

# Investigation of the Scanning Tunneling Microscopy Image, the Stacking Pattern, and the Bias-Voltage-Dependent Structural Instability of 1,10'-Phenanthroline Molecules Adsorbed on Au(111) in Terms of Electronic Structure Calculations

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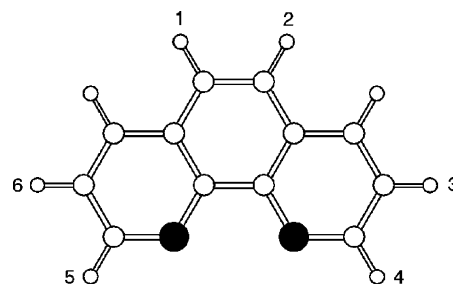
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A self-assembled monolayer of 1,10'-phenanthroline (phen) molecules on Au(111) was found to undergo a structural phase transition when the bias voltage is switched in scanning tunneling microscopy (STM) experiments (*Phys. Rev. Lett.* **1995**, 75, 2376; *Surf. Sci.* **1997**, 389, 19). The nature of two bright spots representing each phen molecule in the high-resolution STM images of phen molecules on Au(111) was identified by calculating the partial density plots for a monolayer of phen molecules adsorbed on Au(111) with tight-binding electronic structure calculations. The stacking pattern of chains of phen molecules on Au(111) was explained by studying the intermolecular interactions between phen molecules on the basis of first-principles electronic structure calculations for a phen dimer, (phen)<sub>2</sub>. The structural instability of phen molecule arrangement caused by the bias-voltage switch was probed by estimating the adsorbate–surface interaction energy with the point-charge approximation for Au(111).

## 1. Introduction

In electrochemical environments individual organic molecules at the solid–liquid interface adsorb onto the substrate surface and form a monolayer, which can be imaged by scanning tunneling microscopy (STM) as a function of the substrate potential.<sup>1–3</sup> The charge on the substrate surface can vary significantly by changing the bias voltage between the substrate and the reference electrode inserted in the liquid. The surface charge density of as high as  $\sim 0.1$  electron per atom is accessible. A change in the surface charge density can affect the stability of a molecular arrangement in an adsorbed monolayer, hence inducing a structural phase transition.<sup>4</sup> For heterocyclic molecules with nitrogen lone pairs, the adsorbate–surface interaction on Au(111) involving the nitrogen lone pair orbitals is strong at high substrate potentials.<sup>5</sup> When the surface is negatively charged, 2,2'-bipyridine (22BPY) on Au(111) adopts a flat orientation in which the two aromatic rings of 22BPY are parallel to the Au(111) surface. When the surface is positively charged, 22BPY adopts a vertical orientation in a coplanar cis configuration in which the two nitrogen atoms face the metal surface. In their STM studies of the monolayers of 1,10'-phenanthroline (phen) on Au(111), Tao and co-workers observed an order–disorder structural phase transition induced by a change in the surface charge.<sup>6,7</sup> Phen molecules self-assemble into polymer-like chains which can organize into either disordered or ordered phases depending on the substrate



**Figure 1.** Structure of phen. The small and large open circles represent the H and C atoms, respectively, and the filled circles the N atoms.

potential and the concentration of phen in the bulk solution. These chains are randomly oriented at low substrate potentials, but are aligned along one of the Au(111) lattice directions as the surface charge is raised beyond a critical value.

