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Description of adenine and cytosine on Au(111) nano surface using different DFT functionals (PW91PW91, wB97XD, M06-2X, M06-L and CAM-B3LYP) in the framework of ONIOM scheme: Non-periodic calculations

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ABSTRACT

In this work, the adsorption of the adenine (AD) and cytosine (CY) on the Au(111) nano surface (AD@Au and CY@Au) have been examined in the framework of combined quantum mechanics/molecular mechanics (QM/MM) methodology using two-layer ONIOM method and different density functional theory (DFT) functionals in the absence of periodic boundary conditions (PBC). It was found by selecting an appropriate size for the Au surface, the results obtained using QM/MM method were in good agreement with those obtained via the periodic DFT calculations with the same functional. The calculated adsorption energies (E_{ad}) using M06-2X and M06-L functional were in good agreement with those, recently, obtained using periodic DFT calculations considering PBC and employing van der Waals (vdW) DFT functionals. The correlation diagram between the molecular orbitals of isolated deformed AD (AD-D) and CY (CY-D) and their molecular orbitals in AD@Au and CY@Au systems have also been investigated in this work.

1. Introduction

Adsorption of DNA bases on the surface of metals is essential to understand the nature of the interaction of entire DNA molecule with the hard substrates. This understanding is a fundamental concern in different subjects, such as the development of DNA microarray techniques [1], portable cost-effective DNA sequencing [2], targeted drug delivery [3] and formation of self-assembled superstructures [4,5]. For example, biochip technology is based on the immobilization of biological macromolecules on the surface of electronic devices [4]. The biochemical properties of the immobilized molecules can be influenced to a large extent by the interaction with the surface. Furthermore, the structure of DNA molecule on a hard substrate is extremely important to determine the ability of molecule to conduct charge in the set-ups relevant for nanotechnologies, because the electronic structure of DNA and charge transfer rates are extremely sensitive to the conformational of DNA on the metal surface [6–9]. The interaction of DNA bases on the Au surface is more interest to researchers compared to the other metals because gold is used as a commonly metal in biochip technology.

Piana et al. [4] studied the nature adsorption of four DNA bases on the Au(111) surface by performing DFT calculations, employing PW91PW91 exchange-correlation functional considering periodic boundary conditions (PBC). They found that the preferred orientations for the DNA bases were parallel to the surface and the interaction between the Au surface and the DNA bases were a physisorption except for adenine (AD), where a weak chemical bond between the amino group and a gold atom was formed. The adsorption of the cytosine (CY) on Au(111) surface was studied by Rosa et al. [10] using DFT periodic calculations, employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation, with the nonlocal van der Waals (vdW) DFT functional. They found that considering of dispersion interactions was crucial for the handling of this system so that increased the value of the adsorption energy and also affects the CY bonding geometry. They also observed a tilted geometry was always favorable relative to a parallel geometry, which is not accessible in standard DFT investigations. Rosa et al. [11] also used the same level of periodic DFT method to investigate several interfaces formed by the CY, AD, guanine (GU) and thymine (TY) with the Au(111) surface with the objectives of interpreting the adsorbate-substrate interaction mechanism and developing a classical force field for the related systems constituted of

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DNA oligomers on Au(111) surface. They concluded that the vdW effects are main determinants to attain a correct description of the computed interfaces, both qualitatively and quantitatively. In addition, they found charge sharing between the substrate and absorbate, the formation of hybrid orbitals and even bonding orbitals. Recently, Rosa et al. [12] studied the effect of vdW effect on the molecule-metal interfaces employing four different DFT functionals including vdW-DF [13], vdW-DF2 [14], C09-vdW-DF [15], and C09-vdW-DF2 [16] implemented in quantum-espresso package considering PBC. They found that there is no unique functional that is optimal for any system and the functionals designed to reduce the short-term repulsion between the adsorbate and substrate usually overestimate the adsorption energy and may even predict the wrong adsorption orientation. In addition, they showed that an accurate description of the substrate does not ensure an accurate evaluation of the adsorption energetics, while the electronic structure is less sensitive to the specific choice. According to the above references, the presence of vdW term in the DFT functional is crucial for the study of the interaction and configuration of the DNA base on the metal surface.

The first aim of this work is the study of the adsorption of AD and CY on the Au surface using QM/MM methodology in the framework of ONIOM method and comparison of the results with those obtained using periodic DFT calculations with different functionals reported in literature [4,10–12]. The question is that how much the calculated adsorption energies and orientations of the DNA bases on the Au nano surface, obtained in the absence of PBC and using QM/MM method, are comparable with those obtained in the presence of PBC using periodic DFT calculations. In the other words, the appropriate description of ONIOM method for studying of the adsorption of DNA bases on Au surface is investigated. The second aim is the evaluation of DFT functionals such as wB97XD [17], M06-2X [18], CAM-B3LYP [19] and M06-L [20] in prediction of the adsorption energies and orientations of the DNA bases on the Au surface in the scheme of ONIOM method and comparison them with the other theoretical results reported in literature [10,11]. Finally, the study of the change in the electronic structure of AD and CY due to the adsorption on the Au surface obtained using ONIOM method is the third aim of this work.

