



Single Molecules on Liquid-Solid Interfaces Probed by Atomic Force Microscopy

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Doctoral Dissertation

Single Molecules on Liquid-Solid Interfaces

Probed by Atomic Force Microscopy

(液中動作する原子間力顕微鏡を用いた単一分子計測)

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Contents

Chapter 1: General Introduction

<i>1.1 Background</i>	<i>4</i>
<i>1.2 History of AFM</i>	<i>6</i>
<i>1.3 Application of AFM for investigations of chemical reactions</i>	<i>8</i>
<i>1.4 Detection of adsorbed species with weak interactions onto surfaces</i>	<i>10</i>
<i>1.5 Aim of this study</i>	
<i>1.5.1. Investigations of single molecular states in chemical reactions</i>	<i>11</i>
<i>1.5.2. Detection of adsorbed single molecules at liquid-solid interfaces</i>	<i>12</i>
<i>1.6 References</i>	<i>13</i>

Chapter 2: Principle and Instrument of FM-AFM

<i>2.1 Operation modes of a cantilever</i>	<i>17</i>
<i>2.2 Applied forces to a probe</i>	<i>21</i>
<i>2.3 Cantilevers</i>	<i>22</i>
<i>2.4 Cantilever oscillation</i>	<i>23</i>
<i>2.5 Experimental setup</i>	<i>25</i>
<i>2.6 Noises in FM-AFM</i>	<i>27</i>
<i>2.7 References</i>	<i>28</i>

Chapter 3: Liquid-Environment FM-AFM Imaging of A Cobalt Porphyrin

<i>3.1 Introduction</i>	<i>29</i>
<i>3.2 Experiment</i>	
<i>3.2.1 Chemicals</i>	<i>32</i>
<i>3.2.2 Substrates</i>	<i>32</i>
<i>3.2.3 Preparation of solutions</i>	<i>34</i>

3.2.4 <i>Microscope and cantilevers</i>	35
3.3 <i>Topography of CoTPP at liquid-solid interfaces</i>	
3.3.1 <i>Topography in wide area</i>	36
3.3.2 <i>Topography in narrow area</i>	40
3.4 <i>Conclusions</i>	44
3.5 <i>References</i>	44

Chapter 4: FM-AFM Imaging of a Platinum Porphyrin in Photooxidation Reaction

4.1 <i>Introduction</i>	47
4.2 <i>Experiment</i>	
4.2.1 <i>Chemicals</i>	49
4.2.2 <i>Substrates</i>	49
4.2.3 <i>Physical measurements</i>	49
4.3 <i>Photooxidation of anthracene in solution</i>	51
4.4 <i>Topography of PtTPP at liquid-solid interfaces</i>	54
4.5 <i>Topography of PtTPP under visible light irradiation</i>	56
4.6 <i>Conclusions</i>	61
4.7 <i>References</i>	61

Chapter 5: Solvent-Sensitive Structures of Interfacial Liquid on Salicylic Acid (110) Surface

5.1 <i>Introduction</i>	63
5.2 <i>Experiment</i>	
5.2.1 <i>Chemicals</i>	65
5.2.2 <i>Substrates</i>	65
5.2.3 <i>Microscope and cantilevers</i>	67
5.3 <i>Topography of SA in liquids</i>	68

<i>5.4. Interfacial structures of liquids over SA</i>	
<i>5.4.1 TES liquid structures over SA</i>	72
<i>5.4.2 Decanol liquid structures over SA</i>	78
<i>5.5 Conclusions</i>	82
<i>5.6 References</i>	83
 Chapter 6 Summary and Future Perspective	 84
 Acknowledgements	 87

Chapter 1: General Introduction

1.1 Background

Liquid-solid interfaces play very important roles in a broad range of daily phenomena and scientific or technological property.¹ These include a variety of fields such as electrochemistry,² self-assemble structure,³ heterogeneous catalyst,⁴ crystal growth,⁵ and biological chemistry,⁶ just to name a few. In various fields, the interesting and complicated behavior has been studied by using many sensitive analytical methods, for instance spectroscopy such as X-ray spectroscopy, infrared absorption spectroscopy, UV-Vis (ultraviolet-visible) absorption spectroscopy, and neutron diffraction.⁷ Although these methods provide numerous information about liquid-solid interfaces, acquired results are averaged and qualitative data without local information as a function of lateral or vertical coordinate to the surface.

On the other hand, scanning probe microscopy (SPM) has been regarded as one of prominent tools for elaborating surface structures with various interactions at interfaces.^{1d, 8} In particular, atomic force microscopy (AFM) has the advantage of possibility to conduct measurements in different environments including ultrahigh vacuum (UHV), ambient conditions, and liquid environments. Especially, the experiments in liquids enable to realize flexible designs or conditions under which chemical or physical phenomena actually proceed, leading to expanded and intrinsic information. Besides, unlike scanning tunneling microscopy (STM), AFM measurements allow imaging topography on even insulant substrates as well as conducting or semiconducting materials.⁹

In addition, recent development of AFM achieved imaging not only surface topography with nanoscale resolution but also solvated structures at liquid-solid interfaces.¹⁰ Solvent molecules often form a characteristic structure with oscillation vertical to the substrate at the interface. Although the oscillatory density profiles

measured by X-ray reflectivity¹¹ or SFA (Surface Force Apparatus)¹² also have been reported, acquiring high lateral resolution is difficult as well as measurements of surface height profiles. The combination of the local structure on the surface and the liquid density profile vertical to the surface leads to revealing the interaction between the substrate or adsorbates on the surface and solvent molecules, where the interfacial interaction is involved in a variety of forces such as van der Waals forces, hydrogen bonds, steric effects, and electrostatic interactions.

The changes of interfacial structures or interactions were also detectable, which were applied to experiments such as imaging of morphological changes of biological materials, structural changes induced by isomerization, lithiation for lithium ion batteries, and phase changes at crystal surfaces.¹³

Such highly sensitive AFM enables to probe single molecules in liquids and elucidate a variety of interfacial phenomena. In this work, AFM is applied as a powerful tool for measurements and investigations of single molecular states at liquid-solid interfaces.

1.2 History of AFM

AFM belongs to a series of SPM and gives a nice tool to image topography of solid surfaces at high resolution. SPM started with STM, which was invented by Binnig and Rohrer¹⁴ and attained to image at atomic resolution of 7×7 lattice arrangements of silicon atoms for Si(111).¹⁵ Before invention of STM, there are no instruments for visualizing surfaces with capability to distinguish individual molecules or atoms. In near period, SNOM (scanning near-field optical microscope) was introduced, which allowed imaging with light below the optical resolution limit.¹⁶

After that, AFM has been invented by Binnig *et al.* in 1986 to measure any type of forces on an atomic scale, and the first AFM imaging was accomplished in air to probe the surface of aluminum oxide with lateral and vertical resolution of 3 nm and less than 0.1 nm, respectively.¹⁷ Furthermore, Giessibl *et al.* succeeded in atomic resolution images of potassium bromide (KBr) at 4 K and taking step line images using contact AFM.¹⁸ However, tip scanning by contact AFM should give a damage to a material surface and would be difficult to achieve reliable atomic resolution.¹⁹

Since then, introduction of the vibrating probe (dynamic mode method) led to significant transformation to achieve high resolution.²⁰ Major two dynamic modes, amplitude modulation AFM (AM-AFM, also known as tapping mode)^{20b} and frequency modulation AFM (FM-AFM, also known as non-contact mode)^{20c} have been developed. In particular, FM-AFM is one of the prominent force detection methods. FM-AFM measurements detect the resonant frequency shift induced by the force applied to the oscillating cantilever from the surface. Therefore, minute forces can be detectable without destruction of surface structures, leading to measurements with high resolution.

In 1995, Giessibl reported the atomic resolved image of Si(111)-(7×7) in UHV at room temperature was obtained using NC-AFM.²¹ In addition, Kobayashi *et al.* showed the image of fullerene molecules on Si(111)-(7×7),²² and Fukui *et al.* reported the dynamic aspects and associated structures of TiO₂(110) and CeO₂(111) surfaces.²³ The

resolution with AFM today is comparable to that achieved with STM in some cases.

In addition to AFM measurements under UHV, images in liquid environments have been achieved. In liquid media, various experimental conditions are tuned such as pH, polarity, and ion strength, which enable to demonstrate *in-situ* studies for investigations of changes of interfacial interactions. It was reported that surface topography on sodium chloride and HOPG (highly oriented pyrolytic graphite) covered in paraffin was observed with lateral and vertical resolution of 0.15 nm and 5 pm, respectively, as the first imaging in liquids.²⁴ The first application of AFM for imaging biological molecules in water was demonstrated by Drake *et al.*²⁵ Ando *et al.* have improved the apparatus, and the imaging data associated with dynamic biomolecules are presented using high-speed AFM.²⁶ In comparison with imaging in air, liquid media could reduce perturbation of samples leading to decline of a damage caused by scanning materials.^{1d, 27} However, a low Q factor induced by imaging in liquids²⁸ and a noise arising from a cantilever sensor resulted in limitation of imaging with high resolution. In 2005, Fukuma *et al.* have developed a low noise cantilever deflection sensor and showed FM-AFM images of a polydiacetylene single crystal and mica in water with molecular and atomic resolution, respectively.²⁹ Furthermore the improvement of FM-AFM has also enabled the visualization of interfacial liquid structures, including 3D water distribution of the water-solid interface.^{10, 30} Additionally, AFM measurements have been applied to observation of organic solvent-solid interfaces,³¹ imaging SAMs (self-assembled monolayers) in liquids,³² detection of single ions adsorbed on the substrate,³³ and investigation of nanoscale mechanism of crystal growth.³⁴ Recently, FM-AFM has also been successfully adopted under liquid environments for soft materials or examination of electrochemical reactions,³⁵ which required measurements at low loading forces.³⁶

1.3 Application of AFM for investigations of chemical reactions

The AFM studies at interfaces applied to various field have played very important roles in a board range of science as mentioned in the previous section. The investigation of chemical reactions at interfaces is also no exception. The imaging of surfaces is one of good methods to reveal phenomena at interfaces, together with other studies, for instance X-ray or neutron reflection analysis.

In particular, atomic or molecular level imaging is crucial for elucidation of the reaction mechanism in detail. For example, the imaging of the catalyst surface with high resolution under UHV conditions has been previously reported together with reactants, intermediates, and final products.³⁷ In addition, the dynamic study of a single molecule visualized even each chemical bond using the modified cantilever with atomic dimension such as CO terminated tip apex.³⁸ However, a lot of chemical reactions around us occur in the presence of liquid media. The UHV conditions give rational environments to achieve well-defined cantilever designs and imaging with extreme high resolution but these measurements provide far information from various actual reactions.

In contrast to observation under UHV, surfaces immersed in solution are completely covered by solvent molecules or solutes such as reactants, intermediates, products including main- and by-products, catalyst molecules, and inert species. The molecular nature such as polarity or hydrophilicity in the vicinity of active sites or adsorbed active species on the surface would restrict or promote other molecules approaching and affect their reactivity or selectivity.³⁹ When new adsorbates exchange another previous adsorbates on adsorption sites, the change in Gibbs free energy for the surface interaction is described below.⁴⁰

(Provided no solvent molecules adsorbed onto adsorption sites)

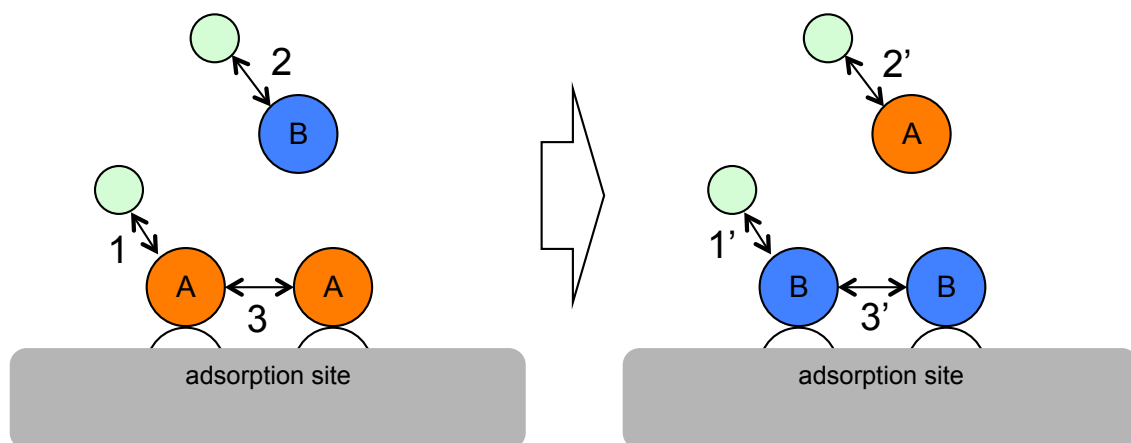


Figure 1.1. Exchange of adsorbates on adsorption sites. A (orange sphere) and B (blue sphere) are adsorbates in solution. A green sphere is a solvent molecule.

$$\Delta G = \Delta G(B) - \Delta G(A) + \Delta G(1') - \Delta G(2) + \Delta G(2') - \Delta G(1) + \Delta G(3') - \Delta G(3)$$

$\Delta G(A)$ or (B) : The free energy change for adsorption of A or B

$\Delta G(1)$ or $(1')$: The free energy change for interactions of A or B on surface with solvent

$\Delta G(2)$ or $(2')$: The free energy change for interactions of B or A with solvent in solution

$\Delta G(3)$ or $(3')$: The free energy change for interactions of A or B each other on surface

Thus, unlike in UHV systems, the driving force of the interfacial reaction includes not only the free energy for adsorption/desorption on adsorption sites but also the interaction involved with other species such as solvent molecules. In addition, it is likely that adsorption occurs in liquids even though the enthalpy change is positive (i.e. endothermic) due to the contribution of the sufficient negative entropic term (i.e. $-T\Delta S$).

However, AFM measurements of chemical reactions in liquid environments are much less developed in comparison to those under UHV conditions. Although the limited AFM studies were carried out in chemical reactions,^{1d, 13b, c, 40} no images of single atoms or molecules in liquids have been acquired under chemical reaction conditions. The imaging of single molecules at interfaces would enable to elucidate chemical reactions induced by homogeneous catalysts or adsorbed active species onto surfaces.

1.4 Detection of adsorbed species with weak interactions onto surfaces

The measurement of adsorption species at the interface is very important to elucidate a chemical reaction on molecular scale as mentioned in the previous section. However, directly scanning the surface with a cantilever could cause desorption of adsorbates with very weak interactions or flexible structures at the solid-liquid interface (Figure 1.2a). On the other hand, recently developed AFM would permit detection of interfacial liquids¹⁰ with softer or more flexible structures than adsorbed species on the surface by the force measurement with the cantilever scanning vertical to the surface. Thus, this method could also apply to detection of weakly adsorbed species at interfaces (Figure 1.2b). Actually, the previous report represented the solvent-sensitive interfacial structure or the localized adsorption structure as a function of lateral coordinate to the surface.⁴¹ The comparison between inert and active species to adsorption onto substrates would lead to confirmation of the concept mentioned above and deep understanding of interfacial structures.

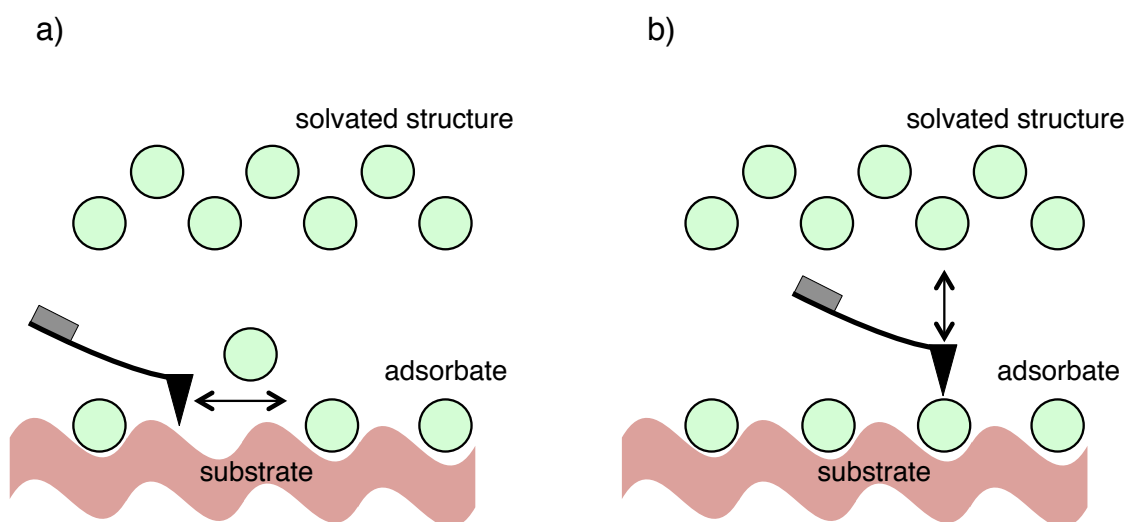


Figure 1.2. Procedure to obtain a) surface topography and b) two-dimensional force (or frequency shift) distribution by scanning lateral and vertical to the surface, respectively.

1.5 Aim of this study

1.5.1. Investigations of single molecular states in chemical reactions

The purpose of this study is detection of single molecules in chemical reactions at liquid-solid interfaces and visualization of single molecular states in solution. To achieve the aim of this study, the author conducted experiments by using FM-AFM as a powerful tool to reveal the interfacial structures. FM-AFM has superior ability to measure in liquid environments with high resolution including insulant materials (such as mica as explained below) as mentioned in the former section and Chapter 2. In addition, the author made choices of mica and metalloporphyrins as a substrate (the detailed structure is showed in Chapter 3) and active species for chemical reactions, respectively. Mica is commercially and easily available and has inert and atomically smooth surfaces prepared by cleavage for very facile procedures.⁴² Metalloporphyrins are attractive compounds involved with a number of synthetic transformations as catalysts⁴³ and have advantage of adsorption due to large planarity. Only a few examples which observed single molecular states of metalloporphyrins by STM have ever been reported.⁴⁴ However, the observed molecules were limited to free or oxidized states bound with atomic or molecular oxygen induced by specific substrates with nature of electron donating such as HOPG or Au, where the adsorbed molecular states were distinct from those in solution. In addition, no organic compounds including reactants or products have been confirmed by STM measurements even when synthetic transformations occurred.

The author started with the AFM study of absorption behavior of metalloporphyrins onto mica without ability of electron donating followed by single molecular states in the chemical reactions, the complex formation reaction (in Chapter 3) and the photo-induced oxidation reaction (in Chapter 4). These direct measurements of molecular states provide deep insights of various chemical reactions. In these studies, the author discussed the possibility to detect not only adsorbed metalloporphyrins but

also organic compounds involved with the chemical reactions by using AFM.

In order to discuss the chemical interactions between metalloporphyrins and reactants, the local molecular states of metalloporphyrins were compared in liquid environments. Imaging cobalt porphyrins with a vacant coordination site was carried out to determine the contribution of organic solvents as coordination ligands as discussed in Chapter 3. As well as the complex formation reaction, single molecular states of platinum porphyrins were compared under reaction conditions. To assess the contribution of synthetic transformations to imaging single molecules at the interface, the sequential observation under light irradiation were conducted. These observations and discussions were described in Chapter 4.

1.5.2. Detection of adsorbed single molecules at liquid-solid interfaces

As described in the previous section 1.4, interfacial structures including adsorbed molecules are intimately linked to surface phenomena such as chemical reactions. The measurements of frequency shift or force distribution could help to uncover not only liquid structures but also existence of directly and weakly adsorbed molecules at liquid-solid interfaces. To confirm this concept, frequency shift distribution was compared between inert or active solvent molecules against the solid surface. In particular, hydrogen bonding formation is useful for adsorption of solvent molecules onto surfaces. In this study, salicylic acid was used as a model for the specific substrate with hydrogen bonding ability. Only liquid structures of inert solvents on salicylic acid were reported previously.⁴⁵ The author discussed solvent-sensitive liquid structures at the liquid-solid interfaces and possibility to determine presence or absence of adsorption species onto the surface.

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Chapter 2: Principle and Instrument of FM-AFM

2.1 Operation modes of a cantilever

In opposite to previous optical microscopy, SPM scans surfaces with a sharp probe to detect near-field interactions between the tip and the material surfaces and constructs surface images.¹ In addition, feedback control is used for keeping the detected stimulation constant.