From the analysis of their high-resolution STM images, Tao and co-workers found that each phen molecule is represented by two bright spots and suggested that these bright spots are associated with the two nitrogen atoms of phen (Figure 1).<sup>7</sup> To a first approximation, the STM image of a sample is well described by the partial electron density plot  $\rho(r_0, e_f)$  of the sample surface.<sup>8–10</sup> These plots calculated using the extended Hückel tight binding (EHTB) electronic band structure method<sup>11</sup> have been indispensable in interpreting STM images of numerous organic and inorganic compounds.<sup>9,10</sup> In particular, calculations for hydrocarbons on graphite<sup>9,10</sup> showed that insulating molecules adsorbed on a metallic substrate are detected by STM for two reasons: the orbitals of the insulating molecules mix,

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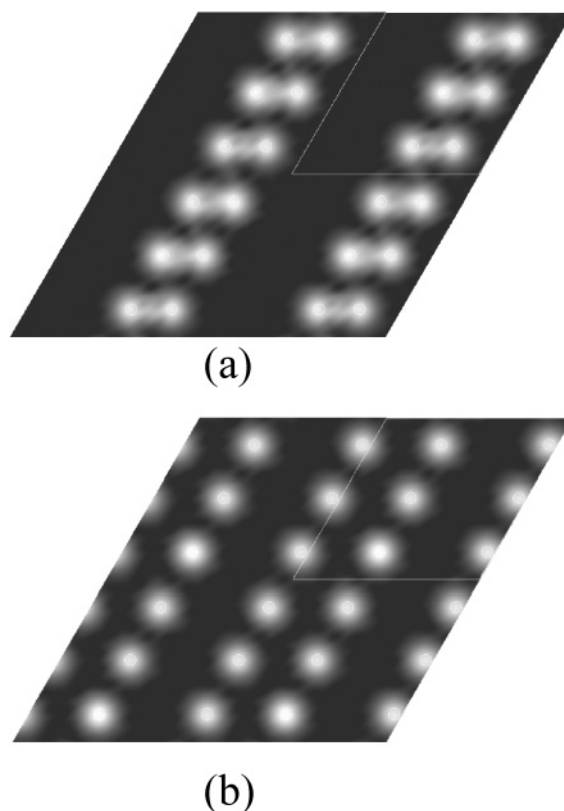
though slightly, into the energy region of the substrate's Fermi level, and the molecules are close to the tip. As the extent of the orbital mixing increases, the electron density of the adsorbed molecules in the associated  $\rho(r_0, e_f)$  plot increases, so the adsorbed molecules appear as bright spots in the corresponding STM images. It is often the topmost atoms of the adsorbed molecules closest to the tip that dominate the  $\rho(r_0, e_f)$  plot and hence are seen in the STM images.<sup>9,10</sup> If the phen molecules adsorbed on Au(111) stand vertically on the surface with the N atoms facing the surface, the two topmost hydrogen atoms of each phen (i.e., H1 and H2 in Figure 1) become closest to the tip. Then, it is expected that the two spots representing each phen in the STM image are associated with the two topmost hydrogen atoms rather than with the two N atoms that are far away from the tip.

The present work is aimed at understanding the nature of two bright spots representing each phen molecule in the high-resolution STM images of phen molecules on Au(111), the stacking pattern of chains of phen molecules on Au(111), and the structural instability of phen molecule arrangement caused by the bias-voltage switch. To achieve this objective, we simulate STM images of phen molecules adsorbed on Au(111) by calculating their partial density plots, study the binding energy of a phen dimer, (phen)<sub>2</sub>, on the basis of first-principles electronic structure calculations, and estimate the surface-charge dependence of the phen–Au(111) interaction with the point-charge approximation for the Au(111) surface.

## 2. Partial Density Plots and STM Images

To simulate the STM images of phen molecules adsorbed on Au(111), we calculated the partial density plots  $\rho(r_0, e_f)$  on the basis of the EHTB method for a monolayer of phen adsorbed on a slab of Au atoms consisting of three layers of Au atoms parallel to the Au(111) surface. A monolayer of phen molecules was constructed using the molecules stacked vertically on Au(111) with an interplanar distance of 3.4 Å (i.e., the van der Waals contact distance between two carbon atoms). We considered two vertical arrangements of phen molecules. In one arrangement the N atoms face the surface, and in the other arrangement the N atoms face away from the surface. The partial density plots were made on the plane lying 3.0 Å above the topmost atoms of the vertically adsorbed molecules (i.e.,  $r_0 = 3.0$  Å).

