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Scanning Tunneling Microscopy on Ordered Self-Assemblies of Cyclodextrin Inclusion Complexes Formed by Substrate-Induced Two-Dimensional Crystal Growth

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Cyclodextrin (CyD) inclusion complexes with water and methanol, both of which had been known to form the cage-type crystal structure in the three dimensional crystal growth mode, were observed to form new self-assembled structures on highly oriented pyrolytic graphite (HOPG) and MoS_2 surfaces. By removing the surface CyD molecular layers using the atom manipulation technique of scanning tunneling microscopy (STM), ordered molecular stacking of the inner layers was observed. The surface of the observed CyD layers was markedly flat, indicating a stronger interaction between CyDs in each layer compared to that between the adjacent CyD layers, which is possibly related to the two-dimensional crystal growth mode induced by the anisotropic hydrogen bonding interaction between CyDs. On MoS_2, CyD has threefold symmetric lattice matching commensurate with the structure of S atoms, which is considered to affect the ordering of the self-assemblies. In fact, numerous defects are observed in the surface layer.

KEYWORDS: STM, self-assemble, cyclodextrin inclusion complex, atom manipulation, crystal growth, catalysis

1. Introduction

Studies on the microscopic molecular arrangements induced by self-assembled ordering have been attracting considerable attention because of their importance from both fundamental and practical points of view.[1–8] Interactions between molecules are reflected on the ordering of self-assembled structures; thus analysis of the structures of the assemblies is extremely important to the development of nanoscience technology in order to realize desired materials. In line with the development of the scanning tunneling microscopy (STM), direct observation of self-assembled molecules has been a recent research trend. However, the analysis by STM has been mainly conducted on molecules exhibiting van der Waals interaction; thus studies on molecules exhibiting anisotropic interaction are lacking.[1–6]

Cyclodextrins (CyDs) are torus-shaped cyclic oligosaccharides consisting of six to nine glucose units linked by a (1-4) glucosidic bond (Fig. 1).[7,8] From the structure of the hydroxyl groups existing on both sides of the cavity, CyD is trapezoidal as shown schematically in Fig. 1, and CyDs show anisotropic interaction due to hydrogen bonding. The hydroxyl groups on each side are called primary and secondary hydroxyl groups. CyD is hydrophilic outside, but hydrophobic inside. From this characteristic, CyDs are soluble in water and they easily form inclusion complexes with guest molecules. Furthermore, they show selective catalysis in the reactions with various organic materials, and are expected to play an important role in the field of artificial enzymes and bio-sensor devices. Therefore, studies on the self-assembled structures of CyDs are necessary not only for a fundamental understanding of the anisotropic molecular interaction, but also for making use of the high potential of CyDs.

Recently, α-and β-CyD-H_2O complexes on highly oriented pyrolytic graphite (HOPG) were directly observed by STM,[9] and they were found to exhibit arrangements different from that expected from the crystal structures determined by the X-ray diffraction method. The new structures were considered to be caused by the difference in growth mechanism; CyD crystals are grown in the three-dimensional mode generally, but on the HOPG surface, CyDs are self-assembled in the two-dimensional growth mode. If the CyDs are arranged in the two-dimensional growth mode, it becomes possible to understand their anisotropic interaction more easily, and the growth and control techniques of ordered CyDs can be realized.

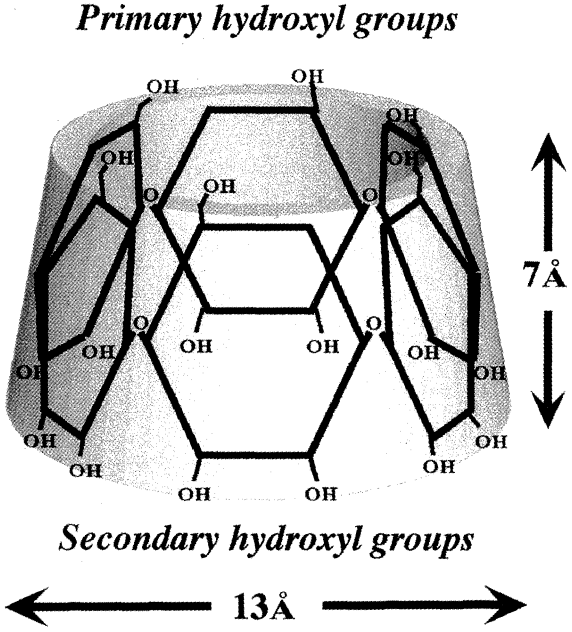

Fig. 1. Schematic model of α-cyclodextrin. Cavity diameter is 0.45 nm, and its depth is 0.7 nm. The CyD outer diameter is around 1.4 nm.

