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Binding configuration, electronic structure and magnetic properties of metal-phthalocyanines on Au(111) surface with ab-initio calculations

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Abstract

Binding configurations, interface electronic structures, and magnetic properties of 3*d*-transition metal phthalocyanine (MPc, where M=Mn, Fe, Co, Ni, Cu or Zn) molecular systems on Au(111) substrate, are systematically investigated with first-principles density functional theory (DFT) calculations using PW91 exchange-correlation functional. We also calculated the corresponding properties of free standing molecules and did comparisons between these two cases. It is found that MnPc, FePc and CoPc have a stronger binding than that of NiPc, CuPc and ZnPc. For the magnetic property of the MPc molecules, it is not affected after the molecular adsorption, except for CoPc. In addition, for the adsorption properties of FePc on Au(111), we find out that the low adsorption energy and small energy differences between different configurations allow the FePc molecules to diffuse on Au(111) substrate easily at certain temperatures.

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Introduction

Molecule-metal systems have attracted much attention[1-5] not only because of fundamental interest[1-3] but also for potential applications in future electronics.[4,5] Among these systems, metal phthalocyanine (MPc) represents one of the most promising and versatile classes for its novel properties, thermal and chemical stability. In recent years, there has been variety of work on the metal-Pc systems. For example, Hipps *et al.* presented the adsorption behavior of FePc, CoPc, NiPc and CuPc on Au(111) surface.[6-8] Kondo effect and its manipulations in MPc on different surfaces (CoPc/Au(111),[9] FePc/Au(111)[10], and MnPc/Pb/Si(111)[11]) were reported. Petraki *et al.* studied the electronic structure of NiPc thin film on inorganic and organic substrates.[12] Energy level alignment at organic semiconductor interfaces of 3*d*-transition metal phthalocyanines was systematically investigated by Grobosch *et al.*.[13] Transport and vibration properties of MPc-metal substrate systems were also studied.[14-17]

In these studies, quantum mechanical calculations based on density functional theory (DFT) were employed to understand and predict the interface properties of MPc-metal systems. Electronic structures of free MPc molecules with 3*d*-transition metal were studied with various exchange correlation functionals.[18-23] It was found out that a hybrid functional could successfully cancel the self-interaction errors (SIE) and described the electronic structure very well for single MPc molecule.[18,19,23] Carefully chosen nonempirical hybrid functional such as HSE03 and PBE0 can also perform good in periodical systems.[24, 25] But because of the expensive time consuming, it is hard to use for the calculations of large molecule-metal systems. For the time being, state-of-the-art DFT calculations of MPc/metal interfaces still mainly use semi-empirical functionals. It was found that DFT calculations with a GGA functional sometimes agreed well with experimental results on the metal-substrate distance and the STM images, especially for CoPc/Ag(111).[26] In this work, we choose PW91 functional and investigate the adsorption behavior of FePc on Au(111) surface. The most stable adsorption configuration, interaction between FePc and Au(111), and magnetic properties are systematically calculated and analyzed. After that we investigate other MPc/Au(111) systems (M=Mn, Co, Ni, Cu or Zn). We find that the adsorption energies of all the configurations are around several hundred *meV*, implying a weak interaction between the molecules and the substrate. And the adsorption has little effect on the magnetic properties of the molecules except for CoPc. The substitution of the central metal ion changes the interface properties of MPc/Au(111). The results of FePc/Au(111) and CoPc/Au(111) calculated with PW91 functional are compared with the results published,[9, 10, 27-29] which is helpful for better understanding the configurations and electronic properties of MPc/Au(111) system.

Selection of Functional and Calculation Method

Various functionals were used in MPc-metal substrate calculations. Hu *et al.* calculated electronic and magnetic properties of MPc on Au(111) system (where M=Mn, Fe, Co, Ni or Cu) at 6-31G**/LSDA level implemented in DMol package.[9, 27] However, because of the over-binding feature caused by LDA functional, the binding energies are around -3.5 eV.[27] We also used the LDA functional to calculate the FePc/Au(111) system and got a binding energy of -3.6 eV and a migration barrier of 0.19 eV, which yields a strong binding and a hopping rate of ~10 times/second at 77K. As a comparison, calculation using PW91 functional gave a weak binding and a migration barrier of 0.04 eV, corresponding to a hopping rate of $\sim 10^{10}$ times/second. Experimentally, time resolved tunneling spectroscopy found that the hopping rate was larger than 10^6 at 77K.[29] Considering the diffusivity was decreased by an electric field, we conclude that the PW91 functional could give a better description than that with the LDA for FePc/Au(111).

Compared with LDA, GGA is believed to give an under-binding picture on molecule-metal substrate systems. Therefore, many van der Waals (vdW) involved methods have been used to improve the description of the dispersion part.[30-32] These methods have given excellent results in many systems such as graphite system and so on.[33] In the last three years, these methods have also been applied to MPc-metal substrate.[34,35] In these studies, the vdW interaction induced a close molecule-substrate distance and then influenced the electronic structure at the interface. However, even though DFT-D method performs pretty well in π-π packing system,[33] it overbinds the molecules to the metal substrate[32, 36-38] and sometimes overestimates the binding energy with an error larger than the underestimates of a PBE functional.[37] One example in which the DFT-D method might give wrong conclusion is the CoPc/Cu(111) system. In this system, a modified DFT-D method gave a stronger binding energy than LDA did.[35] We tested the FePc/Au(111) system with the DFT-D method (Grimme 06 scheme[30] and parameters for gold were chosen the same as Ag). It was found that DFT-D method predicts an adsorption structure similar to LDA result with an average FePc-substrate distance of 2.81Å, while the binding energy is -11.4 eV, which is stronger than that from LDA calculation. This result is similar to CoPc/Cu(111) system.[35] The recently developed vdW-DF method[31] sometimes did not perform well in molecule-metal interface either. According to the published results, vdW-DF calculations predicted a binding distance between aromatic molecules and Cu(111) substrate much larger than experimental results.[39, 40]