The operation modes of a cantilever in AFM measurements were grouped into two general categories, the contact mode and the dynamic mode. In the contact mode operation, the cantilever scans in continuous direct contact with the surface to maintain the repulsive force between the cantilever and the surface (Figure 2.1a). This operation mode has advantage of simple principle and suitability for hard materials. However, since the contact mode operation could scratch or destroy surfaces, it is not appropriate in the case of high mobility materials such as nanoparticles and soft materials, for instance polymer or biological molecules.

On the other hand, a cantilever is oscillated vertical to the surface in the dynamic mode. The dynamic mode is further divided into amplitude modulation AFM (AM-AFM) or frequency modulation AFM (FM-AFM) in respect to a feed back parameter to obtain surface topography. In the AM mode, the amplitude shift (ΔA) is detected as a feed back parameter (Figure 2.2a). The oscillation amplitude decreases in repulsive regime with a constant frequency (tapping mode, Figure 2.1b). The AM mode is often usually used in ambient or liquid environments to prevent frequency from deviation out of resonance peak under UHV conditions with high Q values.

In the FM mode, the frequency shift (Δf) is detected as a feed back parameter (Figure 2.2a). In this case, it is required two feedback loops so that Δf and amplitude are kept constant. Under UHV conditions, a cantilever can be operated in attractive regime (i.e. NC mode, Figure 2.1c). In addition, measurements in liquid environments are also

carried out mainly with positive Δf (repulsive regime, Figure 2.1b) and actually achieved atomic resolution with low noise systems (as described in section 2.6),² leading to an increase of the signal due to attainment of small amplitude. Compared to the AM mode with possibility of deviation from resonant frequency owing to interaction forces, the FM mode has numerous advantages of not only high sensitivity and reproducibility but also prevention of sample degradation due to continuous excitation at resonant frequency and stiff cantilevers, leading stable oscillation. Furthermore, scanning with high sensitivity vertical to the surface also enables to elucidate localized liquid structures at liquid-solid interfaces. In this study, the author conducted experiments by using FM-AFM.

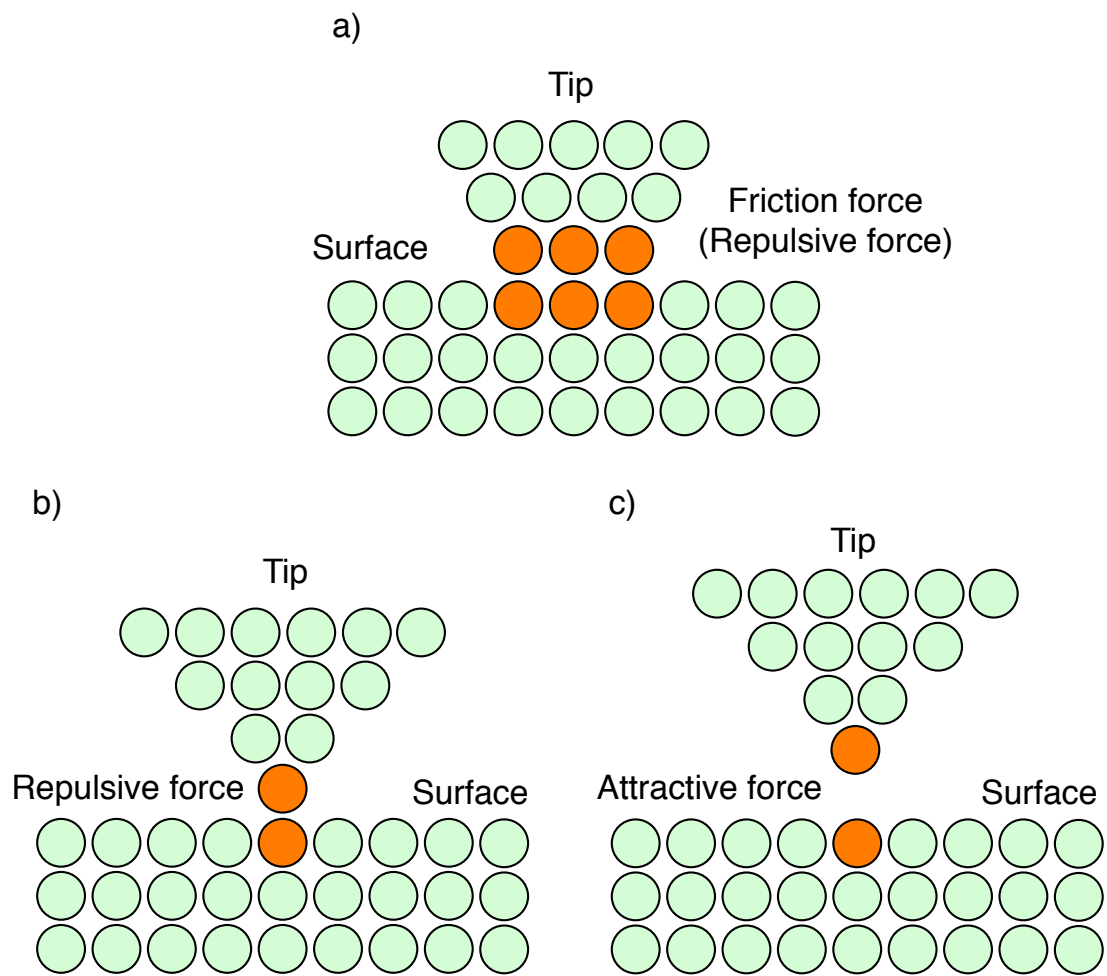


Figure 2.1. Schematic models for cantilever operation of a) the contact mode, b) the tapping mode, and c) the non-contact mode.

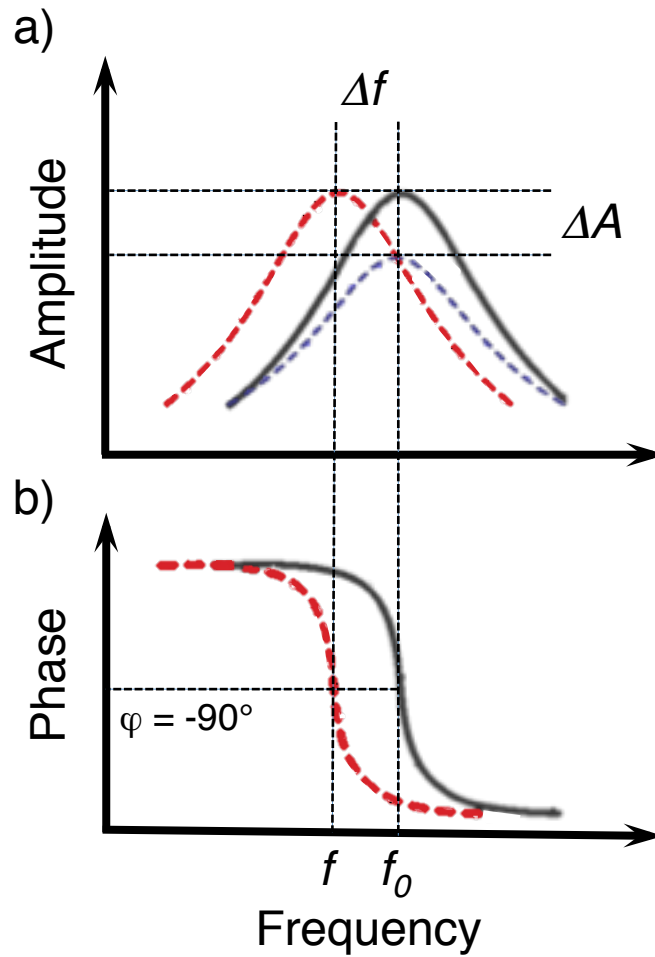


Figure 2.2. a) Amplitude as a function of frequency before (black line) and after approach to the surface in the AM (blue dotted lines) or FM (red dotted line) mode. b) The phase difference between the cantilever excitation signal and the deflection signal as a function of frequency before (black line) and after (red dotted line) approach in the FM mode with one to one relation between line colors in a) and b).

2.2 Applied forces to a probe

As described in the previous section, the cantilever deflection in the contact mode is kept constant to maintain the repulsive force during probing as indicated by¹

$$F_r = k\Delta q \quad (2.1)$$

where F_r , k , and Δq are the repulsive force, the spring constant, and the cantilever deflection, respectively.

In the case of dynamic mode operation, the main applied forces to the cantilever in liquids include large distance forces such as the van der Waals force and the electric double layer force, and small distance forces, for instance the Pauli repulsion and the solvation force. The van der Waals force (F_{van}) between the cantilever and the surface is given by³

$$F_{van} = -\frac{A_H R}{6D} \quad (2.2)$$

where A_H , R , and D are the Hamaker constant, the curvature radius of the tip, and the distance between the tip and the surface. Provided the electric potential of the tip is equal to that of the surface, the electric double layer force (F_{EDL}) is described as³

$$F_{EDL} = \kappa R Z e^{-\kappa D} \quad (2.3)$$

where κ , R , Z and D are the inverse of Debye length, the curvature radius of the tip, the interaction constant, and the distance between the tip and the surface. In addition to such large distance forces, the hard sphere potential given by (2.4) is often used to express the Pauli repulsion.³

$$U(r) = +(\sigma/r)^n (n \rightarrow \infty) \quad (2.4)$$

Here σ and r are the atomic radius and the distance between each atom. Besides, at the tip-surface distance less than about several times as large as solvent molecular distances, the oscillated potential could be obtained due to the discrete nature of solvent molecules.³ The total intermolecular pair potential is often expressed as a Lennard-Jones potential³

$$U_{L-J}(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \quad (2.5)$$

where r is the distance between each atom.

2.3 Cantilevers

A probe is a part of a cantilever together with a support substrate as described in Figure 2.3. In general, the representative shape of the cantilever actually used in this work is a strip of paper type. In addition, a variety of cantilevers were reported, for instance a super sharp type with a small tip curvature radius of less than 2 nm and a probe with a high Q value of more than 30000 in UHV.⁴ These cantilevers are made from various kinds of compounds such as a silicon single crystal, silicon nitride, and silicon oxide. In general, soft cantilevers with a spring constant of 0.1~1 N/m are often used in the contact mode operation to suppress the loading forces. On the other hand, harder cantilevers with a spring constant of 2~50 N/m are usually selected in the dynamic mode relative to the contact mode. In the dynamic mode, only small excitation leads large amplitude at around the resonance frequency.

A back of a cantilever is coated by metal components, for instance gold or aluminum, to reflect laser beam for detection of cantilever deflection. In this study, Au coated cantilevers, which reflect laser beam more strongly than aluminum were used in all AFM measurements.

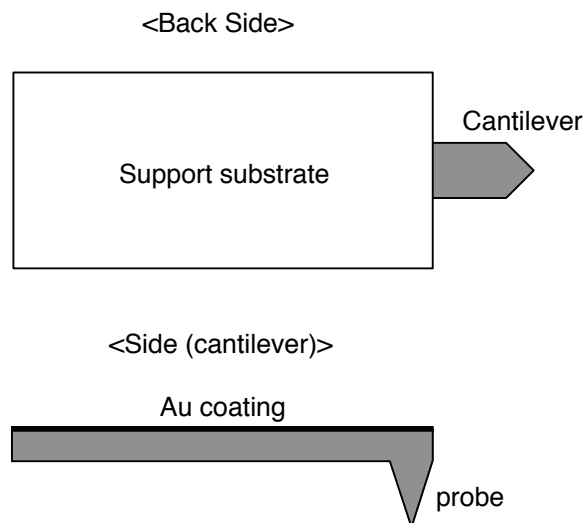


Figure 2.3. Schematic illustration of a cantilever.

2.4 Cantilever oscillation

The motion equation of a vibrating cantilever is indicated by⁵

$$EI \frac{\partial^4 w(x,t)}{\partial x^4} + \rho S \frac{\partial^2 w(x,t)}{\partial t^2} = F(x,t) \quad (2.6)$$

where w , E , I , ρ , S , and F are the transverse displacement of the cantilever, the Young's modulus, the moment of inertia, the density of the cantilever, the cross-sectional area of the cantilever, and the applied force to the cantilever, respectively. Given the consideration of the cantilever as a point mass with the single-degree-of-freedom system to get insights into the cantilever motion, the motion equation of the oscillated cantilever could be approximately expressed as⁵

$$m \frac{dz(t)^2}{dt^2} = -m \frac{\omega_0}{Q} \frac{dz(t)}{dt} - k(z(t) - (A + s)) + F_{int}(z(t)) + F_d(z(t)) \quad (2.7)$$

where m , z , ω_0 , Q , k , A , s , F_{int} and F_d are the effective mass of the cantilever, the position of the cantilever, the resonance angular frequency, the quality factor, the spring constant, the oscillating amplitude, the closest tip-sample distance during an oscillation cycle, the interaction force applied to the tip, and the external driving force (Figure 2.4). F_{int} including the interaction force between the cantilever and the surface and the counteracting force from solution would be so complicated and described by non-linear function as a function of z . F_d is given by $kA_0 \cos \omega t$, where k , A_0 , and ω are the spring constant, the constant number, and the angular frequency. Assumed that F_{int} is regarded as small perturbation, the motion of the cantilever can be represented by

$$z(t) = z_0 + A \cos(\omega t + \phi) \quad (2.8)$$

$$z_0 = A + s \quad (2.9)$$

where ϕ is the phase difference between the cantilever excitation signal and the deflection signal. In FM-AFM, ϕ is adjusted to be -90° at the resonance frequency (Figure 2.2b). Then, $\Delta f(z(t))$ is expressed by¹

$$\frac{\Delta \omega(z(t))}{\omega_0} = -\frac{1}{\pi k A} \int_{-1}^1 F_{int}(z(t) + A(1+u)) \frac{u}{\sqrt{1-u^2}} du \quad (2.10)$$

$$\Delta \omega(z(t)) = 2\pi \Delta f(z(t)) \quad (2.11)$$

where $\Delta\omega(z(t))$ is the angular frequency shift. This equation is converted to⁶

$$F(z(t)) = 2k \int_{z(t)}^{\infty} \left(1 + \frac{\sqrt{A}}{8\sqrt{\pi(v-z(t))}}\right) \Omega(v) - \frac{\sqrt[3]{A}}{\sqrt{2(v-z(t))}} \frac{d\Omega(v)}{dv} dv \quad (2.12)$$

where $\Omega(z(t))$ is $\Delta\omega(z(t))/\omega_0$.

In addition to scanning lateral to the surface to obtain surface topography, the applied force to the cantilever as a function of the tip-surface distance can be acquired by transformation of monitored Δf using equation (2.11). Besides, transformation of applied force distribution into liquid density distribution has been proposed in the previous reports.⁷ Although the versatile approach has not been completely established yet, the applied force distribution has been known to be intimately related to the gradient of the structured liquid density distribution.

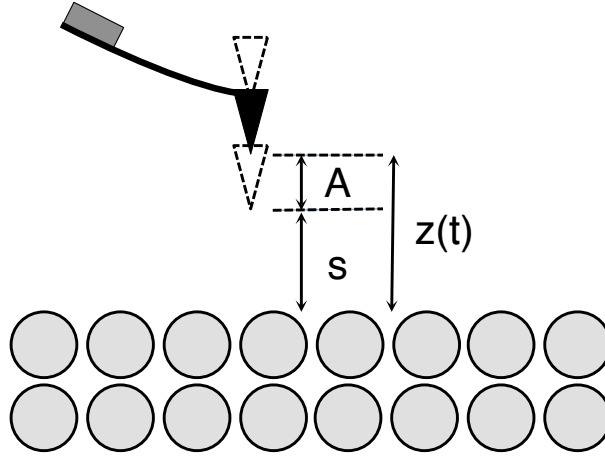


Figure 2.4. Schematic illustration of an oscillation cantilever at the interface.

2.5 Experimental setup

Figure 2.5 shows an experimental setup for AFM measurements. A cantilever is oscillated at its resonance frequency (f_0) before approaching to the surface by a piezoelectric actuator or photothermal excitation. Whereas the former method has the advantages of availability and a simple setup, the latter could decrease spurious resonance to improve stability and accuracy of AFM measurements.⁸ To detect the deflection of the oscillating cantilever, the light from a diode laser is irradiated onto a backside of the cantilever and reflected toward the position-sensitive photodetector (PSPD), where four photodiodes are oriented vertically or laterally to direction of laser displacement.⁹ The photo-induced currents from the photodiode were converted to voltages in the current-to-voltage (IV) converter. The amplifier outputs the vertical (A+B-C-D) or lateral (A+C-B-D) difference of the photodiode signal by their sum. The position of the laser spot is adjusted at the boundary between four photodiodes and output changes can be regarded as the deflection signal.

The deflection signal is cut off the noise by the band pass filter (BFP) around center f_0 . Then, the signal is branched into the automatic gain control (AGC) circuit through the phase-shifter and the frequency shift detector. The AGC circuit modifies the cantilever oscillation to maintain a constant amplitude.⁹

The deflection signal ($V_{ex}\cos 2\pi ft$) distributed into the frequency conversion circuit is multiplied by the signal with middle frequency ($\cos 2\pi(f_x+f_0)t$, $f_x = 4.5$ MHz, eq. (2.13)) followed by removal of high frequency component ($\cos 2\pi[(f_x+f_0)+f]t$) through the band pass filter.¹⁰

$$\begin{aligned} \cos(2\pi ft) \cos[2\pi(f_x + f_0)t] &= \frac{1}{2} \{ \cos 2\pi[(f_x + f_0) - f]t \\ &\quad + \cos 2\pi[(f_x + f_0) + f]t \} \quad (2.13) \end{aligned}$$

Then the deflection signal was routed through the PLL (phase locked loop) detector. The phase difference between the deflection signal and the input signal is detected by

the phase detector and used as the input signal of the VCOX (voltage controlled crystal oscillator) though the loop filter. When the circuit is convergent, this filtered signal can be used for feedback and imaging.

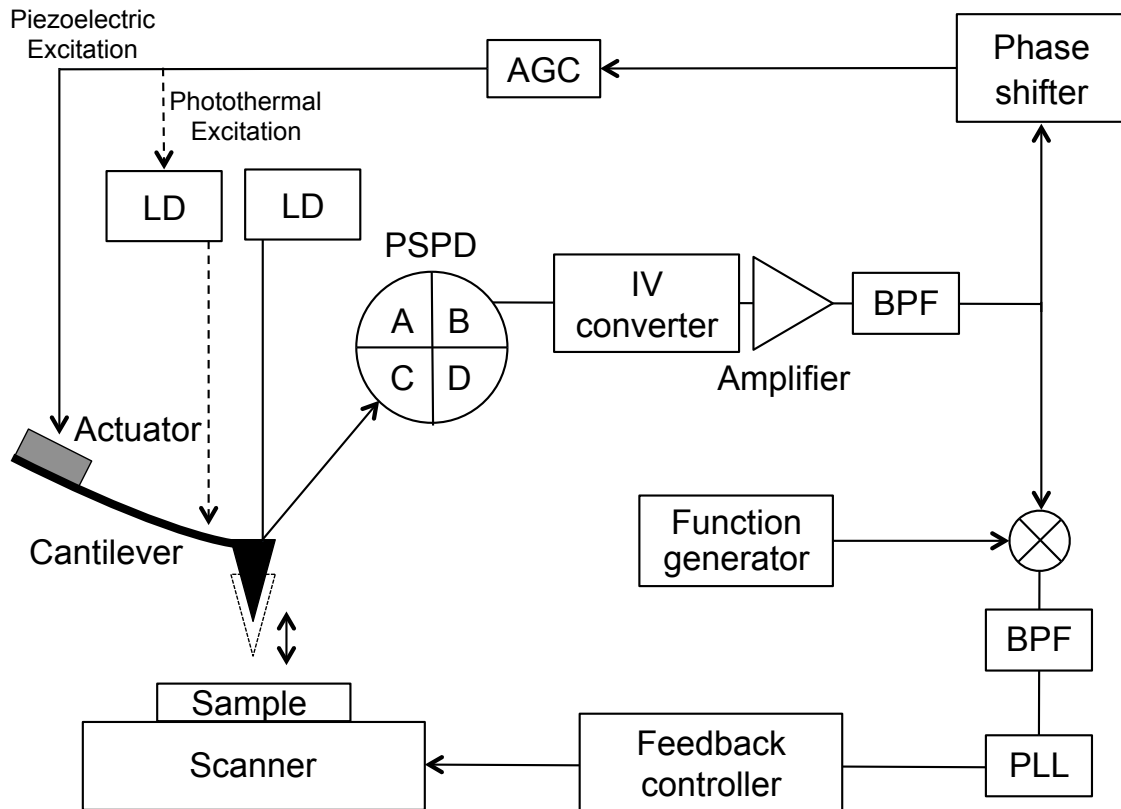


Figure 2.5. An experimental setup of FM-AFM.