In order to understand the characteristics of self-assembled ordering of CyD molecules on HOPG, self-assembled CyD

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structures were analyzed by using STM on an atomic scale. We first compare the structures of α-CyD-H_2O and α-CyD-CH_3OH complexes on HOPG, both of which have the same crystal structure according to X-ray diffraction analysis. Then, we present the results of STM observation of the inner layers of CyD thin films performed by removing the CyD surface layers using the atom manipulation technique of STM. Finally, structural differences observed in the α-CyD-CH_3OH complexes on HOPG and MoS_2 will be discussed to study the interaction between CyDs and the substrates.

2. Experimental

Specimens were prepared by adding aqueous solutions of α-CyD and guest compounds dropwise onto a freshly cleaved HOPG or MoS_2 surface. For the study of the α-CyD-H_2O complex, 1 mM α-CyD solution was added dropwise. Two water molecules are automatically included into the cavity of α-CyDs. On the other hand, for the study of the α-CyD-CH_3OH complex, an aqueous solution containing 1 mM α-CyD-CH_3OH complex was added dropwise onto the substrates. After drying step samples, STM observations were performed in air at room temperature using a PtIr tip. All images were taken by the constant height mode. For the analysis of inner structures, surface CyD layers were removed by applying pulse voltages onto the surface using the STM tip.

3. Result and Discussion

3.1 Self-assembled α-CyD-H_2O and α-CyD-CH_3OH complexes on HOPG

Figures 2(a) shows the STM image of α-CyD inclusion complexes with H_2O ($V_t = 30$ mV, $I_s = 0.63$ nA). The crystal structure of the α-CyD inclusion complexes with H_2O is known to form the cage-type structure.[9] The crystal structures of the CyD inclusion complexes determined by X-ray diffraction analysis are schematically shown in Fig. 3 ((a) three-dimensional view, (b) *a*-*c* plane, (c) *a*-*b* plane, (d) *b*-*c* plane). The crystal data are $a = 1.4856$, $b = 3.3991$, $c = 0.9517$ nm for α-CyD-H_2O complex, and $a = 1.394$, $b = 3.683$, $c = 0.947$ nm for α-CyD-CH_3OH complex.[10,11] As reported previously,[9] the observed structure of the α-CyD-H_2O molecules on HOPG surface differs, for example, in molecular orientation and distance, from the surface structures expected from the cage-type crystal structure.

In order to confirm the observed difference, STM measurement was performed on the α-CyD inclusion complex with CH_3OH molecules. According to the results of X-ray diffraction analysis, the α-CyD-CH_3OH complex also forms the cage-type crystal structure shown in Fig. 3 for the α-CyD-H_2O complex.[11] Figure 2(b) shows an STM image of α-CyD-CH_3OH on HOPG ($V_t = 30$ mV, $I_s = 1$ nA). As expected from the comparison between Fig. 2(b) and Fig. 3, α-CyD-CH_3OH formed a structure similar to α-CyD-H_2O, and the arrangement of the CyDs observed in the STM images is clearly different from that on the surface of the cage-type structure.

