



Adsorption of Metal-Phthalocyanine Molecule on Aluminum (100) Surface: The DFT Study

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ABSTRACT

Adsorption of various metal-phthalocyanine (MPc) molecules on Al(100) substrate were investigated by using the Density functional Theory (DFT). There are six transition metal atoms substituted in phthalocyanine skeleton ranking from d^5 to d^{10} of the 1st row of transition metal and metal free phthalocyanine (H_2Pc) molecule were studied. After adsorption, we found that the interaction between MPc molecules and substrate depended on the central metal of MPc molecule. The interaction between the ZnPc, CuPc and NiPc molecules on Al substrate are relatively weak comparing to the adsorption of H_2Pc molecule, while the CoPc, FePc, and MnPc adsorptions show stronger interaction. This work are further investigated the vacuum level shift by extracting the information from the density of state (DOS) calculation. The shift of DOS of MPc molecule effect to the charge barriers at the interface.

Keywords: Metal-Phthalocyanine (MPc); Density functional Theory; Metal-Organic interface

1. Introduction

Today, many commercial electronic devices are made of organic semiconductor materials such as organic solar cell (OSC), organic light emitting diodes (OLED) and organic photovoltaic (OPV). In the field of interface science and engineering research,

charge barrier is of vital importance to the successful operation of any electronic device and, therefore, is one of the most interesting properties of any metal-organic contact. In past decades, the Schottky-Mott rule can be used to predict charge barriers at the interface

of metal-semiconductors devices [1]. Hole barrier is defined by the energy difference between the substrate work function and the electron affinity of the semiconductor while electron barrier is defined by the energy difference between the substrate work function and the electron ionization of the semiconductor. However, this rule is deficient in describing the metal-organic devices [2].

Since, the work done by Ishii and Seki was clearly demonstrated the break-down of the assumption of a common vacuum level [3]. They showed that the vacuum level did not align but shift at the metal-organic interface [2]. The vacuum level shift was found in, for example, adsorption of π -conjugated polymers or noble gasses on metal surface [4-5]. Moreover, the vacuum level shift was observed although such an interaction between the adsorbate and substrate is very weak (the shift found even though the electrons of the adsorbate are fully occupied (close-shell) which should be not to be reacted to the substrate). Nevertheless, this model is known later as "the push-back model" [6] and it can well describe the vacuum level shift for such a weak interaction or most of physisorption cases.

Metal-Phthalocyanine molecules are interested organic semiconductor which has been used to assemble many electronic devices as seen from past decades [7-13]. There were several studies on various substrates previously, for example, Au, Ag, Cu, and Pt [14-18]. These substrates have intrinsic metal d-band states which play a crucial role in determining the interfacial electronic structure [19]. However, there is a few studies on a highly active metal, e.g. alkali, alkali earth and post transition metal [20-24]. Aluminum is an interesting one which is commonly used for making an electrode in the low-cost electronic devices.

In this work, various MPc/Al(100) systems are studied using the first-principle density functional theory calculation. We

focus on the vacuum level shift and the charge barrier formation at the interface because these parameters can influence the device performance.

2. Materials and Methods

The calculations were performed by ABINIT software [25-27] which used the first principles calculation and successfully studied metal surfaces and also metal-organic interfaces. The projector augmented wave method (PAW) [28] and the Perdew-Burke-Ernzerhof (PBE) parameters of the generalized gradient approximation (GGA) [29] were employed. The plane-wave cutoff energy and the augmented charge density were set to 400 and 800 eV, respectively. In a unit cell, the k-point of $2 \times 2 \times 1$ grid was applied for Brillouin zone integration. When calculated the density of state (DOS) and its projection on atom, a smearing energy of 0.05 eV was applied throughout the calculations.

The Al substrate was constructed from the optimum value of Al bulk calculation with Al-Al bond length of 2.85 Å. In slab model, there are four Al layers with surface size of $14.248 \times 14.248 \text{ Å}^2$ and a vacuum space of 15 Å is provided to avoid self-interaction between the nearest slabs. During the optimization, only the top two Al layers were allowed to relax. After optimization, it was found that the two topmost Al layers are slightly expand by 5% compared to the bulk lattice constant. The surface work function was estimated from $\Delta W = V_\infty - E_F$, where V_∞ is the electrical potential energy far from the top of Al surface and E_F is the Fermi energy of Al substrate. The calculated Al work function yields 4.23 eV which is in agreement with the previous work [30].