2.6 Noises in FM-AFM

In UHV conditions, high resolution could be attainable in the FM mode due to high Q factors and the low noise system. On the other hands, the viscous and inertial resistance cause a decline in Q factors in liquid environments, leading deterioration of resolution. The noises in FM-AFM are required to be suppressed to achieve high resolution. The phase noise in the FM mode, namely the ratio between fluctuation of cantilever deflection and amplitude is converted into the frequency noise.^{1,2} The spectral density of the frequency noises (n_f) includes the thermal noise density (n_{th}) arising from Brownian motion, the displacement sensor noise (FM noise) density (n_{ds}), and the noise density (n_{osc}) deriving from frequency fluctuation of oscillating cantilever, which are given by^{1, 11}

$$n_f = \sqrt{n_{th}^2 + n_{ds}^2 + n_{osc}^2} \quad (2.14)$$

$$n_{th} = \sqrt{\frac{f_0 k_B T}{\pi k Q A^2}} \quad (2.15)$$

$$n_{ds} = \frac{\sqrt{2} n_{det} f_m}{A} \quad (2.16)$$

$$n_{osc} = \frac{n_{det} f_0}{\sqrt{2} Q A} \quad (2.17)$$

where f_0 , k_B , T , k , Q , A , n_{det} , and f_m are the resonance frequency, the Boltzmann constant, the temperature, the spring constant, the quality factor, the amplitude of the cantilever, the noise-equivalent displacement density, and the modulation frequency.

Assumed that Q is sufficiently large in UHV, n_{osc} becomes negligible.^{1,2} Besides, when the contribution of n_{ds} becomes small in the range of low modulation frequency, n_{th} is dominant to n_f . However, in the case of low Q factors such as liquid environments, n_{osc} considerably affects measurements and becomes important factors for improvement of sensitivity.

Yamada *et al.* improved the instrument to reduce the noise of the deflection sensor such as optimization of laser beam output and realization of highly effective laser beam detection.² Thus, the reduction of frequency noise enabled to operate with small

vibrating amplitude, leading a increase of interfacial interactions between the tip and the surface and improvement of sensitivity.

2.7 References

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Chapter 3: Liquid-Environment FM-AFM Imaging of A Cobalt Porphyrin

3.1 Introduction

A metalloporphyrin (Figure 3.1a) consisting of a metal cation in the molecular center and four pyrrole rings bound with methine groups has been known to show various catalytic performances,¹⁻⁴ including epoxidation,¹ photosensitization,² and C-H functionalization.³ In particular, cobalt (Co) porphyrins have much attention as functional catalysts,⁵ for example water oxidation,^{5a} oxidative coupling,^{5b} and reduction of carbon dioxide.^{5c} These characteristics are inherently based on electronic interactions between a central cation and a porphyrin ligand, which could be modulated by substituent groups in the ligand.^{2c, 2f, 5c}

The detail knowledge about metalloporphyrin molecules under the reaction conditions gives a deep understanding of catalytic performance or mechanism. Hence, many groups have investigated metalloporphyrins in liquid environments using various methods, including STM (scanning tunneling microscopy),⁶ AFM (atomic force microscopy),⁷ XPS (X-ray photoelectron spectroscopy),⁸ and UV-Vis (ultraviolet-visible) spectroscopy.^{7b} Especially, the imaging by AFM gives one of nice tools to reveal the mechanism of catalyst reactions. As described in Chapter 1 and 2, the recent progress in FM-AFM measurements opens up the possibility of subnanometer-scale imaging under liquid environments.⁹ In addition, observation by AFM can be carried out on various substrates including insulant substrates. Although some groups reported topography of metalloporphyrins at solid-liquid interfaces,⁷ to our knowledge, no examples have been reported to image discrete single molecules by using AFM. The previous AFM study under UHV conditions¹⁰ showed the discrete metalloporphyrin molecules to be sure as shown in Figure 3.1b. However, as mentioned in Chapter 1, probing under limited conditions without surrounding

molecules such as solvent or solute gives effective information but is difficult to reflect the behavior in solution.

Here we refocus on the coordination structure of the central metal cation. Depending on a metal atom, the metalloporphyrin at the liquid-solid interface could possess four coordinated geometry or further one axial coordination ligand. Imaging of a metalloporphyrin in liquid environments also enables to get information about coordination states of axial ligands.

In this chapter, we first investigated the adsorption behavior of 5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphyrin cobalt (CoTPP, Figure 3.1c) at liquid-solid interfaces, where solvents were 1-hexanol, 1-phenyloctane, and 1-chlorohexane, and substrate was muscovite mica. CoTPP has advantage in adsorption onto substrates due to the substituents of phenyl groups, leading large solubility and planarity in comparison with non-substituted Co porphyrins. Furthermore, the binding state of a Co porphyrin with an axial ligand was studied in narrow-area topography. Imaging of CoTPP bound with an axial ligand would play a key role in establishment of analysis methods of intermediate states in catalyst reactions since CoTPP has been reported to have catalytic functions, and the metal cation has been known to be active center. Besides, the coordination ability of axial ligands (solvent molecules) is also the very important factor in complex formation. In general, donor number (DN) is known as one of the indicators of coordination ability. OH-group-substituted hydrocarbon has larger DN than that of phenyl- or chloride-group-substituted hydrocarbon (for instance, DN of ethanol, 2-ethylhexanol, toluene, dichloromethane, and 1,2-dichloroethane are 20, 48, 0.1, 1, and 0, respectively).¹¹ The measurements by using advanced FM-AFM indicated whether the axial ligand was detectable in the presence of only molecules with large DN (i.e. strong coordination ability) or even molecules with small DN (i.e. weak coordination ability).

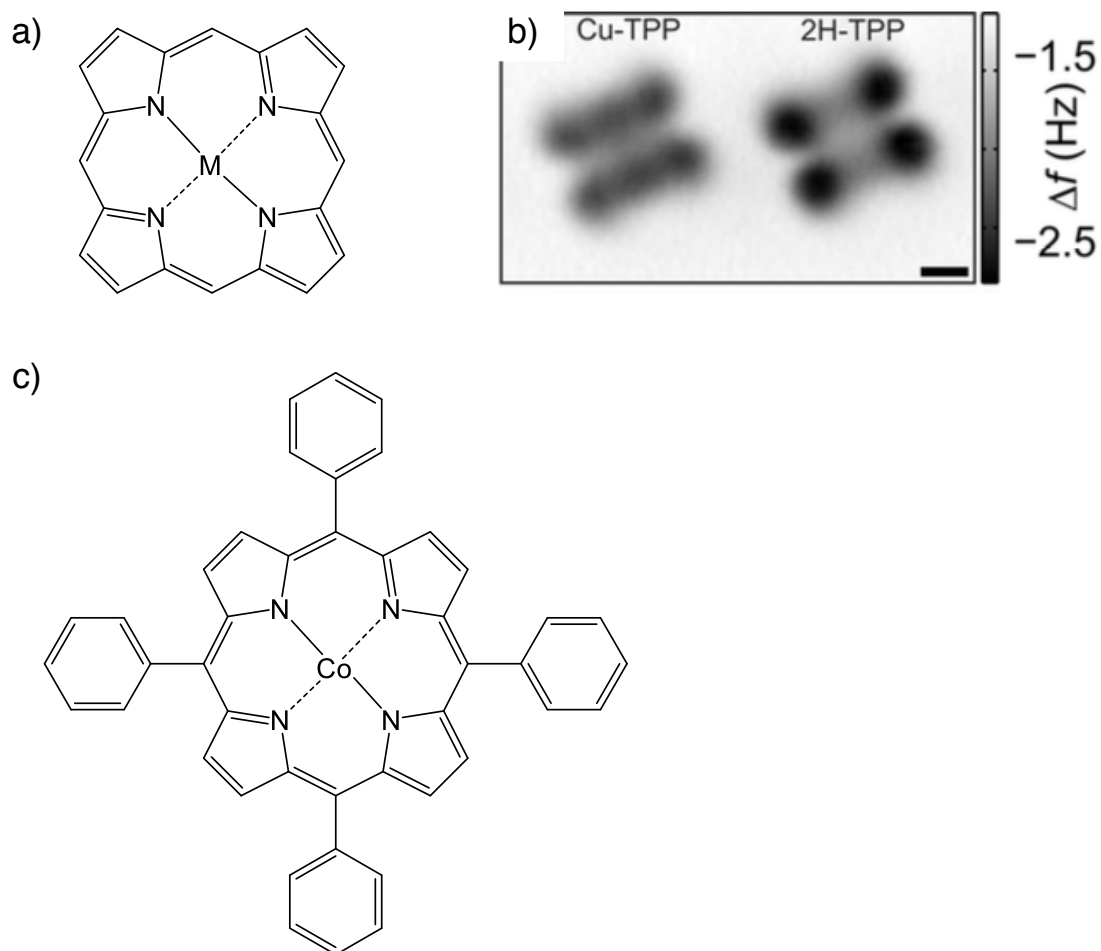


Figure 3.1. Molecular Structures of a) metalloporphyrin and c) 5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphyrin cobalt (CoTPP). b) Imaging of discrete single molecules of porphyrins by using AFM under the UHV condition in the previous report (scale bar is 0.5 nm).¹⁰

3.2 Experiment

3.2.1 Chemicals

5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphyrin cobalt (CoTPP, photosensitizer >85%) and 1-Hexanol (>99%) were purchased from Sigma-Aldrich. 1-Phenyloctane (>98%), 1-Chlorohexane (>95%), and 1-hexylamine (>99%) were purchased from Tokyo Chemical Industry Co., Ltd. All reagents were used without further purification.

3.2.2 Substrates

Idealized structures of muscovite mica are shown in Figure 3.2.¹² The muscovite mica has a layered structure consisting of two tetrahedral sheets either side of octahedral sheets, and these 2:1 layers and potassium cations (K^+) are alternately assembled each other. The tetrahedral sheets have the honeycomb-layer-structure which is composed of SiO_4 tetrahedra, where each tetrahedron shares three oxygen with adjacent tetrahedra. The electron deficiency (negative charge) arising from a 1 in 4 substitution of SiO_4 for AlO_4 is neutralized by K^+ . In each side of tetrahedral sheets in a 2:1 layer, two oxygen atoms from adjacent tetrahedra and OH locating below the center of the hexagon of the honeycomb layer form the six corners of the AlO_6 octahedron. The composition of muscovite mica is $KSi_3Al_3O_{10}(OH)_2$, and the unit cell is monoclinic consisting of 4 formula units of composition. The unit cell parameters are $a = 0.519$ nm, $b = 0.901$, $c = 2.00$ nm and $\beta = 95.8^\circ$. The weak interlayer electrostatic interaction leads ease of cleave along with (001) plane.

Muscovite mica (Furuuchi Chemical) was obtained as a substrate with 10 mm $\times$ 10 mm $\times$ 0.3 mm. In this chapter, the author takes the term, mica, to mean specifically muscovite mica. The mica was glued on a sample holder (Figure 3.3) and cleaved with an adhesive cellophane tape just before dropping the solution onto the substrate.

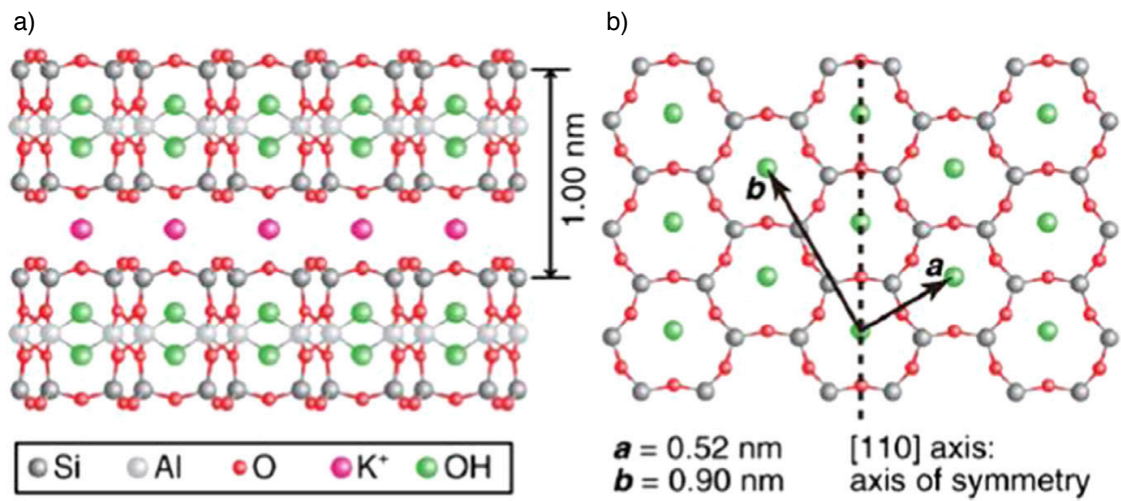


Figure 3.2. Idealized structures of muscovite mica.¹² a) [110] projection showing the assembled structure consisting of 2:1 layers and cations. b) The cleaved plane (001) showing the honeycomb layer of SiO₄ and OH.

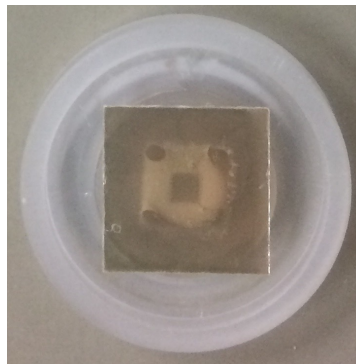


Figure 3.3. The photograph of a mica substrate glued on a sample holder.

3.2.3 Preparation of solutions

CoTPP / 1-hexanol solution

To prepare a CoTPP solution, an excess of CoTPP powder was added to 1-hexanol. After stirring for several minutes and filtration, a solution (9×10^{-4} M) was obtained and used for FM-AFM measurements.

CoTPP / 1-phenyloctane solution

A CoTPP powder (2.2 mg, 3.3×10^{-3} mmol) was dissolved to 1-phenyloctane (1000 mg). In the case of 1-phenyloctane, FM-AFM measurements were performed at lower concentration (3×10^{-3} M) than saturated solution to prevent the laser from shielding.

CoTPP 1-chlorohexane solution

A CoTPP powder (0.2 mg, 3×10^{-4} mmol) was dissolved to 1-chlorohexane (250 mg). In the case of 1-chlorohexane, FM-AFM measurements were performed at lower concentration (1×10^{-3} M) than saturated solution to prevent the laser from shielding.

3.2.4 Microscope and cantilevers

A microscope compatible to SPM-8000FM was manufactured by Shimadzu Corporation and used in this study. The low-noise force detection system described in Chapter 2 was installed in the microscope. The surface topography was obtained in pure solvent or CoTPP solution as mentioned above.

A phase-locked loop (PLL) was used for oscillating a cantilever at its resonance frequency (f_0) and detecting its frequency shift (Δf) induced by the tip-surface interaction force. The amplitude was regulated to be constant with automatic gain controller (AGC). The cantilever was oscillated by a piezo actuator.

Silicon cantilevers (Nanoworld, NCH-W, Au coating) with a nominal spring constant of 42 N/m were used. FM-AFM images presented in this chapter were obtained at constant Δf and vibration amplitude as described in each caption.

The solution was deposited onto a freshly cleaved mica surface and covered with a clear thin glass sheet just before measurements. All measurements were performed at room temperature and under ambient atmosphere.

3.3 Topography of CoTPP at liquid-solid interfaces

3.3.1 Topography in wide area

The constant Δf topography of the mica surface in CoTPP dissolved 1-phenyloctane and 1-chlorohexane solution was shown in Figure 3.4a and b. In solution, a number of discrete molecule-sized protrusions appeared on mica. The lateral dimension of the each protrusion was slightly larger than a CoTPP molecule flat-lying on the surface due to high mobility of CoTPP resulting from weak adsorption onto the surface as described below. On the other hand, the protrusions were absent in pure solvent. These results indicated CoTPP in 1-phenyloctane and 1-chlorohexane solution adsorbed onto mica.

After cleavage of mica, it could be simply thought half of K^+ are expected to remain on each created surface to keep charge valance. Actually, the recent study indicated surface K^+ on cleaved surfaces tended to be high dispersion owing to repulsive interactions between cations and the surface coverage (approximately 45%) was very close to that as expected.¹³ In addition, formation of row-like and small hexagonal domains composed of K^+ was also confirmed due to high surface coverage. Immersed in aqueous ionic solution, distribution of surface cations changes, and surface charge is balanced by adsorbed ions including original K^+ , dissolved cations, H_3O^+ , and OH^- depending on solution pH. Ricci *et al.* reported ordered arrangements of adsorbed cations onto mica in aqueous solution induced by interfacial water using dissipation microscopy.¹⁴ On the other hand, distribution of K^+ on cleaved mica would be expected to roughly remain even after immersion into organic solvent due to low solubility of ionic substances and no existence of another ions in solution contrary to aqueous solution.

Although the CoTPP molecule is the neutral molecule, positive charge is localized on the Co atom in molecular center. Hence, even though high distribution of K^+ counteracted electrostatic interactions between CoTPP and mica, weakly attractive forces between CoTPP and negatively charged domains could act as the driving force

for stabilization.

In order to obtain information about the interaction between CoTPP and mica at the solid-liquid interface, observation in CoTPP dissolved 1-phenyloctane solution including 1-hexylamine (0.1 M) was carried out (Figure 3.4c). The amine derivatives are known for molecules with large DN (for example, DN of ethylamine is 55).¹¹ As a result, the protrusion disappeared on mica, which would imply the axial ligand, 1-hexylamine bound to Co resulting in increasing electron density of Co and a decline in the electrostatic interaction at the CoTPP-mica interface.

Figure 3.5a represents constant Δf topography in 1-hexanol solution with larger DN relative to 1-phenyloctane or 1-chlorohexane. The single molecule-sized protrusions on mica also appeared, which indicated solvent coordination ability of 1-hexanol was negligible in respect to adsorption of CoTPP onto mica in contrast to 1-hexylamine. Beside, in spite of nearly the same CoTPP concentration in each solution, the CoTPP adsorption density is slightly different, which might result from difference of surface K^+ density, coordination ability of solvent, and solvent polarity (large solvent polarity might lead large interactions between solvent and substrates, resulting in prevention of CoTPP adsorption).

In the literature previously reported,¹⁵ a cobalt porphyrin tends to take specific coordination number in a given oxidation state; Co(III) has two axial ligands (six-coordinated structure), Co(II) has one axial ligand (five-coordinated structure), and Co(I) has no axial ligands (four-coordinated structure). The Co cation in the center of CoTPP is divalence and easy to ligate one axial ligand. Thus, it could be considered most CoTPP at the liquid-mica interface took the five-coordination state. In the meantime, a small part of protrusions, for example marked with orange circles in Figure 3.5a, showed different heights (Figure 3.5c), where the height of protrusions could changed with time as described in Figure 3.5b and d. These results would imply the different coordination states of CoTPP could be locally existed and observed in AFM measurement time scale. The further discuss is found in the next section.

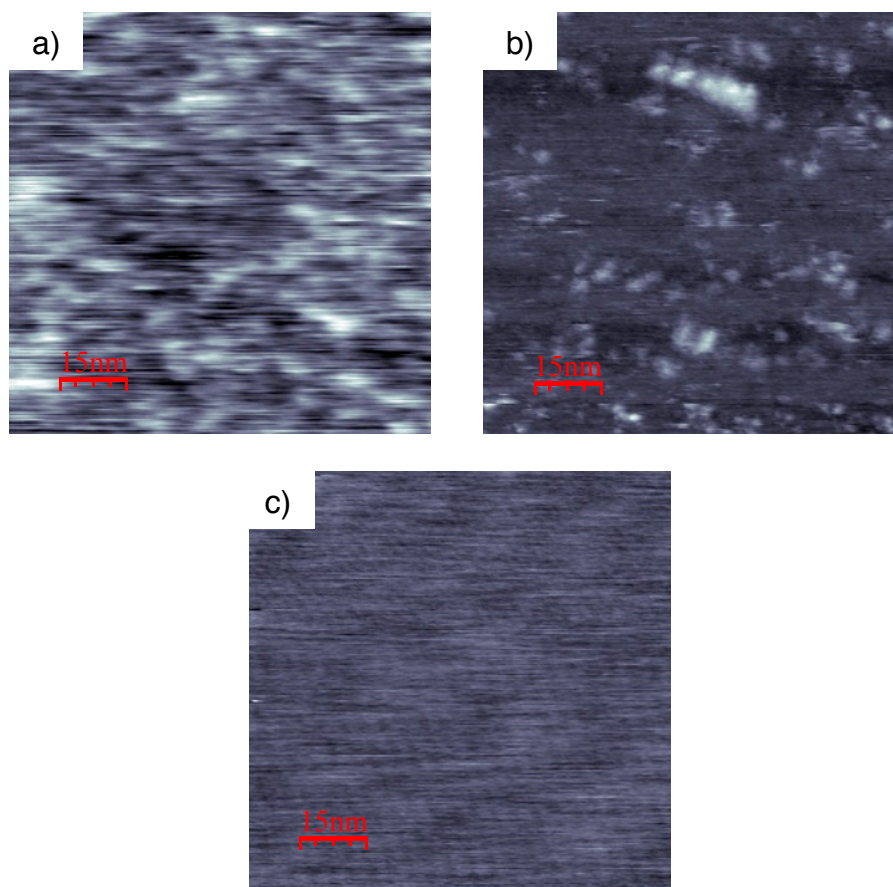


Figure 3.4. Constant Δf topography observed in CoTPP dissolved a) 1-phenyloctane solution, b) 1-chlorohexane solution, and c) 1-phenyloctane solution including 1-hexylamine (0.1 M).

