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Reversible Switching of the Spin State in a Manganese Phthalocyanine Molecule by Atomic Nitrogen

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Abstract

Reversible control of the spin state of an organic molecule is significant for the development of molecular spintronic devices. Here, density functional theory calculations have been performed to study the adsorption of atomic nitrogen on a single manganese phthalocyanine (MnPc) molecule, three-layered MnPc, and MnPc on an Fe(100) surface. For all three cases, the N atom strongly adsorbs on the top of the Mn atom and induces a significant variation of the geometric, electronic and magnetic properties. After N adsorption, an energy gap appears and the electronic states become unpolarized. Different functionals including three hybrid functions are used in these calculations, and all yield the switchable spin state.

I. INTRODUCTION

Metal phthalocyanine (MPc) and metal porphyrin (MPP) molecules are organometallic molecules that have a planar geometry with unsaturated coordination. Reversible control of a spin state at a molecular level is of great interest due to the wide range of potential applications that rely on such a phenomenon, especially single-molecular devices and spintronic devices.[1-12] Due to the activity of the metal center, external chemical stimuli are often used to modify the electronic structure and the molecular spin state.[9,10,13] The spin of a MnPc molecule on a Bi(110) surface has been found to reduce from S=1 to S=1/2 through adsorption of a CO molecule, as observed using a combination

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of scanning tunneling microscopy (STM) and density functional theory (DFT) calculations.[10] Further work has shown that the adsorption of a NO molecule switches off the spin state of a metal porphyrin molecule, cobalt-tetrapheylporphyrin (CoTPP), on a Ni(001) surface.[9] Most previous studies have focused on the coordination of small molecules although the coordination of single atoms is also essential, not only for revealing the elementary chemical binding mechanism, but also for manipulating the spin state at the atomic scale in spintronic devices. Atomic nitrogen adsorption has been experimentally studied on many metal surfaces, and is known to significantly modify geometric and electronic properties, for example, by decreasing the work function the W(100) surface,[15] inducing a lower-symmetry reconstruction of a Cu(100) surface,[16] or through the formation of surface-nitride-like Fe_4N.[17] Recently, Zhang *et al*. reported scanning tunneling spectroscopy (STS) and photoelectron spectroscopy measurements that showed the electronic structure of the center Mn atom in MnPc to be greatly modified upon N atom coordination.[1]

Despite the above studies, the effect of N adsorption on the spin state of MnPc molecules has received much less attention and needs further investigation. This is particularly true when considering that most recent reports have focused on controlling the spin state of a single MPc molecule on a specific substrate[9-14]. A spin switch is not a suitable possibility for all substrates since the influence of the adsorbed MPc often differs considerably depending on the underlying surface. For example, the magnetic moment of the central Mn atom in a MnPc molecule is nearly preserved on a Cu(001) surface but significantly reduced on Co(001), Au(111), and Bi(110) substrates.[10-13] Magnetic quenching of a CoPc molecule also occurs when it adsorbs on a Au(111) surface.[14] With this in mind, it is important to find a universal way to switch the spin state of MPc molecules, not only on weakly-coupled substrates but on strongly-interacting ones as well.

Finally, control of spin typically occurs by switching from high spin states to low spin states such as S=3/2 to 1 or S=1 to 1/2 transitions [9,10,13,14]. Complete quenching of the magnetic moment has been reported on Co-centered molecules such as CoPc, CoTPP, etc.,[9, 14] but rarely for other MPc molecules, particularly MnPc which has a high magnetic moment associated with the central Mn atom. Demonstration of reversible quenching of the magnetic moment of Mn in MnPc would be a significant step in the development of molecular spintronics.

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In this study, a single N atom is used to coordinate with the central magnetic Mn atom of a MnPc molecule. The atomic N is chosen to decorate MnPc based on the following reasons. First, the magnetic moment of Mn atom in MnPc is considerably large (>3.0 μB). It is hardly to quench its magnetic moment with any molecule. On the contrary, N atom has three unpaired spins and could greatly reduce the magnetic moment of Mn in MnPc. Second, the interaction of N atom with metallic atom or ion is usually very strong with significant electron transfer. This property might weaken the interaction between Mn in MnPc and substrates, decrease the influence on MnPc from substrates. Our calculation shows that reversible switching of the spin state in MnPc can be obtained by adsorption/desorption of a single N atom. Importantly, the adsorption-induced spin switch is predicted to not only occur in a single MnPc molecule and the topmost MnPc molecule of a three-layered weakly-bonded structure, but also in MnPc molecules that are strongly adsorbed on a ferromagnetic Fe(100) surface. Calculations with different functionals performed for single MnPc and three-layered MnPc molecules lead to the same conclusions.

II. COMPUTATIONAL METHODS

All calculations are performed within the framework of DFT using a plane-wave basis set via the Vienna Ab-initio Simulation Package (VASP).[18,19] The electron-ion interaction is described using the projector augmented wave (PAW) method[20,21] with the spin interpolation reported by Vosko *et al.*[22] adopted for spin-polarized calculations. The plane-wave energy cutoff is set to 400 eV for all calculations. For the results presented here, the nitrogen atoms that are nearest and second-nearest to the central Mn atom in MnPc molecule are labelled as N1 and N2, respectively, to distinguish between the two inequivalent nitrogen sites. The adsorbed nitrogen atom is labelled as N and three-layered MnPc is abbreviated to 3MnPc.