Experimentally, the surface of the self-assembled CyD structures was found to be markedly flat, which strongly suggests that CyDs grew in the two-dimensional mode on HOPG. In general, CyD crystals, structures of which have been determined by X-ray diffraction analysis, are obtained by the three-dimensional growth mode. A supersaturated aqueous

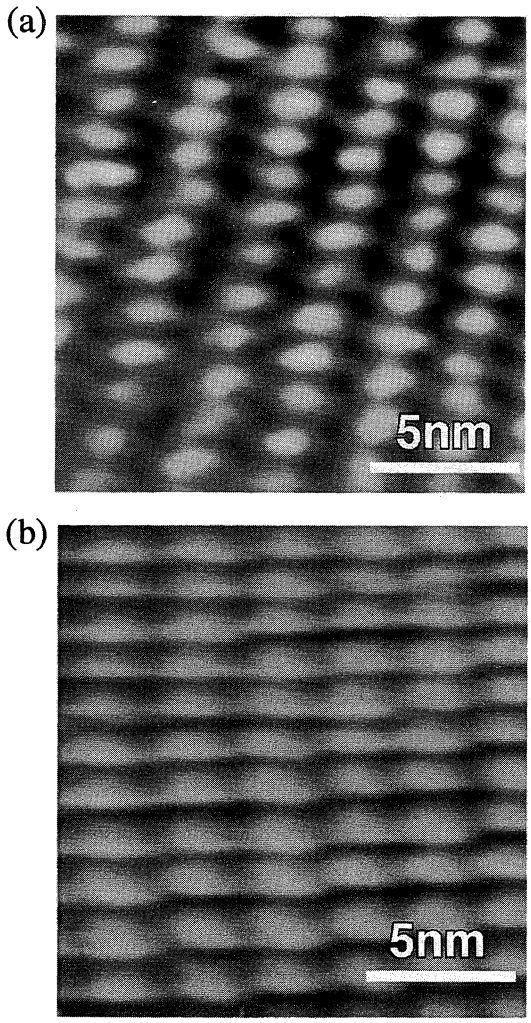

Fig. 2. STM images obtained on HOPG for the self-assembled complexes of (a) α-CyD-H_2O ($V_t = 30$ mV, $I_s = 0.6$ nA) and (b)α-CyD-CH_3OH ($V_t = 30$ mV, $I_s = 1$ nA).

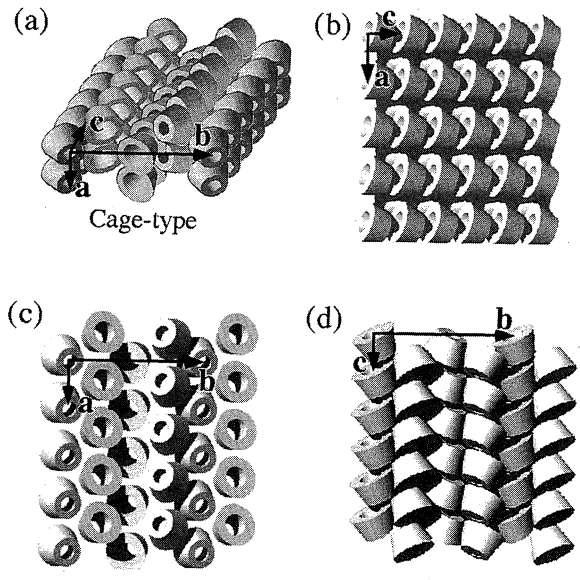

Fig. 3. Schematic of the cage-type structure determined by the X-ray diffraction method. (a) three-dimensional view, (b) *a*-*c* plane, (c) *a*-*b* plane, and (d) *b*-*c* plane.