At the same time, the traditional GGA functional works well in some MPc/metal systems. Baran *et al.*'s calculation results of CoPc(SnPc)/Ag(111) using PBE-GGA functional showed excellent agreement with experiments. Taking SnPc/Ag(111) system for example, the calculated 3.7 Å Pc-surface distance was pretty close to the experimental result (3.6Å).[26] The Sn-surface distance also fit very well. In PW91 functional, there is an overbinding coming from the exchange part. Zhang *et al.* shows this will make PW91 functional sometimes works pretty well in a vdW dominated system.[41] Therefore, we used a PW91-GGA functional to make a systematic study of MPc (M=Mn, Fe, Co, Ni, Cu or Zn) on Au(111) surface, which may be helpful for the further understanding of the interaction between MPc molecules and Au(111) substrate.

Quantum mechanical calculations were performed within density functional theory and the generalized-gradient approximation using the VASP code.[42,43] Exchange-correlation effects were carefully checked and finally modeled using the Perdew-Wang functional (PW91).[44] The projector augmented wave method was employed.[45,46] Periodic boundary conditions were applied. When calculating the properties of a free single molecule, a 30Å×30Å×15Å supercell was used. The MPc molecule was placed in the *x-y* plane. When calculating the MPc/Au(111) systems, the supercell consisted of a *c*(8×7) repeated Au (111) slabs and separated by 18 Å vacuum. We used four-layer gold atoms to model the substrate. The first two layers and the molecules are fully relaxed, which should give a better description for the interaction between central metal atom in MPc and the gold atom beneath it. This supercell consisted 281 atoms. The electronic wave functions were expanded in plane waves with a kinetic energy cutoff of 400 eV. Γ point k-sampling was used. The structures were relaxed until residual forces were smaller than 0.02 eV/Å. Other parameters such as the smearing type were described when they were used. The calculated lattice constant for bulk Au is 4.174Å. Comparing with the experimental result 4.078Å, there is a 2% discrepancy. Adsorption energy for MPc on Au(111) is defined as: $E_{\mathrm{ads}}=E_{\mathrm{MPc/Au(111)}}-E_{\mathrm{MPc}}-E_{\mathrm{Au(111)}}$.

Freestanding single molecule

In order to investigate how the substrate influences the electronic structures and magnetic properties of MPc molecules, free standing single MPc molecules were calculated first. Figure 1 shows the schematic structure of MPc (M=Mn, Fe, Co, Ni, Cu or Zn). Compared with H_2Pc molecule, the two central hydrogen atoms of H_2Pc are replaced by a 3*d* transition metal atom. The molecule can be treated as a cross with each leg about 1.5 nm long, depending on the kind of central metal atom.

Spin polarized calculations were carried out first for all the six molecules. NiPc and ZnPc are found as $S = 0$, which means that these two molecules are not spin polarized. The spin quantum numbers of other molecules are 1/2, 1/2, 1, 3/2 for CoPc, CuPc, FePc and MnPc, respectively. It is the same with the calculations using other methods [18-20] and can be explained by simple ligand field theory. As NiPc and ZnPc are not spin polarized, in the following we just do the non-spin polarized calculations. One interesting thing that should be mentioned here is the magnetic moment of the CuPc molecule. Previous calculations and experiments did not have consistent results about whether CuPc molecule was spin polarized and what was the total magnetic moment for a single CuPc molecule. In our calculation, we support that CuPc is an $S = 1/2$ system and the magnetic moment is 1 μ_B, which is the same as that in ref. 18-20 and different from that in ref. 27.

Density of states (DOS) of a free MPc molecule is shown in Fig. 2. The black lines are the projected DOS (PDOS) on the Pc frame of MPc. The red lines are the PDOS on the central metal atom. Gaussian smearing was used in these calculations and the width of 0.05 eV was adopted. To show the effect of different central atoms on the DOS, we aligned the highest occupied molecular orbit of H_2Pc and the corresponding orbitals of the other MPc molecules. The positions of Fermi level for each molecule were marked with blue lines. The results show that the original highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) contributed from the Pc skeleton were nearly unchanged, even though their geometric structures and electronic properties were changed as the central metal atom changed. We also drew the shape of the wave functions of these two orbitals (not shown here), and they exhibit the same shape as the corresponding ones of the H_2Pc molecule. Compared to the LUMO of H_2Pc molecule, the corresponding orbitals of MnPc and FePc are strongly spin polarized. The existence of the Fe or Mn atom also induces extra states coming from the metal atom in the band gap of Pc skeleton. These states decrease the band gap in the molecular crystal. For CoPc and CuPc, the orbital corresponding to the LUMO of H_2Pc is only slightly spin polarized. The new states coming from the metal atoms in the original gap are close to the original HOMO and LUMO, which means the gap of CoPc and CuPc is only slightly decreased compared to that of MnPc and FePc. For NiPc and ZnPc, which are not spin polarized, the existence of the central metal atom does not influence the original electronic structures of the Pc skeleton much. Comparing with the experimental data, [18, 19, 23] the occupied states of free MPc molecules are squeezed, due to the choice of the PW91 functional. Jahn-Teller effect may change the D_{4h} symmetry to D_{2h} and thus influences the electronic structure especially for the charged case.[48, 49] These will cause the disagreement between scanning tunneling spectroscopy (STS) and the calculated local density of states (LDOS), but the main essential experimental feathers can be reproduced.[50]

FePc/Au(111) system

Au(111) is a well investigated surface.[51, 52] The herringbone structure provides a good template for the adsorption of molecules and ad-atoms. At low coverage, molecules and atoms prefer to adsorb on the FCC packing region.[53-55] So an un-reconstructed FCC packing slab model is a good approximation for studying the electronic properties of MPc on Au(111) at low coverage deposition. When one MPc molecule adsorbs on this FCC packing substrate, there are four typical adsorption sites: top, hcp hollow, fcc hollow and bridge. While considering the angle between the lobe of an MPc molecule and the crystalline direction of the substrate, it becomes more complicated. Combining experimental results with the symmetry of substrate and the molecule, we can get ten independent configurations named as top-angle, top, bridge-I, bridge-II, bridge-III, bridge-IV, fcc, fcc-angle, hcp, and hcp-angle. This notation is also used in the other part of this article. Figure 3 is the top view of these ten configurations.