For N-adsorbed MnPc on an Fe(100) substrate, the unit cell and surface model are the same as our previous calculation of MnPc/Fe(100).[23] The MnPc molecule is predicted to adsorb on the top site of the Fe(100) surface with the Mn-N1 bonds along the <110> direction.[23] The generalized gradient approximation (GGA) approach based on the Hubbard model (GGA+U)[24] is used. During structural optimizations, the bottom three substrate layers are fixed. The adsorbed N atom,

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all atoms in the MnPc molecule, and the topmost substrate layer are allowed to relax freely until all forces are less than 0.01 eV/Å. A single Γ point is used due to numerical limitations.

For N-adsorbed 3MnPc, all atoms are allowed to relax freely except the *z* coordinates of atoms at the bottom layer. The van der Waals interaction is incorporated through the DFT-D3 method with Becke-Jonson damping.[25,26] Different functionals are used for the N-adsorbed single MnPc molecule and 3MnPc stacking structure through GGA, GGA+U, hybrid functionals of B3LYP [27], HSE06 [28], and PBE0 [29]. In GGA+U method, the value of *U* should be carefully chosen due to the calculated spin states of MPc can be varied by using different *U* values.[33] As discussed in our previous study, an effective *U* value (3 eV) for the Mn atom has been determined by comparison of the energy levels and ordering of the molecular orbitals for MnPc calculated at different *U* values (from 2 to 8 eV) referenced using the results from the HSE06 or PBE0 hybrid functionals, because these can provide better agreement with the experimental results.[23]

III. RESULTS AND DISCUSSION

The stacking geometry of CoPc multilayers on a Pb substrate has previously been observed by Chen *et al*. using STM.[30] Here, the same stacking geometry as that of CoPc is adopted for 3MnPc. The Mn atoms of MnPc in the middle layer lie directly on the top of those in the bottom layer, but with the in-plane molecular axes rotated by 45° (middle panel of Fig. 1a). The planar MnPc in the topmost layer has the same molecular orientation as the MnPc in the middle layer but laterally shifted by 1.668 Å. Our calculation shows that ferromagnetic coupling between neighboring layers of MnPc is more energetically favorable than antiferromagnetic coupling by 0.101 eV and 0.116 eV as determined using the GGA and GGA+U methods, respectively.

Compared to ligand atoms (N1, N2, C), the adsorbed N atom prefers the top site of the central Mn atom, consistent with STM observations of MnPc confined by highly-oriented pyrolytic graphite (HOPG).[1] The adsorption energies calculated using GGA+U are -2.91, -2.88 and -2.56 eV for N-adsorbed single MnPc, 3MnPc and MnPc/Fe(100), respectively. These values are much smaller the GGA-calculated energy of -6.63 eV for N-MnPc/HOPG,[1] but closer to the experimental value obtained using an STM tip-bias-induced desorption measurement (1.7-2.9 V). The N

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adsorption-induced geometric variation is mainly focused on the central Mn atom and insignificant on the Pc macrocycle. As shown in Fig. 1a, the central Mn atom is obviously shifted to the vacuum side by the adsorption of a N atom for all three cases. The height deviation (Δh) of the central Mn atom from the plane composed of the nearest eight C atoms is about 0.425-0.486 Å, as predicted by different functionals for the N-adsorbed single MnPc (top panel of Fig. 1b). The Δh value for the Mn of the topmost layer (0.302-0.409 Å) in N-3MnPc is slightly smaller than that in N-MnPc. The weak interaction between neighboring MnPc layers in 3MnPc may be responsible for the smaller height deviation. However, for N-adsorbed MnPc on the ferromagnetic Fe(100) substrate, the height deviation calculated through GGA+U (0.701 Å) is obviously larger than those in N-adsorbed MnPc and 3MnPc. Correspondingly, the bond length of Mn-Fe is evidently elongated from 2.592 Å to 3.062 Å. As indicated in the bottom panel of Fig. 1a, there are some direct bonds between C atoms in the Pc macrocycle and substrate Fe atoms. The Pc plane is shifted toward the surface by strong hybridization with the substrate atoms. On the contrary, the Mn atom is pushed toward vacuum side by N adsorption. The reverse shift direction causes the large height deviation. The bond lengths of N-Mn (1.498-1.531 Å, middle panel of Fig. 1b) are very similar for the three adsorption cases and much shorter than those for N1-Mn (>1.9 Å), indicating a strong interaction between the adsorbed N and Mn atoms. N adsorption also induces a slight increase of the N1-Mn bonds by about 0.031-0.038 Å for N-MnPc and N-3MnPc, and 0.072 Å for N-MnPc/Fe(100) (bottom panel of Fig. 1b). Other changes in the geometric structure of the Pc macrocycle are negligible.