The geometry and the electronic structure of all isolated MPc molecules were carried out before study the adsorption. The results were shown in Table 1. This calculations were done without consideration of magnetic properties of MPc molecules which should be depended on the central

metal substitution. It is important to note that the magnetic properties of MPc molecules is, therefore, not our scope and may be studied elsewhere.

There are indeed many laboratory works and there are very difficult to find the minimum adsorption configuration due to numerous parameters needed to consideration. Thus, for the comparison purposed among these MPc, the adsorption configuration as shown in Fig. 1a were carried out in this work. The pyrrole-ring arm of MPc molecule was set to be oriented at 30° counterclockwise with respect to [011] direction, which is similar the experimental works [15,16, 31-34]. This orientation of each MPc molecule was fixed for all calculations.

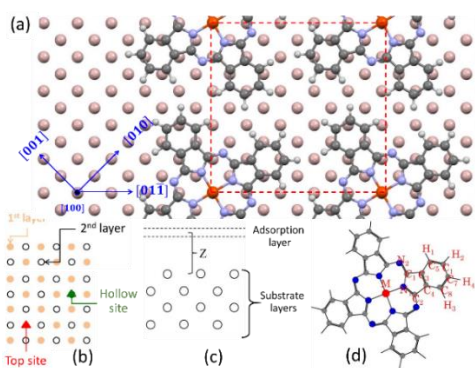


Fig. 1. (a) The unit cells of MPc adsorbed on Al(100) substrate used in this work, (b) Definition of the hollow and the top site of MPc adsorbed on Al(100) substrate. (c) Cross-section view shows the adsorption layer and the substrate layers. (d) Structure of MPc molecule.

Table 1. The optimized interatomic distances of various MPc molecules

Distance (Å)	H ₂ Pc	MnPc	FePc	CoPc
M-N ₁	1.024	1.947	1.933	1.923
N ₁ -C ₁	1.384	1.398	1.395	1.390
C ₁ -N ₂	1.324	1.326	1.326	1.324
C ₁ -C ₃	1.456	1.452	1.453	1.456
C ₃ -C ₅	1.400	1.401	1.400	1.399
C ₅ -H ₁	1.092	1.092	1.092	1.092
C ₅ -C ₆	1.396	1.397	1.397	1.398
C ₆ -H ₂	1.093	1.093	1.093	1.093

Distance (Å)	NiPc	ZnPc	CuPc
M-N ₁	1.908	1.966	2.004
N ₁ -C ₁	1.390	1.382	1.38
C ₁ -N ₂	1.322	1.331	1.336
C ₁ -C ₃	1.455	1.461	1.464
C ₃ -C ₅	1.399	1.399	1.399
C ₅ -H ₁	1.092	1.092	1.093
C ₅ -C ₆	1.398	1.398	1.399
C ₆ -H ₂	1.093	1.093	1.093

Fig. 1b shows two configurations of adsorption, namely, the hollow and the top configuration. The top configuration means that the central metal of MPc molecule is located on the top of an Al atom underneath, while the hollow configuration is defined as the central metal of MPc molecule is located above the center of four Al atoms underneath.

The extrapolation was used to obtain the minimum interaction distance with respect to the lowest energy by plot graph between the adsorption energy vs. distance. All data were collected for extrapolation by examining the total energy with respect to the distances z from 3.0 to 4.5 Å with 0.25 Å adjust step as shown in Fig.1c. During the extrapolation, the position of MPc and Al substrate were not allowed to move. The interaction distance between the adsorbate and substrate is only the parameter to be examined.