Figure 2a shows the partial density plot  $\rho(r_0, e_f)$  calculated for the case when the N atoms of the phen molecules face the Au(111) surface, i.e., when the H1 and H2 atoms are closest to the tip. The plot shows that each phen molecule is represented by the electron densities of the H1 and H2 atoms. The distance between the H1 and H2 atoms is about 2.14 Å,<sup>12</sup> which is consistent with the distance between the bright spots representing each phen molecule in the high-resolution STM images.<sup>7</sup> Figure 2b shows the partial density plot  $\rho(r_0, e_f)$  calculated for the case when the N atoms of phen molecules face away from the Au(111) surface, i.e., when the H4 and H5 atoms are closest to the tip. The plot shows that each phen molecule is represented by the electron densities of the H4 and H5 atoms, with no contribution from the N lone pair orbitals. The distance between the H4 and H5 atoms of phen is much longer than 2.14 Å, which is not consistent with the distance between the bright spots representing each phen molecule in the high-resolution STM images. Consequently, the bright spots in the STM images of the phen molecules adsorbed on Au(111) should be assigned to the H1 and H2 atoms of the phen molecules, which in turn



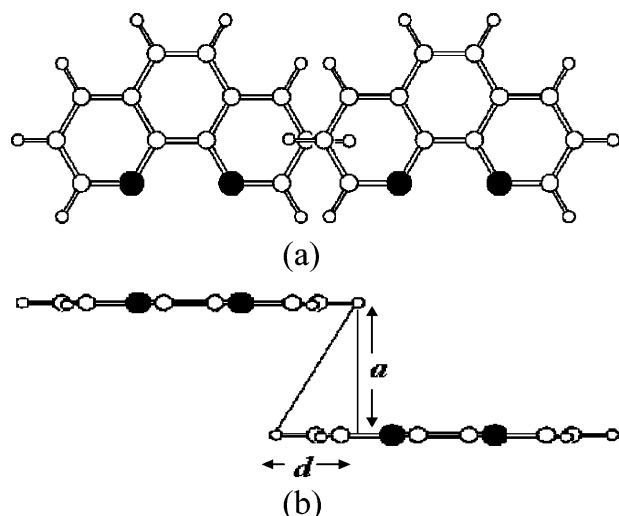
**Figure 2.**  $\rho(r_0, e_f)$  plots calculated for a monolayer of phen molecules adsorbed vertically on the Au(111) surface with  $r_0 = 3$  Å: (a) with the N atoms facing the surface and (b) with the N atoms facing away from the surface. The white circles in (a) refer to the H1 and H2 atom positions, and those in (b) the H4 and H5 atom positions. The contrast covers electron density variations in the  $(0.0\text{--}1.2) \times 10^{-8}$  electron  $\text{au}^{-3}$  in (a), and  $(0.0\text{--}1.9) \times 10^{-8}$  electron  $\text{au}^{-3}$  in (b).

means that the phen molecules are adsorbed on Au(111) through the nitrogen lone pair–Au interactions.

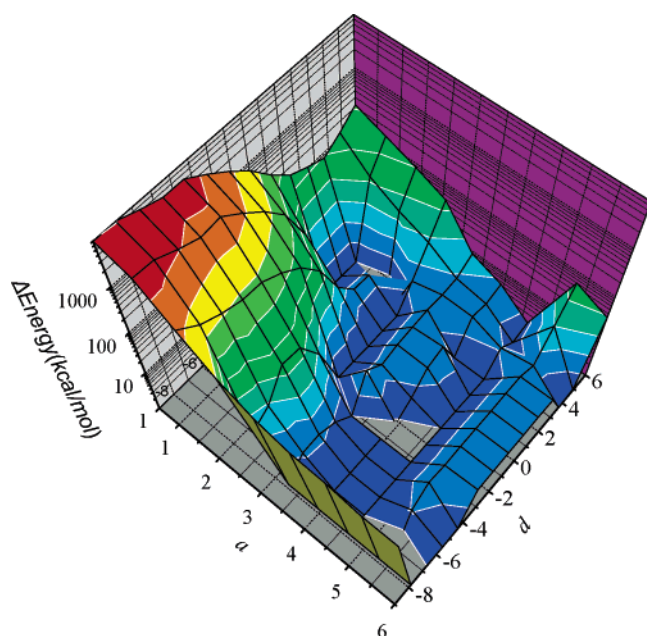
## 3. Interaction between Phen Molecules

