Research Article

Structure of chloroaluminum phthalocyanine (ClAlPc) on SiO₂(100) surface: A combined molecular dynamics(MD) and density functional theory (DFT-D) study

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ABSTRACT

In this study, we systematically investigated the adsorption of chloroaluminum phthalocyanine (ClAlPc) on SiO₂ (100) surface using molecular dynamics (MD) combined density functional theory including a semiempirical dispersion correction (DFT-D). Chloroaluminum phthalocyanine (ClAlPc) molecule can adsorb on surfaces in two distinct adsorption configurations, depending on if the central Cl atom points toward (Cl-down) or away (Cl-up) from the surface. Our calculation results indicated that the Cl-down configuration is slightly stable than the Cl-up one because of the interaction between the surface SiO₂ (100) and ClAlPc is stronger in the former than in the latter.

Key words: adsorption; ClAlPc; SiO₂; DFT-D; Molecular dynamics

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INTRODUCTION

Metal-phthalocyanines (MPcs) are very promising species for organic electronics because of their remarkable organoelectronic properties, air stability and low cost[1]. Most investigations in this field focused mainly on the structural and electronic properties of the MPcs, such as vanadyl-phthalocyanine(VOPc)[2], chloroaluminum phthalocyanine(ClAlPc)[3], chlor-ogallium phthalocyanine(GaClPc)[4], and titanyl-phthalocyanine(TiOPc)[5]. However, the adsorption morphology of MPcs on the surface is a critical factor for optimizing the performance of electronic devices[6-10]. Recently, few studies have been carried out on the correlation between the charge state and molecular conformations on various substrates[11,12].

Tianchao Niu and co-workers[13] discussed the dipole orientation dependent symmetry reduction of 4-fold symmetric chloroaluminum phthalocyanine (ClAlPc) molecules on a Cu(111) surface by combined low temperature scanning tunneling microscopy(LT-STM) and density functional theory (DFT) calculations. It has been demonstrated that ClAlPc with Cl-up configuration reserved C4 symmetry, while Cl-down adsorbed ClAlPc reduced symmetry from C4 to C2. The molecular dipole chain arrays of chloroaluminium phthalocyanine (ClAlPc) on the graphite surface were analyzed using scanning tunneling microscope (STM) by Huang et. al[14]. The pure ClAlPc single layer films on graphite were found neatly aligned with the Cl-up configuration formed a well-ordered molecular dipole monolayer on graphite (0001). Li[15] investigated the adsorption morphology of ClAlPc molecules and found the MPc molecules preferred to lie parallel to the pure SiO₂ surface and grow into an island mode resulting in a high density and a regular cone array by the atomic-force microscopy(AFM). This kind of film with face-on orientation and conical structure is highly suitable for the organic solar cells applications.

In this work, we carried out a combined molecular dynamics (MD) and density functional theory (DFT) investigations of the adsorption morphology of ClAlPc on the SiO₂(100) as well as the inner driving force for this architecture. Our calculation results show that the stable adsorption configurations of ClAlPc on the SiO₂(100) in this work are quite similar to the previous experimentally reported configurations of ClAlPc on Cu(111) or graphite

surfaces. The two different morphologies, Cl-down configuration and Cl-up configuration, are explained by the intermolecular interaction and illustrated with charge-density difference plot.

COMPUTATIONAL DETAILS
MOLECULAR DYNAMICS (MD)
With the advent of the information age, there is more and more number of traffic information. The sources of traffic We performed molecular dynamics (MD) simulations with quantum annealing implemented in the Forcite module of Materials Studio[16] to elucidate the adsorption motif of the chloroaluminium phthalocyanine (ClAlPc) molecule on the $SiO_2(100)$. Molecular dynamics methods were used to obtain information about the dynamic behavior and orientation of phthalocyanine molecule on the surface in time dependence. Quantum annealing is a new method to search for the minimum of a cost function through a control of quantum fluctuations. Quantum annealing is used mainly for finding solutions combinatorial optimization problems. According to the previous studies, although the quantum annealing algorithm is not capable, in general, of finding solutions to NP2 complete problems in polynomial time, quantum annealing is still a promising optimization technique, which exhibits good performances on some typical optimization problems.