3. Results and Discussion

3.1 Adsorption energy

The adsorption energy (E_{ads}) is derived from Eq. (3.1) where, the $E_{\text{MPcs+Al}}$ is the total energy of adsorbate molecule and substrate, the E_{Al} is the total energy of clean Al substrate and the E_{MPcs} is the total energy of an isolated MPc molecules, respectively. The results are shown in Table.2.

$$E_{\text{ads}} = E_{\text{MPcs+Al}} - E_{\text{MPcs}} - E_{\text{Al}}. \quad (3.1)$$

According to Eq. (3.1), a negative energy value indicates molecule is adsorbed on the substrate.

The adsorption energies of ZnPc, CuPc and NiPc molecules were slightly

lower than the case of H₂Pc adsorption. The case of CuPc adsorption showed the lowest adsorption energy with the hollow configuration. Nevertheless, the interaction distances between these molecules and Al substrate were approximately 4.2 Å long.

Table 2. Adsorption energies and interaction distance of various MPcs adsorbed on the hollow and the top site of Al(100) surface

Adsorbate molecules	Hollow site		Top site	
	E _{ads} (eV)	Distance (Å)	E _{ads} (eV)	Distance (Å)
H ₂ Pc	-0.146	4.25	-0.134	4.34
ZnPc	-0.170	4.20	-0.154	4.27
CuPc	-0.183	4.17	-0.172	4.24
NiPc	-0.152	4.23	-0.146	4.14
CoPc	-0.632	3.75	-0.643	3.75
FePc	-0.644	3.52	-0.673	3.50
MnPc	-0.561	3.50	-0.598	3.46

On the other hand, the results showed that the bonding of CoPc, FePc and MnPc molecules and Al substrate were much stronger than the previous cases. Their adsorption energies were drastically decreased which were in consistent to the shorter interaction distance of around 3.6 Å long. The case of FePc adsorption showed the best geometry for adsorption and this molecules was more favorable adsorbed on the top site instead of the hollow site.

According to the results, one can be divided into two categories, the weak and the strong interaction compared to the case of metal free H₂Pc adsorption. In the case of weak interaction, the CuPc showed the lowest stable with the hollow adsorption configuration than the other, ZnPc and NiPc. Nevertheless, among all of MPc molecules, the binding between FePc and Al(100) showed the most stable geometry of adsorption with the top configuration. The strong interaction of Cu, Co, Fe and Mn on Al atoms underneath were implied as shown in Fig. 3 and 4. At the Fermi energy level, the atomic orbital of these metals maintained contributing to the Fermi energy level of the MPc/Al(100) system. It is the clear evidence implied the strong bonding between the adsorbate and substrate.

3.2 Electron transfers after adsorptions

The total amount of electrons transferred across interface, $\rho'_{\text{ads}}(z)$ can be calculated by using Eq. (3.2),

$$\rho'_{\text{ads}}(z) = \int_A (\rho_{\text{MPc/Al}}(x, y, z) - \rho_{\text{Al}}(x, y, z) - \rho_{\text{MPc}}(x, y, z)) dx dy, \quad (3.2)$$

where, $\rho'_{\text{MPc/Al}}(x, y, z)$, $\rho'_{\text{Al}}(x, y, z)$ and $\rho'_{\text{MPc}}(x, y, z)$ are electron density of the adsorbate molecule on substrate, the Al substrate and the isolated MPc molecule at the (x, y, z) position, respectively.

According to Eq. (3.2), a positive value indicates the total amount of electron increase while a negative value indicates the total amount of electron decrease. The calculated $\rho'_{\text{ads}}(z)$ are shown in Fig. 2. In all cases, the density $\rho'_{\text{ads}}(z)$ shows that electrons are transferred from the substrate to the adsorbate molecules. The only difference between two groups is the degree of electron transfer. The adsorption of ZnPc, CuPc and NiPc molecules show the same degree of electron transfer as that of H₂Pc adsorption. It is to be noted that the case of CuPc adsorption shows slightly different result from the others. There is a peak located dominantly at the adsorbed molecule and a deep dipped curve near the top of the 1st layer of Al substrate. The degree of electron transfer in the case of CoPc, FePc and MnPc adsorption are increased dominantly than the previous group. As a results, it suggests that the interaction between the MPc molecule and Al substrate depended on the central metal in parent Pc skeleton.