MnPc is known to be a magnetic molecule with the magnetic moment of the Mn atom larger than 3.0 μ_B. For N-adsorbed MnPc, the magnetic moment of the Mn atom is initially set as 4.0 μ_B. It gradually decreases to zero during the self-consistent field (SCF) calculation through GGA, indicating a magnetic quenching due to N adsorption. Similar magnetic quenching has been reported by Nguyen *et al*. in NO-adsorbed MnPc using GGA calculations.[31] However, our recent investigation indicates that the magnetic moment of the Mn atom is zero when calculated using GGA but still larger than 3.0 μ_B when GGA+U and hybrid functionals of HSE, PBE0, and B3LYP are used for NO-adsorbed MnPc.[32] It is possible that GGA predictions lead to a misrepresentation of geometric, electronic and magnetic properties of

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NO-adsorbed MnPc. Here, different functionals including GGA, GGA+U and hybrid functionals are used to investigate the variation of the magnetism before and after N adsorption. An energy difference (ΔE_1) is calculated between spin unpolarized and polarized configurations (Fig. 2a) for free MnPc and N-adsorbed MnPc:

$$\Delta E_1 = E_{Spin\ unpolarized} - E_{Spin\ polarized} \tag{1}$$

For free MnPc, positive values of ΔE_1 are obtained through not only GGA but also GGA+U and three hybrid functionals, indicating that a spin polarized configuration is energetically favorable. A considerable magnetic moment (>3.0 μ_B) is obtained in the Mn atom, consistent with all existing calculations and experiments. On the contrary, the value of ΔE_1 is negative for N-adsorbed MnPc when using all five functionals (middle panel of Fig. 2a), indicating the preference of the spin unpolarized configuration. This means that, in contrast to NO-adsorbed MnPc, the switch of the spin state of a single MnPc molecule by atomic N adsorption is independent of the functional. For N-adsorbed 3MnPc, low spin (6.0 μ_B) and high spin (8.0 μ_B) configurations are calculated using different functionals. ΔE_2 is the energy difference between the two spin configurations.

$$\Delta E_2 = E_{Low\ spin} - E_{High\ spin} \tag{2}$$

A negative value of ΔE_2 is obtained for all five functionals, indicating that the low spin configuration is energetically favorable. For this spin state, the magnetic moments of the adsorbed N and the Mn1 atom at the topmost layer of 3MnPc decreases to zero (Fig. 2b). In contrast, the variation of the magnetic moment of Mn2 at the middle layer and Mn3 at the bottom layer are very small (Fig. 2b). The negligible variation can be attributed to the weak interaction between neighboring layers, indicated by their typical van der Waals layer distance which is 3.352 Å between the topmost and middle layers and 3.184 Å between the middle and bottom layers.

Figure 3a shows the density of states (DOS) of Mn in the free MnPc molecule as calculated using different functionals. The conventional GGA functional underbinds some molecular orbitals and introduces disorder, as specified by blue arrows in Fig. 3a. In comparison, the GGA+U method shows that both the energy levels and the ordering of molecular orbitals are

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much closer to those obtained with hybrid functionals (HSE, B3LYP and PBE0). The occupied states of Mn close to the Fermi level mainly consist of *z*-derived components (d_{xz}/d_{yz}, d_{z2}). The electronic states are strongly positively spin polarized at levels below -1.0 eV and negatively spin polarized near to the Fermi level.

After N adsorption on the single MnPc, an obvious energy gap can be observed between the highest occupied state and the lowest unoccupied state (Fig. 3b). The gap calculated using GGA+U is larger than that for GGA but smaller than those for the hybrid functionals. Such a trend for the different functionals is common for molecules and semiconductors. Unlike the free MnPc, the orbital ordering of Mn in N-adsorbed MnPc is in agreement for both the GGA and GGA+U methods and the three hybrid functionals (Fig. 3b). The occupied states close to the Fermi level are not derived from a *z* component of the *d* orbital but from the d_{x2-y2} state. This is due to the strong hybridization with the p_z orbital of the adsorbed N atom, resulting in significant donation from the Mn 3*d* to this atom and a considerable electron redistribution in the *d* orbitals of the Mn atom and a deep level shift of the d_{z2} orbital. The enlargement of the energy gap is consistent with the disappearance of the highest occupied molecular orbital (HOMO), dominated by the Mn 3*d* orbital, as observed in STS N-MnPc/HOPG.[1] Another prominent feature is that all electronic states become spin unpolarized after N adsorption.

Fig. 3c shows the DOS of the three Mn atoms in 3MnPc calculated using the HSE hybrid functional before and after N adsorption. Before N adsorption, the DOS of the Mn atom in each layer (labelled as Mn1, Mn2, Mn3) are similar and very close to that in free MnPc. After N adsorption, the variation is significant in the N-bonded Mn atom (Mn1), but negligible in the Mn atoms at the middle and bottom layers (Mn2 and Mn3). Also caused by the strong hybridization with the adsorbed N atom, the occupied states of Mn1 close to the Fermi level are not derived from a *z* component of the *d* orbital but by a d_{xy} orbital. It should be mentioned that here the d_{xy} orbital is the same as the d_{x2-y2} orbital in the N-adsorbed MnPc in Fig. 3b, since the molecule rotates for 45^{o}. The orbital ordering of Mn1 in N-adsorbed 3MnPc is the same as that of Mn in N-adsorbed MnPc and independent of the functional. The energy gap agrees well with that in N-adsorbed MnPc. Noticeably, the electronic states of the Mn1 atom become spin unpolarized while those of Mn2 and Mn3 atoms remain highly spin polarized.