2. Computational details

In the present work, the QM/MM method in the ONIOM scheme has been used for studying the adsorption of the AD and CY on the Au(111) nano surface. The QM/MM method has been widely used for dealing with numerous complex systems in chemical phenomena [21,22]. It treats a relatively small localized region of the system at a high level of theory (QM) where the key chemical process takes place, while the remainder of the system can be sufficiently calculated using computationally efficient lower level methods (MM). For the calculations in this work, two-layer ONIOM method was used which is a subtractive QM/MM scheme developed by Morokuma et al. [23]. The “ONIOM” term is abbreviative of “our own *n*-layered integrated molecular orbital and molecular mechanics”. The nano-surface was modeled as a two-dimensional array consisting of 232 Au atoms with a hexagonal surface structure. The reason for selecting this size of the surface will be explained in the next section. To construct the Au surface, the unit cell of the Au(111) surface with cubic symmetry and the lattice constant of $a_{lattice} = 4.077$ Å for solid Au was optimized using the selected DFT functionals (PW91PW91, wB97XD, M06-2X, M06-L and CAM-B3LYP), separately employing LANL2DZ for the Au atoms. The lattice parameters of the unit cell after optimization were $a = b = c = 3.921$, 4.016, 3.959, 3.941, and 3.912 Å for CAM-B3LYP, M06-2X, M06-L wB97XD and PW91, respectively.

The surface cleavage was performed on the optimized unit cells to construct two-layer Au(111) supercells. Each supercell was re-optimized again using the ONIOM method so that the first and second layer were considered in the QM and MM regions, respectively and the Au atoms of the second layer was considered rigid during the optimization. The level of the theory selected for the QM part in the optimization of each supercell was the DFT functional which had been used for the optimization of its unit-cell and the universal force field (UFF) was applied for the MM region. Similarly, the structures of the isolated AD and CY were optimized in the gas phase using the selected DFT functionals and 6-311++G(d,p) basis set, separately.

The optimized AD and CY molecules were placed on the optimized surface at a certain distance in parallel orientation. The molecule and the Au layer below it were selected as QM region (high layer) and the second Au layer was considered in the MM region (low layer) (see Fig. 1). The DFT method was used for the QM region and the UFF was applied for the MM region. All of the Au atoms of the surface were considered rigid during the optimization process. The other reason for considering the rigid structure for the Au surface in the optimization of AD@Au and CY@Au is that the deformation of the metal surface due to the adsorption is very small and it can be ignored. For example, Kelly et al. have shown using periodic DFT calculations that the deformation of the Au surface due to the interaction with the AD dimers is very small (0.00–0.01 eV) [24]. Piana et al. [4] showed that the largest displacement of the Au atom due to the adsorption of DNA basis is <0.005 nm. The 6-311++G(d,p) basis set, for C, N, O and H atoms of AD and CY, and LANL2DZ for the Au atoms in the QM region were used for the ONIOM calculations. The calculated interaction and adsorption energies were corrected by the basis set superposition error (BSSE) [25]. All calculations were performed using Gaussian 09 quantum chemistry package [26].

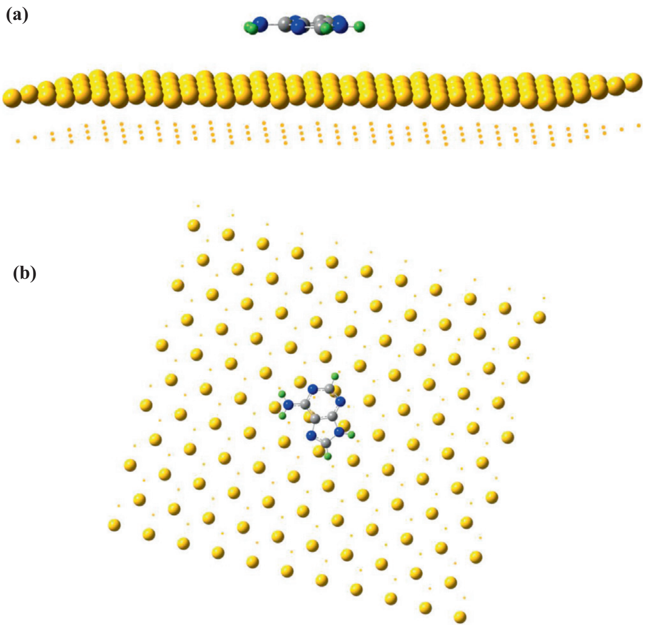

Fig. 1. The two-layer ONIOM model selected for the QM/MM calculations on the adsorption of AD on Au(111) surface (AD@Au). The selected Au atoms with dots are in the low layer and AD and Au atoms identified with big spheres are in the high layer.