To analyze the stacking pattern between phen molecules, we examined the intermolecular interaction between phen molecules by performing first-principles electronic structure calculations for a dimer, (phen)<sub>2</sub>, in which the two molecules are arranged parallel to each other as shown in Figure 3. The relative positions of the two phen molecules in this dimer are determined by the two geometrical parameters  $d$  and  $a$ .  $a$  is the intermolecular distance, and  $d$  measures the extent of overlap between two phen molecules in the top projection view of the dimer.  $d = 0$  signifies that the nearest terminal H atoms of two phen molecules just touch in the top projection view, while a negative  $d$  value indicates that the phen molecules overlap in the top projection view of (phen)<sub>2</sub>. For our electronic structure calculations we employed the hybrid density functional method at the level of B3LYP/6-311G(d,p) implemented in the Gaussian98 code.<sup>13</sup> The structure of phen was kept constant at the structure optimized with the same level of calculations.

The dimerization energy of (phen)<sub>2</sub>,  $\Delta E$ , defined as the energy of the dimer minus 2 times the energy of the monomer, was calculated as a function of the geometrical parameters  $d$  and  $a$ . The computational results for (phen)<sub>2</sub> are summarized in Supporting Information Table S1. The essential trends in the calculated dimerization energies are summarized as a three-dimensional surface plot in Figure 4. As a function of  $a$  and  $d$ , the energy surface of Figure 4 is quite flat in the range of  $a =$



**Figure 3.** Arrangement of two phen molecules in a dimer, (phen)<sub>2</sub>, where  $d$  is the overlap distance between two monomers and  $a$  is the interplanar distance between the monomers.



**Figure 4.** Three-dimensional surface plot of the binding energy  $\Delta E$  (kcal/mol) of (phen)<sub>2</sub> as a function of the geometrical parameters  $d$  and  $a$  (Å).

1.665–5.828 Å. The occurrence of such a large flat area is consistent with the observation that two kinds of kinks occur in the STM images of phen molecules on Au(111).<sup>7</sup> One is a sudden translation of a section of a chain in the direction perpendicular to the chain by about 2 Å without the orientation of the chain with respect to the underlying Au(111) lattice direction being changed. The other is a sudden bending of a chain by 120°, which allows the chain to follow an equivalent direction on the Au(111) lattice.

The dimerization energies  $\Delta E$  calculated for local minimum-energy structures of (phen)<sub>2</sub>, obtained under the constraint that the phen monomers are parallel to each other, are summarized in Table 1. Note that, in the region of  $a = 2.08$ –3.30 Å, there occur two minimum-energy structures with differing degrees of overlap between the two phen molecules, i.e., one with overlap ( $d < 0$ ) and the other without overlap ( $d > 0$ ). Only when the intermolecular spacing is close to the van der Waals sum of two carbon atoms (i.e., 3.4 Å), the two local minimum-energy structures are comparable in stability (Table 1).

