

Mechanism of two-dimensional superstructure formation of self-assembled adenine molecules

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One of the DNA bases, adenine molecules spontaneously form superstructures on the Cu(111) surface. Under an experimental condition, a characteristic chain structure, in which adenine molecules form two rows, *i.e.* 'double-chain', was observed, coexisting with a hexagonal structure, though the former is less favorable than the latter in energy. In this study, molecular arrangements of the 'double-chain' structure were analyzed. A series of inter-chain potential energy surface (PES) calculations revealed that there were two types of two-chain systems: one had both hexagonal and double-chain structures, and the other had only double-chain structures, as the stable structures. Furthermore, thermal stability of the double-chain structures was investigated by means of two-dimensional molecular dynamics (MD) simulation. The MD simulation revealed that some double-chain structures were stable even at 300 K and some transformed into a hexagonal structure. The former accounts for the coexistence of double-chain and hexagonal structures observed in the STM experiment, and the latter suggests that an energetically favorable hexagonal structure can be attained by way of a double-chain structure.

Key words: two-dimensional self-assembled structure, adenine, molecular dynamics simulation, potential energy surfaces

1. INTRODUCTION

Recently, many studies aiming at the fabrication of molecular devices by means of self-assembly phenomena of molecules on solid surfaces have been done actively. In such systems, molecules assemble through the non-covalent interactions, such as the hydrogen-bonding and electrostatic interactions [1-3].

The DNA base adenine molecules are known to assemble spontaneously on substrates through the hydrogen-bondings, and form the characteristic two-dimensional ordering structures, *i.e.* superstructures, reflecting the molecular shape. The self-assembled superstructures have been analyzed on various substrates, including gold [4], molybdenite [5], graphite [6-8] and copper [9-14]. Adenine self-assembly on Cu(111), which is a chemically less active surface, shows various two-dimensional ordering structures depending on the deposition conditions [9-13]. It has been reported in the previous high resolution Scanning Tunneling Microscopy (STM) studies that, although disordered chains emerged at a high deposition rate and a high surface coverage, a characteristic chain structure, in which adenine molecules form two rows, *i.e.* 'double-chain', was observed, coexisting with a hexagonal structure at a low deposition rate and a low surface coverage [11]. In the current system, the resultant ordered molecular arrangements are sustained mainly by intermolecular hydrogen-bonding energy. Therefore, the stabilization energy of the self-assembled

structure is highly correlated with the number of hydrogen-bondings. Thus, it is expected that a molecule in a hexagonal arrangement gains larger stabilization energy than that in a double-chain does. In this sense, the coexistence of two different structures is inexplicable. The analyses of the molecular arrangement of the double-chain structure and the process of its formation are necessary to understand the observation.

In this study, possible molecular arrangements in double-chain structures were systematically examined. For simplicity, an adenine molecule was treated as a rigid body. The potential energy surfaces (PESs) between various two adenine chains were calculated. Furthermore, in order to investigate the thermal stability of the double-chain structures that observed at local energy minima in the PESs calculation, molecular dynamics simulations of these model systems were performed.

2. Modeling of Adenine Chains systems

According to the preceding experimental observation [6-13], we assumed that a dimer is the basic unit of the superstructure of adenine. Based on the assumption, in this section, three possible single chains were selected after the analysis of stable dimer configurations, and then two-chain systems composed of two possible chains were examined.

At first, we calculated the stabilization energy of several dimers using *ab initio* method (MP2/6-311G**).

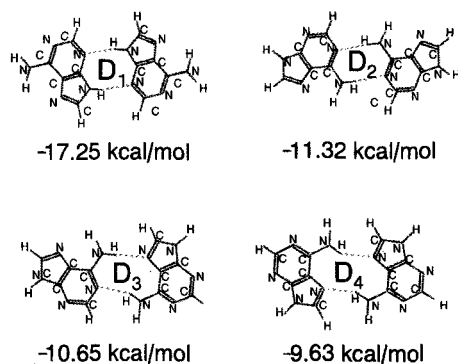


Fig. 1 The hydrogen bonding pattern of adenine dimers and the stabilization energies of the dimers.

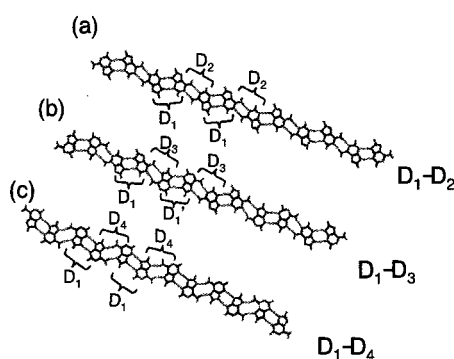


Fig. 2 Adenine molecular chains. (a) D_1 - D_2 , (b) D_1 - D_3 , (c) D_1 - D_4 chain. D_1 dimers are linked with D_2 , D_3 or D_4 types hydrogen-bonding in each chains.