Because different stable configurations of FePc on Au(111) have been claimed in previous studies[10, 27], we first investigate the FePc/Au(111) system to point out what the discrepancy is. In this calculation, we use a PW91 exchange-correlation functional, a four layer-Au(111) substrate slab and Methfessel-Paxron order 1 smear type with a 0.1 eV width. The adsorption energies (E_{ads}) and geometric parameters of different configurations are listed in Table 1. D_1 is the average vertical distance between the FePc molecule and substrate. D_2 is the vertical distance between the iron atom and the gold atom under it. D_3 is the vertical distance between the highest gold atom (attracted by the iron atom) and the rest of the gold atoms in the first layer. We found that top-angle was the most stable configuration, which is in agreement with previous experimental observations and calculations in ref. [10, 28, 29]. And fcc, hcp, bridge-I and bridge-III were relatively meta-stable ones. So for other MPc/Au(111) system, we just calculated and analyzed these five configurations. The adsorption energy differences between these states are small (several tens meV). It thus suggests that these configurations can co-exist at certain temperatures, such as 300K. The adsorption energy for the most stable adsorption configuration is -436 meV. This adsorption energy is higher than that of a typical physical adsorption but is much lower than that of a chemical adsorption. The calculated migration barrier is 38 meV, which is large enough to make the molecule frozen at 4K but small enough to make it fast diffusing at 77K, and this conclusion has also been supported by the experiments in ref. [28, 29] which shows that FePc diffuses easily on Au(111) substrate at 77K but gets fixed on the substrate at 4K. The magnetic moment of an FePc molecule, before it is deposited on Au(111), is 2 μ_B. While FePc is deposited on Au(111) surface, our calculations still give a 2 μ_B magnetic moment, which means the adsorption does not quench the spin of the FePc molecule.

These results are different from those in ref. [27], in which the most stable configuration is hcp hollow, the adsorption energy is much lower (-3.67 eV) and the magnetic moment for FePc is half-quenched when adsorbed on Au(111). Comparing these with our calculation results, the differences could come from either the different exchange correlation functionals or the different considerations for substrate while relaxing the configurations. For different exchange correlation functionals, we have checked our results using LDA functional. The result shows that the most stable configuration is top-angle, which is the same with that obtained from the PW91 calculations. Different from PW91 calculation results, the magnetic moment changes to 1 μ_B and the distance between the Fe and gold atoms is short. Therefore, different exchange correlation functionals is the reason of the magnetic moment change. For the consideration of the substrate, the first two layers of gold atoms were fully relaxed in our calculation while they were fixed in ref. [27]. After the first two layers of gold atoms were relaxed, some gold atoms were pulled out at certain adsorption site. Take the top-angle configuration as an example, the gold atom directly under Fe was lifted up as high as 0.3 Å in our PW91 calculation and 0.17 Å in our LDA calculation. This uplift of Au atom will lower the energy of the system, and thus change the energy sequence between different adsorption configurations. Therefore, it is clear that the fixation of the substrate contributes to the discrepancy of the most stable adsorption configuration between our calculation and the calculation in ref. [27]. Different choice of exchange correlation functional contributes to the quench of the magnetic moment of the iron atom. As mentioned above, LDA calculation gives a higher migration barrier comparing with the experiments. We can conclude that the choice of functional and the relaxation of the first few layers under the adsorbed molecule are both very important for correctly understanding the electronic properties of molecules on substrate and the interaction between the molecules and the substrate.

The effect of different adsorption sites on the electronic structure was carefully analyzed. The projected DOS (PDOS) of a FePc molecule on each of several typical adsorption sites is shown in Fig. 4a-c. The PDOS of the Pc skeleton in each of these configurations is nearly the same and also much the same as that in free FePc molecule. This means the interaction between the Pc and Au(111) is weak, and the adsorption has little influence on the electronic structure of the Pc skeleton. The PDOS of the Fe atom is different for different adsorption sites. And it is also different from that of free FePc, especially near the Fermi level. This indicates the interaction between the iron atom and the metal substrate is stronger than that between Pc and the substrate. This interaction is also site specific, which has been used to explain the site-specific Kondo effect.[10]

Charge transfer is an important aspect of molecular electronics. Here we also calculated the electron density difference in FePc/Au(111) system. The electron density difference used here was defined as follow:

$$\Delta\rho=\rho_{\mathrm{MPc/Au(111)}}-\rho_{\mathrm{MPc}}-\rho_{\mathrm{Au(111)}}$$

Negative $\Delta\rho$ means electrons loss, while positive $\Delta\rho$ means electron accumulation.

Figure 5 shows the iso-surfaces of the electron density differences of the most stable configuration in real space. Iso-surfaces of ±0.002 $Å^{-3}$ are selected, which is quite a small change in the FePc/Au(111) system. It is found that there is a small charge redistribution. For the Pc skeleton of a FePc molecule, the electrons in p_z orbitals transfer to the in-plane orbitals (p_x and p_y). The conjugate properties are slightly weakened and the σ bonds in the molecular plane are enhanced. For the iron atom, the d_{xz} and d_{yz} orbitals are weakened and d_{z2} orbital is enhanced. A few electrons transfer from FePc molecule to the interface between the molecule and substrate. This charge transfer forms a dipole pointing from the substrate to the molecule. The dipole moment in the top-angle configuration is about 1.32 eV•Å.