MD simulation with the DREDING force field was used to investigate the adsorption morphology[17]. All simulations started from the energy-minimized structures. Minimize the structure using the conjugate gradient method to remove unphysical overlap of the molecules for maximum of 1×106 steps. The simulations were performed with a step of 1 femtosecond in vacuum and the total simulation time was 1000ps, which is enough time for system analysis. We set the initial temperature of the system as 298 K and after annealing at temperatures up to 598°C. Anneal the structure by ramping the temperature from 298 to 500 to 298 K over 1000 ps followed by additional minimization.Constant volume and temperature (NVT) simulations were performed on our simulation cells. The nonbonded energies were calculated using the Atom-based summation method instead of the popular Ewald summation[18]. Transients of 1 ns were collected for the simulated models at the various temperatures and degrees of hydration. Afterward, 1 ns Annealing simulations at 298K were performed for reproduction of the exsitupattern by restarting from the last snapshot of the trajectory at the selected temperature. In all cases the integration time step was 1fs and the sampling interval was 100 time steps.
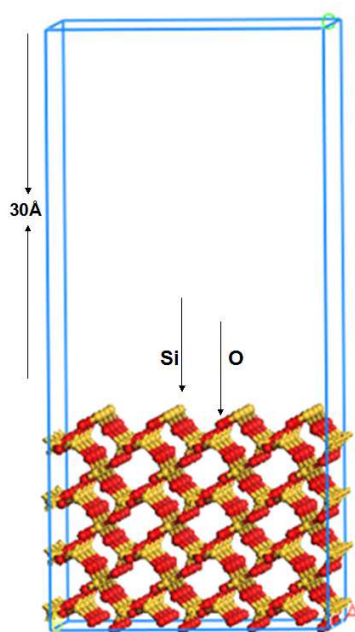

Fig. 1: Optimized $SiO_2(100)$ vacuum slab

DENSITY FUNCTIONAL THEORY (DFT-D)
Based on above MD simulation results, the adsorption mechanism of ClAlPc on a SiO_2 (100) surface was further analyzed by using density functional theory (DFT) implemented in the Dmol3 program[19,20]. In order to account for the missing dispersion effects in the standard implementation of DFT, several approaches have been proposed, which were recently discussed in the review by Tkatchenko et al.19 In this work we used the computationally inexpensive semiempirical dispersion correction scheme to standard DFT proposed by Grimme[21](DFT-D method) to study the adsorption of ClAlPc on the $SiO_2(100)$ surface. The DFT-D is dispersion corrections to standard Kohn–Sham density functional theory (DFT) and can be used in combination with standard or slightly modified

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(short-range) exchange–correlation functionals. A Periodic super cell of $SiO_2(100)$ surface was constructed using 304[SiO_2] units with a thickness of four layers and 30 Å vacuum regions between the slabs, which is large enough to avoid the interaction between periodic images. The supercell with cell dimension of 19.600 Å × 21.600 Å × 46.000 Å was used. The optimized $SiO_2(100)$ surface is shown in Fig. 1.

Here, the double-numeric quality basis set (DN) is adopted, the size of which is comparable to Gaussian 6-31G (d) basis set[22]. The core electrons were treated with all electrons. Generalized gradient-corrected (GGA) function by Perdew, Burke, and Ernzerhof (PBE) was employed for geometrical optimization with the Fermi smearing of 0.005 hartree (1 Ha=27.2114 eV) and global orbital cutoff of 4.5 Å adopted. The tolerances of the energy, gradient, and displacement convergences were 2×10-5 Ha, 4×10-3 Ha/Å-1and 5×10-3 Å, respectively.

RESULTS AND DISCUSSION
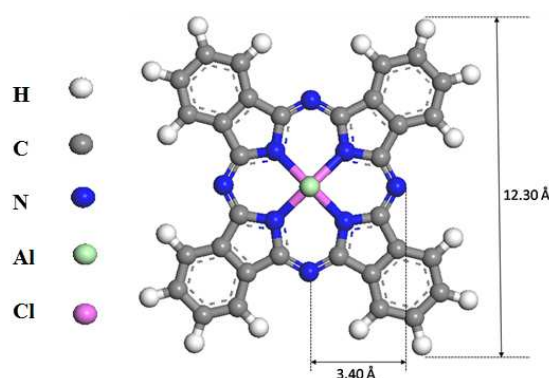
ADSORPTION MODES

Fig. 2: ClAlPc molecular structure and its dimensions

The optimized ClAlPc molecular structure is shown in Fig. 2, where the Al-Cl bond is out-of-plane with a length of 2.174 Å. As the Al atom is positively charged and Cl atom is negatively charged, the molecule has an electric dipole moment of 1.87 debye pointed from Cl to Al, which is quiet similar to previous publish[23,24].