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The coupling between MnPc and HOPG or neighboring MnPc layers is dominated by weak van der Waals interactions. Therefore, the variation of electronic and magnetic properties of MnPc in the N-MnPc/HOPG studied by Zhang *et al*. and in the N-3MnPc calculated above is primarily determined by the hybridization between the adsorbed N and the center Mn atom. However, the substrates typically used in spintronic devices often exhibit strong coupling with the MnPc molecule. It is therefore essential to determine if the atomic N could also switch off the spin state of MnPc on these strongly-coupled substrates. Our previous study shows MnPc strongly chemisorbs on a ferromagnetic Fe(100) surface with an adsorption energy of -6.31 eV, much larger than for Cu(001) (-0.5 eV), Co(001) (-2.2 eV), and Au(111) (-3.58 eV).[11-12] Here, we study N adsorption on a MnPc that is confined by the Fe(100) surface.

Hybrid functionals are not used due to the computational limitation and metallic substrate. All results discussed below are based on calculation through the GGA+U method. Before N adsorption, the central Mn atom strongly hybridizes with the underlying Fe atom and the electronic states are spin polarized (second panel of Fig. 3d).[23] The d_{z2} orbitals at -0.8 eV and -3.0 eV are shifted to a deeper level at -4.5 eV by the adsorbed N atom and an increase in the energy gap is observed (top panel of Fig. 3d). It is worth noting that the ordering of orbitals is the same as that in N-MnPc and N-3MnPc without a metallic substrate. The electronic states of Mn and the adsorbed N atom become nearly spin unpolarized even on the ferromagnetic substrate. Any variation of the electronic and magnetic properties mainly occurs on the central Mn atom with no obvious change in the Pc macrocycle or the underlying Fe atom (Fig. 3d).

Charge density maps along the [100] direction are plotted in Fig. 4 to visualize the bonding between MnPc and the Fe(100) substrate as well as the adsorbed N atom. Before N adsorption, the charge density between the Mn atom and the underlying Fe atom is condensed, indicating a strong interaction (Fig. 4a). This is consistent with the short bond length of Mn-Fe (2.592 Å) and prominent DOS composed of d_{z2} orbitals close to the Fermi level. After N adsorption, the charge density between Mn and Fe is very sparse and the isosurface becomes invisible under the same threshold value (Fig. 4b) indicating considerable weakening of the Mn-Fe bond. This agrees with the substantial elongation of the Mn-Fe bond (3.062 Å) after N adsorption. On the contrary, no significant variation is found for the charge density between the Pc

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macrocycle and the substrate. In the region of the adsorbed N and Mn, very dense charge can be observed indicating strong hybridization. Such a strong interaction is also indicated by the short bond length of N-Mn (1.529 Å) which is much smaller than that of N1-Mn (2.030 Å) in MnPc.

Differential charge density is shown in Fig. 5 to visualize the electron transfer process induced by N adsorption. For N-adsorbed MnPc, the differential charge density is calculated by

$$\Delta\rho = \rho_{N-MnPc} - \rho_{MnPc} - \rho_{N} \tag{3}$$

where $\rho_{\text{N-MnPc}}$ is the charge density of N-adsorbed MnPc. ρ_{MnPc} and ρ_{N} are the charge densities of a single MnPc molecule and a N atom, respectively. The latter two systems have the same geometry and same unit cell as for N-MnPc. The spin up (↑) and spin down (↓) differential charge density is respectively calculated by

$$\Delta\rho(\uparrow) = \rho_{N-MnPc}(\uparrow) - \rho_{MnPc}(\uparrow) - \rho_{N}(\uparrow) \tag{4}$$

$$\Delta\rho(\downarrow) = \rho_{N-MnPc}(\downarrow) - \rho_{MnPc}(\downarrow) - \rho_{N}(\downarrow) \tag{5}$$

In the differential charge density map, yellow/blue represents the increase/decrease of the electron density. Electron transfer primarily occurs between the adsorbed N and the bonded Mn atom. In total, electrons are donated from the Mn atom to the adsorbed N atom (Fig. 5a), forming a strong bond between them. However, as indicated by blue color in Fig. 5b, an apparent decrease of the spin-up electron density can be observed around the adsorbed N atom. Conversely, the yellow color in Fig. 5c around the same region demonstrates a substantial increase of the spin-down electron density of the adsorbed N atom. A similar phenomenon is observed along the vertical direction around the central Mn atom. Namely, the variation of the charge density is opposite for spin up and spin down electrons around the adsorbed N atom and the d_{z2} orbital of the Mn atom. This indicates that besides the process of electron transfer from the underlying Mn atom to the adsorbed N atom, the electron redistribution between different spin configurations is also considerable. Both processes cause the spin states in Mn and the adsorbed N atoms to effectively ‘switch off’. The differential charge densities of N-adsorbed 3MnPc and MnPc/Fe(100) surface (middle and right panels of Fig. 5) are very similar to that in N-adsorbed MnPc. Electron transfer mainly occurs between the adsorbed N and the top-layered Mn atom. An opposite variation can

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also be observed for spin-up and spin-down electron density in the adsorbed N and the d_{z2} states of the Mn atom. The charge transfers between neighboring layers of MnPc (Fig. 5a′) and MnPc-Fe substrate (Fig. 5a″) are negligible with no significant influence on the electronic or magnetic structures.

