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Effect of the Dipole-Dipole Interaction on the Self-Assembly of Cyclodextrin Inclusion Complexes

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We performed scanning tunneling microscopy (STM) observations on self-assembled α-cyclodextrin (CyD) inclusion complexes on HOPG for the guest compounds of (1) H_2O, (2) MeOH (Methanol) and (3) *p*-NP (*p*-nitrophenol). The observed structures of α-CyD-H_2O and α-MeOH complexes were channel-like with twofold symmetry, however, α-CyD-*p*-NP showed a structure different from that of the others, namely, a threefold symmetric arrangement. On the other hand, the dipole moments calculated for α-CyD-H_2O and α-MeOH complexes were similar and directed from the secondary to the primary hydroxyl groups of the α-CyD. However, the dipole moment on the α-CyD-*p*-NP complex was oblique to the axis for the other two complexes. Taking into account this difference in the dipole moment and the hydrogen bonding between the CyDs, the structural differences observed by STM could be explained comprehensively. The obtained results indicate the existence of a high potential for the structural control of the self-assembled α-CyD complexes by changing the guest compounds.

KEYWORDS: STM, Cyclodextrin, self-assemble, inclusion complex, dipole moment

1. Introduction

Recently, self-assembly of molecular arrangements has been attracting considerable attention because of its high potential as a nano-science technology for the realization of desired materials. Since the ordering of a self-assembled molecular arrangement depends on the intermolecular forces, microscopic analysis is important for understanding the self-assembly mechanism.

Scanning tunneling microscopy (STM) is a very powerful tool for studying nanostructures on an atomic scale and has been widely used for the direct observation of self-assembled molecules. Many STM observations have been conducted, such as for linear n-alkanethiol,[1)] planar liquid crystal[2,3)] and spherical Fullerene molecules.[4)] However, the intermolecular interactions in these materials are mainly due to van der Waals forces, and studies on molecules with anisotropic interactions are still insufficient.

Cyclodextrins (CyDs) are cyclic oligosaccharides and consist of 6–12 glucopyranose units in a chair conformation. Schematic model of α-CyD, which consists of six glucopyranose units, is shown in Fig. 1.[5,6)] Hydroxyl groups are located on both ends of the torus-shaped structure, and are termed the primary and secondary hydroxyl groups. Due to the presence of these hydroxyl groups, the external wall of a CyD is hydrophilic and there is a strong anisotropic interaction between CyDs. On the other hand, many methyl groups exist on the inner wall of the cavity, and the nonbonding electron pairs of the glucosidic oxygen bridges are directed towards the cavity interior. Therefore, the cavity has a hydrophobic characteristic, and CyDs include various hydrophobic molecules therein. From these characteristics, CyDs are expected to play an important role in the field of artificial enzymes and biosensor devices. Therefore, the study of CyD self-assembly is very important from both the fundamental and practical points of view.

Recent STM observations revealed that α-CyD inclusion complexes were self-assembly-ordered on a HOPG substrate, and their arrangements were different from those of the three-dimensionally grown crystals.[7,8)] The arrangements of the α-CyD inclusion complexes differed, and the included guest molecules were considered to strongly influence the interactions between the CyDs. However, since the effect of the guest-dependent conformation is not sufficient to explain the differences in the arrangements, it is necessary to provide some other mechanism to understand the phenomenon.

A rather large dipole moment (10–20 D) is known to exist on CyDs, and its effect on the formation of inclusion complexes was reported in a previous paper.[9)] Until now, no attention has been paid to the relation between the dipole moment and CyD molecular arrangement. In this paper, we analyze the effect of the dipole moment on the arrangement of the self-assembly-ordered α-CyD inclusion complexes.

2. Experimental and Calculation

Three types of inclusion complexes, (1) α-CyD-H_2O, (2) α-CyD-MeOH, and (3) α-CyD-*p*-NP, were prepared as samples by dropping a 1.0 mM solution of each onto a freshly cleaved HOPG surface, and then drying naturally. As is schematically shown in Fig. 2, each α-CyD cavity includes (a) two H_2O molecules, (b) a single MeOH molecule and (c) a single *p*-NP molecule.[10–12)] STM observations were per-

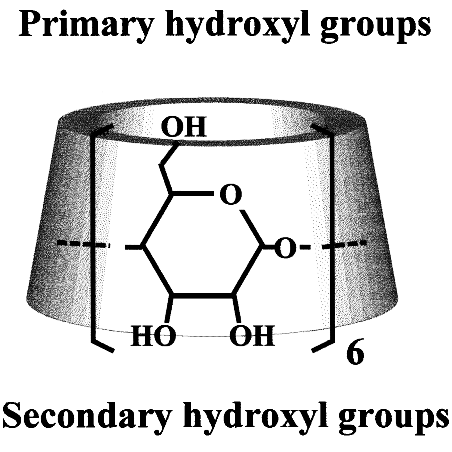

Fig. 1. Schematic structure of α-cyclodextrin (α-CyD).