In this work, the annealing dynamic simulation was adopted to study the possible orientation of ClAlPc on a SiO_2 (100) surface using the forcite module within Materials Studio. Two initial modes (1 and 2) for the ClAlPc standing on SiO_2 (100) are shown in Fig. 3.
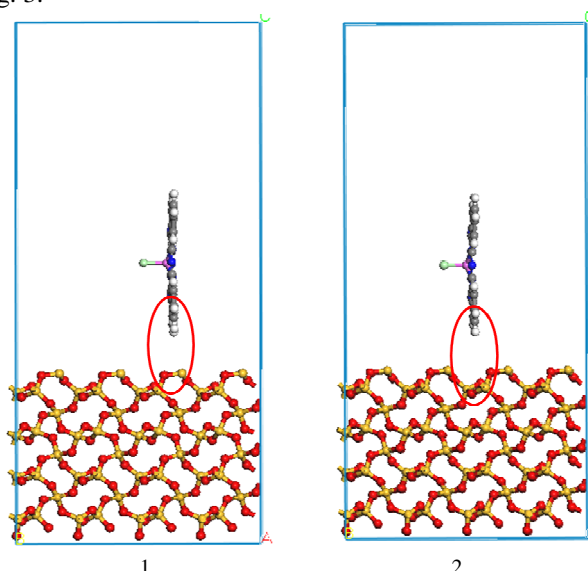

Fig. 3: Molecule ClAlPc adsorbed on a SiO_2 (100) substrate with Cl-up(a) and Cl-down(b) configurations respectively

CHARGE-DENSITY DIFFERENCE PLOT
To get a better understanding of the mechanism of the Cl-up and Cl-down configurations, we explored the variation of charge density at the molecule-substrate interface due to the adsorption. Here, a simple SiO_2 cluster was selected to illustrate the interfacial interaction between ClAlPc and $SiO_2(100)$ surface. Previous theoretical works has demonstrated the validity of using small SiO_2 clusters instead of the whole substrate in the simulation of the

electronic structures of molecule-substrate system[25].
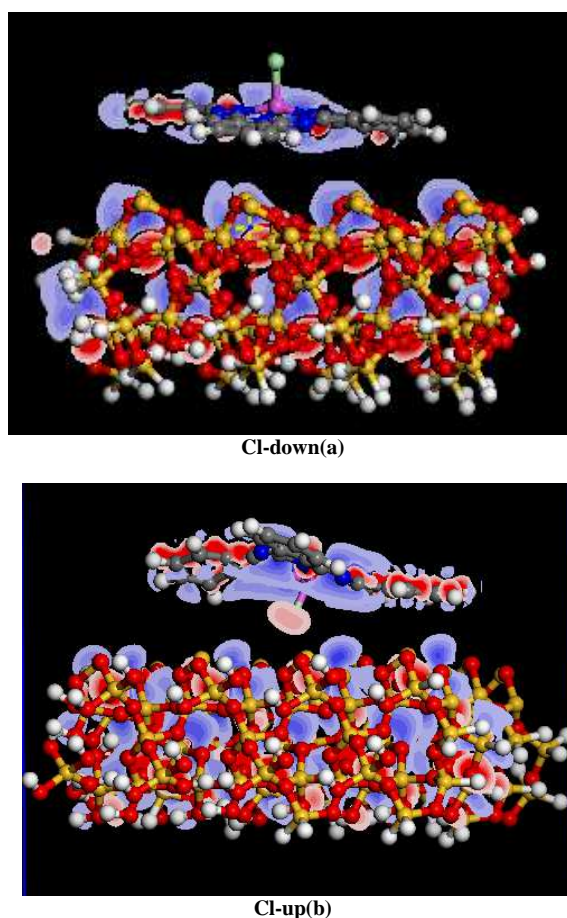

Cl-down(a)

Cl-up(b)

Fig. 4: Total charge-density difference plot for Cl-up and Cl-down adsorption configurations. Regions of electron depletion /accumulation are displayed in blue(+)/red(−) isosurface value: ±0.05 e/ Å³

Fig. 4 shows the charge density difference $\Delta\rho = \rho ClAlPc/ SiO_2(100) - \rho ClAlPc - \rho SiO_2(100)$ obtained with DFT-D method for the cluster models "Cl-up"and "Cl-down", where $\rho ClAlPc/ SiO_2(100)$, $\rho ClAlPc$ and $\rho SiO_2(100)$ are the charge densities of the full system, the isolated ClAlPc, and the SiO_2 substrate, respectively. In Fig. 4, the blue gray color indicates positive charge accumulation, while red color indicates the negative charge accumulation. In the case of Cl-down configuration, significant charge transfer can be detected between the Cl and $SiO_2(100)$ surface; the negative charge accumulation is visible at the Cl atom in Fig. 4a and the positive charges are distributed on the silicon atoms of SiO_2 surface. These results unequivocally demonstrate the strong attractive electrostatic interactions between the ClAlPc molecule and the SiO_2 substrate in the Cl-down adsorption mode. However, for the Cl-up configuration, the electrostatic repulsive interaction between the positively-charged benzene rings of ClAlPc and the similarly-charged silicon of substrate seems slightly larger than the molecule-substrate attractive interactions (Fig. 4b), which will provide a rationalization for the enlargement of ClAlPc-SiO_2 distance in Cl-up than that in Cl-down configuration.