The interaction between the adjacent molecules was also considered. A small supercell with a top-angle configuration was used to simulate the monolayer structure of FePc/Au(111).[54] The parameters to optimize the structure and calculate the adsorption properties were the same as described above but with a c(5×6) supercell and a 2×2×1 *k*-sampling. The adsorption energy for this full-coverage system is -489 meV, which is only 53 meV lower than that with a big supercell. The PDOS on

FePc molecule in the monolayer structure is shown in Fig. 4d. Compared with that of single molecule adsorption (Fig. 4a), there are no obvious differences. All of this indicates the interaction between the molecules is weak.

Other MPc/Au(111) systems

Since the PW91 calculation results of FePc/Au(111) agree well with the experimental observations, such as the fast diffusion,[28] we further do similar calculations on other MPc/Au(111) systems (M = Mn, Co, Ni, Cu or Zn). The supercells used in these calculations are the same as that used in FePc/Au(111) calculations. For MnPc, CoPc and CuPc, in which the free standing molecules have significant magnetic moment, we did the spin polarized calculations when we considered the adsorption on Au(111) surface. For NiPc, ZnPc, we tested whether it was spin polarized when adsorbed on Au(111) surface. The calculations show that both the molecules and the substrate are not spin polarized. So we calculated these two systems without spin polarization.

First of all, the geometric structures were relaxed and the adsorption energies of the five selected adsorption configurations were calculated, see Table 2. The average vertical distance between an MPc molecule and Au(111) substrate (D_1) for the most stable structure is 3.77, 3.64, 3.84, 3.88 and 3.68 Å for MnPc, CoPc, NiPc, CuPc and ZnPc on Au(111). The gold atom beneath the metal atom is lifted up (D_3) 0.35, 0.2, 0.04, 0.02 and 0.02 Å and the metal-gold distance (D_2) is 3.00, 3.27, 3.78, 3.86 and 3.56 Å, for the same sequence, respectively. Here we find that the geometric distortion of MnPc, FePc and CoPc is larger than that of NiPc, CuPc and ZnPc, which means a stronger adsorption for MnPc, FePc and CoPc molecules. These distances also suggest a relatively weak interaction between molecules and substrate.

For the spin-polarized systems (MnPc and CuPc) the magnetic moments of the adsorbed MPc molecules are not different than if the molecules were free. For CoPc, the magnetic moment changes from 1 μ_B in a free molecule to 0.58 μ_B after adsorption. As the adsorption energy of the CoPc/Au(111) system is smaller than that of MnPc/Au(111) and FePc/Au(111), indicating a weaker binding between CoPc and the Au(111) substrate, this decreased magnetic moment is surprising. We then checked both smearing and k-sampling. It was found that with a 0.02 eV smearing width and 13 irreducible k points, the magnetic moment increases to 0.8 μ_B. These results indicate that the improper treatment of the fractional occupation near Fermi level in the calculation may "cause" the decrease of magnetic moment but not the adsorption. Whether the magnetic moment of CoPc is quenched by the adsorption or not should be further investigated by both experiments and theoretical calculations.

We also carefully analyzed the electronic properties of these systems and compared them with corresponding free standing molecules. The DOS information before and after adsorption on a top-angle site is shown in Fig. 6. For MnPc, FePc and CoPc, the electronic states near the Fermi energy changed significantly, while for NiPc, CuPc and ZnPc they did not change that much. This means the interaction between MPc (M=Mn, Fe or Co) and Au(111) is stronger than that between MPc (M=Ni, Cu or Zn) and Au(111) substrate. This is consistent with the adsorption energies and the vertical distance between central atom of MPc and the first layer of Au(111). With regard to adsorption energy, MnPc/Au(111), FePc/Au(111) and CoPc/Au(111) are relatively more stable than NiPc/Au(111), CuPc/Au(111) and ZnPc/Au(111). Considering the vertical distances between the central metal atom and the underneath gold atom, we can conclude that the smaller the distance, the more stable the configuration.

Following from the discussion above, we find that the interaction between the central metal atom and the gold atom underneath it plays an important role in these systems, while the electronic structures of Pc skeletons change only slightly. Figure 7 shows the PDOSs of the central metal atoms before and after being adsorbed on top-angle sites. For all the MPc/Au(111) systems, the in-plane orbitals (d_{xy} and d_{x2-y2} orbital,

|m|=2) of the metal atoms in MPc (blue lines here) do not change much. The d_{xz} and d_{yz} orbitals ($|m| = 1$) of MnPc, FePc and CoPc shift a little, while those of NiPc, CuPc and ZnPc remain almost unchanged. In the MnPc/Au(111), FePc/Au(111), and CoPc/Au(111) systems, the black lines changed, which means that the d_{z2} orbital plays an important role in the interaction between the MPc (M=Mn, Fe or Co) molecules and the metal substrate. For NiPc/Au(111), ZnPc(111), CuPc/Au(111) systems, the d_{z2} orbitals do not change that much. Now we can conclude that the MnPc, FePc and CoPc have stronger interactions with Au(111) than NiPc, CuPc and ZnPc have.

