

DFT+U Studies of MnP Adsorption on Au(111) Surface and Electric Field Effectsby **K. Leung, S. Rempe, P. Schultz, M. Chandross, and C. Medforth**

Motivation—Transition metal porphyrin molecules exhibit a wide range of electronic and magnetic properties. They have the potential to be deposited on metal electrodes and used as memory and molecular electronics elements, sensors, and other nanoscale devices. Recently, Shelnett, Medforth, and coworkers proposed a novel nanomechanical application of “bridled” Ni(II) porphyrins based on a ligand-binding induced increase of the Ni²⁺ effective radius (Fig. 1).¹ This molecule can potentially exhibit nano-tweezer motion that can be used to grab on to/release toxin or drug molecules, and thus have national security implications. In this theoretical work, we consider Mn(II) porphine (MnP) deposited on Au(111) as a simple mimic of nickel porphyrin which may exhibit similar effective metal ion size changes when subject to an electric field.

Accomplishment—Accurate modeling of this composite Mn(II)P/Au(111) system is extremely challenging. Density Functional Theory (DFT) with the Perdew-Burke-Brazerhof (PBE) exchange correlation functional, routinely used in surface science calculations, is accurate for the Au(111) surface but does not predict the correct spin state for isolated MnP. Quantum chemistry methods work much better for the latter but are not feasible (~100 times more costly than PBE) to apply to a periodically replicated model of a gold electrode.

Here we apply for the first time the DFT+U method to a 1st row transition metal center in a molecule.² DFT+U has been successfully used to treat strongly correlated electron systems such as nickel (II) oxide and LaCoO₃ (related to

the colossal magnetoresistance materials). We parameterize the “U” in DFT+U (the intra-d band coulomb term) with spin-spittings predicted using quantum chemistry method.

Table 1 illustrates the success of this approach for the isolated MnP molecule. PBE predicts incorrect spin states and molecular geometries. Tuning U=4.2, DFT+U yields both the correct high-spin ground state and a Mn(II)-N bond length similar to experimental values.

Figure 2 depicts MnP deposited on Au(111) and the resulting change in its electron density distribution. The binding energy is 0.7, and the spin polarization changes from s=5/2 to s=2, consistent with a change of the Mn(III) oxidation state and the interpretation that Mn has donated an electron to the gold substrate. This apparent electron transfer can be reversed by applying a 0.7 eV/Å electric field, which recovers the high spin state associated with Mn(II). The field-induced 0.13 Å increase in Mn-N distance is reminiscent of that in bridled nickel porphyrins, and suggest that manganese porphyrins (or expanded porphyrins) may be tailor-made into electric-field triggered, switchable molecular devices.

Significance—Our theoretical predictions provide impetus to future atomic force microscope experiments aimed at demonstrating and exploiting switchable molecular devices assembled on gold electrodes. Our novel application of the DFT+U method will enable *ab initio* molecular dynamics studies of reactions involving 1st row transition metals in aqueous and biological environments, and open up new areas of theoretical research.

¹Song, *et al.*, J. Am. Chem. Soc. 127:1179 (2005)

²Lichtenstein *et al.*, Phys. Rev. B 60:8257 (1994).

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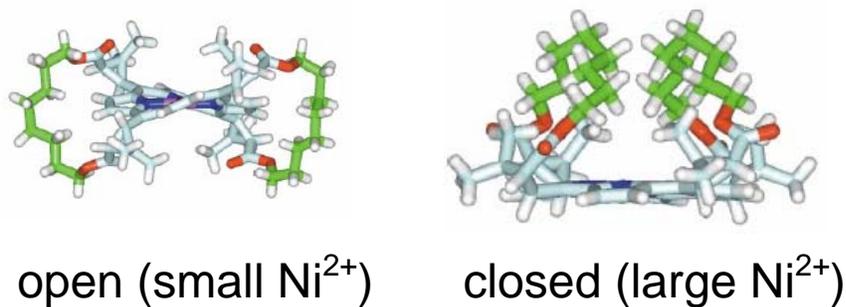


Figure 1. Open and closed conformation of a bridled Ni(II) porphyrin [1].

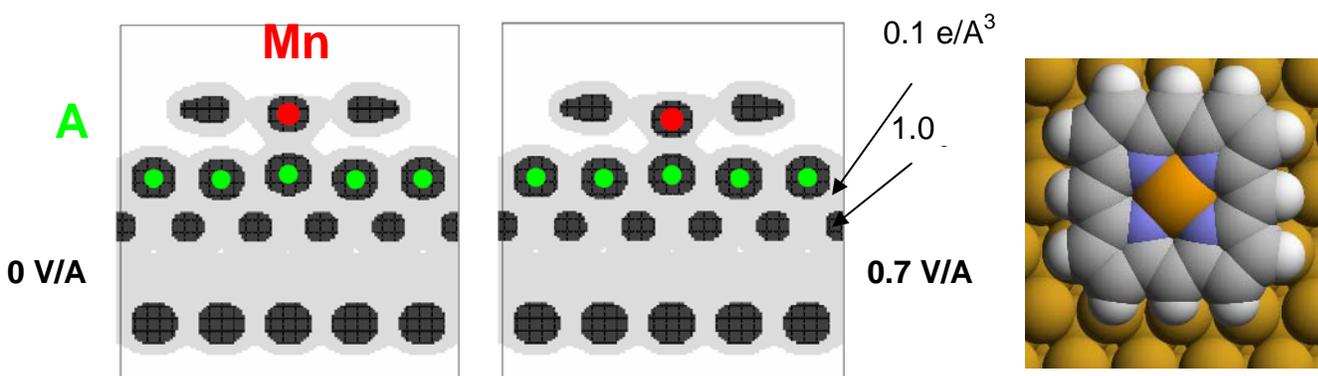


Figure 2. MnP deposited on Au(111): electron charge densities in absence/presence of electric field.

	Mn(II)P	Mn(II)P*	MnP/Au(111)	MnP/Au(111)+field	MnP/Au +field*
d(Mn-N)	2.09 Å	2.05 Å	2.02 Å	2.15 Å	2.02 Å
E _{bind}	NA	NA	0.7 eV	0.1 eV	0.2 eV
total spin	5/2	3/2	2	5/2	3/2

Table 1: The Mn-N distance in the porphine ring, the binding energy on Au(111), and total spin polarization of manganese (II) porphines. Computed using the DFT+U method except where marked by an asterisk (those use the PBE functional, which is inadequate for isolated manganese porphines).