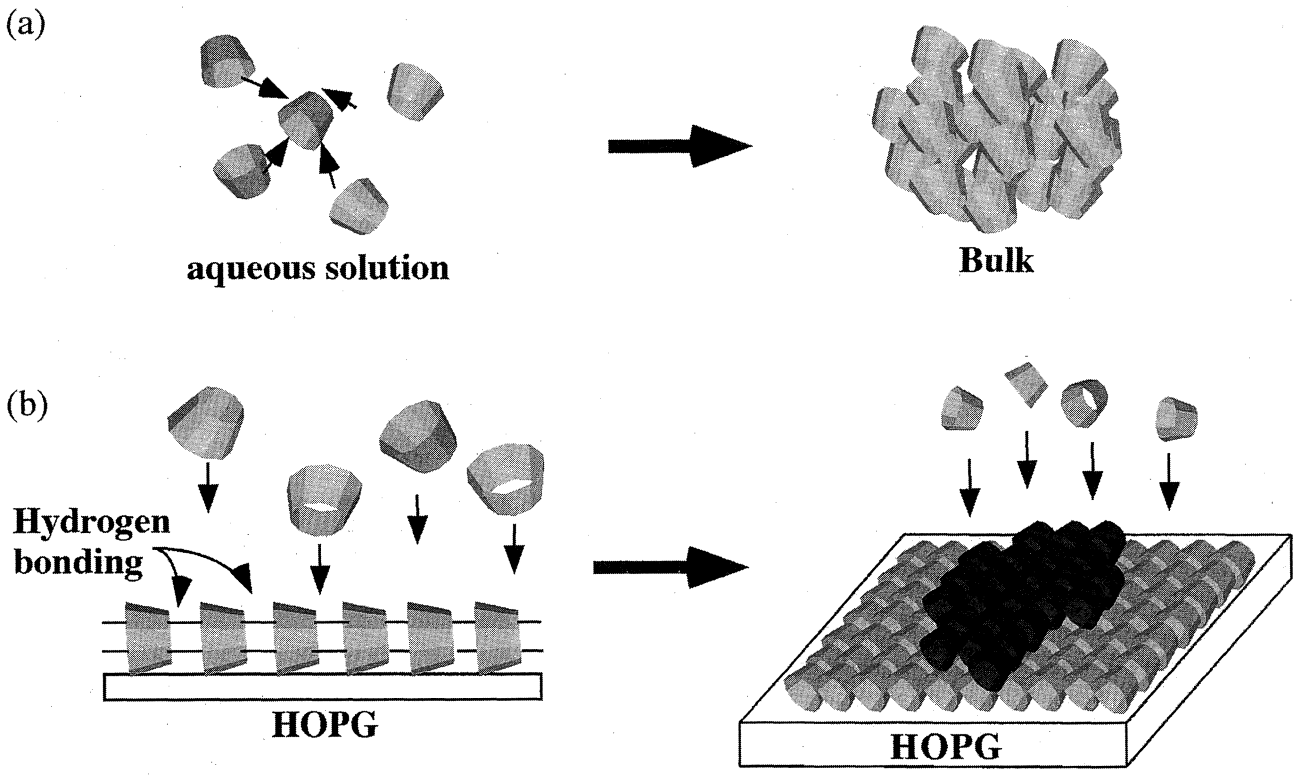

Fig. 4. Schematic models of the crystal growth modes. (a) Three dimensional and (b) two dimensional.

solution containing CyD inclusion complexes is cooled and crystals grow from the seeds as shown in Fig. 4(a). However, since samples whose structures are shown in Fig. 3 were prepared by the dropwise addition of an aqueous solution of low-density CyD inclusion complexes, single CyD molecules are expected to interact with the HOPG surface first. Concerning the conformation of the CyD molecules on HOPG, they are preferably lying on the surface with their apolar outer wall on the apolar graphite substrate. CyDs interact with each other through hydrogen bonding, and tend to form a linear chain. Since kink sites are the highest coordination sites, CyDs are mostly stabilized at kink sites, which also results in the two-dimensional growth mode as shown in Fig. 4(b). Interaction between CyDs and the HOPG surface will be discussed in detail in §3.3.

3.2 *Observation of CyDs in inner layers using the atom manipulation technique*

In order to confirm the ordering of the inner layers, we tried to remove the surface CyD layers by using the atom manipulation technique. Namely, a pulse voltage of 10 V was applied to the surface by the STM tip during STM measurement. After the modification, STM observations were performed over the same surface to analyze the structures of the CyD inclusion complexes in the inner layers.

Figure 5 shows an example of an STM image of the α-CyD-CH_3OH complex acquired after applying a pulse voltage of 10 V. As shown in Fig. 5(a), a hole is made on the surface by the treatment. The cross section along line A-B in Fig. 5(a) is shown in Fig. 5(b), The height of the step is 1.3 nm, which is close to the diameter of a single CyD, 1.4 nm. Figure 5(c) shows the magnified image of the squared area in Fig. 5(a). Since the arrangement is slightly disordered around the step edge, it is difficult to compare the positional relationship of CyDs on the two terraces. However, CyDs are clearly ordered on both terraces. In addition, the observed surface layers are extremely flat even in the hole made by STM, which indicates the existence of a stronger interaction between CyDs in each layer compared to that between two adjacent CyD layers. The observed result supports the mechanism that the ordering of the self-assembled structure is formed in the two-dimensional growth mode as discussed in §3.1.