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formed in air at room temperature using a Pt/Ir tip. All STM images were obtained in the constant height mode.

In order to analyze the molecular interactions, the dipole moment was calculated for each case. For the atomic coordinates of the guest compounds, the parameters determined for the crystal structures by the X-ray diffraction method were used.[10–12]

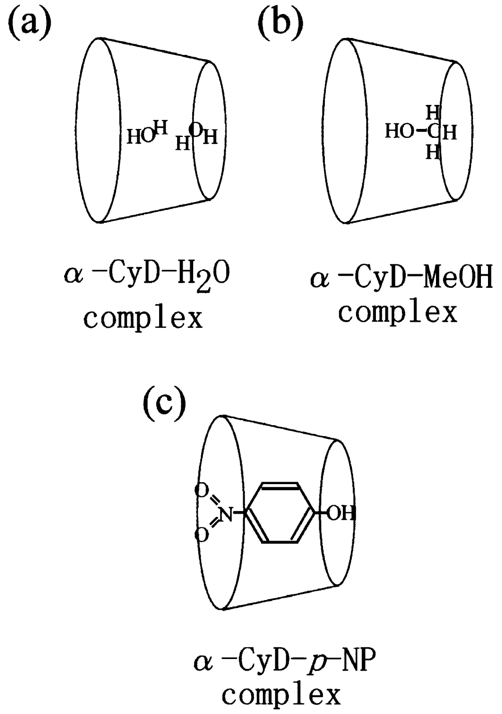

Fig. 2. Schematic structures of (a) α-CyD-H_2O, (b) α-CyD-MeOH, and (c) α-CyD-p-NP inclusion complexes.

3. Results and Discussion

3.1 *α-CyD-self-assemblies observed by STM*

Figure 3 shows STM images of (1) α-CyD-H_2O, (2) α-CyD-MeOH, and (3) α-CyD-p-NP. As shown in Figs. 3(a) and 3(b), α-CyD-H_2O and α-CyD-MeOH complexes show channel-like structures with twofold symmetry, which is schematically shown in Fig. 3(d). On the other hand, the α-CyD-p-NP complex (Fig. 3(c)) has a threefold symmetric arrangement as schematically shown Fig. 3(e). Since all molecules are completely included in the α-CyD cavity as shown in Fig. 2, they could not have a direct influence on the arrangement. Therefore, some secondary effect on the interaction is expected. In the following sections, we analyze the effect of the dipole moment on the self-assembly arrangement of CyD inclusion complexes.

3.2 *Dipole moment induced on α-CyD inclusion complexes*

The dipole moments calculated for (1) α-CyD-H_2O, (2) α-CyD-MeOH, and (3) α-CyD-p-NP inclusion complexes are shown in Fig. 4. The dipole moments induced on α-CyD-H_2O and α-CyD-MeOH complexes are directed from the secondary to the primary hydroxyl groups, as shown in Figs. 4(a) and 4(b), respectively. However, on the α-CyD-p-NP complex, the dipole has an oblique orientation relative to the other cases. (Fig. 4(c)).

Since the dipole moment of the p-NP molecule itself is directed from the primary hydroxyl groups to the secondary hydroxyl groups, the component from the CyD molecule must contribute to the dipole structure. How does this occur? When α-CyD includes small molecules, such as H_2O and MeOH, two glucose residues of the CyD molecule are rotated inward, so that the CyD molecule has a distorted structure.[11,12] However, when α-CyD includes a larger molecule such as p-NP, the rotation of the glucose residue is suppressed, and little distortion is induced on the CyD.[10] Therefore, the difference