Oscillation amplitude: a) 0.6 nm, b) 0.6 nm, c) 0.6 nm. Δf setpoint: a) +200 Hz, b) +120 Hz, c) +200 Hz.

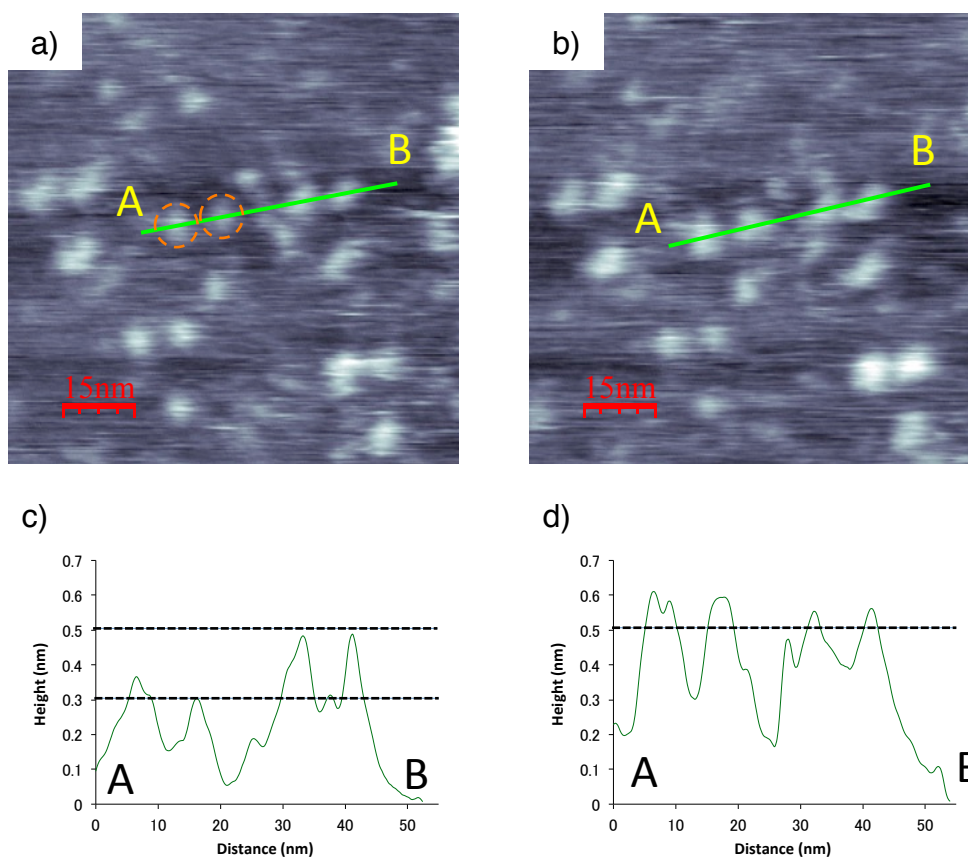


Figure 3.5. a) First constant Δf topography observed in CoTPP dissolved 1-hexanol solution and b) after 60 seconds. c) and d) Cross-sectional height profiles along the green lines on the image a) and b), respectively.

Oscillation amplitude: a) 0.6 nm b) 0.6 nm. Δf setpoint: a) +140 Hz b) +140 Hz.

3.3.2 Topography in narrow area

The constant Δf topography at the liquid-solid interface in CoTPP dissolved 1-hexanol solution was shown in Figure 3.6a. The width of protrusions was slightly larger than the CoTPP molecular size owing to large mobility caused by weak interfacial interactions. In addition, two states of adsorption were also further identified. The topographic height of the protrusion marked with the orange circle was about 0.4 nm relative to the mica surface. On the other hand, the protrusion with the blue circle presented a smaller height of about 0.2 nm. CoTPP molecules in solution could stack on the CoTPP molecule adsorbed on mica. However, CoTPP is required to stack off-center to avoid the electrostatic repulsion between each cobalt center. The width of the protrusion with a larger height was approximately coincident with that with a smaller height, which would imply it is unlikely to form the CoTPP dimer. Hence, these protrusions with distinct heights suggested both the coordination state (major state) and the state without an axial ligand (minor state) existed and could be detected in AFM measurement time scale.

It would be thought the possible axial ligand is the dissolved oxygen molecule or the solvent molecule. Summers *et al.* reported the crystal structure of Co porphyrin bound with pyridine and the bond distance between Co atom in the molecular center and N atom from pyridine, which is about 0.2 nm¹⁶ and approximately consistent with the difference between two states of adsorbed CoTPP on mica (Figure 3.6) though it is not equal in the coordination atom. In comparison with the solution study and the STM study in the previous reports,^{6f} it was shown the solid support with electron-donating ability leading to a increase in affinity of cobalt porphyrin for oxygen molecules was essential. However, mica would only act to stabilize CoTPP and have almost no electronic interactions with CoTPP. For this reason, it is less likely that CoTPP on mica binds an oxygen molecule at the liquid-solid interface.

Solvent molecules could also act as axial ligands. The acquired data was reasonable to explain the adsorption molecule aligned parallel to the substrate, and different states

of CoTPP were ascribed to the chemical interaction between the solvent molecule and Co in the molecular center. As well as topography in 1-hexanol solution, the two states of protrusions were also observed in 1-phenyloctane or 1-chlorohexane solution (Figure 3.6c, e), which suggested the different states of CoTPP sensitive to axial ligands were also detectable in the presence of even weak coordination ligands (solvent molecules with small DN).

In addition, Figure 3.7 shows the successive constant Δf topography at the liquid-mica interface in CoTPP dissolved 1-chlorohexane solution. The protrusion marked with the blue circle was nearly the same height as the one marked with the orange circle in the first image (Figure 3.8a, b). After that, the state of the protrusion marked with the blue circle changed to the state with a smaller height. As the time further progressed, the height of the protrusion marked with the blue circle returned to the original state, which is the same as the protrusion marked with the orange circle. It was found that FM-AFM measurements showed coordination state has changed, which could be detectable in AFM measurement time scale.

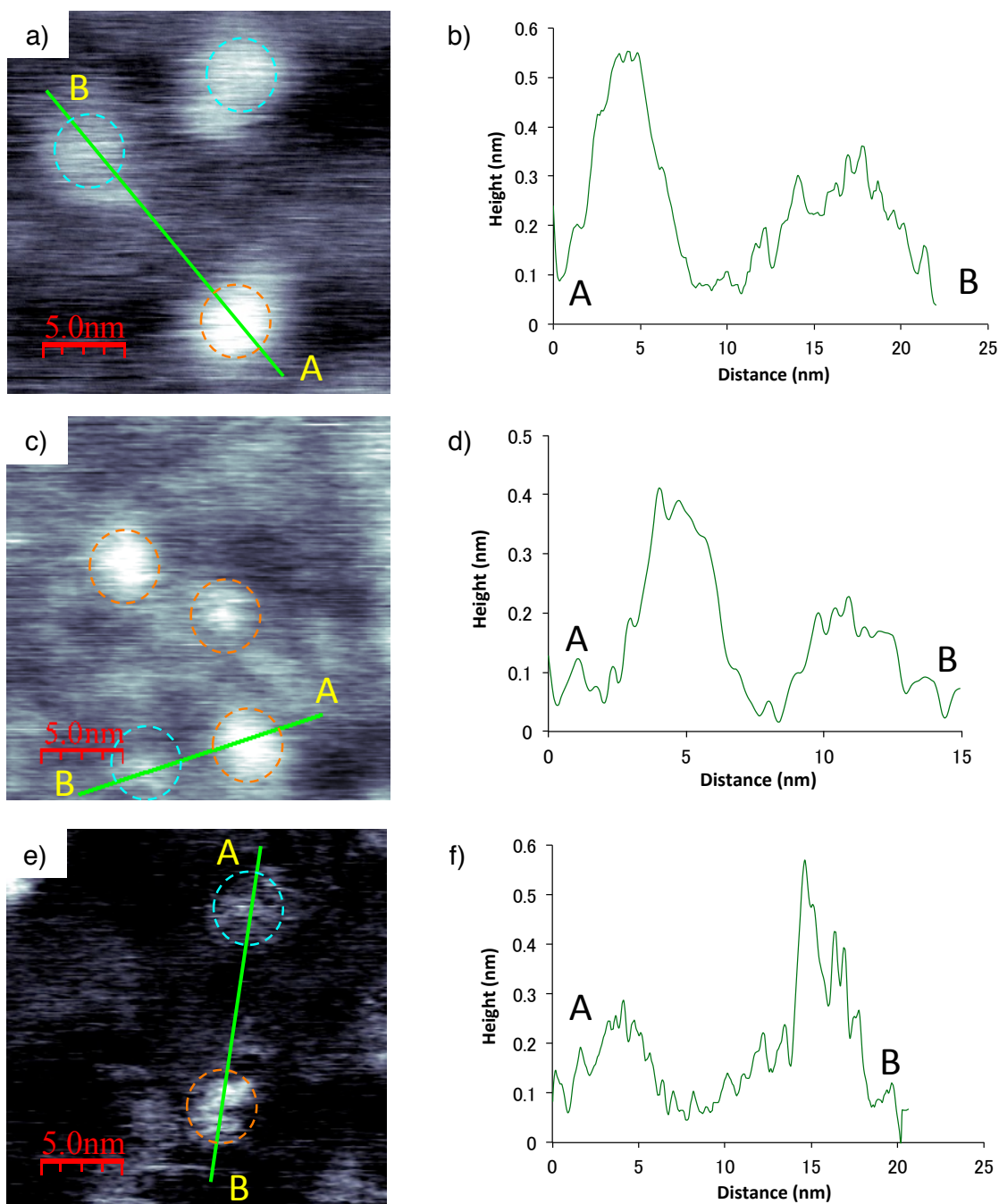


Figure 3.6. Constant Δf topography observed in CoTPP dissolved a) 1-hexanol solution, c) 1-phnyloctane solution, and e) 1-chlorohexane solution. b), d), and f) Cross-sectional height profiles along the green lines on the image a), c), and e), respectively.

Oscillation amplitude: a) 0.6 nm b) 1.0 nm c) 0.6 nm. Δf setpoint: a) +140 Hz b) +100 Hz c) +120 Hz.

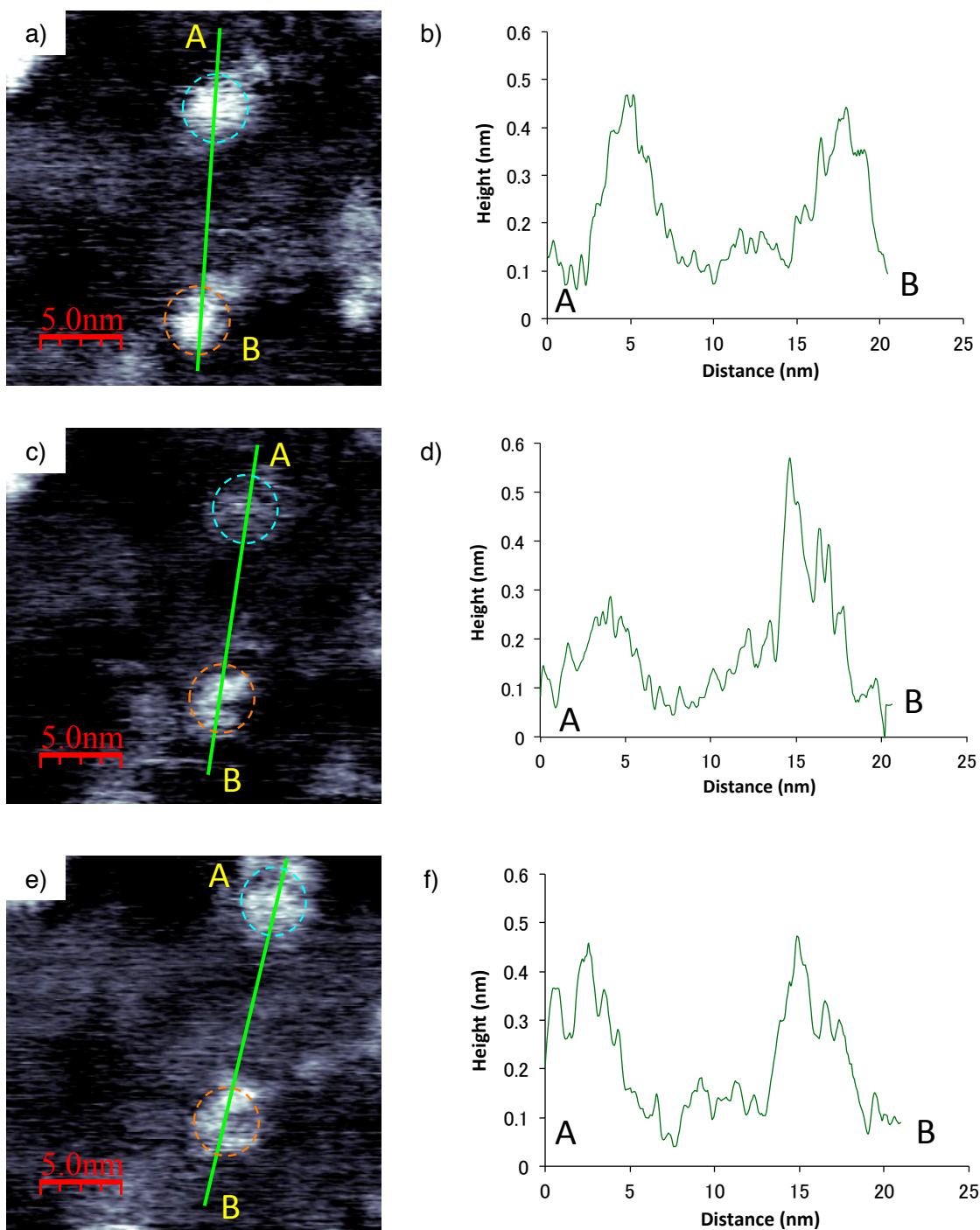


Figure 3.7. Consecutive constant Δf topography observed in CoTPP dissolved 1-chlorohexane solution. a) First image, c) 21seconds, and e) 41seconds after a). b), d), and f) Cross-sectional height profiles along the green lines on the image a), c), and e), respectively.

Oscillation amplitude: 0.6 nm. Δf setpoint: +120 Hz.

3.4 Conclusions

In this chapter, the constant Δf topography at the interface in CoTPP solution was obtained and topographic protrusions were identified in 1-hexanol, 1-phenyloctane, and 1-chlorohexane solution. Electrostatic interactions across the CoTPP-mica interface would lead stabilization of CoTPP adsorption on mica. Besides, two states of adsorption were further identified, and the difference of topographic height was about 0.2 nm, which indicated adsorbed solvent molecules would be arranged parallel to the substrate, and different states of CoTPP were ascribed to the coordination states in the Co metal center. In addition, the coordination states of axial ligands have changed with time, and it could be detectable in AFM measurement time scale in the presence of even weak coordination ligands.

3.5 References

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Chapter 4: FM-AFM Imaging of a Platinum Porphyrin in Photooxidation Reaction

4.1 Introduction

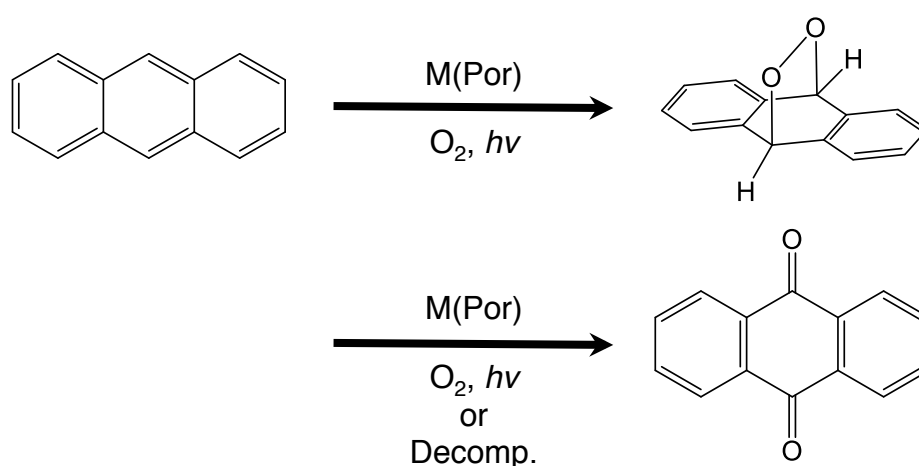
Porphyrins and their analogs including metal complexes are known to be highly effective and environmental friendly triplet state photosensitizers for formation of singlet molecular oxygen.¹ In presence of visible light, porphyrin derivatives produce singlet molecular oxygen selectively (type II process). The singlet oxygen generated by porphyrin with light irradiation could be evidenced by electron paramagnetic resonance (EPR).² Besides, anthracene derivatives are also employed to detect singlet molecular oxygen as chemical trapping to form endoperoxide or further oxidized species, anthraquinone by decompose or additional oxidation (scheme 4-1).³

The major analyses of these photoreactions are performed in solution, such as spectroscopy, ¹H NMR, and EPR.⁴ On the other hand, no real-time imaging of these reactions at solid-liquid interfaces have been reported. It does not apply only to metalloporphyrin in light-induced reactions, and only a few limited examples have been reported to image single molecules in reaction conditions, for instance oxidation of manganese porphyrins⁵ or oxygenation of cobalt porphyrins.⁶ These studies described the single molecular images in several redox states of manganese or cobalt porphyrins by STM. However, reactants except for oxygen were not detected in spite of catalytic reactions (only result of GC was provided).^{5b} Additionally, these oxidation of metallocomplexes occurred only in the presence of specific substrates with electronic interactions at interfaces, from which reactions in solution were intrinsically different.

In the previous chapter, the author indicated it was possible to monitor discrete metalloporphyrins with organic molecules as coordination ligands. The AFM has proven to be a good tool for imaging molecules including reactants at solid-liquid interfaces. However, detected organic molecules were not transformed to another

chemical structures. In fact, real-time imaging of individual molecules in chemical reactions by AFM was limited under UHV (ultra high vacuum),⁷ where solvent-induced factors such as interactions with reagents, competitive adsorption, diffusion, and concentration are absent.

Here, the author reported the AFM study of the photooxidation of anthracene catalyzed by 5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphyrin platinum (PtTPP) at the solid-liquid interface. PtTPP has been known as not only sensitizers of singlet molecular oxygen generation with high quantum yield but also photooxidation catalysts.³ Recently advanced AFM enabled to demonstrate dynamic studies in liquid environments, leading to imaging discrete catalyst molecules together with reagents or products under reactive conditions as expected.



Scheme 4.1. Photooxidation of anthracene by metalloporphyrin.

4.2 Experiment

4.2.1 Chemicals

5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphirin platinum (PtTPP, >95%, Figure 4.1) was purchased from Funakoshi Co., Ltd. 1-Phenyloctane (>98%), anthracene (>97%), and anthraquinone (>98%) were purchased from Tokyo Chemical Industry Co., LTD. All reagents were used without further purification.

4.2.2 Substrates

Muscovite mica (Furuuchi Chemical) was obtained as a substrate with 10 mm × 10 mm × 0.3 mm. The composition of muscovite mica is $\text{KSi}_3\text{Al}_3\text{O}_{10}(\text{OH})_2$, and the unit cell is monoclinic consisting of 4 formula units of the composition. The unit cell parameters are $a = 0.519$ nm, $b = 0.901$ nm, $c = 2.00$ nm and $\beta = 95.8^\circ$.⁸ The detail crystal structure of mica was described in Chapter 3. In this chapter, the author takes the term, mica, to mean specifically Muscovite mica. The mica was glued on a sample holder (Figure 3.3) and cleaved with an adhesive cellophane tape just before dropping the solution onto the substrate.