In conclusion, the adsorption of ClAlPc on the $SiO_2(100)$ surface in the "Cl-down" configuration involves a strong interaction between the molecule and the substrate, while in the "Cl-up" the interaction between the ClAlPc and surface is weaker.

CONCLUSION

We have demonstrated the adoption mode of ClAlPc on the SiO_2 (100) surface by annealing dynamic simulation. Using the DFT-D calculation, we find a strong interaction between the molecule and the substrate in the Cl-down configuration. The results shown here exemplify the critical role of the electrostatic interaction dependent molecule-substrate adsorption mode, which can influence the potential application of the molecule as electronic device elements.

REFERENCES

[1] H Fukagawa; S Hosoumi; H Yamane; *S Kera.N Ueno. Physical Review B*, **2011**, 83(8), 085304.

[2] T Niu; C Zhou; J Zhang; S Zhong; H Cheng.W Chen. *The Journal of Physical Chemistry C*, **2012**, 116(21), 11565-11569.

[3] T Chao Niu; Y Li Huang; J Tao Sun; S Kera; N Ueno; *A Thye Shen Wee.W Chen. Applied Physics Letters,* **2011**, 99(14), 143114.

[4] A Gerlach; T Hosokai; S Duhm; S Kera; OT Hofmann; E Zojer; J Zegenhagen.F Schreiber. *Physical Review Letters*, **2011**, 106(15).156102.

[5] KM Burson; Y Wei; WG Cullen; MS Fuhrer.JE Reutt-Robey. *Nano Lett,* **2012**, 12(6), 2859-2864.

[6] H Wang; D Song; J Yang; B Yu; Y Geng.D Yan. *Applied Physics Letters,* **2007**, 90(25), 253510.

[7] Liqiang Li; Qingxin Tang; Hongxiang Li.W Hu. J. Phys. Chem. B, **2008**, 112, 10405-10410.

[8] L Wang; G Liu; F Zhu; F Pan.D Yan. *Applied Physics Letters,* **2008**, 93(17), 173303.

[9] L Huang; C Liu; X Qiao; H Tian; Y Geng.D Yan. *Advanced Materials*, **2011**, 23(30), 3455-3459.

[10] C Wang; H Dong; W Hu; Y Liu.D Zhu. *Chem Rev*, **2012**, 112(4), 2208-2267.

[11] YY Zhang; SX Du.HJ Gao. *Physical Review* B, **2011**, 84(12), 125446.

[12] A Mugarza; R Robles; C Krull; R Korytár; N Lorente.P Gambardella. *Physical Review B,* **2012**, 85(15), 155437.

[13] T Niu; M Zhou; J Zhang; Y Feng.W Chen. *The Journal of Physical Chemistry* C, **2013**, 117(2), 1013-1019.

[14] YL Huang; R Wang; TC Niu; S Kera; N Ueno; J Pflaum; AT Wee.W Chen. *Chem Commun (Camb)*, **2010**, 46(47), 9040-9042.

[15] L Li; W Hu; H Fuchs.L Chi. *Advanced Energy Materials,* **2011**, 1(2), 188-193.

[16] D Module. San, Diego, CA, **2003**.

[17] SL Mayo; BD Olafson.WAG III. J. *Phys. Chem.*, **1990**, 94, 8897-8909.

[18] JL Lenhart; DA Fischer; TL Chantawansri.JW Andzelm. *Langmuir,* **2012**, 28(44), 15713-15724.

[19] T Yakhanthip; S Jungsuttiwong; S Namuangruk; N Kungwan; V Promarak; T Sudyoadsuk.P *Kochpradist. J Comput Chem*, **2011**, 32(8), 1568-1576.

[20] S Jungsuttiwong; T Yakhanthip; Y Surakhot; J Khunchalee; T Sudyoadsuk; V Promarak; N Kungwan.S Namuangruk. J *Comput Chem,* **2012**, 33(17), 1517-1523.

[21] A Tkatchenko.M Scheffler. *Physical Review Letters,* **2009**, 102(7), 073005.

[22] S Grimme. J *Comput Chem,* **2006**, 27(15), 1787-1799.

[23] S Kera; H Yamane; H Honda; H Fukagawa; KK Okudaira.N Ueno. *Surface Science,* **2004**, 566-568, 571-578.

[24] Y Azuma; T Yokota; S Kera; M Aoki; KK Okudaira; Y Harada.N Ueno. *Thin Solid Films*, **1998**, 327, 303-307.

[25] R Sanchez-de-Armas; MA San-Miguel; J Oviedo; A Marquez.JF Sanz. *Phys Chem Chem Phys*, **2011**, 13(4), 1506-1514.