In Fig. 1, four stable dimers and their stabilization energies are shown. Since the D_1 type hydrogen-bonded dimer structure showed the lowest energy, the dimer was adopted as the basic unit of stable adenine chains throughout the following analyses. Secondly, possible single chains composed of D_1 type dimers are considered. We assumed that, in a stable chain, the D_1 type dimers should connect with each other by two hydrogen-bondings (N-H...N): D_2 , D_3 and D_4 types hydrogen-bondings. As a result, three types of chains were selected: D_1 - D_2 , D_1 - D_3 and D_1 - D_4 chains (Fig. 2 (a)-(c)). It should be noted that, although the free, planar adenine molecule has a single mirror symmetry, and is achiral, it become chiral when it is adsorbed onto a surface in such a way that it loses its mirror plane symmetry. The basic unit dimer also exhibits chirality on the surface. Therefore, we should take into account the two-dimensional chirality for chain modeling. The D_1 - D_2 and D_1 - D_4 chains consist of a single two-dimensional enantiomer of the type D_1 dimer, while the D_1 - D_3 chain consists of both enantiomers, namely, one enantiomer alternates with its mirror image in the D_1 - D_3 chain. All these chains also show two-dimensional chirality themselves. Lastly, using these D_1 dimer based chains, 12 independent two-chain systems were examined in this work. The calculated two-chain systems can be classified into two groups: one

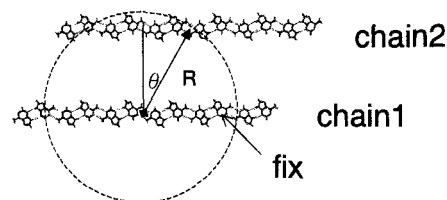


Fig. 3 Reaction coordinates (R , θ) for inter-chain energy potential energy surfaces.

consists of the same kind of single chains (HOCH) and the other consists of two different chains (HECH). HOCH can be further classified whether the two chains have same chirality (HOCH-S) (e.g., $D(1-2, 1-2)$; "1-2" denotes D_1 - D_2 chain.) or those have different one (HOCH-R) (e.g., $D(1-2, \underline{1-2})$). Here, the underline of $\underline{1-2}$ denotes that the D_1 - D_2 chain orients the opposite side to the surface.

3. COMPUTATIONAL DETAILS

As mentioned above, among the intermolecular interactions hydrogen-bonding interaction should play the most important role in determining molecular configuration on the C(111) surface. Our preliminary DFT calculation revealed that the energy between an adenine molecule and Cu(111) surface was about 2.3 kcal/mol, which was much less than the single hydrogen-bonding energy, 5.9 kcal/mol. In addition, it has been confirmed that the adenine molecules is lying flat with the molecular plane parallel to the Cu(111) surface. Therefore, for simplicity, we treated an adenine molecule as a two-dimensional rigid body. The all-atom Amber force field [15] was used to determine the intermolecular interaction. The partial charge of the adenine was determined by *ab initio* calculation at the MP2/6-311G** level after optimization of the geometry of an isolated adenine molecule at the HF/6-311G** level.

Calculation of Potential Energy Surface of Adenine Chains

The inter-chain potential energy is defined as

$$\Delta E = E_{total} - (E_{chain1} + E_{chain2}),$$

where E_{total} , E_{chain1} , and E_{chain2} are energies of the two chain system, chain 1, and chain 2, respectively. The inter-chain energies were calculated as a function of the distance R between centers of mass of each chain and the angle θ (see Fig. 3). The calculation was repeated from -90 to 90 degrees, at the interval of 0.5 degree for θ , from the smallest contact distance to 50 Å, at the interval of 0.05 Å for R .

Each single chain composed of six dimers was used for the calculations of potential energy surfaces and MD simulation.