As discussed above, the adsorbed N atom induces a significant shift of Mn from the Pc macro plane and considerably weakens the hybridization between Mn and Fe. The main role of the Fe(100) substrate then is to pin the molecule through its Pc macrocycle. The metallic substrate does not have substantial influence on the electronic and magnetic properties of the central Mn atom once N has adsorbed to the molecule. The N-induced switch off of the spin state of MnPc could be expected on other metallic substrates such as Cu, Co, Au, or nonmetallic substrates such as HOPG, because their hybridization with a MnPc molecule would be much weaker than for Fe(100)[11,12]. The flexibility of such a phenomenon would be significant to applications in spintronics where a wide variety of substrates are employed. The desorption of N atoms from MnPc/HOPG is observed to commence at 260 ^{o}C and complete at 305 ^{o}C. An STM tip has also been used to detach or reattach the N atom to the Mn center.[1] Therefore, controllable adsorption/desorption of N atoms provides a reversible way of switching the spin state of MnPc molecules.

IV. CONCLUSION

The electronic and magnetic structure of MnPc in different environments has been investigated using DFT calculations. We have shown that the spin state of MnPc can be ‘switched off’ through atomic N adsorption for a variety of systems, from a single MnPc molecule and weakly-bonded three-layered MnPc, to MnPc strongly coupled to an Fe(100) surface. The switch off of the spin state is obtained not only using calculations with conventional GGA, but also with the GGA+U method and three hybrid functionals for N-adsorbed MnPc and three-layered MnPc. Two processes, electron donation from the Mn atom to the adsorbed N atom and electron redistribution between different spin configurations, are considered to be responsible for the N-induced magnetic quench. This study demonstrates an effective way of reversibly controlling spin states in organic MnPc molecules in a variety of environments.

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REFERENCES

[1] J. Q. Zhong, Z.Z. Wang, J. L. Zhang, C. A. Wright, K. Yuan, C. Gu, A. Tadich, D. Qi, H. X. Li, M. Lai, K. Wu, G. Q. Xu, W. Hu, Z. Li, and W. Chen, Reversible tuning of interfacial and intramolecular charge transfer in individual MnPc molecules, *Nano Lett.* **2015**, 15, 8091−8098.

[2] J. Kügel, M. Karolak, A. Krönlein, J. Senkpiel, P. J. Hsu, G. Sangiovanni, and M. Bode, State identification and tunable Kondo effect of MnPc on Ag(001), *Phys. Rev. B* **2015**, 91, 235130.

[3] J. Uihlein, H. Peisert, H. Adler, M. Glaser, M. Polek, R. Ovsyannikov, M. Bauer, and T. Chassé , Strong interaction of MnPc on Ni(111): influence of graphene buffer layer, *J. Phys. Chem. C*, **2014**, *118* , 28671–28678.

[4] S. Lindner, B. Mahns, U. Treske, O. Vilkov, F. Haidu, M. Fronk, D. R. T. Zahn, and M. Knupfer, Epitaxial growth and electronic properties of well ordered phthalocyanine heterojunctions MnPc/F16CoPc, *J. Chem. Phys.* **2014,** 141, 094706.

[5] P. Sessi, T. Bathon, K. A. Kokh, O. E. Tereshchenko, and M. Bode, Probing the electronic properties of individual MnPc molecules coupled to topological states, *Nano Lett.*, **2014**, *14* , 5092–5096.

[6] L. Bogani, W. Wernsdorfer, Molecular spintronics using single-molecule magnets. *Nat. Mater.* **2008***,* 7, 179–186.

View Article Online
DOI: 10.1039/C7CP06641D

[7] N. Atodiresei, J. Brede, P. Lazić, V Caciuc , G. Hoffmann, R. Wiesendanger, S. Blügel, Design of the local spin polarization at the organic ferromagnetic interface. *Phys. Rev. Lett.* **2010**, 105, 066601.

[8] T. Komeda, H. Isshiki , J. Liu , Y. F. Zhang , N. Lorente , K. Katoh, B. K. Breedlove, and M. Yamashita, Observation and electric current control of a local spin in a single-molecule magnet. *Nat. Commun.* **2011**, 2, 217.

[9] C. Wäckerlin, D. Chylarecka, A. Kleibert, K. Müller, C. Iacovita, F. Nolting, T. A. Jung, and N. Ballav, Controlling spins in adsorbed molecules by a chemical switch, *Nat. Commun.* **2010**, 1, 61-67.