**TABLE 1: Dimerization Energies  $\Delta E$  (kcal/mol) of the Dimer (phen)<sub>2</sub> at Local Minimum-Energy Structures under the Constraint that the Monomers Are Parallel to Each Other**

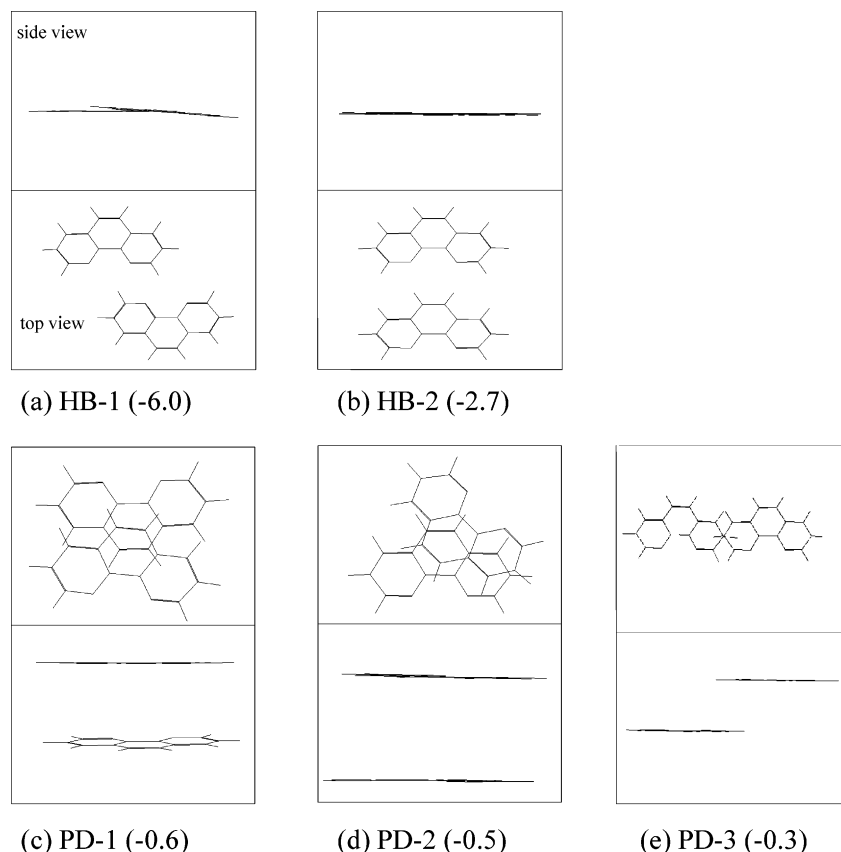
$a$ (Å)	$d$ (Å)	$\Delta E$	$a$ (Å)	$d$ (Å)	$\Delta E$
0.833	−5.622	3278.0	2.884	0.774	5.0
1.665	2.379	5.3		−5.922	8.2
	−5.622	229.6	3.330	0.579	4.9
2.081	1.720	5.2	3.746	−0.324	4.9
	−5.621	69.0	4.163	−1.621	4.8
2.498	1.378	5.0	4.995	−1.622	5.0
	−5.622	22.1	5.828	−0.619	5.1

The calculated dimerization energies  $\Delta E$  are all positive (i.e., the dimer formation is not energetically favorable) under the constraint that the monomers of (phen)<sub>2</sub> are parallel (Figure 4 and Table 1). Nevertheless, the energy surface plot of Figure 4 clearly indicates the regions of low-energy structures for (phen)<sub>2</sub>. Full geometry optimizations for (phen)<sub>2</sub> in the regions of low-energy structures lead to five local minimum-energy structures with negative  $\Delta E$  (i.e., the dimer formation is energetically favorable) shown in Figure 5. The two most stable structures of (phen)<sub>2</sub> have C–H···N hydrogen bonds between the two monomers. The remaining three dimer structures originate from the interplanar van der Waals interaction between the two monomers. Thus, the stacking of phen molecules on Au(111) observed in the STM images should be described in terms of the interaction between the nitrogen lone pair and gold atom as well as the interplanar van der Waals interactions.