We did the electron density difference analysis for two typical systems: MnPc/Au(111) as an example of relatively strong adsorption and ZnPc/Au(111) as an example of relatively weak adsorption. The integrated electron density difference in the *x-y* plane is shown in Fig. 8. As described above, the adsorption of MnPc is stronger than that of ZnPc, and the geometric distortion for MnPc is larger than that of ZnPc, which can be seen in Figs. 8a and 8c. It also shows clearly that the charge transfer in MnPc/Au(111) system is larger than that in ZnPc/Au(111) system. Still, they follow the same pattern. This charge transfer induces a dipole moment perpendicular to the surface. The interactions among these dipole moments play an important role in the self assembly behavior in this system.[53]

Summary

The adsorption properties of 3*d*-transition metal MPc molecules (MnPc, FePc, CoPc, NiPc, CuPc and ZnPc) on Au(111) substrate were investigated. We found that the small energy differences between different configurations allow the FePc molecules to diffuse on the substrate easily at certain temperatures, which is in good agreement with experimental observations. The electronic properties and the magnetic properties of the molecules on Au(111) were compared with those of the free standing molecules. The electronic structures of the Pc skeleton do not change much as the molecules adsorb on Au(111), for all the molecules we studied. The magnetic properties of the central metal atoms are unchanged by adsorption for all the molecules except for CoPc.

Acknowledgements

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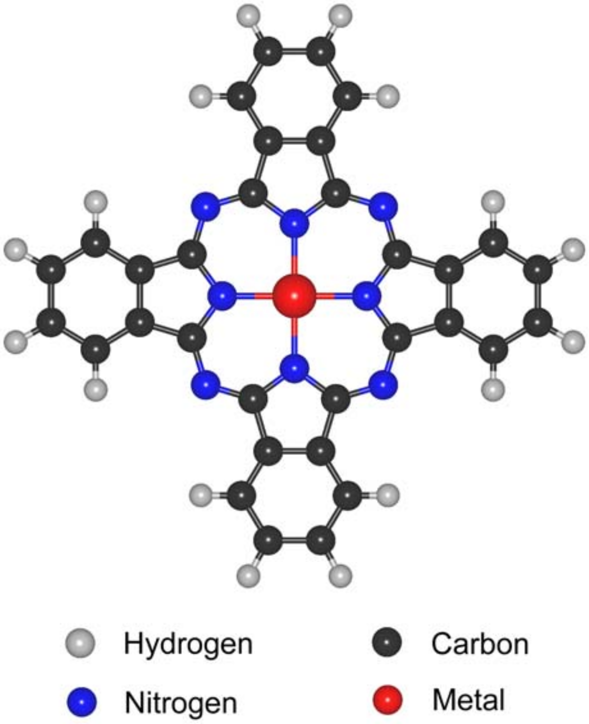

Fig. 1. Schematic structure of 3*d* transition metals MPc (M=Mn, Fe, Co, Ni, Cu or Zn).

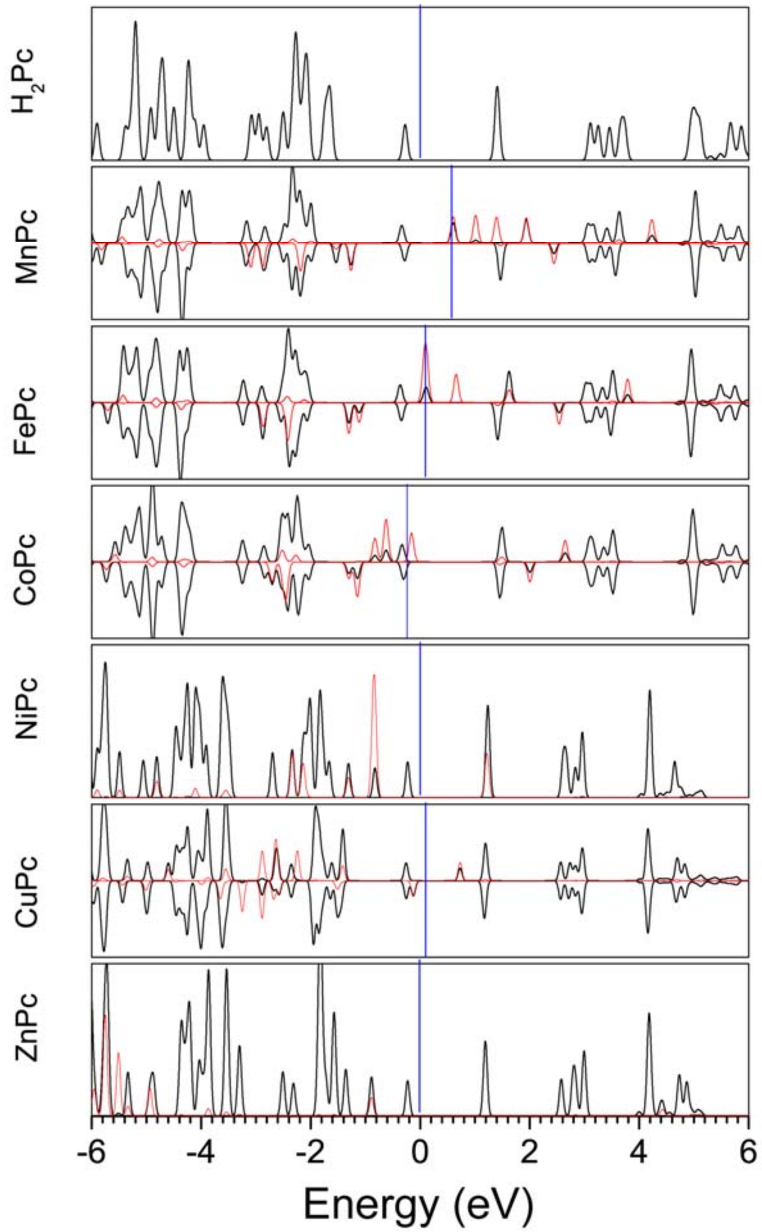

Fig. 2. DOS of H_2Pc and PDOS of MPc, which are projected on the Pc framework (black line) and metal atoms (red line). The HOMO of H_2Pc and corresponding orbitals of MPc are aligned. The Fermi level is marked as a blue line in each panel.