3.3 *Comparison of self-assembled α-CyD-H_2O complexes on HOPG and MoS_2*

Next, in order to study the effect of the interaction between CyDs and the substrate, we performed STM observations by changing the substrate from HOPG to MoS_2. Figure 6 shows an STM image of α-CyD-H_2O complexes on MoS_2 ($V_t = -600$ mV, $I_s = 0.8$ nA). Since MoS_2 is semiconductive, a higher bias voltage was necessary to acquire the images. The observed arrangement is similar to that of α-CyD-H_2O complexes on HOPG shown in Fig. 2(a). However, there numerous defects are observed on the surface, such as mis-orientation and absence of CyD molecules. Since the molecules and the formation process used were the same, comparison of the STM images suggests the effect of CyD-substrate interaction on surface morphology.

Figure 7 shows the positional relationship between α-CyD and the HOPG and MoS_2 substrates. As shown in Fig. 7(a), there exist many similar stable positions for α-CyD on HOPG surface; therefore, a small degree of sliding of α-CyD will lead to the creation of another symmetric configuration on HOPG, indicating the instability of α-CyD on this substrate. Therefore, CyD layers are expected to be formed with less defect introduction. In contrast, on the MoS_2 substrate surface,

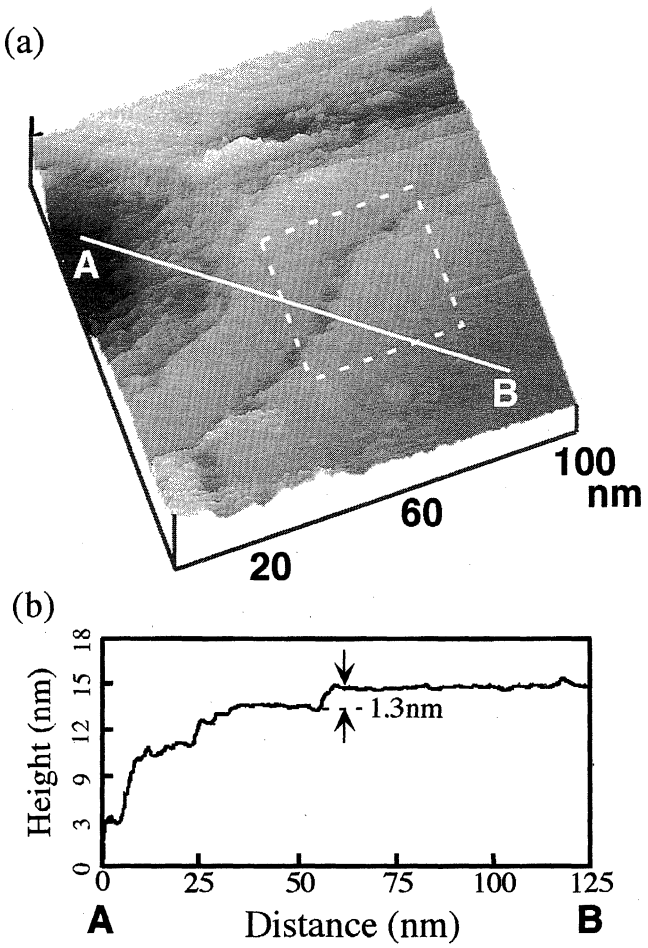

Fig. 5. (a) STM image of the surface of α-CyD-CH_3OH (V_s = 30 mV, I_t = 0.63 nA) complexes on HOPG with a hole made by applying 10 V with STM tip and (b) cross section along line A-B in (a). (c) Magnification of the squared area in (a).