Two-dimensional MD simulation

Several MD simulations of the two chain systems starting from double-chain structures obtained in the PESs as their stable configurations were carried out. The simulation was performed in the canonical ensemble (NVT) in a square box (210 Å \times 210 Å) with periodic boundary conditions. The cut off radius was as long as

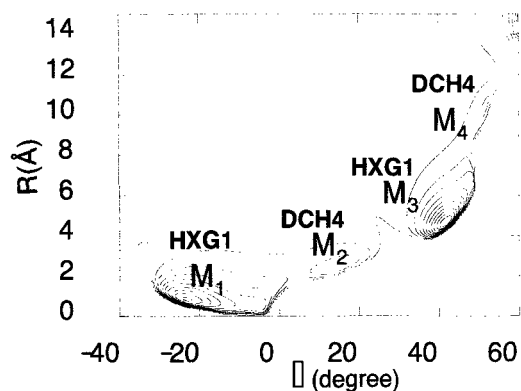


Fig. 4 Potential energy surface of D(1-4,1-4). The contour lines are drawn every 5 kcal/mol. DCH1 and HXG1 are double-chain and hexagonal structures defined in section 4. M_1 – M_4 indicate the positions of the potential minima of the map.

105 Å, and a switching function was applied to reduce an artifact caused by the cutoff. The equations of motion were integrated using the rRESPA algorithm with a time step of 2fs.[16]. 5ns-MD calculations were undertaken at 50 K, 100 K, 150 K, 200 K, 250 K, and 300 K, respectively.

4. RESULTS AND DISCUSSION

4.1 Potential Energy Surfaces of Adenine Molecular Systems

The PES of HOCH-S, D(1-4,1-4) and stable structures of the system (DCH4 and HXG1; “DCH” and “HXG” indicate double-chain and hexagonal structure, respectively.) are shown in Fig. 4 and Fig. 5(a) and (c), respectively. The patterns of hydrogen-bonding network formed at M_1 and M_2 are identical to those at M_3 and M_4 , respectively. In the DCH4 structure (M_2 , M_4 potential minima of the PES), the two single chains are placed in parallel with a minimal distance between them. This structure is defined as double-chain. On the other hand, the HXG1 structure at M_1 or M_3 is a stable structure in which the basic unit connects with each other through two hydrogen-bondings, this structure is defined as hexagonal. The stabilization energy of the structure at M_3 , -54.3 kcal/mol, is the lowest on the PES map. The HXG1 structure (see fig.5(b)), in which the basic unit dimers connect to the neighboring dimers with D_2 and D_4 types hydrogen-bondings, has p211 symmetry with the unit cell containing two molecules. This structure is identical to the model of the adenine superstructure on moribdenite proposed by Sowerby et al. [5]. In the HXG1 conformation, D_1 - D_4 type hydrogen-bonding pattern stretches along the axis *a* (dashed lines), and D_1 - D_2 type pattern extends along the axis *b* (dotted lines). Therefore, HXG1 is found in D(1-2, 1-2) and D(1-4, 1-4) chain systems. Figure 6 shows the PES of a HOCH-R, D(1-4, 1-4). The stabilization energy at M_1 is the lowest on the map, -23.2 kcal/mol. The structures at M_1 and at M_2 correspond to the double-chain structures DCH-R6 (Fig.5 (c)) and DCH-R7, respectively. Any hexagonal molecular arrangement was geometrically prohibited in the HOCH-R system. The DCH-R6' double-chain structure observed at M_3 corresponds to

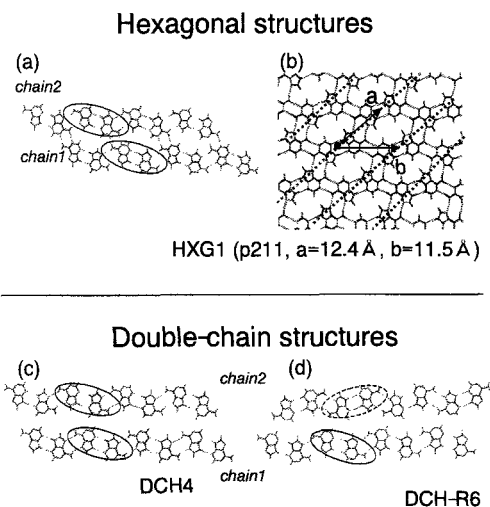


Fig. 5 Hexagonal and double-chain structures. A dimer in a solid ellipse is the basic unit of the chains (D_1 type dimer) and a dimer in a dashed ellipse is the mirror image of the basic unit.

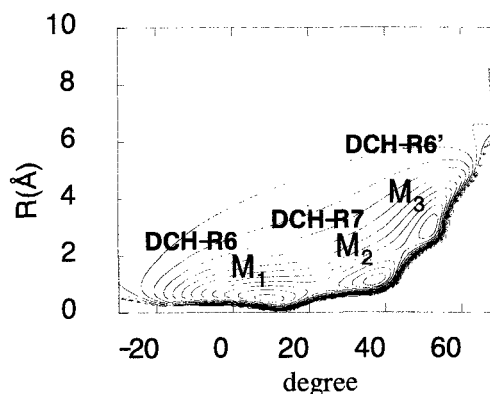


Fig. 6 Potential energy surface of D(1-4,1-4). The contour lines are drawn every 4 kcal/mol interval. DCH-R6 and DCH-R7 are double-chain structures defined in section 2. DCH-R6' is the mirror image of the DCH-R6. M_1 – M_3 indicate the positions of the potential minima of the map.

the mirror image of DCH-R6 at M_1 .