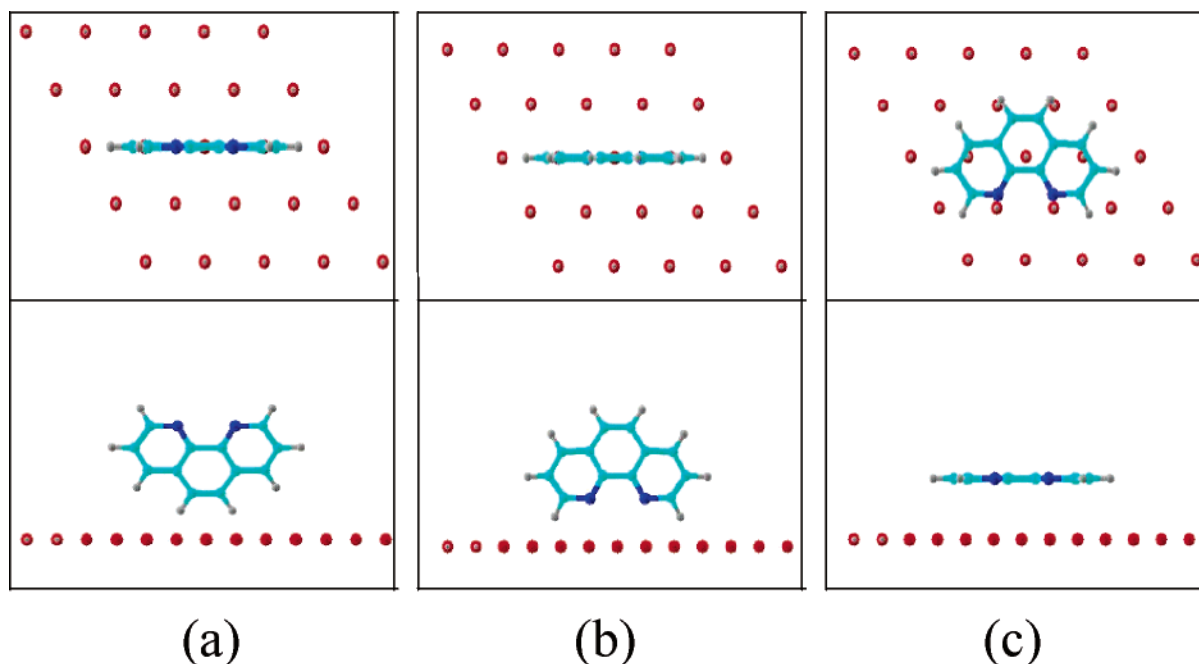
#### 4. Substrate–Adsorbate Interaction in Terms of the Point-Charge Approximation

To examine how the stability of the monolayer structure of phen molecules on Au(111) might be affected by the bias-voltage change, it is necessary to estimate the dependence of the phen–Au(111) interaction on the charge of the Au(111) surface induced by the bias voltage. To simulate the effect of the charge on Au(111), we represent the Au(111) surface by a single sheet of 25 point charges  $\delta$  located at the  $5 \times 5$  Au positions on the Au(111) surface (Figure 6) and then perform first-principles electronic structure calculations with the B3LYP hybrid method for a phen molecule plus the model surface. As shown in Figure 6, we considered three kinds of arrangements between a phen molecule and the model surface with  $\delta = +0.05$  and  $-0.05$ . For other  $\delta$  values examined, we obtain similar results. Thus, in the following, we discuss only those based on  $\delta = +0.05$  and  $-0.05$ .