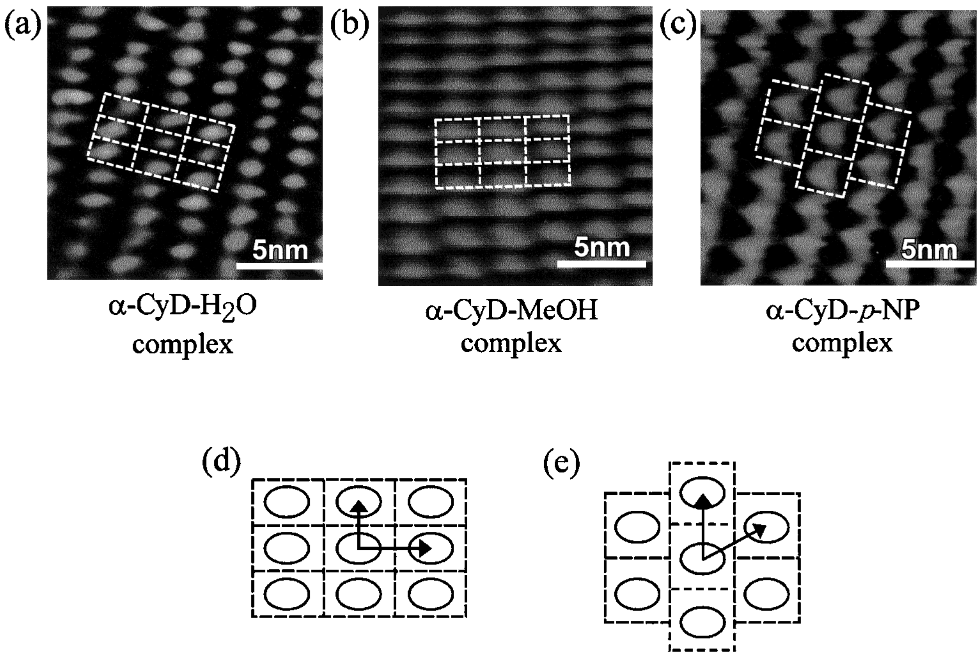

Fig. 3. STM images of (a) α-CyD-H_2O, (b) α-CyD-MeOH, and (c) α-CyD-p-NP inclusion complexes and their structural models with (d) twofold and (e) threefold symmetric arrangement.

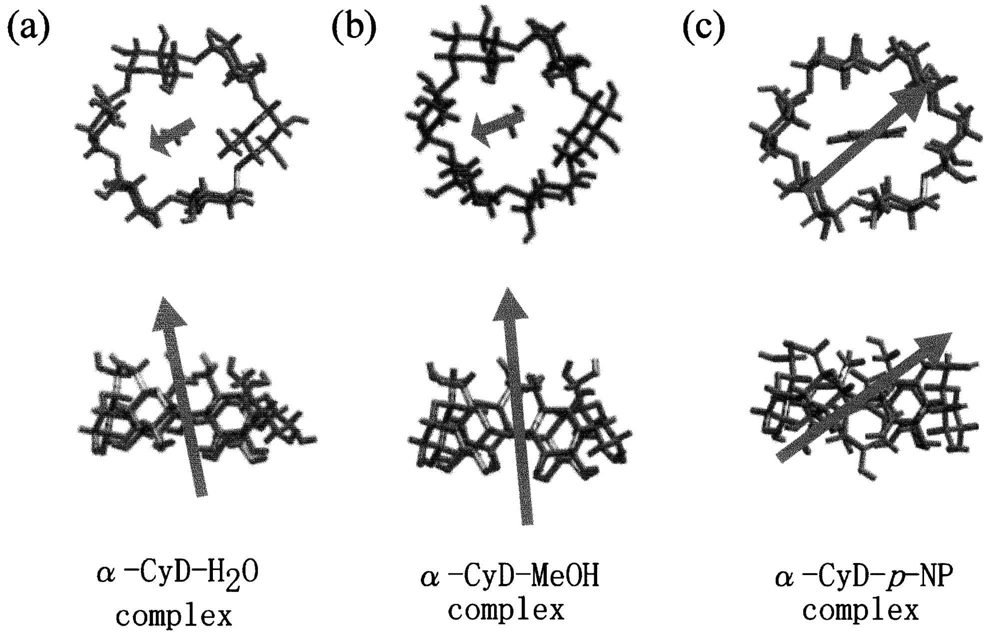

Fig. 4. Dipole moments induced on (a) α-CyD-H_2O, (b) α-CyD-MeOH, and (c) α-CyD-p-NP inclusion complexes.

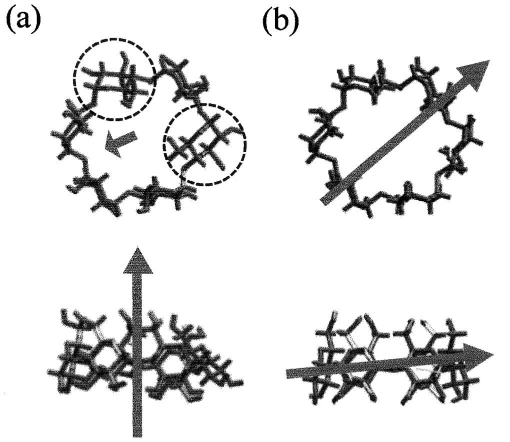

Fig. 5. Dipole moments induced on (a) distorted and (b) non-distorted α-CyD molecules.

in the distortion may influence the electronic structure of the inclusion complexes. In order to clarify this point, we calculated the dipole moments of distorted and undistorted α-CyD molecules without any guest compounds.