4.2.3 Physical measurements

A microscope compatible to SPM-8000FM was manufactured by Shimadzu Corporation and used in this study. The low-noise force detection system described in Chapter 2 was installed in the microscope. Topography was obtained in PtTPP solution as mentioned below.

A phase-locked loop (PLL) was used for oscillating a cantilever at its resonance frequency (f_0) and detecting its frequency shift (Δf) induced by the tip-surface interaction force. The amplitude was regulated to be constant with amplitude feed back controller. The cantilever was oscillated by a piezo actuator. Silicon cantilevers (Nanosensors, PPP-NCH AuD-50) with a nominal spring constant of 42 N/m were used.

FM-AFM images presented in this chapter were obtained at constant Δf and vibration amplitude as described in each caption. The solution was deposited onto the freshly cleaved mica surface and covered with a clear thin glass sheet just before FM-AFM measurements.

UV-Vis (ultraviolet-visible) spectra in solution were recorded on a JASCO V-570 spectrophotometer using a quartz cell (with an optical path length of 10 mm). An Asahi spectra 300 W xenon light source MAX-303 was used as a light source with a light intensity of 110 mW/cm². For light irradiation at >500 nm, a 500 nm band pass filter (HOYA, colored optical glass Y50) was used. The light intensity was tuned by the continuous variable ND filter built in the spectrophotometer as described in each experimental data to avoid prevention of AFM measurements.

All measurements were performed at room temperature and under ambient atmosphere.

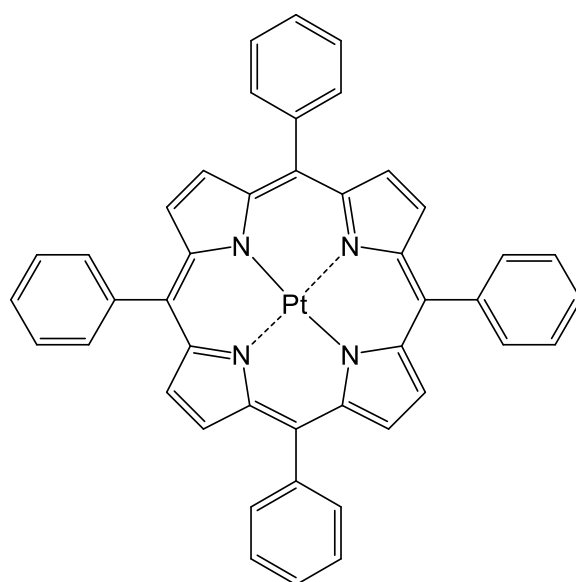


Figure 4.1. A molecular structure of 5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphyrin platinum.

4.3 Photooxidation of anthracene in solution

As described in the previous section, the photooxidation of anthracene with porphyrin derivatives has been well-known. To confirm the reaction proceeding under AFM operative conditions, we first performed consecutive UV-Vis absorption spectra under light irradiation.

The UV-Vis spectra of PtTPP, anthracene, and anthraquinone measured in 1-phenyloctane are shown in Figure 4.2, and the relevant experimental data are listed in Table 4.1. PtTPP exhibits the characteristic bands at 402 nm and in visible region (510 and 538 nm), which could be assigned to the Soret band and the Q bands, respectively.⁹ On the other hand, anthracene and anthraquinone demonstrated bands in only UV region.

Figure 4.3 presents consecutive changes of UV-Vis spectra in anthracene and PtTPP dissolved 1-phenyloctane solution under light irradiation in visible region (>500 nm), identical to PtTPP Q bands. The irradiation of visible light led to a decrease of the absorbance at 359, and 378 nm assigned to anthracene, whereas no changes were observed in visible region. In addition, the light irradiation generated new absorption bands at 283 and 326 nm, assigned to anthraquinone. These spectral changes were similar to data in the literature⁴ and indicated the light-induced oxidation of anthracene into anthraquinone by PtTPP occurred in 1-phenyloctane solution (i.e. under AFM operative conditions). The conversion rates calculated from the anthracene absorption intensity were 2, 4, 8, and 12% after 30, 60, 120, and 180 min light irradiation, respectively. In the subsequent section, the author performed PtTPP adsorption behavior at solid-liquid interfaces in 1-phenyloctane solution and obtained images of PtTPP involved with photooxidation.

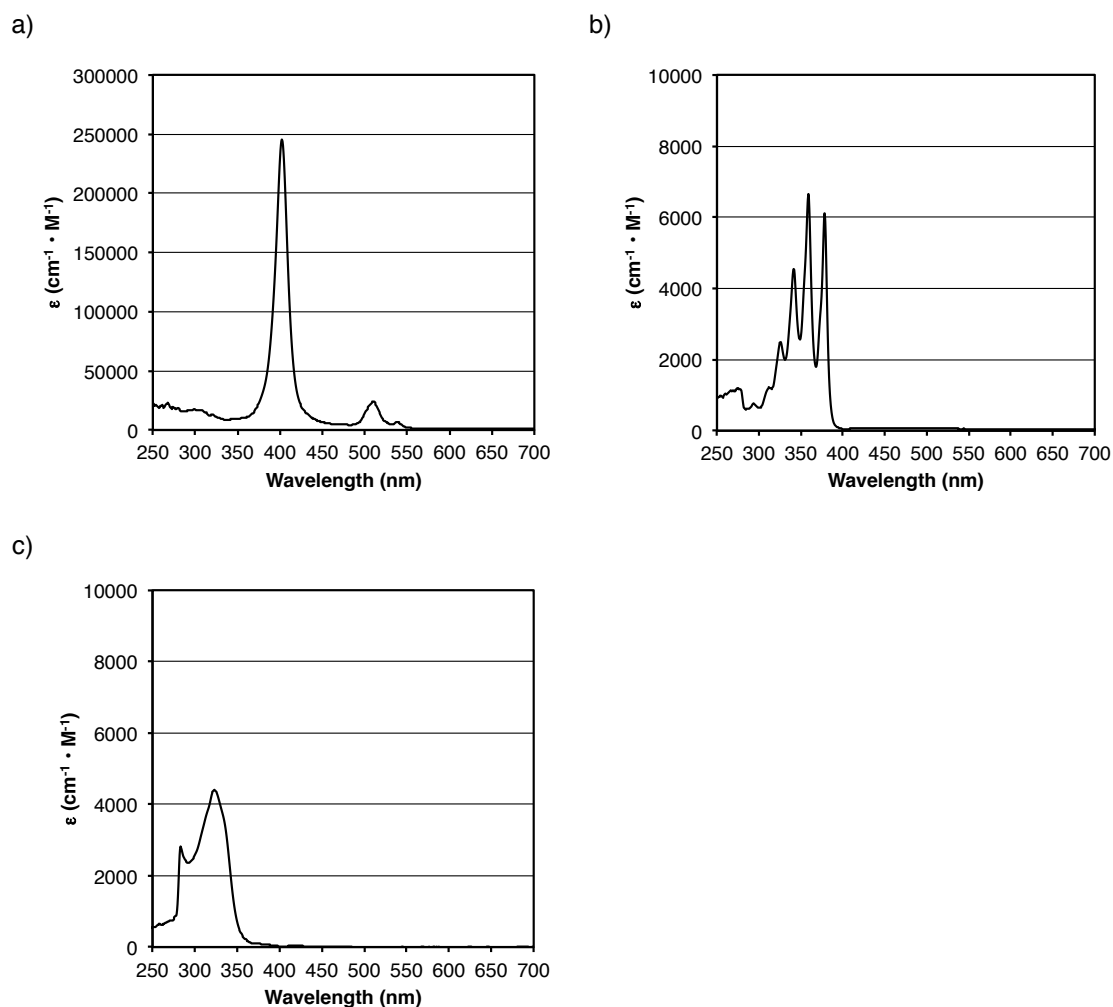


Figure 4.2. UV-Vis absorption spectra of a) PtTPP at 4.1×10^{-6} M, b) anthracene at 1.4×10^{-4} M, and c) anthraquinone at 2.3×10^{-4} M in 1-phenyloctane.

Table 4.1. Experimental absorption spectral data of PtTPP, anthracene, and anthraquinone in 1-phenyloctane.

Compound	Solvent	Concentration (mol · L ⁻¹)	λ_{abs} / nm (ϵ / cm ⁻¹ · M ⁻¹)
PtTPP	1-Phenyloctane	4.1×10^{-6}	402 (245,320), 510 (23,970), 538 (6,700)
Anthracene	1-Phenyloctane	1.4×10^{-4}	293 (770), 312 (1,220), 326 (2,490), 341 (4,550), 359 (6,650), 378 (6,110)
Anthraquinone	1-Phenyloctane	2.3×10^{-4}	283 (2,820), 323 (4,400)

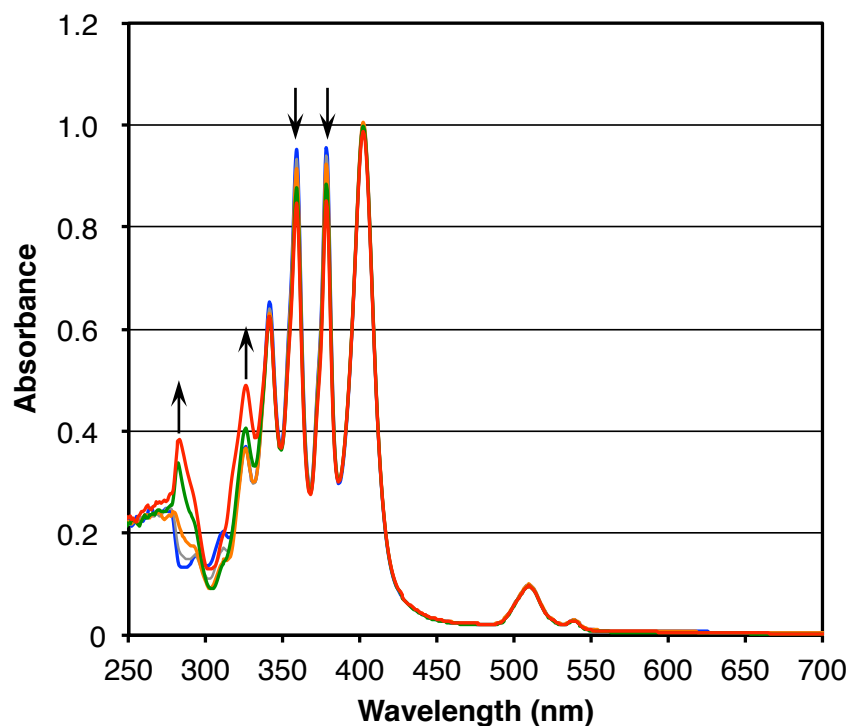


Figure 4.3. Changes of the UV-Vis absorption spectra in PtTPP and anthracene dissolved 1-phenyloctane solution at 4.6×10^{-6} M and 1.4×10^{-4} M, respectively. Upon light irradiation (>500 nm) for 0 (blue line), 30 (gray line), 60 (orange line), 120 (green line), and 180 min (red line). The light intensity was tuned to 75% from the original light source.

4.4 Topography of PtTPP at liquid-solid interfaces

Initially, adsorption property of PtTPP at the liquid-mica interface in 1-phenyloctane solution was investigated under the ambient condition. Figure 4.4a shows the wide-area constant Δf topography at the liquid-mica interface. The bright protrusions with approximately the single molecular dimension appeared instantaneously after immersion, indicating PtTPP was adsorbed face-on to the surface. Of these, a lot of protrusions appeared to be dispersed with only partially agglomerated protrusions. Actually, the height distribution from the mica surface (the darkest area in Figure 4.4a) showed nearly uniform protrusions with a dimension of approximately 0.3-0.4 nm (Figure 4.4b). As described in Chapter 3, adsorption of metalloporphyrins could be stabilized by weak electrostatic interactions at interfaces in spite of the neutral complex. The presumable reason of large dispersion is the distribution of negative charged domains at the mica-liquid interface.

Divalent Pt complexes are known to take d^8 electronic configuration and have an occupied p_z electronic orbital vertical to the molecular plane. Although electron configuration of PtTPP adsorbed face-on to the surface is disadvantage of electrostatic interactions at the interface, the results described above revealed the difference of electronic states between Co and Pt was negligible for adsorption onto the mica surface.

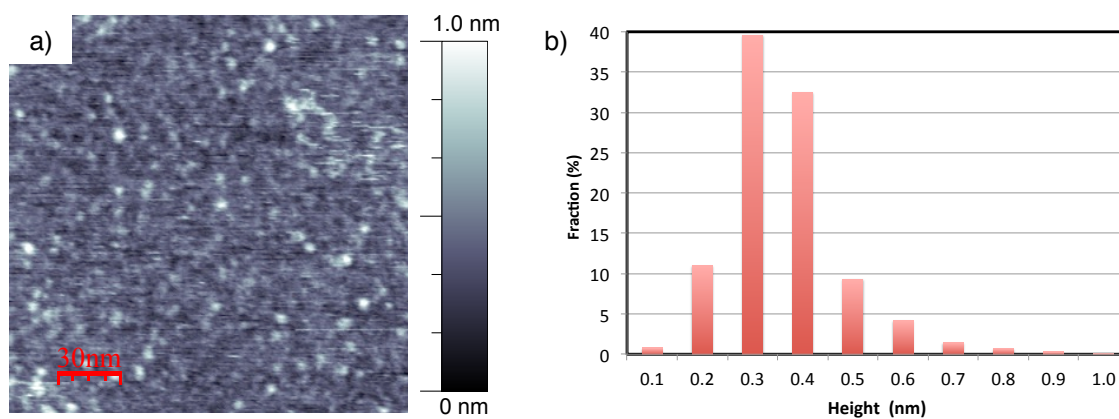


Figure 4.4. a) Constant Δf topography observed in PtTPP dissolved 1-phenyloctane solution at 3.3×10^{-4} M. b) Height histogram of a). Oscillation amplitude: 1.0 nm. Δf setpoint: +50 Hz.

4.5 Topography of PtTPP under visible light irradiation

The author observed PtTPP adsorbed at the interface in the presence of anthracene under visible light (>500 nm) irradiation. Figure 4.5a represents the constant Δf topography in anthracene and PtTPP dissolved solution before light irradiation. Topographic features and corresponding height distribution from the mica surface (given by red histogram in Figure 4.5c) were roughly maintained relative to those in absence of anthracene (Figure 4.4a and b).

On the other hand, constant Δf topography in anthraquinone and PtTPP dissolved solution as shown in Figure 4.5b presented protrusions with a distinct height about 0.2 nm larger relative to those in anthracene dissolved solution in comparison with histogram (Figure 4.5c). These different features might be attributed to different adsorption structures onto PtTPP between anthracene and anthraquinone.

Subsequently, the constant Δf topography in anthracene dissolved PtTPP solution upon the light irradiation is shown in Figure 4.6a. In comparison with topography before light irradiation (Figure 4.5a), subsequent light irradiation led to new appearance of approximately 0.2-0.3 nm larger protrusions relative to the original state (Figure 4.6b). The shift amount of the height was roughly coincident with the difference of protrusion heights between in anthracene and anthraquinone dissolved solution (Figure 4.5c). These results suggested the appearance of protrusions with a larger dimension would be attributed to the conversion of anthracene into anthraquinone on PtTPP.

Upon the irradiation, singlet oxygen generated on PtTPP and instantaneously reacted with adjacent anthracene or diffused and/or deactivated. Singlet oxygen has sufficiently small excited state life time in organic solvent relative to AFM time scale,⁹ for instance, life time in *n*-decane was 27.6 μ s in the literature, which results in no contribution of singlet oxygen to the change in topography under irradiation.

Nevertheless, the concern about influence of generated anthraquinone in solution still remains. In this experiment system, not only interfacial anthracene molecules but also

those in solution would be reacted and converted into anthraquinone molecules. The anthraquinone molecules generated in solution also could be diffused and adsorbed onto PtTPP. Actually, Figure 4.6a was acquired under irradiation in 28 min. When light irradiation to solution was carried out as indicated in Figure 4.3, however, conversion rate into anthraquinone in solution was only 2% after 30 min irradiation with the light intensity even 2.5 times as large as that in the AFM measurement. (As shown in each caption, the light intensity in the absorption spectroscopic measurement and the AFM measurement are 75% and 30% relative to the original light source, respectively.) Besides, the AFM measurement in 2% anthraquinone solution relative to anthracene was demonstrated to give the image and histogram (Figure 4.7a and b) similar to those without anthraquinone. Taking such small conversion rate and reproductive experiment into account, it would be implied the anthraquinone generated in solution was negligible or sufficiently small for the AFM measurement.

The change of the protrusion height was also confirmed in images of discrete single molecules. Figure 4.8 shows the subsequence of topographic images from one experiment under visible light (>500 nm) irradiation in narrow area. The protrusion described in Figure 4.8a was transformed into the higher protrusion (Figure 4.8b), whose shift amount of the dimension was about 0.2 nm approximately according to that in histogram observed in wide-area, which suggested such a dimension change of the single protrusion (i.e. single molecule) was ascribed to generation of anthraquinone. These results indicated the conversion into anthraquinone observed in wide-area was also detected in the single molecular measurement.

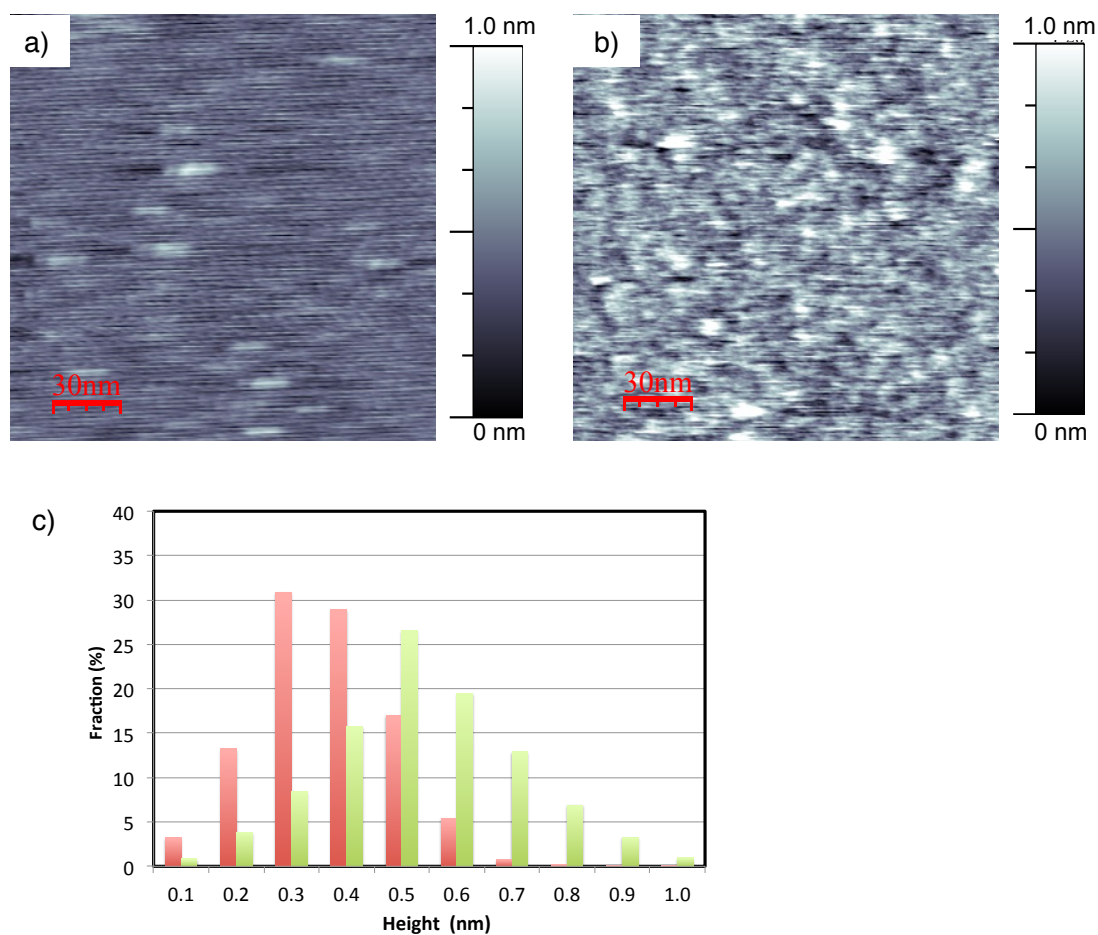


Figure 4.5. Constant Δf topography observed in a) PtTPP (3.3×10^{-4} M) and anthracene (2.2×10^{-2} M) dissolved 1-phenyloctane solution and b) PtTPP (3.3×10^{-4} M) and anthraquinone (4.2×10^{-3} M) dissolved 1-phenyloctane solution. c) Height histogram of a) (red bars) and b) (green bars).