[10] A. Strózecka, M. Soriano, J. I. Pascual, J. J. Palacios, Reversible change of the spin state in a manganese phthalocyanine by coordination of CO molecule. *Phys. Rev. Lett.* **2012**, 109, 147202.

[11] S. Javaid, M. Bowen, S. Boukari, L. Joly, J. B. Beaufrand, X. Chen, Y. J. Dappe, F. Scheurer, J. P. Kappler, J. Arabski, W. Wulfhekel, M. Alouani, and E. Beaurepaire, Impact on interface spin polarization of molecular bonding to metallic surfaces. *Phys. Rev. Lett.* **2010,** 105, 077201.

[12] Z. P. Hu, B. Li, A. D. Zhao, J. L. Yang, and J. G. Hou, Electronic and magnetic properties of metal phthalocyanines on Au(111) surface: a first principles study, *J. Phys. Chem. C* **2008,** 112, 13650–13655.

[13] L. Liu, K. Yang, Y. Jiang, B. Song, W. Xiao, L. Li, H. Zhou, Y. Wang, S. Du, M. Ouyang, W. A. Hofer, A. H. C. Neto, and H. Gao, Reversible single spin control of individual magnetic molecule by hydrogen atom adsorption, *Sci. Rep.* **2013,** 3, 1210.

[14] A. D. Zhao, Q. X. Li, L. Chen, H. J. Xiang, W. H. Wang, S. Pan, B. Wang, X. D. Xiao, J. L. Yang, J. G. Hou, and Q. S. Zhu, Controlling the Kondo effect of an adsorbed magnetic ion through its chemical bonding, *Science* **309**, 1542–1544 (2005).

View Article Online
DOI: 10.1039/C7CP06641D

[15] A. Michaelides, P. Hu, M.-H. Lee, A. Alavi, and D. A. King, Resolution of an ancient surface science anomaly: work function change induced by N adsorption on W{100}, *Phys. Rev. Lett.* **90**, 246103, (2003).

[16] S. M Driver, J. T. Hoeft, M. Polcik, M. Kittel, R. Terborg, R. L. Toomes, J. H. Kang and D. P. Woodruff, Cu(100)c(2×2)-N: a new type of adsorbate-induced surface reconstruction, *J. Phys.: Condens. Matter* **13,** L601–L606, (2001).

[17] R. Imbihl, R. J. Behm and G. Ertl, The structure of atomic nitrogen adsorbed on Fe(100), *Surf. Sci.* **123**, 129-140 (1982).

[18] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total energy calculations using a plane-wave basis set, *Phys. Rev. B,* **1996,** 54, 11169– 11186.

[19] G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* **1996,** 6, 15–50.

[20] G. Kresse and D. Joubert, From ultrasoft pseudo potentials to the projector augmented-wave method, *Phys. Rev. B* **1999**, 59, 1758–1775.

[21] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **1994,** 50, 17953–17979.

[22] S. H. Vosko, L. Wilk, and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis, *Can. Phys. J.* **1980,** 58, 1200–1211.

[23] X. Sun, B. Wang, and Y. Yamauchi, Electronic structure and spin polarization of metal (Mn, Fe, Cu) phthalocyanines on an Fe(100) surface by first-principles calculations, *J. Phys. Chem. C.* **2012,** 116, 18752–18758.

[24] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Band theory and Mott insulators: Hubbard U instead of StonerI, *Phys. Rev .B,* **1991,** 44,943–954.

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[25] S. Grimme, J. Antony, S. Ehrlich, and S. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements H-Pu, *J. Chem. Phys.* **2010**, 132, 154104.

[26] S. Grimme, S. Ehrlich, and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comp. Chem.* **2011,** 32, 1456.

[27] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, Ab-initio calculation of vibrational absorption and circular-dichroism spectra using density-functional force-fields, *J. Phys. Chem.* **1994,** 98, 11623.

[28] J. Heyd, G. E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential , *J. Chem. Phys.* **2006,** 124, 219906.

[29] C. Adamo, V. J. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *Chem. Phys.* **1999**, 110, 6158−6170.

[30] X. Chen, Y. S. Fu, S. H. Ji, T. Zhang, P. Cheng, X. C. Ma, X. L. Zou, W. H. Duan, J. F. Jia, Q. K. Xue, Probing superexchange interaction in molecular magnets by spin-flip spectroscopy and microscopy, *Phys. Rev. Lett.* **2008**, 101, 197208.

[31] T.Q. Nguyen, M.C.S. Escano, H. Kasai, Nitric oxide adsorption effects on metal phthalocyanines, *J. Phys. Chem. B* **2010,** 114, 10017.

[32] Z. Y. Li, M. Jibran, X. Sun, A. Pratt, B. Wang, Y. Yamauchi, Z.J. Ding, Influence of electron correlation on the electronic and magnetic structures of nitric-oxide-adsorbed manganese phthalocyanine, *Chem. Phys. Lett.* **2017**, 675, 15-19

[33] W. Wang, R. Pang, G. Kuang, X. Shi, X. Shang, P. N. Liu, and N. Lin, Intramolecularly resolved Kondo resonance of high-spin Fe(II)-porphyrin adsorbed on Au(111) , *Phys. Rev. B* **2015**, 91, 045440.