The phen–Au(111) interaction energy  $\Delta E_s$  was calculated as a function of the distance  $r$  between the phen and the model surface, where the distance  $r$  is given from the surface to the closest atoms of phen. Results of our calculations are summarized in Figure 7, where the interaction energy  $\Delta E_s$  refers to the energy of a phen molecule interacting with the model surface minus that of an isolated phen. The  $\Delta E_s$  values, which are calculated to be positive for all cases examined, are meaningful only in their relative values. That is, the smaller the  $\Delta E_s$ , the more energetically favorable the adsorption. When a phen molecule is perpendicular to the Au(111) surface with the N atoms facing away from the surface, the negative surface charge is more favorable for the adsorption than the positive surface charge (Figure 7a). When a phen molecule is perpendicular to the Au(111) surface with the N atoms facing the surface, the positive surface charge is more favorable for the adsorption than the negative surface charge (Figure 7b). In the flat arrangement of a phen molecule, the positive surface charge is more favorable



**Figure 5.** Local minimum-energy structures of  $(\text{phen})_2$  optimized without the constraints at the level of B3LYP/6-311G(d,p). The acronyms HB and PD refer to the hydrogen-bonded and the parallel-displaced structures, respectively. The number in parentheses refers to the binding energy (kcal/mol) of the dimer.



**Figure 6.** Vertical and parallel arrangements of a phen molecule on the model surface made up of point charges located on the  $5 \times 5$  mesh points. observation<sup>6,7</sup> that a self-assembled monolayer of phen molecules on Au(111) undergoes a structural phase transition when the bias voltage is switched in STM experiments.

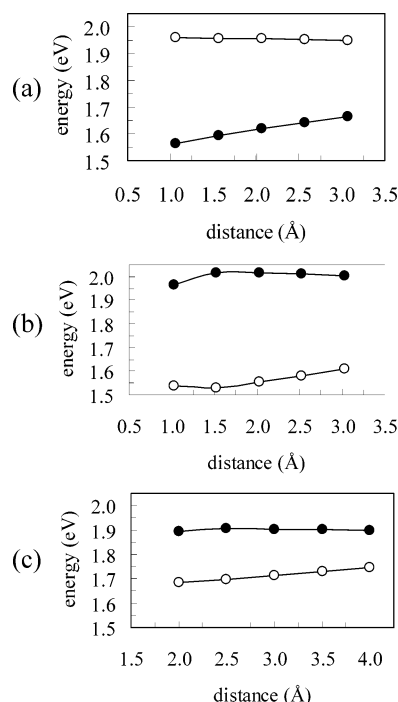
than the negative surface charge (Figure 7c). Nevertheless, comparison of parts a–c of Figure 7 indicates that, regardless of the sign of the surface charge, the perpendicular arrangements of phen molecules are more favorable than the flat arrangement on the Au(111) surface.

It is clear from our model calculations that the stability of the phen adsorption on Au(111) depends on the charge of the Au(111) surface. This result is consistent with the experimental

## 5. Concluding Remarks

Our partial density plots show that the bright spots of the high-resolution STM images of phen on a Au(111) surface





**Figure 7.** Phen–Au(111) interaction energy  $\Delta E_s$  calculated as a function of the distance between the model surface of point charges  $\delta$  and the closest atoms of phen to the surface: (a) a phen molecule is perpendicular with the N atoms facing away from the surface, (b) a phen molecule is perpendicular with the N atoms facing the surface, and (c) phen lies flat and parallel to the surface. The  $\Delta E_s$  values for  $\delta = -0.05$  are represented by filled circles, and those for  $\delta = +0.05$  by empty circles.

correspond to the hydrogen atoms H1 and H2 of phen, which means that in the monolayer of phen molecules adsorbed on Au(111) the molecules stand vertically with their nitrogen lone pairs interacting with the surface. The calculated binding energies of (phen)<sub>2</sub> explain the “slipping” in the chains of phen molecules observed in the high-resolution STM images of phen molecules on Au(111). The phen–Au(111) interaction energies indicate that the chain structures of phen molecules in the monolayer on Au(111) can become destabilized when the bias voltage is switched from a positive to a negative value because the switch of the bias voltage induces a reversal of the sign of the surface charge.

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**Supporting Information Available:** Table S1 of the dimerization energies of the dimer (phen)<sub>2</sub> calculated as a function of the intermolecular structural parameters  $a$  and  $d$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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