Oscillation amplitude: a) 1.0 nm b) 1.0 nm. Δf setpoint: a) +120 Hz b) +105 Hz.

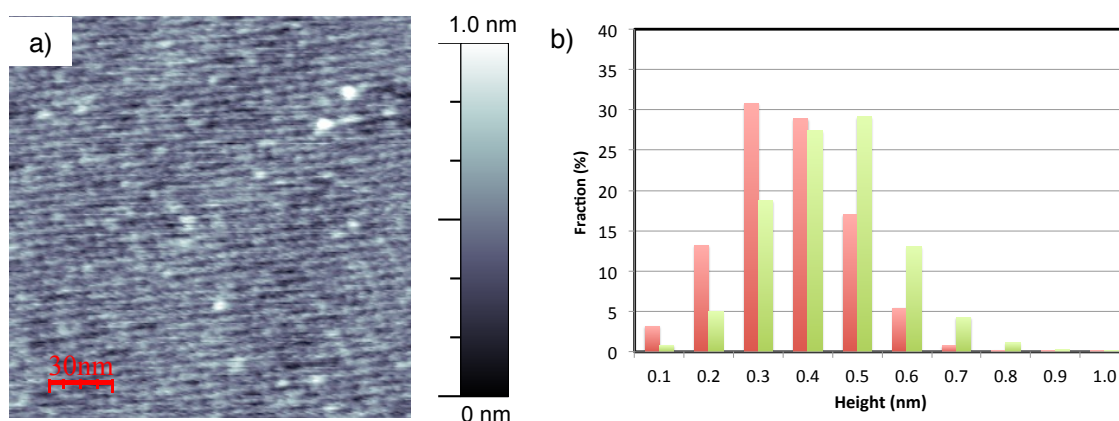


Figure 4.6. a) Constant Δf topography observed in PtTPP (3.3×10^{-4} M) and anthracene (2.2×10^{-2} M) dissolved 1-phenyloctane solution under light irradiation in 28 min. The light intensity was tuned to 30% from the original light source. b) Height histogram of Figure 4.5a (red bars) and Figure 4.6a (green bars). Oscillation amplitude: 1.0 nm. Δf setpoint: +120 Hz.

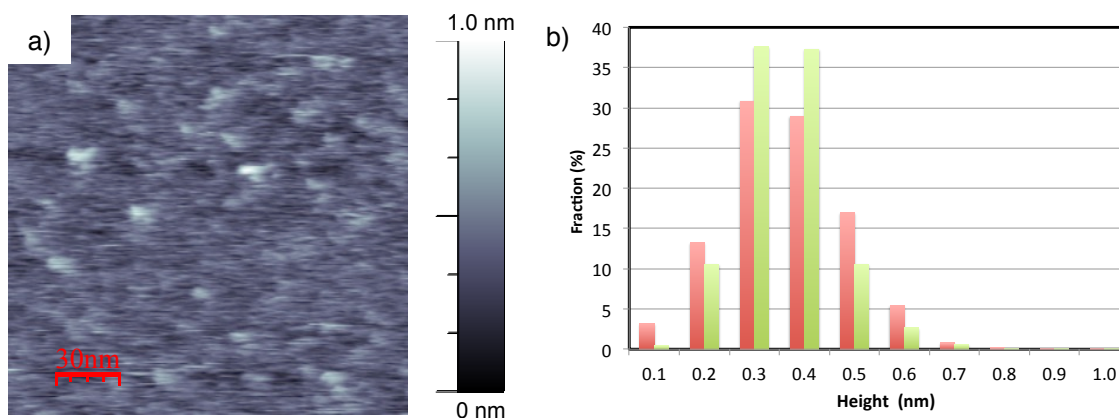


Figure 4.7. a) Constant Δf topography observed in PtTPP (3.3×10^{-4} M), anthracene (2.2×10^{-2} M) and anthraquinone (4.6×10^{-4} M) dissolved 1-phenyloctane solution. b) Height histogram of Figure 4.5a (red bars) and Figure 4.7a (green bars). Oscillation amplitude: 1.0 nm. Δf setpoint: +80 Hz.

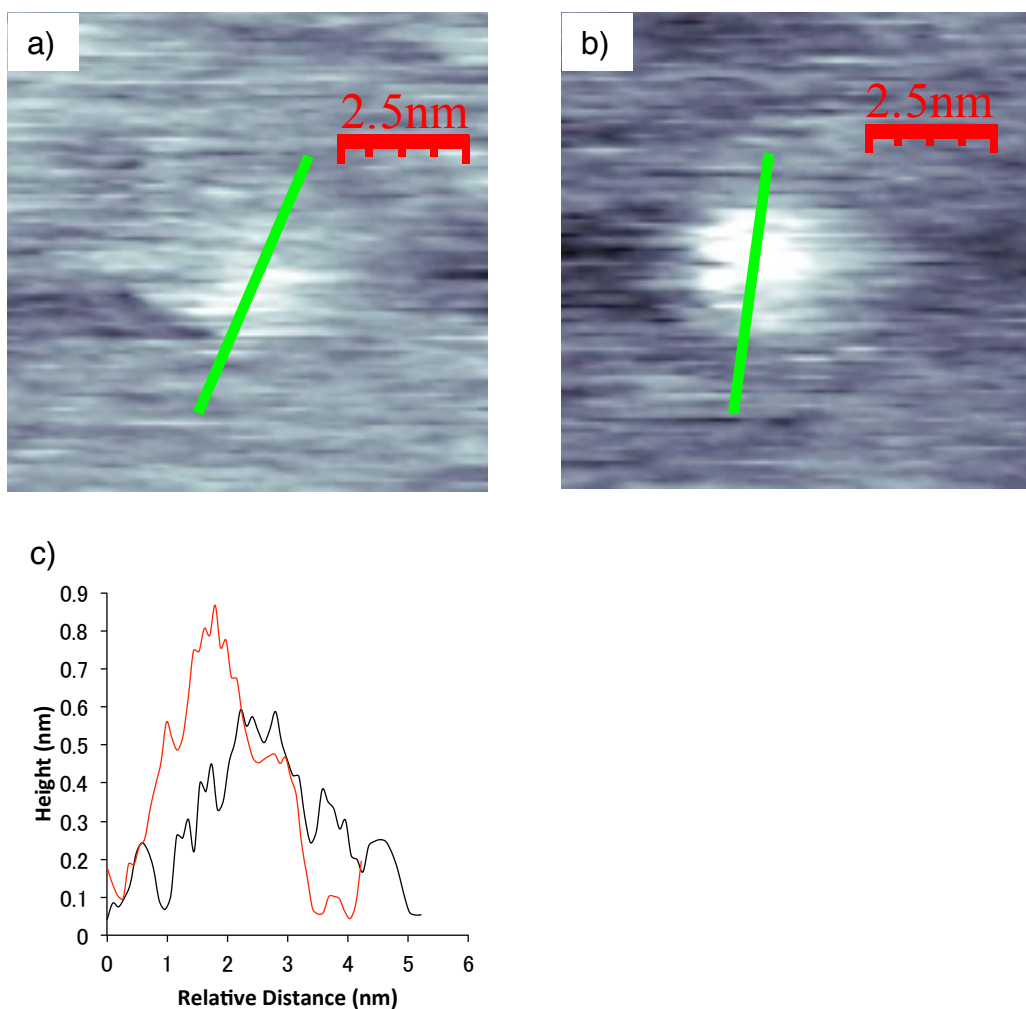


Figure 4.8. a) and b) Sequential constant Δf topography observed in PtTPP (3.3×10^{-4} M) and anthracene (2.2×10^{-2} M) dissolved 1-phenyloctane solution under light irradiation with a measurement interval of 27 sec. c) Cross-sectional height profiles indicated by black and red lines along the green lines on images of a) and b), respectively. The light intensity was tuned to 10% from original light source.

Oscillation amplitude: 1.0 nm. Δf setpoint: +170 Hz.

4.6 Conclusions

In this chapter, single molecular imaging by FM-AFM was reported about photooxidation of anthracene induced by PtTPP. First, the UV-Vis absorption measurements were carried out to confirm the visible-light-induced reaction in 1-phenyloctane solution followed by the AFM studies under light irradiation.

Before irradiation, PtTPP was dispersed on the mica surface presumably due to electrostatic interactions at the solid-liquid interface. Upon the visible (>500 nm) light irradiation, new protrusions with a 0.2-0.3 nm larger dimension were generated in wide-area, whose shift amount was approximately coincident with the difference of protrusion heights between in anthracene and anthraquinone solution. In addition, single molecular imaging in narrow-area also showed the change of the protrusion height similar to that in wide-area, which suggested the interfacial behavior in the chemical reaction was detectable in even single molecular images using FM-AFM. It was expected to lead to application to other various reactions in liquid environments.

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Chapter 5: Solvent-Sensitive Structures of Interfacial Liquid on Salicylic Acid (110) Surface

5.1 Introduction

Local structures of solvent at interfaces play very important roles in application in chemistry, biochemistry and material science.¹ The precise understanding of interactions at solid-liquid interfaces leads to determination of not only various properties but also mechanism of adsorption/desorption behavior. In addition, solvent affinity for solid surfaces with a variety of functional groups is also thought to be the key role in catalyst reactions at solid-liquid interfaces, which directly affects catalyst activity or selectivity.² As described in Chapter 1, however, limited methods are available for experimental determination of interfacial liquid structures, for instance X-ray diffraction, neutron reflection, and SFA (surface force apparatus).³ In addition, these analyses give only average data lateral to the surface and it is difficult to reveal local liquid structures.

On the other hand, AFM has been applied as an effective tool for liquid distribution sensors at interfaces as a function of lateral and vertical coordinate with spatial resolution owing to development of FM-AFM as described in Chapter 2, which has enabled to achieve piconewton-order force sensitivity.⁴ In fact, AFM measurements have been demonstrated for metal carbonate,⁵ metal oxide,⁶ SAMs (self-assembled monolayers),⁷ graphite,⁸ and organic crystals.⁹ Besides, AFM measurements could help to reveal not only liquid structures but also adsorbed molecules with even weak interactions as mentioned in Chapter 1.

In an earlier study,¹⁰ the constant frequency shift (Δf) topography of salicylic acid (SA) on (110) surface in *n*-hexadecane, *n*-decane, 1-phenyloctane and octamethylcyclotetrasiloxane (OMCTS) has been reported by using FM-AFM, whose features are consistent with the crystal structure reported in the literature.¹¹

Additionally it was found that a checkerboard-like structure of liquids in accordance with surface corrugation was formed perpendicular to [001] direction over (110) surface.

Organic crystals are suitable as substrates for investigation of interactions at liquid-solid interfaces due to a variety of surface figure or substituents. In terms of liquids or adsorbed molecules, molecular features of organic solvent such as symmetry, bulkiness, and substituent affect interfacial interactions. As mentioned above, the reported liquid structures at the liquid-SA interfaces were limited in solvent with one-dimensional structures (rod-like shape) or planar molecules. A structure of solvent with three-dimensional structures such as spherical molecules was attractive in terms of fitness onto the corrugated surface. Besides, formation of hydrogen bonds is also the very important factor for determination of interfacial structures. Taking other report for example, Nishioka *et al.* presented the localized structure of water on *p*-nitroaniline.⁹ Although SA also has the interesting surface figure and hydroxyl groups, no measurements in spherical molecular solvent or solvent with hydrogen bond ability have been performed using FM-AFM. In this chapter, the surface topography and the liquid structures at the SA-liquid interfaces were investigated in tetraethylsilane (TES, Figure 5.1a) and 1-decanol (Figure 5.1b) to reveal the sensitivity to molecular figure or substituent groups for the interfacial structures in comparison with what was observed in hexadecane. Moreover, the possibility of application to detect weakly adsorbed molecules was also discussed.

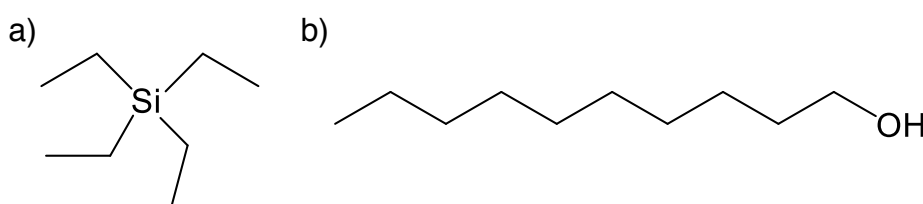


Figure 5.1. Molecular structures of a) TES and b) 1-decanol.

5.2 Experiment

5.2.1 Chemicals

Salicylic acid (SA, >99.5%), 1-decanol (>95%) and ethanol (>99.5%) were purchased from Wako. Tetraethylsilane (TES, >97%) was purchased from Tokyo Chemical Industry Co., LTD. *n*-Hexadecane (>99%) was purchased from Sigma-Aldrich. All reagents were used without further purification.

5.2.2 Substrates

In this study, crystals of SA were prepared by recrystallization.¹¹ A saturated solution of SA was prepared in ethanol. After cooling from 303 K to 298 K in 7 days using an incubator, single crystals were precipitated.

In the literature,¹¹ the crystals of SA are monoclinic with $a = 1.152$ nm, $b = 1.121$ nm, $c = 0.492$ nm, and $\beta = 90.50^\circ$, and with space group $P2_1/a$. The (110) or (210) planes of SA seemed to be preferred orientation planes. Figure 5.2a and b show (001) and (010) planes of the crystal structure.^{11b, d} Each SA molecule forms dimers with hydrogen bonds. The molecular columns consisting of the dimers with 44.7° distortion against (110) plane and a distance of 0.49 nm form protrusions with a width of 0.70 nm. The molecular columns consisting of the dimers with 47.5° distortion against (001) plane form trenches with a width of 0.91 nm.¹⁰ The carboxylic acid groups of surface SA molecules in trenches are occupied with hydrogen bonds and remaining hydroxyl groups are exposed to the crystal surface.

The prepared crystal with 6 mm $\times$ 0.6 mm $\times$ 0.4 mm was fixed on a sample holder (Figure 5.3) followed by heating the crystal surface using dryer to become clear for sublimation just before installing on the stage of FM-AFM and dropping the solution onto the crystal.

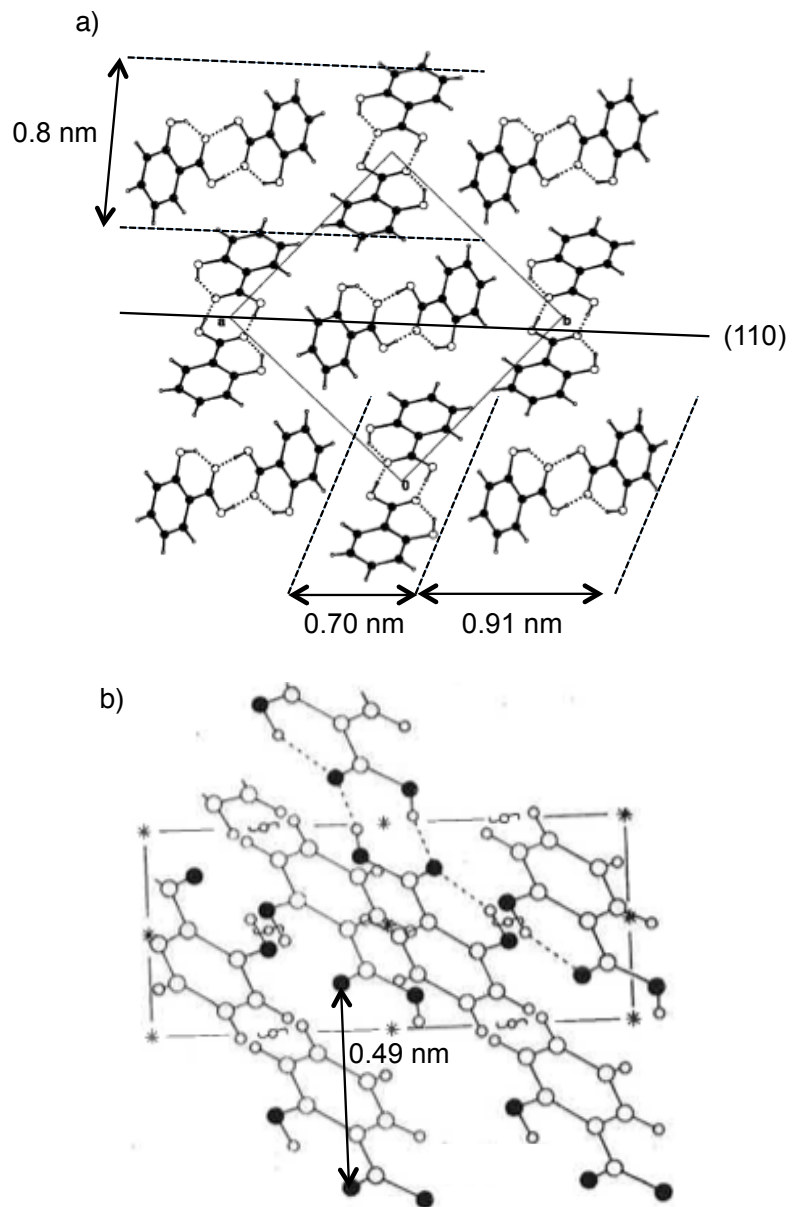


Figure 5.2. a) and b) Structure projection on (001) and (010) surfaces, respectively.^{10, 11b, d}

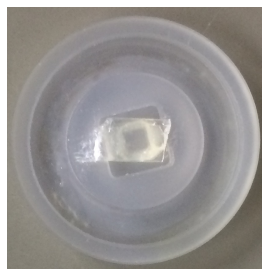


Figure 5.3. The photograph of a single SA crystal glued on a sample holder.

5.2.3 Microscope and cantilevers

A microscope compatible to SPM-8000FM was manufactured by Shimadzu Corporation and used in this study. The low-noise force detection system described in Chapter 2 was installed in the microscope. Topography was obtained in neat TES or SA saturated 1-decanol solution.

The Δf of cantilever oscillation was detected with a phase-locked loop (PLL). The amplitude was regulated to be constant with amplitude feed back controller. The cantilever was oscillated by using photothermal excitation method except for Figure 5.9 (using a piezo actuator) as described in Chapter 2.

Silicon cantilevers (Nanoworld, NCH-W, Au coating) with a nominal spring constant of 42 N/m were used. FM-AFM images presented in this chapter were obtained at constant Δf and vibration amplitude as described in each caption.

The solution was deposited onto a fresh crystal surface after the pretreatment described in the previous section and covered with a clear thin glass sheet just before measurements. All measurements were performed under ambient temperature and atmosphere.

5.3 Topography of SA in liquids

The author started with observation of SA (110) surface topography in TES. Figure 5.4a presents the wide-area constant Δf topography. A terrace and step appeared typically 10 min after immersion (Figure 5.4b). Although only terraces and steps formed artificially by tip-surface collision were observed in the previous report,¹⁰ the height of the single step confirmed this time was coincident with the spacing of (110) surfaces of SA, which suggested the surface feature formed in saturated ethanol has been kept owing to low solubility (less than 0.1g-SA/100g-TES, molar ratio of less than 0.001). On the other hand, no step were observed in SA saturated 1-decanol solution (Figure 5.5a and b), which would be attributable to faster solution equilibrium for the cause of larger SA solubility (7g-SA/100g-decanol, molar ratio of 0.08).

The narrow-area topography in TES and SA saturated 1-decanol solution was traced with constant Δf as shown in Figure 5.4c and 5.5c, respectively. The topography commonly showed the columns of stacked SA molecule pairs along [001] direction. A two-dimensionally ordered structure appeared with a column-to-column distance of 1.6 nm as described in cross-sectional height profiles (Figure 5.4d and 5.5d). In addition, stacked molecule pairs were also resolved along the column axis with a pair-to-pair distance of 0.5 nm in 1-decanol solution due to a good tip condition (Figure 5.5e). These features reproduced what was observed in hexadecane (Figure 5.6),¹⁰ which indicated surface topography was insensitive to solvent molecular dimension and SA solubility.