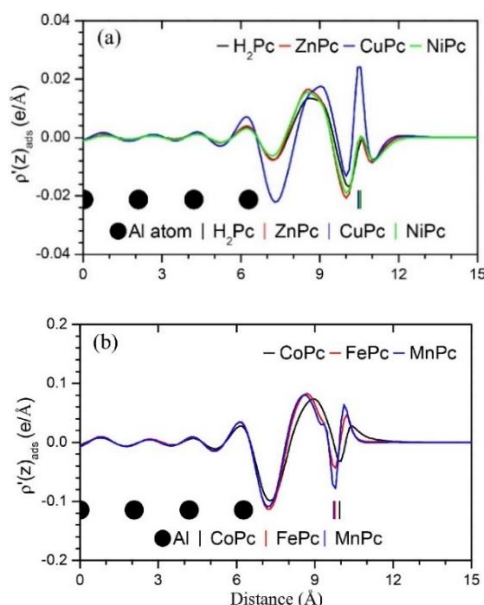


Fig. 2. Two dimensional electron density function as a function of surface direction for (a) H_2Pc , ZnPc , CuPc , NiPc and (b) CoPc , FePc , MnPc on Al(100) surface. The vertical line is located at the positions of the MPc molecules on the top layer of Al surface while the sphere indicates the position of Al layers.

3.3 Electronic structure of MPc molecules after adsorption

In experimental studies by Ultraviolet Photoelectron Spectroscopy (UPS), at some particular thickness after deposition of organic molecule on substrate, the energy spectrum of metal-organic film is mostly belonged to the adsorbed molecule. Moreover, according to the DFT calculation, it is inconvenient to observe electronic structure change after adsorption by looking at the total DOS (Al+MPc) because the main contribution to the DOS spectrum is overwhelmed by Al energy states. As a result, we performed the projected density of state (PDOS) calculation to reveal the physical underlying metal-organic adsorption as previous work did before [35]. The calculations were also compared the spectrum of two MPc molecules; one was solely DOS of isolated MPc molecule before

adsorption and another was the MPc spectrum that was comprised from PDOS of each atom in MPc molecule after adsorption. The purpose is to observe any changes on MPc electronic structure only whereas any changes on electronic structure of Al substrate are neglected.

3.4 H_2Pc , ZnPc and NiPc adsorption

Fig. 3 shows DOS of H_2Pc , ZnPc and NiPc molecule after adsorption. In Fig. 3a, the frontier state of H_2Pc molecule are comprised of ligand atomic orbitals where two center H atomic orbitals lie below the frontier state. The highest occupied molecular orbital (HOMO) of H_2Pc molecule is at -0.75 eV while the lowest unoccupied molecular orbital (LUMO) is at 0.65 eV. Hence, the energy gap between the HOMO and LUMO of isolated H_2Pc molecule is 1.4 eV which is in good agreement with the previous calculation [36]. Fig. 3b and 3c show the DOS of ZnPc and NiPc molecules. It is noticeable that the HOMO and LUMO of ZnPc and NiPc locate nearly at the same position as H_2Pc molecule. As a result, it suggests that the frontier energy level of these molecules are contributed mainly from the Phthalocyanine (Pc) ligand skeleton.

After adsorption, overall energy spectrum are shifted to the lower energy while retaining the main features similar to those before adsorption. In the case of H_2Pc and ZnPc adsorption, the energy spectrum are shifted by 0.4 eV to the lower energy. In the case of NiPc adsorption, the peak occurred at 0.6 eV was found after adsorption therefore this additional state belongs to the C atomic orbitals of the Pc ligand skeleton.