All observed structural patterns are summarized in Table 1. We found two novel hexagonal structures, HXG3 and HXG4, both of which have p211 symmetry with the unit cell containing two (HXG3) and four (HXG4) dimers, respectively. The HXG2 structure proposed by Furukawa et al.[10] has p2gg symmetry with the unit cell containing four molecules. This structure is two-dimensionally achiral while all other hexagonal and double-chain structures exhibit two-dimensional chirality. Table.1 revealed that PESs of the adenine two-chain system could be classified into two groups: one had both double-chain and hexagonal stable structures and the other had only double-chain stable structures. In the latter case, the hexagonal pattern of the hydrogen-bonding network is geometrically prohibited.

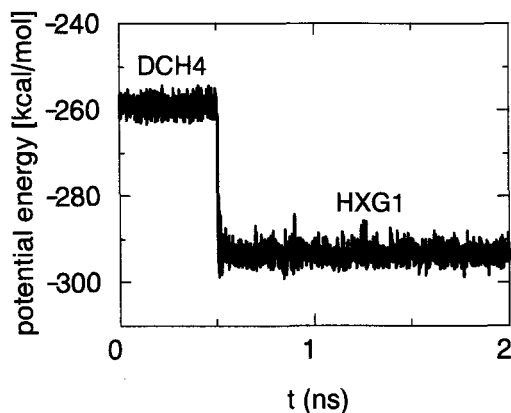


Fig. 7 The time change of the potential energy of the double-chain structure DCH1 of the D(1-4,1-4) at 150 K

4.2 2-dimensional MD simulation of adenine double-chain

In order to assess the thermal stability of the double-chain structures that showed local stability in the PESs map, two-dimensional MD simulations were performed at each temperature. In the HOCH-R, the double-chain structures at the deepest well of each PES, *e.g.* DCH-R6, held their molecular arrangements at 300K, and all metastable double-chains transformed to the most stable ones at lower temperature than 300K. The several double-chain structures of HECH broke into small clusters at 300 K, because their stabilization energy is much smaller than the kinetic energy at 300K. The double-chain structures of HOCH-S, *e.g.* DCH4 and those several of HECH spontaneously transformed into hexagonal structures. It is expected from Fig. 4 that in the D(1-4, 1-4) chain system, the structure at M_2 will not transform to the HXG1 at M_3 but the HXG1 at M_1 , because the potential energy barrier between M_2 and M_1 (about 15 kcal/mol) is lower than that of between M_2 and M_3 (about 20 kcal/mol), albeit the fact that the stabilization energy of structure at M_3 is lowest in the system.

Figure 7 shows the time change of the potential energy of the double-chain structure DCH4 of the D(1-4, 1-4). The discontinuous change in the plot confirms that the double-chain structure (DCH4) transformed into the hexagonal structure HXG1. The observation that there are double-chain structures that maintain their molecular arrangements even at 300 K explains the coexistence of a double-chain and a hexagonal structure observed in the STM experiment. Furthermore, our observation suggested that the hexagonal structure was attained by way of a transient double-chain structure.

5. ACKNOWLEDGMENT

This work was partly supported by NAREGI Nanoscience Project, Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Table. 1 Adenine chains systems and their stable structures obtained from PESs calculations. "x" indicates that the chains system has no hexagonal structures in its potential energy map.

		System	Double-chain	Hexagonal
HOCH	HOCH-S	D(1-2,1-2)	DCH1	HXG1
		D(1-3,1-3)	DCH2 DCH3	HXG2 HXG3
		D(1-4,1-4)	DCH4	HXG1
	HOCH-R	D(1-2,1-2)	DCH-R1 DCH-R2	x
		D(1-3,1-3)	DCH-R3 DCH-R4 DCH-R5	x
		D(1-4,1-4)	DCH-R6 DCH-R7	x
HECH	D(1-2,1-3)	DCH-X7	HXG4	
	D(1-2,1-3)	DCH-X3 DCH-X4	x	
	D(1-2,1-4)	DCH-X1 DCH-X2	x	
	D(1-2,1-4)	DCH-X8	HXG3	
	D(1-3,1-4)	DCH-X5 DCH-X6	x	
	D(1-3,1-4)	DCH-X9	HXG4	

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(Received October 13, 2003; Accepted March 17, 2004)