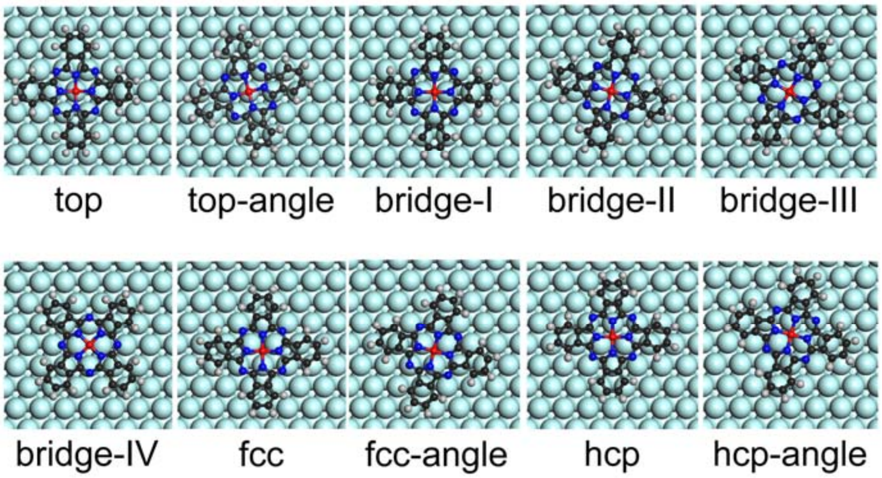

Fig. 3. Typical adsorption configurations of MPc adsorbed on Au(111) FCC terrace.

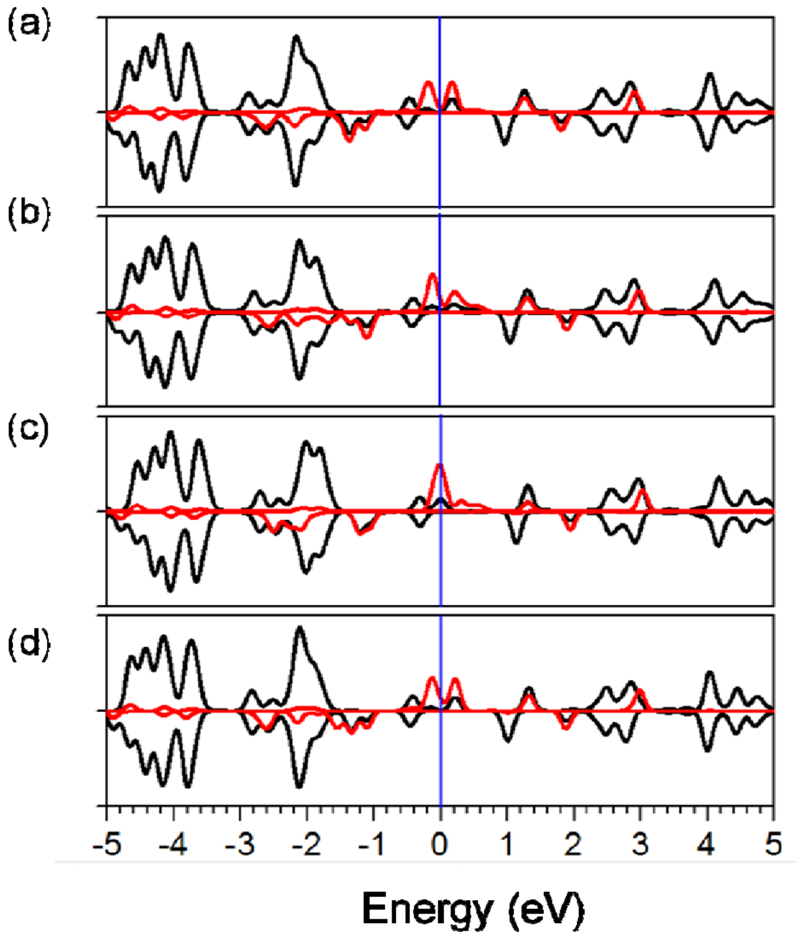

Fig. 4. DOS of FePc/Au(111) system with different adsorption configurations. Black lines are the PDOS on the Pc framework, and red lines are the PDOS on the iron atom. (a) top-angle. (b) hcp. (c) bridge-III. (d) DOS of the configuration for one layer of FePc on Au(111).