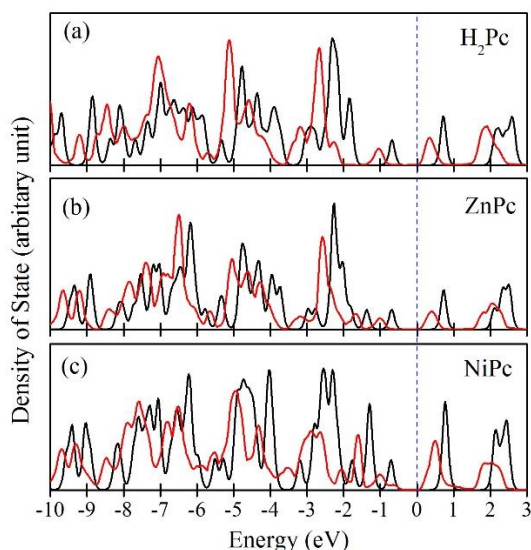


Fig. 3. Partial density of state after adsorbed on Al substrate (red line) for (a) H_2Pc , (b) $ZnPc$ and (c) $NiPc$ molecules comparing to density of state before adsorption of the isolated molecules (black line). The Fermi level is indicated by the vertical blue dash line at zero energy.

3.5 CuPc, CoPc, FePc and MnPc adsorption

Electronic structures of CuPc, CoPc, FePc and MnPc molecules were calculated and the DOS are showed in Fig. 4. Our calculations are in agreement to the previous works of the isolated MPc molecules calculations [37,38]. After adsorption, overall DOS changes similar to the previous cases. All DOS are shifted to lower energy. However, the peak located at the Fermi energy does not shift. The feature at the Fermi level is ambiguous. This may be due to the interaction between the metal atom in MPc molecule and Al underneath because the metal atomic orbitals of these four MPc molecules are located at this energy level. The interaction was found similarly from the other studies on other substrates [39-41].

In the case of CuPc adsorption, the PDOS calculation revealed that both atomic

orbital of Cu atom and Pc ligand skeleton are contributed to the frontier state. By comparing the CuPc DOS to the isolated H_2Pc DOS, there is additional energy states of Cu atom emerged between the HOMO and LUMO. After adsorption, the DOS comprised of Pc skeleton atomic orbitals are shifted to the lower energy while the Cu state still remains at the Fermi level.

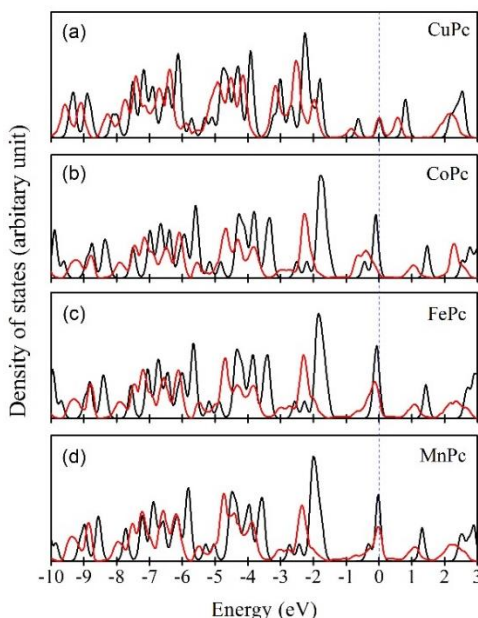


Fig. 4. Partial density of state after adsorbed on Al substrate (red line) for (a) CuPc, (b) CoPc, (c) FePc and (d) MnPc molecules comparing to density of state before adsorption of the isolated molecules (black line). The Fermi level is indicated by the vertical blue dash line at zero energy.

3.6 Work function, vacuum level shift and band offset

Since, the electron transfer occurred at interface results in a localization of charges [42,43], i.e. positive and negative layers. Therefore, they form the dipole moment surface between two contacts [2]. The net dipole moment contributing to the work function can be calculated by using the follow equation [44,45],

$$\Delta W = \frac{e|\bar{P}|}{\epsilon_0 A}, \quad (3.3)$$

where, e is the charge of electron, ϵ_0 is the vacuum permittivity, A is the surface area and $|\bar{P}|$ is the total dipole moment at the interface. The calculated ΔW is shown in Table 3.

In Table. 3, the adsorption of H₂Pc on Al(100) surface results in a marginal change in work function and similar trends are found in the adsorption of ZnPc, CuPc and NiPc molecules. On the other hand, the adsorption of CoPc, FePc and MnPc molecules significantly increased the surface work function because net electrons were greater accumulated at the adsorbate side than that in Al substrate.

