, 101, 819; A.Bencini, F. Totti, *J. Chem. Theory Comput.* 2009, 5, 144