α-CyD has threefold symmetric lattice matching commensurate with the structure of S atoms (Fig. 7(b)), and ionic interaction between hydroxyls in CyD molecules and S atoms in the surface layer of MoS_2 is expected to stabilize CyDs on this surface. Therefore, it is difficult to achieve an adjacent stable conformation. From these results, the arrangement of α-CyD on MoS_2 must be strongly affected by the interaction with

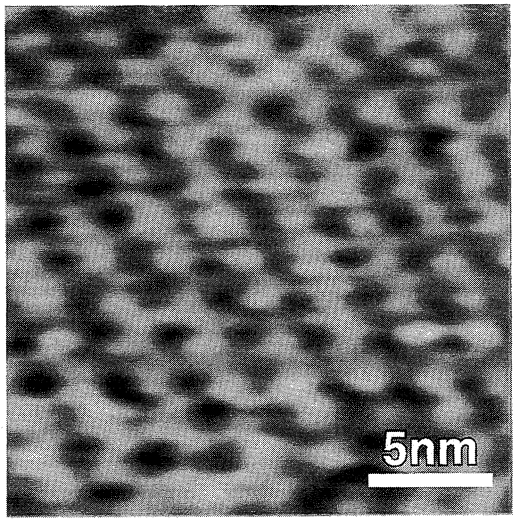

Fig. 6. STM image of the α-CyD-H_2O complexes on MoS_2 (V_s = −600 mV, I_t = 0.8 nA).

the substrate. Several possible structures caused by the lattice matching between CyDs and MoS_2 are shown in Figs. 7(c) and 7(d) ((c) head-to-head, (d) head-to-tail).[11] In consideration of the structures shown in Figs. 7(c) and 7(d), CyDs are thought to form defects on the MoS_2 surface in the first layer, such as misorientation and disordering of molecules, which will affect surface morphology, as observed.

When CyD-substrate interaction is well controlled, substrate-induced control of CyD arrangement, a kind of epitaxial growth in a broad sense, may be possible. CyD-CyD and CyD-substrate interactions can also be controlled by changing the guest compounds.

3.4 Electronic structure of α-CyD

For further study on CyD-CyD interaction and its applications, information on the electronic structures of self-assembled CyDs is necessary. As an example, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) calculated for a α-CyD with the same conformation as the α-CyD-H_2O complex are shown in Fig. 8 ((a) HOMO, (b) LUMO). Here, HOMO and LUMO are localized as shown in Fig. 8; however, the observed electronic structure is rather metallic, and bias dependence of the STM image is unclear. The obtained results suggest that CyDs in the assembled structures have an electronic structure different from that expected from a single molecule. In order to discuss the electronic structures of CyDs in the self-assembled structures, further analysis is under way.

4. Conclusion

We performed STM observations of the self-assembled CyD inclusion complexes on HOPG and MoS_2, and found that their arrangements were different from that expected from the crystal structure determined by X-ray diffraction analysis. By removing the surface CyD molecular layers using the atom manipulation technique of STM, ordering of the molecules in the inner layers was observed. From the analysis based on the observed STM images, ordering of the self-assembled structures on HOPG and MoS_2 surfaces was concluded to take place in the two-dimensional growth mode. On