Table 3. The net change of work surface work function after adsorption (ΔW), and band offset, ϵ_V^F and ϵ_{vac}^F , respectively

	ΔW (eV)	ϵ_V^F (eV)	ϵ_{vac}^F (eV)
H ₂ Pc	-0.028	1.0	0.4
ZnPc	-0.035	1.0	0.4
CuPc	+0.027	0.0 ²	0.6
NiPc	-0.035	0.6 ¹	0.5
CoPc	+0.160	0.0 ²	1.0
FePc	+0.140	0.0 ²	1.0
MnPc	+0.120	0.0 ²	1.0

¹ The present of adsorption state cause the reduction of electron barrier in NiPc/Al system.

² Due to the occupation of atomic orbitals of central metal at the Fermi level, the estimated band offset of CoPc, and FePc and MnPc adsorptions show the zero ϵ_{vac}^F .

According to Schottky-Mott rule, the electron barrier height is defined by the difference between the ionization energy of the adsorbate layer and the metal work function. The hole barrier height is defined by the difference between the adsorbate electron affinity and the metal work function. In this work, the PDOS calculation allowed the estimation of the band offset of various MPC/Al(100) systems. The valence band offset and the conduction band offset are defined by the energy difference between the HOMO and the LUMO of the isolated MPC molecule and the Fermi level of

MPC/Al(100) as ϵ_V^F and ϵ_{vac}^F , respectively. The results are also summarized in Table. 3.

The effect of adsorption to the electronic property of MPC/Al(100) system can be summarized in Fig. 5. Before adsorption, electronic structures of clean Al substrate and isolated MPC molecule have shared vacuum level, E_{vac} , which is where a stationary of electron [2]. After deposition by a monolayer (ML) of MPC molecule, the energy level of the adsorbate is aligned to the metal substrate. Consequently, the vacuum level of the interface is shifted to the lower energy which is independently on central metal substituent. The illustration of vacuum level shift (Δ) are summarized in Fig. 5b.

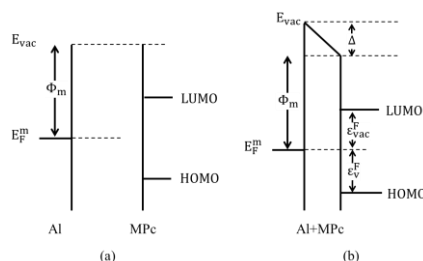


Fig. 5. Energy level of (a) clean Al substrate and isolated MPC molecule before adsorption and (b) the model illustrates the energy level alignment and vacuum level shift at the metal-organic interface.

The future work will be consider the spin polarization and therefore the van der Waals force. Nevertheless, our calculation showed the influence of central metal substituent that effect to physical and electronic properties at the interface. One concern to the physical properties is that the interaction strength between the adsorbate and the substrate. As shown in Fig. 3 and 4, if there is metal atomic orbitals contributed to the Fermi energy level, the strong interaction would be observed. The examples are the case of CuPc, FePc, MnPc and CoPc adsorptions. Whereas, if there is no metal atomic orbitals contribution to the Fermi energy level, the weak interactions are observed as the case of H₂Pc, ZnPc and NiPc cases. According to the results, we suspect to

this information that the electronic state of metal might be induced by adsorption on Al substrate. This topic should be studied for the future work.

4. Conclusion

The adsorption of various MPc molecule on Al(100) surface was investigated by using DFT calculation. The results showed that the central metal atom in Pc skeleton has the crucial role in the forming of surface dipole at MPc/Al(100) interface. The adsorption of ZnPc, CuPc and NiPc molecule on Al substrate result in the marginal induction to the surface work function comparing to the case of H₂Pc adsorption. On the other hand, the adsorption of CoPc, FePc and MnPc molecule cause explicitly the greater change of the surface work function. The vacuum level shift in MPc/Al(100) systems are indicated by PDOS calculations. All energy spectrum are shifted by 0.4 eV to the lower energy. Since, electronic structures of MPc molecules depend on the metal substituent. As a result, both charge barriers, as ϵ_V^F and ϵ_{vac}^F , are based on two factors, their electronic structure origin and the vacuum level shift at the interface.

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