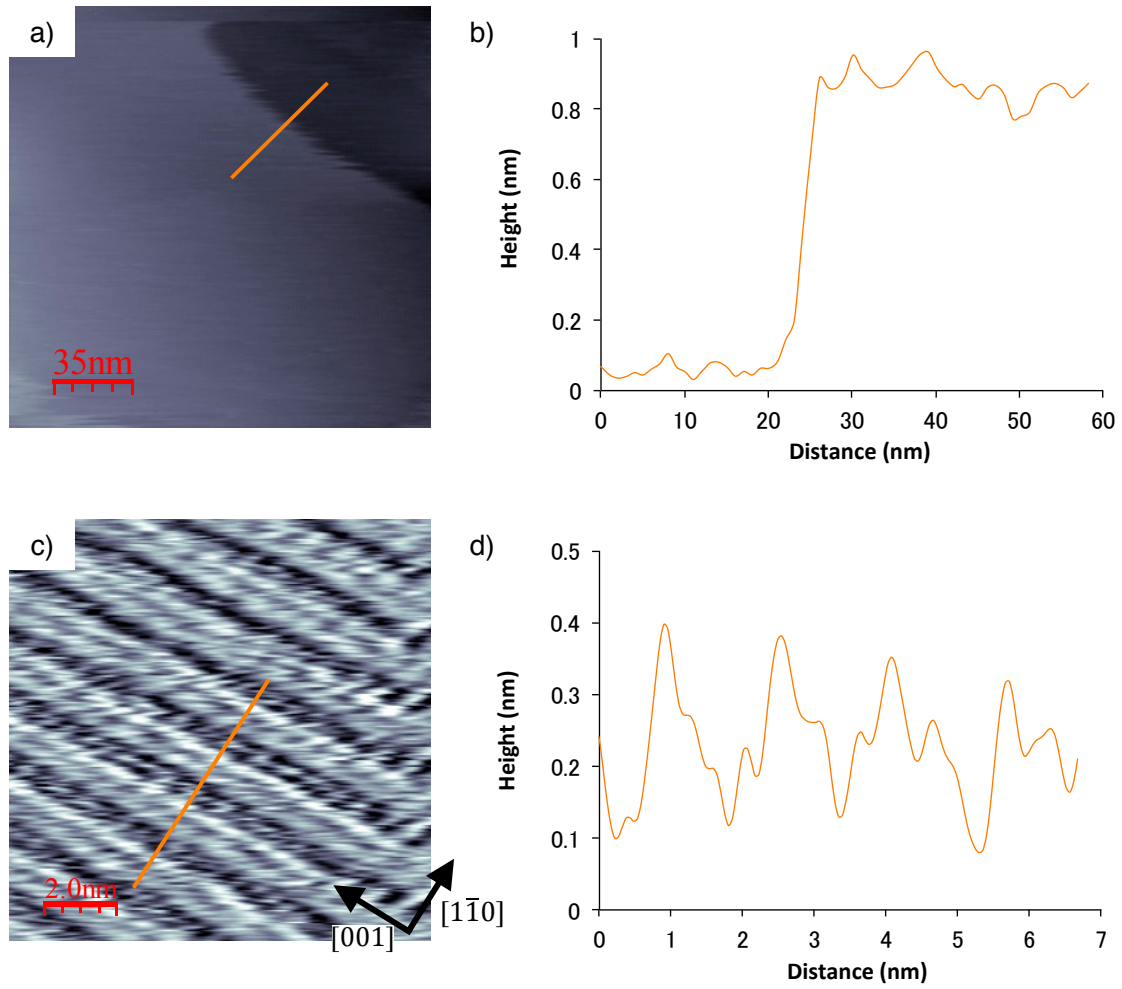


Figure 5.4. a) and c) The constant Δf topography observed in pure TES. b) and d) The cross-sectional height profiles on the orange lines in a) and c), respectively.

Oscillation amplitude: a) 1.0 nm, c) 0.6 nm. Δf setpoint: a) +90 Hz, c) +350 Hz.

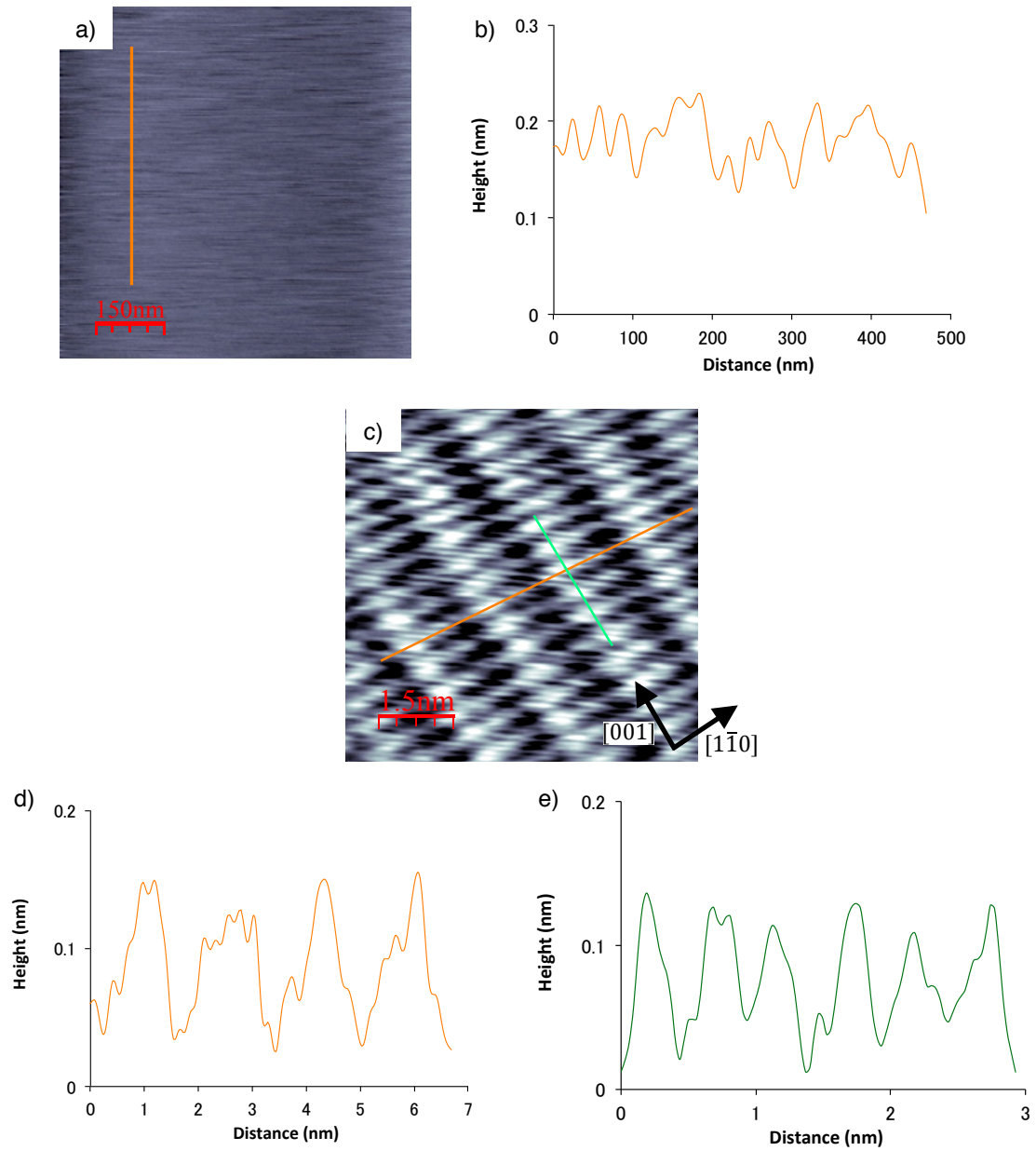


Figure 5.5. a) and c) The constant Δf topography observed in SA saturated 1-decanol solution. b) The cross-sectional height profile on the orange line in a). d) and e) The cross-sectional height profiles on the orange and green lines in c), respectively.

Oscillation amplitude: a) 0.6 nm, c) 0.3 nm. Δf setpoint: a) +180 Hz, c) +250 Hz.

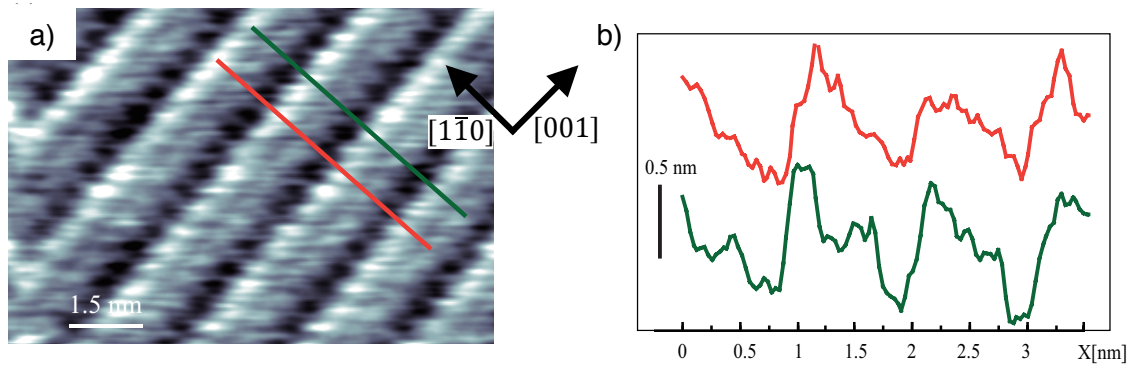


Figure 5.6.¹⁰ a) The constant Δf topography observed in hexadecane. b) The cross-sectional height profiles on the red and green lines in a).

Oscillation amplitude: 0.3 nm. Δf setpoint: +580 Hz.

5.4. Interfacial structures of liquids over SA

5.4.1 TES liquid structures over SA

In order to determine liquid structures on the (110) facet, cross-sectional Δf distribution was obtained. Positive and negative Δf is shown to be bright and dark, respectively. As described in Chapter 2, Sader-Jarvis transformation can be applied to conversion of Δf to force distribution.¹²

First, Figure 5.7a presents Δf distribution in TES perpendicular to [001] direction together with selected force-distance curves. The oscillating tip was scanning from the bulk to the surface. When the tip went down near the surface, Δf increased monotonously and intensively. Thus, the brightest region appeared in the bottom and represented the boundary of solution and solid. Additionally, the brightest line periodically corrugated along the lateral coordinate was slightly tilted upward due to the effect of the drift.

On the solution side of the interface, bright and dark patches were identified to present a checkerboard-like structure of TES in accordance with surface corrugation perpendicular to [001] over SA (110) surface (Figure 5.7a and b). This feature reproduced what was observed in hexadecane (Figure 5.8a).¹⁰ The peak-to-peak distances of force curves (indicated by black dotted lines in Figure 5.7c) over different surface positions determined on red, green, and blue lines were 0.80 nm, 0.75 nm, and 0.77 nm, respectively, insensitive to surface positions. In comparison with the liquid spacing over HOPG with atomic level flatness, the layer-to-layer spacing was found to be 0.81 nm as shown in Figure 5.9a and b. In spite of the corrugated surface structure of SA, the liquid spacing over SA was corresponding to the result over HOPG, which suggested occupied spacing of TES was approximately coincident with the width of protrusions (0.70 nm) or trenches (0.91 nm), leading to ease of arrangement over SA and densely packing as is the case in HOPG.

In fact, a layer-to-layer spacing of hexadecane over SA was 0.67-0.76 nm (Figure

5.8),¹⁰ larger than that over HOPG with a spacing of 0.59 nm (Figure 5.9c and d). In the case of hexadecane with rod shape, molecules would take favorable orientation with molecular axis parallel to the SA molecular column and fit into the trench, leading to contraction of spacing over trench relative to protrusions. However, occupied molecular spacing was smaller than the width of column or trench on SA resulting into instability and dilutely packing for hexadecane over SA.

Second, Figure 5.10a shows a two-dimensional Δf distribution along molecular columns in TES as a function of the vertical and lateral coordinates to elucidate the interfacial liquid structure. Although the SA molecular column has corrugated structure with a spacing of 0.5 nm as described in the previous section, the brightest region presented indefinite surface topography. The uniform liquid layered structure appeared lateral to the surface (Figure 5.10a and b). The each Δf distribution marked with dotted line was extracted and converted to the force-distance curves depicted in Figure 5.10c. The force curves were modulated with a peak-to-peak spacing of 0.79 nm, corresponding to those over HOPG. These results suggested the TES molecular dimension was approximately coincident with the spacing of the corrugated SA structure leading to densely packing and uniform layer-to-layer spacing over SA regardless of crystal positions.

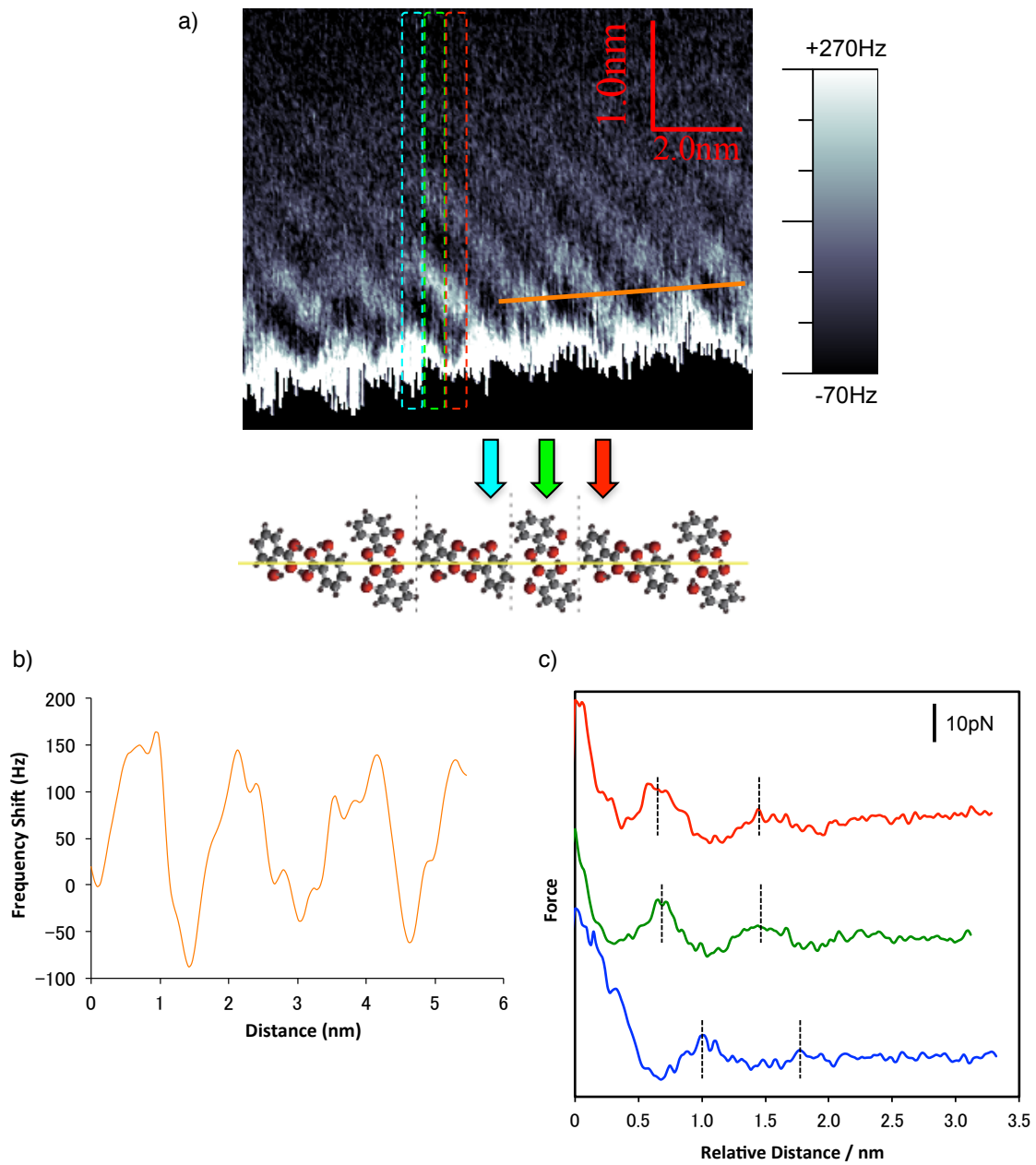


Figure 5.7. Interfacial liquid structures of TES over SA. a) A two-dimensional Δf distribution perpendicular to [001] direction observed with a cantilever oscillation amplitude of 0.6nm. b) A Δf -distance curve on orange line in a). c) A set of force-distance curves with one to one relation between dotted line colors in a) and force curve colors.

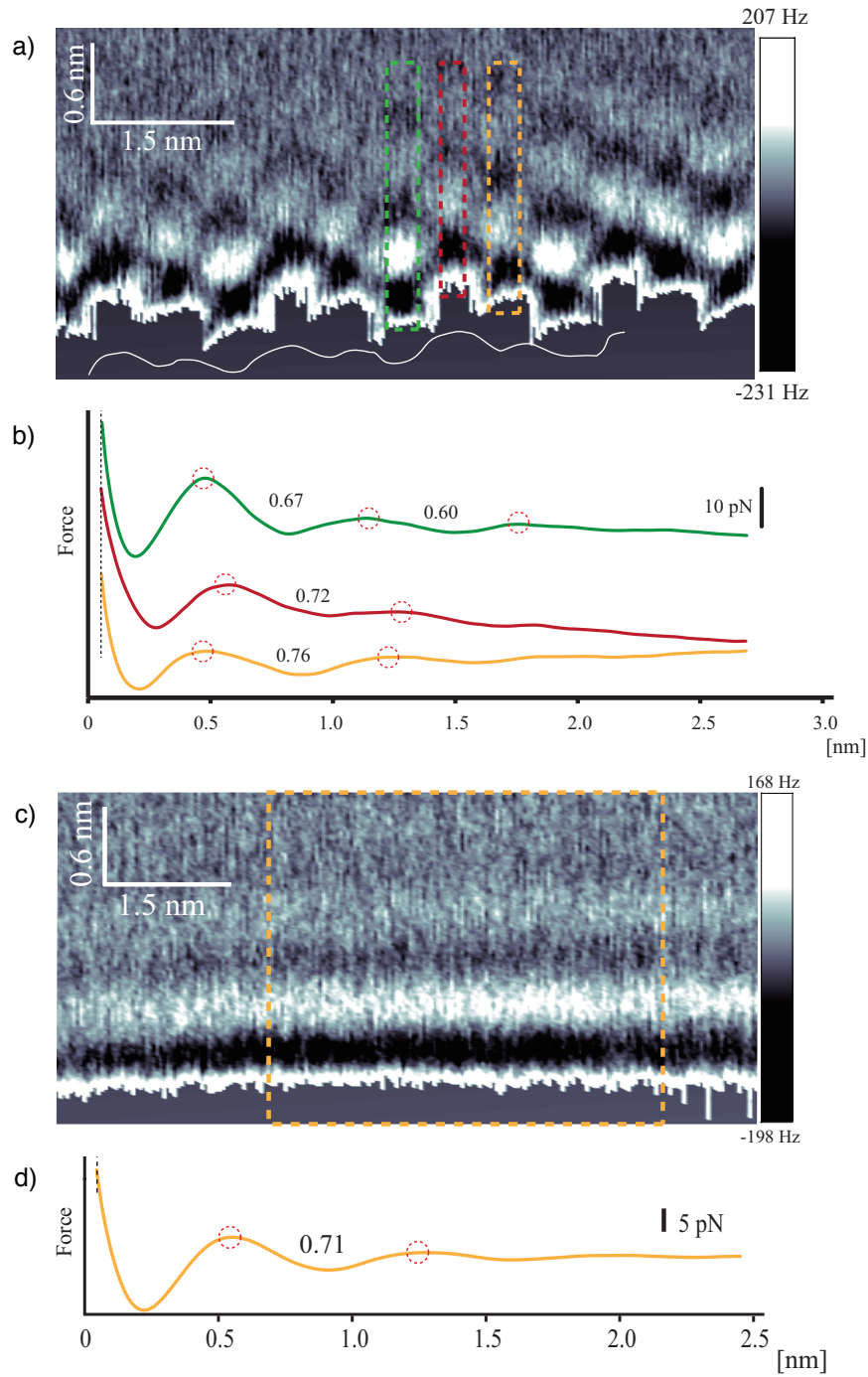


Figure 5.8.¹⁰ Interfacial hexadecane over SA. a) and c) Two-dimensional Δf distribution perpendicular and parallel to [001] direction observed with a cantilever oscillation amplitude of 0.2nm, respectively. b) and d) A set of force distance-curves with one to one relation between dotted line colors in a) or c) and force curve colors, respectively.