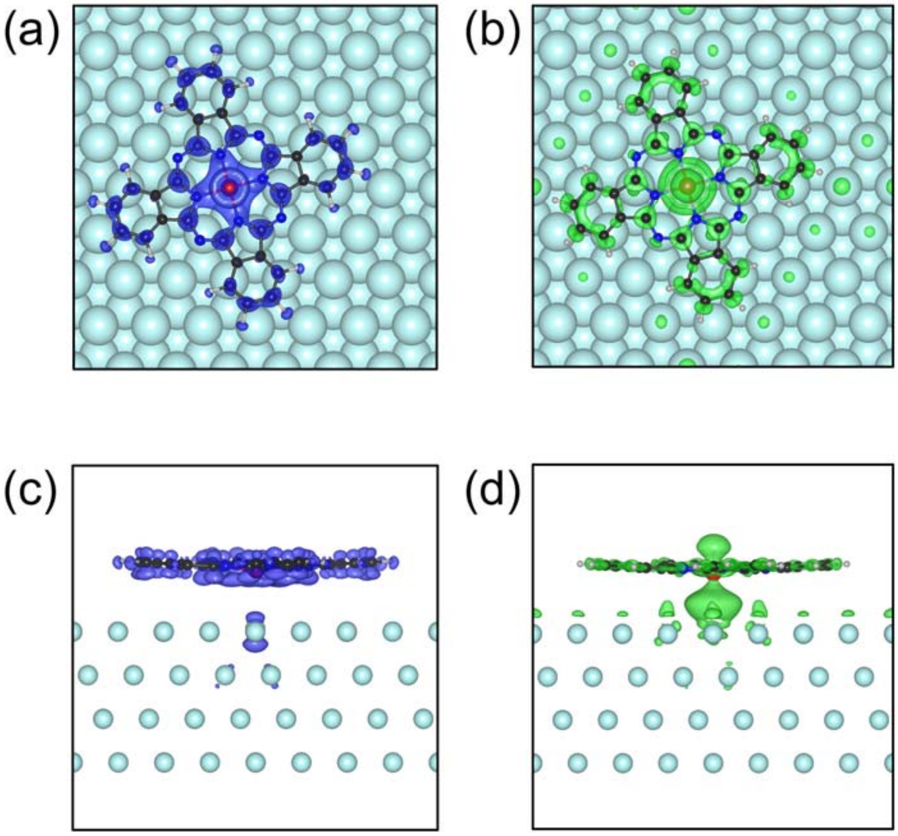

Fig. 5. Iso-surface of electron density difference of FePc/Au(111) system. (a) and (c) are the top view and side view of the negative iso-surface of electron density difference. $\Delta\rho$ = -0.002 Å^{-3}. (b) and (d) are the top view and side view of the positive iso-surface of electron density difference. $\Delta\rho$ = 0.002 Å^{-3}.

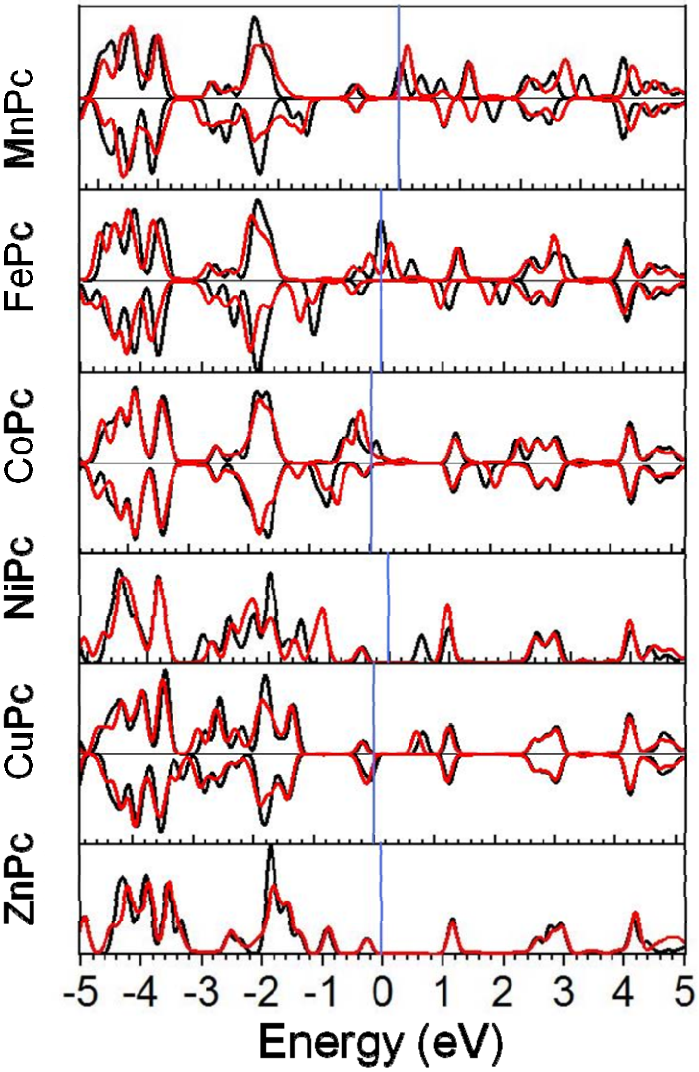

Fig. 6. DOS of MPc and MPc/Au(111) system. The black lines are DOS of free single MPc molecule. Red lines are DOS projected on the MPc molecule adsorbed on Au(111) surface. The blue lines indicate the Fermi energy.