View Article Online
DOI: 10.1039/C7CP06641D

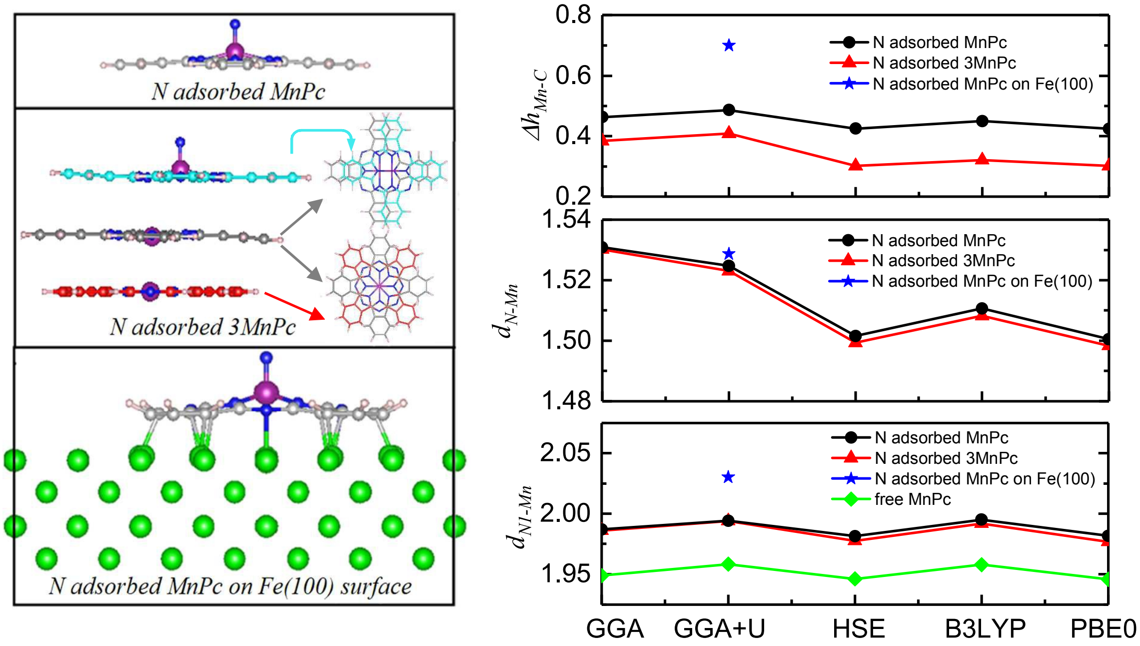

Fig. 1. (a) side view of N-adsorbed MnPc, 3MnPc and MnPc/Fe(100). The green, purple, blue, grey and pink spheres represent Fe, Mn, N, C and H atoms, respectively. In N-adsorbed 3MnPc, red, grey and cyan spheres all represent C atoms in order to distinguish them in different layers. The top view of the 1st-2nd layers and the 2nd-3rd layers of 3MnPc are inserted in the middle panel. (b) Functional dependence of the height deviation (Δ*h*) of the central Mn atom from the plane composed of the nearest eight C atoms, and the bond lengths of N-Mn and N1-Mn.

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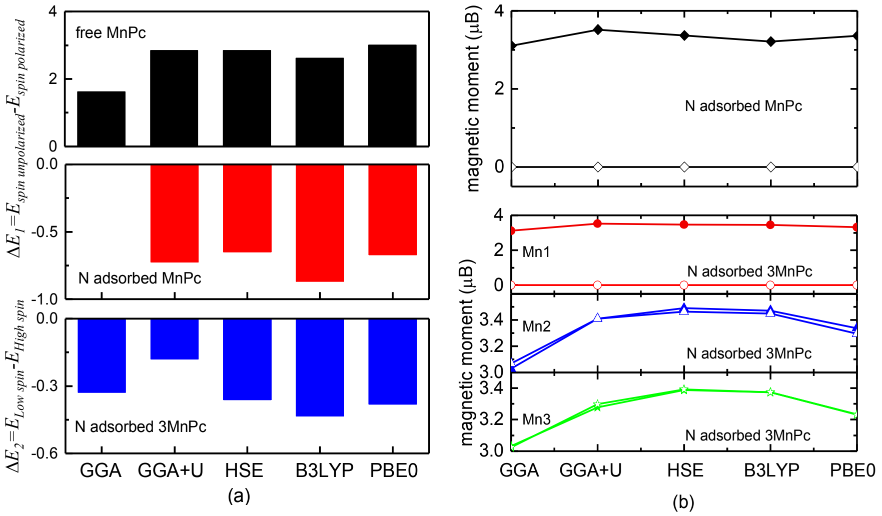

Fig. 2. (a) Energy difference between spin unpolarized and polarized configurations (ΔE_1) for free MnPc and N-adsorbed MnPc (top two panels). Energy difference between low and high spin configurations (ΔE_2) for N-adsorbed 3MnPc calculated using different functionals (bottom panel). (b) The magnetic moment of Mn in MnPc and 3MnPc before (solid symbols) and after (hollow symbols) N adsorption as calculated using the different functionals indicated.