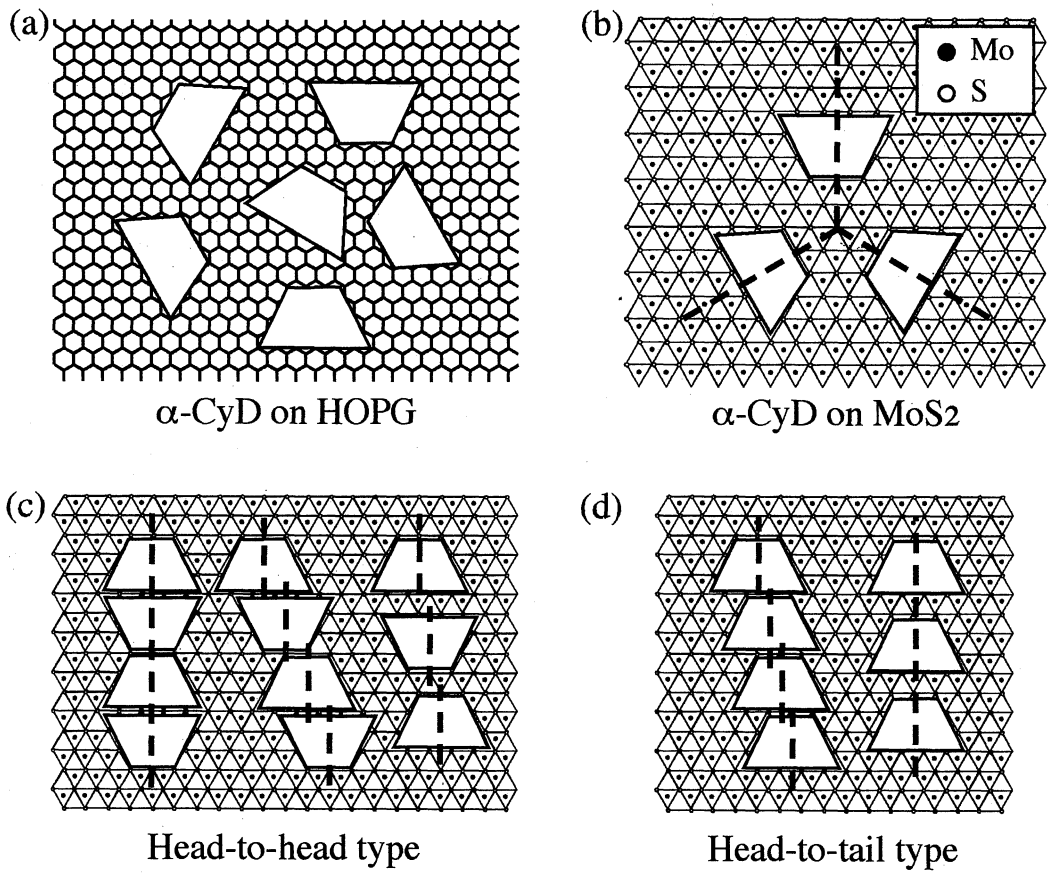

Fig. 7. Schematics of the lattice matching of α-CyDs on (a) HOPG and (b) MoS_2. Ordering of α-CyDs with conformations (c) head-to-head type, and (d) head-to-tail type.

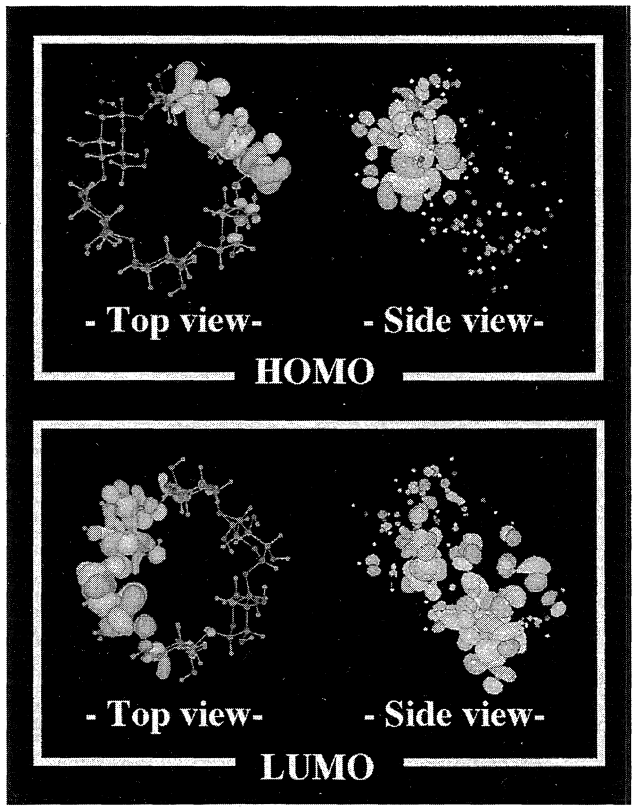

Fig. 8. Electronic structures of (a) HOMO and (b) LUMO calculated for CyD with the same conformation as the α-CyD-H_2O structure.

MoS_2 CyD has an threefold symmetric lattice matching commensurate with the structure of S atoms, which strongly affected the ordering of self-assemblies. Moreover, numerous deffects are observed in the suface layer.

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