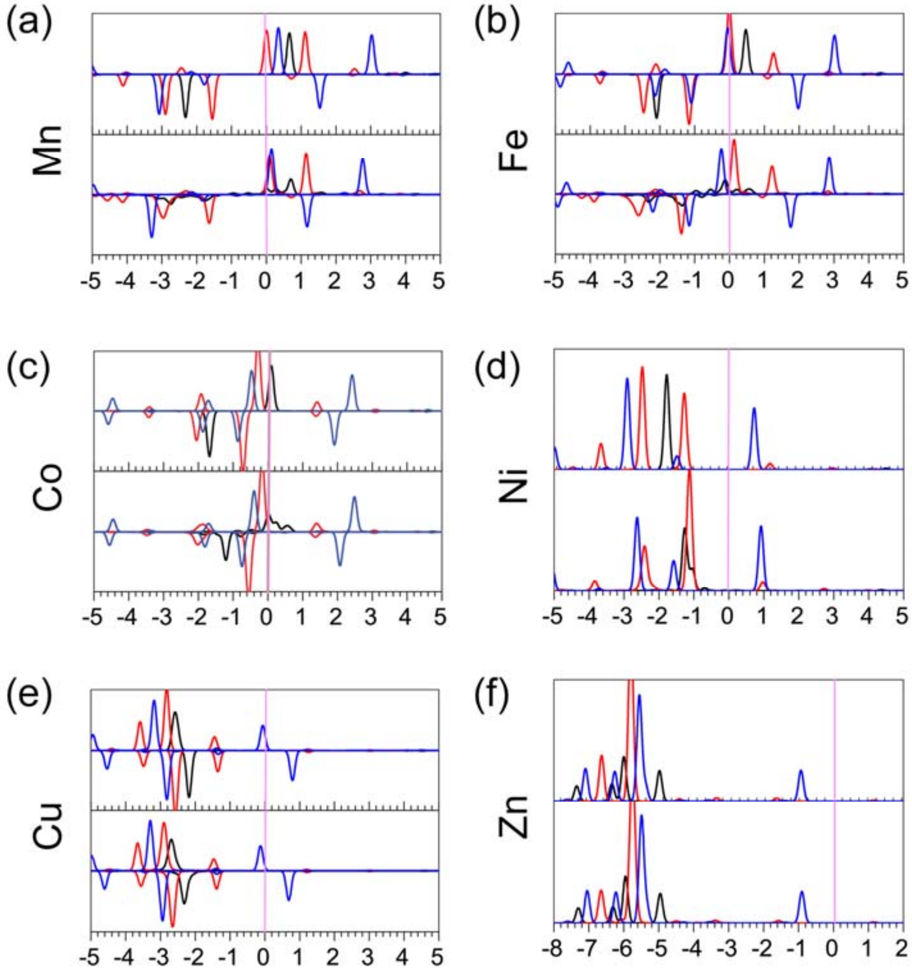

Fig. 7. PDOS of the metal before and after adsorbed on Au(111) surface. (a) MnPc; (b) FePc; (c) CoPc; (d) CuPc; (e) NiPc; (f) ZnPc. Upper panel in each figure is the PDOS of metal atom in free MPc, and lower panel is that after adsorption. Black lines are for d_{z2} ($m = 0$). Red lines are for $d_{xz} + d_{yz}$ ($|m| = 1$). Blue lines are for $d_{xy} + d_{x2\text{-}y2}$ ($|m| = 2$). The purple lines indicate the Fermi energy.

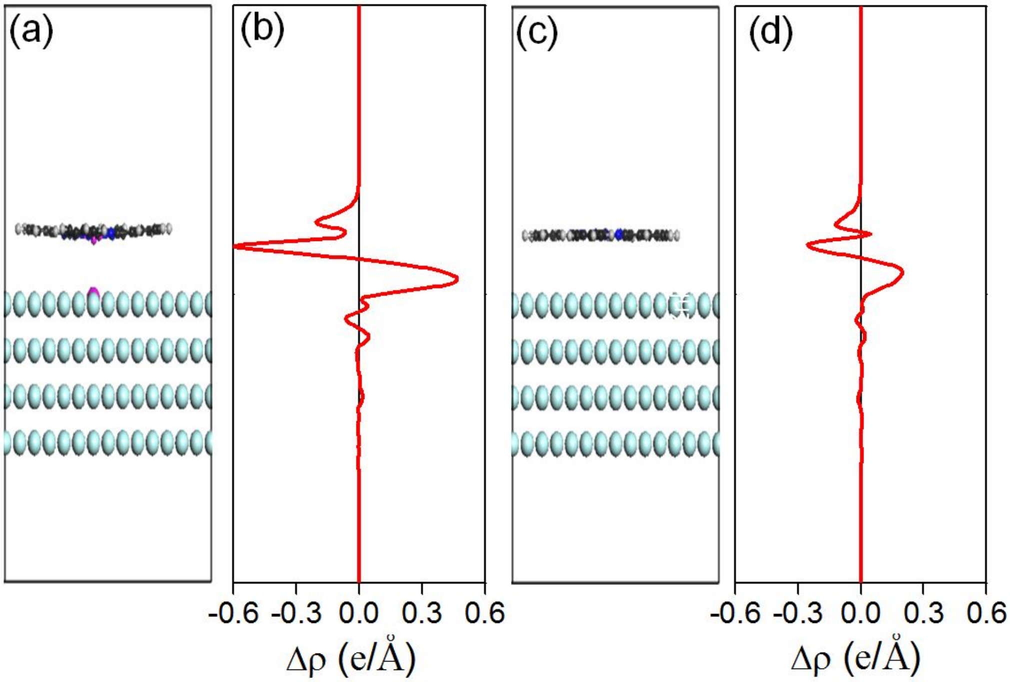

Fig. 8. Integrated electron density difference for MnPc/Au(111) and ZnPc/Au(111) systems in top-angle configuration. (a) and (c) are side views of the adsorption configurations for MnPc/Au(111) system and ZnPc/Au(111) system. (b) and (d) are the integrated electron density difference for MnPc/Au(111) system and ZnPc/Au(111) system in *z*-direction. The charge transfer in MnPc/Au(111) system is larger than in ZnPc/Au(111) system. Negative $\Delta\rho$ means electrons loss, while positive $\Delta\rho$ means electron accumulation.

Table 1. Properties of different configurations of FePc adsorbed on Au(111) surface.

Index	E_{ads} eV	D_1 Å	D_2 Å	D_3 Å
top	-0.377	3.81	3.32	0.31
top-angle	-0.436	3.76	3.28	0.28
bridge-I	-0.414	3.71	3.55	0.04
bridge-II	-0.379	3.74	3.60	0.04
bridge-III	-0.424	3.67	3.60	0.05
bridge-IV	-0.407	3.76	3.70	0.03
fcc	-0.419	3.68	3.60	0.03
fcc-angle	-0.397	3.88	3.81	0.03
hcp	-0.421	3.69	3.60	0.02
hcp-angle	-0.403	3.87	3.78	0.02

Table 2. Adsorption energies of MPc/Au(111) system in the unit of *meV*. E^{0}_{ads} is the adsorption energy of the most stable configuration. The others are relative energies compared with E^{0}_{ads}.

	E^{0}_{ads}	top-angle	bridge-I	bridge-III	fcc	hcp
MnPc/Au(111)	-533	0	44	15	39	26
FePc/Au(111)	-436	0	22	12	17	15
CoPc/Au(111)	-430	0	17	23	15	10
NiPc/Au(111)	-340	0	11	11	22	21
CuPc/Au(111)	-333	8	5	9	14	0
ZnPc/Au(111)	-327	16	0	16	5	1

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