Figure 5(a) shows the dipole moment for a distorted α-CyD. Rotated glucose residues are indicated by dotted circles. The dipole is directed from the secondary to the primary hydroxyl groups. On the other hand, for the undistorted α-CyD, the dipole is induced differently from the case involving distortion, as shown Fig. 5(b). The result indicates that the distortion of one glucose residue strongly influences the dipole moment induced on the α-CyD molecule as predicted.

3.3 *Structural analysis of α-CyD self-assemblies*

Next, taking into account the effect of the dipole moment, we consider the difference in the arrangement observed by STM. For the α-CyD-H_2O and α-CyD-MeOH complexes, their dipole moments are directed from the secondary to the primary hydroxyl groups as shown in Figs. 4(a) and 4(b).

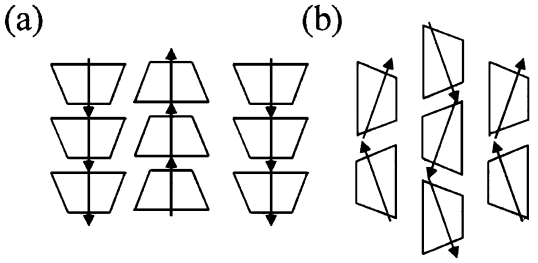

Fig. 6. Structural models with (a) twofold and (b) threefold symmetric arrangement. Arrows indicate the dipole moments induced on CyD inclusion complexes.

Therefore, the dipole-dipole interaction works together with the hydrogen bond interaction in the same direction, and possibly results in the arrangement of the channel-like structure with twofold symmetry as shown in Fig. 6(a). On the other hand, the dipole moment of the α-CyD-p-NP complex is obliquely induced as shown in Fig. 4(c), and the strongest orientation of the dipole-dipole interaction is different from that of the hydrogen bonds. Therefore the channel-like arrangement shown in Fig. 6(a) may be suppressed for the α-CyD-p-NP complex. A possible structure for the α-CyD-p-NP complex is shown in Fig. 6(b). These models show good agreement with the observed structures.

4. Conclusion

We performed STM observations of the self-assembled CyD inclusion complexes by changing the guest compounds. The structure of the α-CyD-p-NP complex was different from those of α-CyD-H_2O and α-CyD-MeOH complexes, which could not be explained solely by the conformational difference related to the guest molecules. Taking into consideration the effect of the induced dipole moment on the molecules, we could comprehensively explain the structural arrangement observed by STM. In addition, the change in the distortion of the α-CyD molecules was found to strongly influence the direction of the dipole moment. These results strongly indicate the high possibility of the structural control of the self-assembly of α-CyD by changing the guest compounds.

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1) D. M. Cyr, B. Venkataraman, G. W. Flynn, A. Black and G. M. Whitesides: J. Phys. Chem. **100** (1996) 13747.
2) F. Charra and J. Cousty: Phys. Rev. Lett. **80** (1998) 1682.
3) D. M. Walba, F. Stevens, D. C. Parks, N. A. Clark and M. D. Wand: Science **267** (1995) 1144.
4) J. K. Gimzewski, S. Modesti, T. David and R. R. Schlittler: J. Vac. Sci. Technol. **B12** (1994) 1942.
5) J. Szejtli: *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn (Pergamon, London, 1996) 1st ed., Vol. 3, Chap. 2, p. 5.
6) K. Harada: *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn (Pergamon, London, 1996) 1st ed., Vol. 3, Chap. 9, p. 279.
7) H. Shigekawa, T. Morizumi, M. Komiyama, M. Yoshimura, A. Kawazu and Y. Saito: J. Vac. Sci. Technol. **B9** (1991) 1189.
8) S. Yasuda, K. Miyake, Y. Goto, M. Ishida, K. Hata, M. Fujita, M. Yoshida, J. Sumaoka, M. Komiyama and H. Shigekawa: Jpn. J. Appl. Phys. **37** (1998) 3844.
9) M. Sakurai, M. Kitagawa, H. Hoshi, Y. Inoue and R. Chujo: Carbohydr. Res. **198** (1990) 181.
10) K. Harata: Bull. Chem. Soc. Jpn. **50** (1977) 1416.
11) P. C. Manor and W. Saenger: J. Am. Chem. Soc. **96** (1974) 3630.
12) B. Hingerty and W. Saenger: J. Am. Chem. Soc. **98** (1976) 3357.