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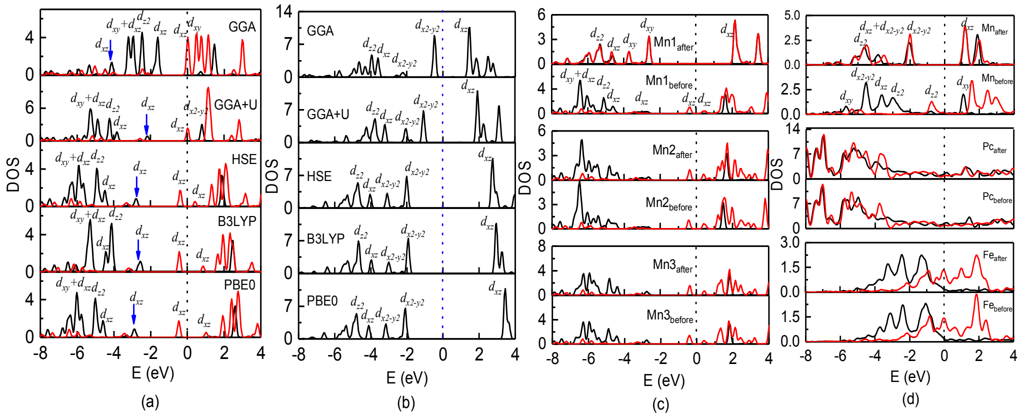

Fig. 3. Density of states (DOS) of the Mn atom in free MnPc (a) and N-adsorbed MnPc (b) calculated using different functionals. (c) DOS of Mn atoms in 3MnPc before and after N adsorption using the HSE functional. (d) DOS of Mn, the Pc macrocycle, and Fe for MnPc/Fe(100) before and after N adsorption calculated using the GGA+U method.

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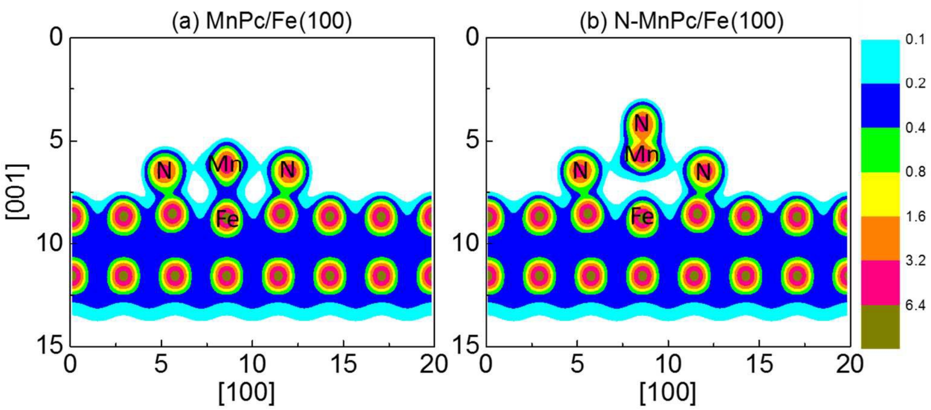

Fig. 4. Charge density (e/Å^3) map along the [100] direction for (a) MnPc/Fe(100) and (b) N-MnPc/Fe(100).

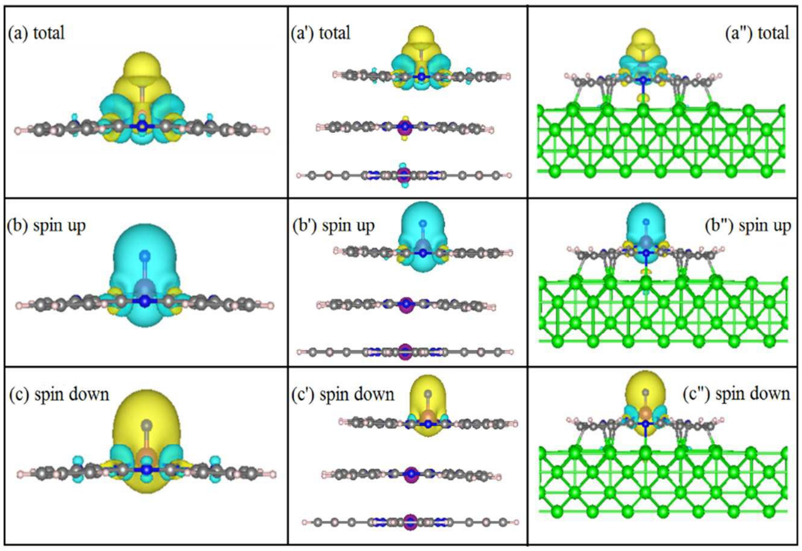

Fig. 5. Differential charge density of N-adsorbed MnPc, 3MnPc and MnPc/Fe(100) surface. (a) (a′) (a″) total, (b) (b′) (b″) spin up, (c) (c′) (c″) spin down electrons. The yellow or blue color indicates a gain or loss of electrons, respectively. The iso-surface level is 0.001 e/Å^3.