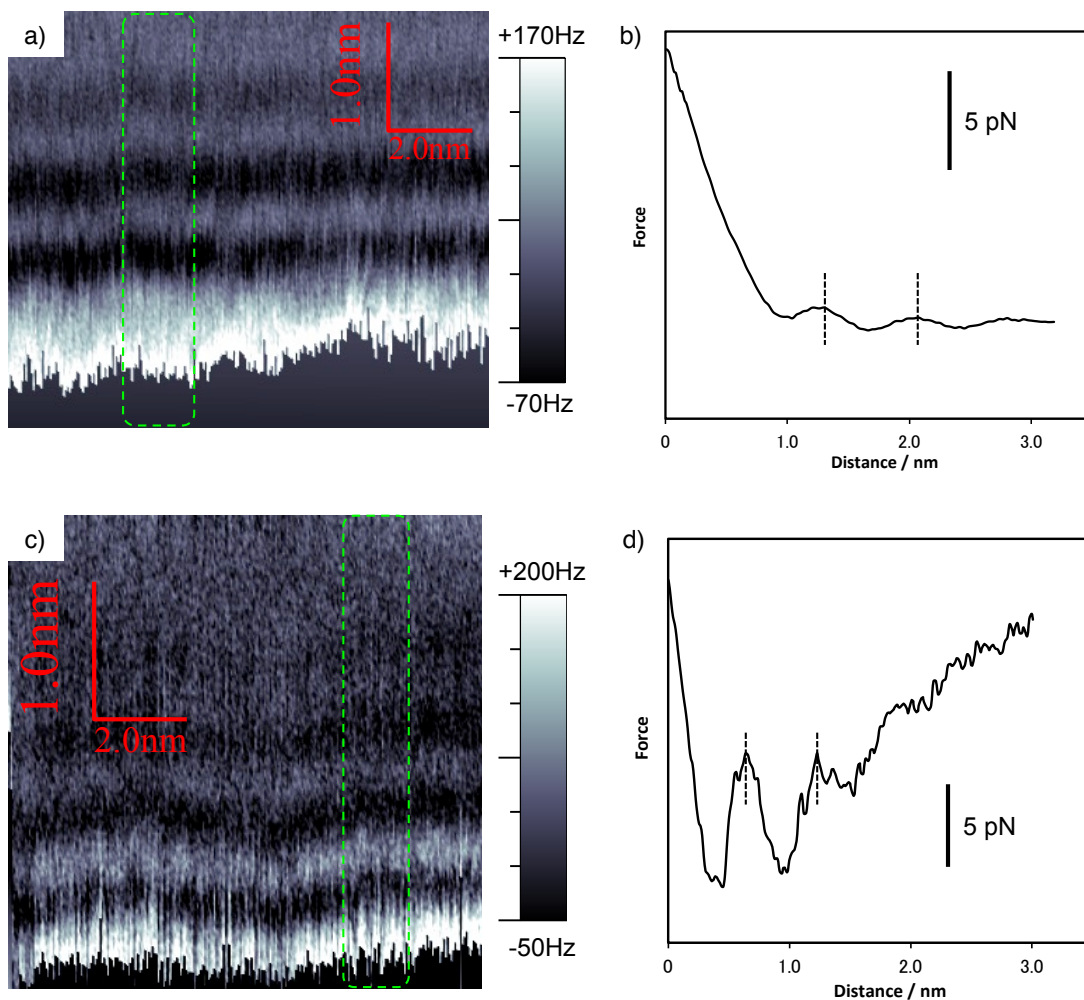


Figure 5.9. Interfacial liquid structures of TES or hexadecane over HOPG. a) and c) Two-dimensional Δf distribution observed in TES and hexadecane with a cantilever oscillation amplitude of 0.3 nm and 0.6 nm, respectively. b) and d) Averaged force-distance curves observed in area marked with the green dotted lines in a) and c), respectively.

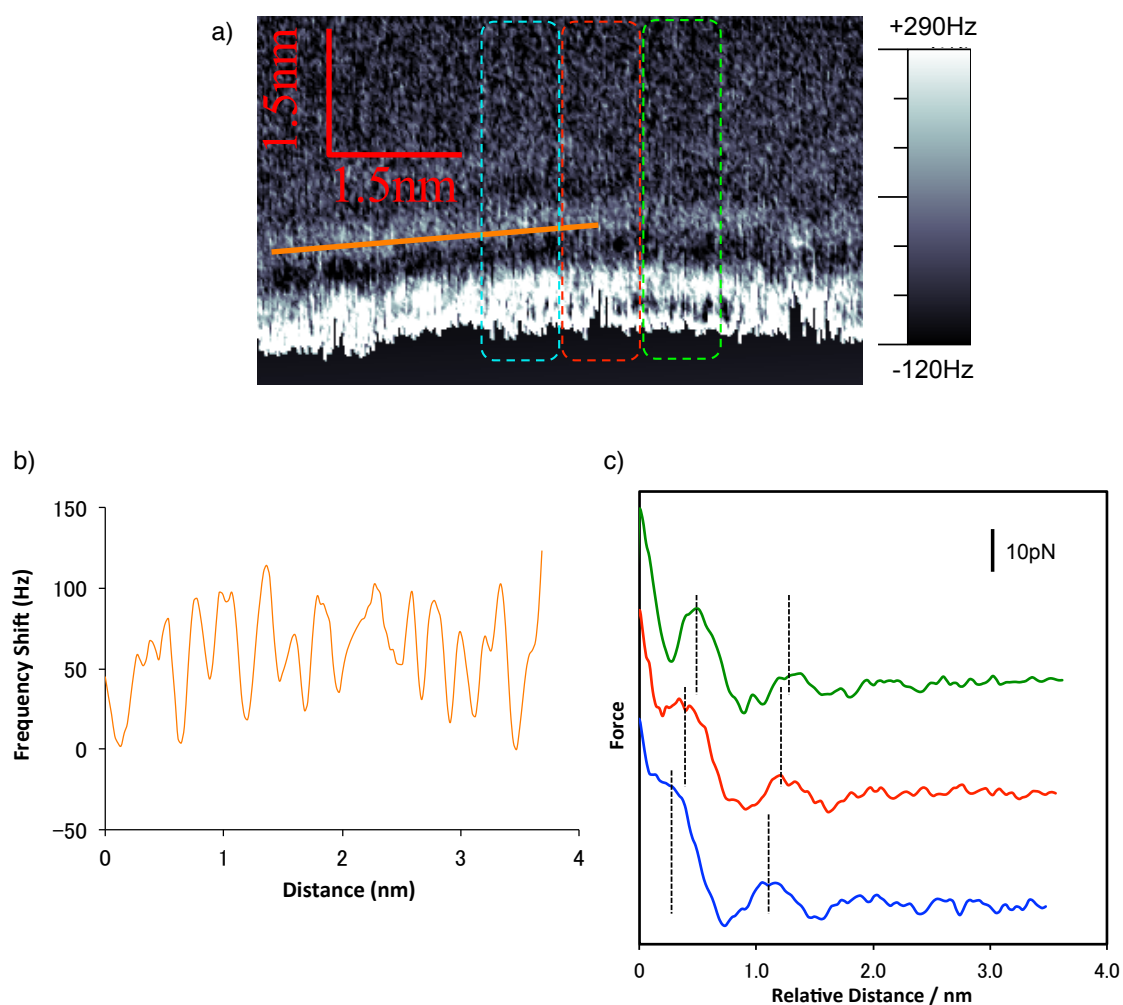


Figure 5.10. Interfacial liquid structures of TES over SA. a) A two-dimensional Δf distribution along [001] direction observed with a cantilever oscillation amplitude of 0.3nm. b) A Δf -distance curve on the orange line in a). c) A set of force-distance curves with one to one relation between dotted line colors in a) and force curve colors.

5.4.2 Decanol liquid structures over SA

The cross-sectional Δf distribution in SA saturated 1-decanol solution over SA perpendicular to [001] direction is shown in Figure 5.11a as a function of the vertical and lateral coordinates together with the averaged force-distance curves (Figure 5.11b) to elucidate the interfacial liquid. The brightest region at the bottom represents the corrugated surface. Although the topographic line was tilted as a result of the drift of the object in the vertical coordinate, the protrusions and trenches assigned to the SA molecular columns appeared alternately with a spacing of approximately 1.6 nm in accordance with the crystal structure.

On the liquid side, in contrast to the checkerboard-like structure observed in TES or hexadecane¹⁰ over SA, the considerably distinct structure with a single uniform layer lateral to the crystal surface appeared and the two force-distance curves averaged in area marked with each colored line represented the peak and valley indicated by dotted circles (Figure 5.11b). However, the Δf -distance curve along the liquid layer depicted in Figure 5.11c showed a weakly corrugated feature with Δf peak positions (indicated by arrows) in accordance with lateral positions of OH groups (located on trenches indicated by arrows in Figure 5.11a). Although the similar corrugated feature was also confirmed in TES (Figure 5.7b), only the first and indefinite layer was observed in the case of saturated 1-decanol solution. This characteristic structure would be attributed to hydrogen bonds between OH groups of SA and interfacial 1-decanol molecules. It could be thought the adsorbed 1-decanol molecules were localized on surface OH groups and aligned vertically or tilted somewhat to the surface in comparison with the liquid structure of hexadecane in lateral alignment to the surface. Besides, 1-decanol molecules were bound with not covalent bonds but weak hydrogen bonds, which would lead to not only fast association/dissociation equilibrium between OH groups of SA and the bulk liquid but also migration between each OH group of SA. In addition, interfacial SA would be dissolved and precipitated repeatedly in solution equilibrium due to the large solubility of SA (7g-SA/100g-decanol, molar ratio of 0.08), which also

gave rise to flexibility of the 1-decanol adsorption layer. These vertical alignment and significantly flexible structure would result in instability of the adsorption layer and difficulty of formation of further liquid layers on the adsorption layer.

Figure 5.12a represents the cross-sectional Δf distribution in SA saturated 1-decanol solution over SA parallel to [001] direction. Although the SA molecular column has corrugated structure with a spacing of 0.5 nm, the brightest region presented no periodicity. The bottom line was tilted as a result of the drift of the object in the vertical coordinate.

On the liquid side, the single uniform layer appeared, and the force-distance curves averaged in area marked with colored lines showed the peak and valley indicated by dotted circles (Figure 5.12b). However, the Δf -distance curve depicted in Figure 5.12c also showed the weakly periodic structure with a spacing of approximately 1.5 nm dissimilar with that in TES (Figure 5.10b). These results suggested 1-decanol molecules would be localized on OH groups to a certain extent at variance with the TES molecules with mobility in lateral liquid layers, and averagely 1 in 3 OH groups of SA would be bound with 1-decanol molecules.

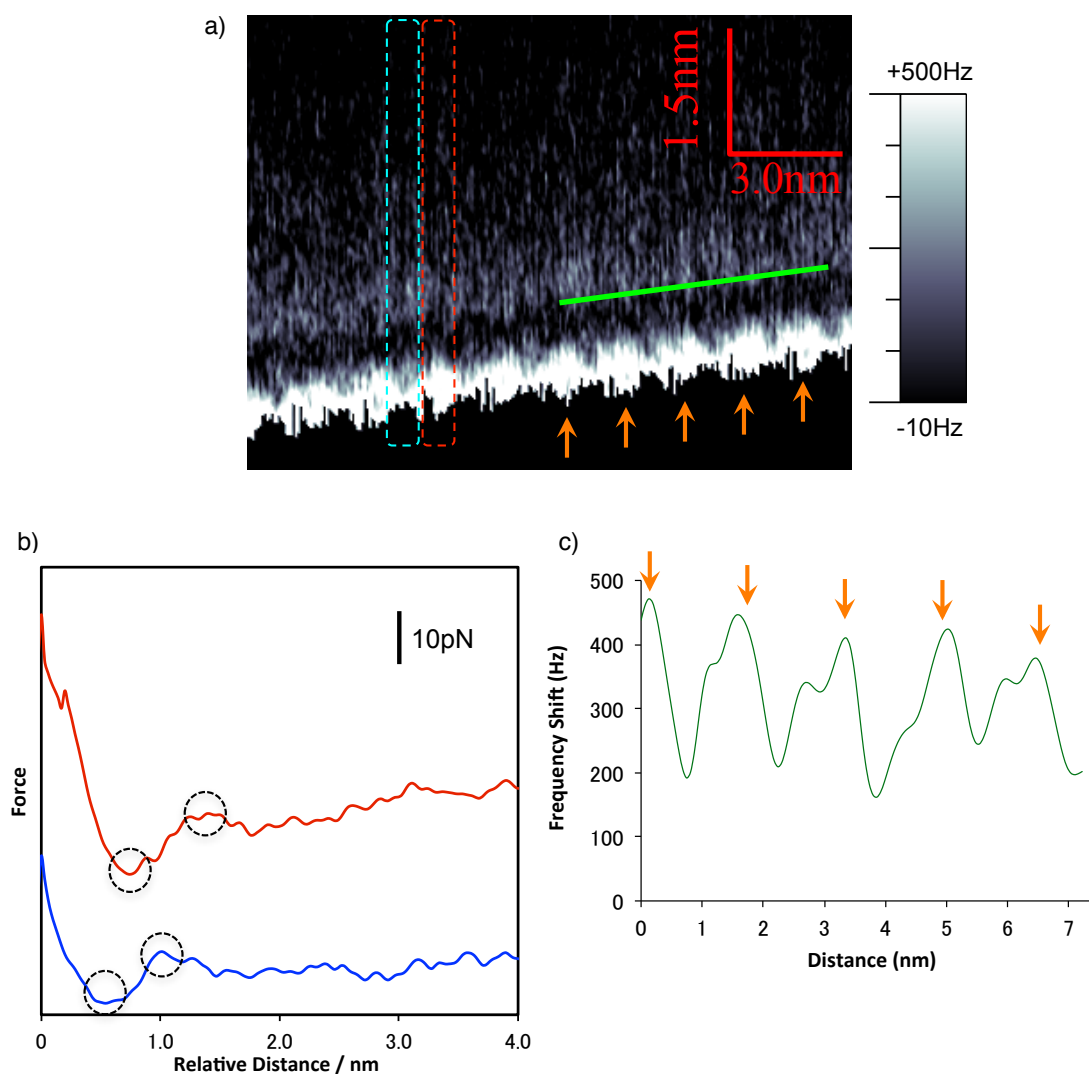


Figure 5.11. Interfacial liquid structures of 1-decanol over SA. a) A two-dimensional Δf distribution vertical to [001] direction observed with a cantilever oscillation amplitude of 0.3 nm. b) A set of force-distance curves with one to one relation between dotted line colors in a) and force curve colors. c) A lateral Δf -distance curve on the green line in a).

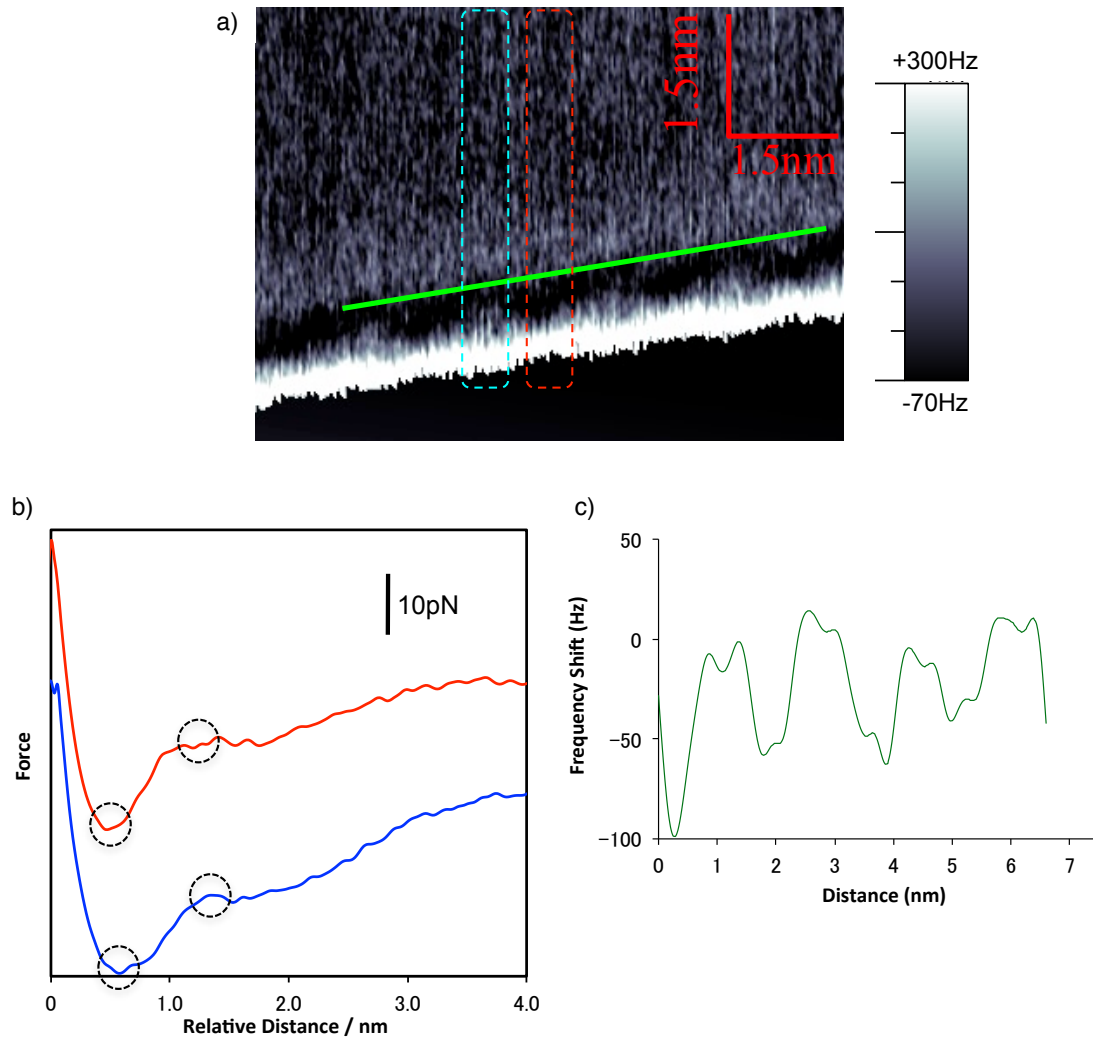


Figure 5.12. Interfacial liquid structures of 1-decanol over SA. a) A two-dimensional Δf distribution along [001] direction observed with a cantilever oscillation amplitude of 0.3nm. b) A set of force-distance curves with one to one relation between dotted line colors in a) and force curve colors. c) A lateral Δf -distance curve on the green line in a).

5.5 Conclusions

In this chapter, constant Δf topography and two-dimensional Δf distribution together with force-distance curves were acquired over SA (110) surface in pure TES and SA saturated 1-decanol in comparison with hexadecane. A step and terrace with a height of about 0.8 nm in accordance with the spacing of (110) planes appeared in TES and the topography identified in TES and 1-decanol commonly showed the columns of stacked SA molecule pairs along [001] direction coincident with the crystal surface structure, which indicated surface topography was insensitive to SA solubility.

Two-dimensional Δf distribution in TES represented a checkerboard-like structure of the liquid in accordance with surface corrugation perpendicular to [001] over SA (110) surface, which reproduced what was observed in hexadecane. The layer-to-layer spacing of TES was approximately corresponding to that on HOPG. On the other hand, the spacing of hexadecane was larger than that on HOPG. These results suggested occupied spacing of TES was approximately coincident with corrugated spacing of SA, which allowed TES to be densely packed over SA.

In contrast to the liquid structure in hexadecane or TES, Δf distribution in saturated 1-decanol showed only the first and uniform layer with the weakly corrugated feature. This characteristic structure would be attributable to weak hydrogen bonds between OH groups of SA and 1-decanol molecules. In fact, localized adsorption molecules on OH groups were detected (averagely 1 in 3 OH groups of SA was occupied by 1-decanol molecules at the interface) in spite of the association/dissociation or solution equilibrium state. In addition, the vertical alignment and significant flexibility of the adsorbed molecular layer led to prevention of forming additional liquid layers on the adsorption layer. Thus, these results showed AFM measurements at liquid-solid interfaces could enable to not only elucidate liquid structures but also detect adsorbed molecules.

5.6 References

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Chapter 6 Summary and Future Perspective

In this study, the FM-AFM measurements to reveal liquid-solid interfacial phenomena at single molecular level were demonstrated. In Chapter 1, the background and history of AFM were described. AFM was a good tool to reveal surface structures including insulant. In particular, AFM measurements in liquids give more effective information about liquid-solid interfacial phenomena than that in UHV in respect to achievement of actual environments. As described in Chapter 2, recently advanced FM-AFM enables to realize the imaging with atomic or molecular resolution even in liquids. Such excellent instruments also could help elucidate chemical reactions in liquid-solid interfaces. In this study, observation of metalloporphyrins as active species on mica, an inactive substrate was carried out to attain not only imaging of single metalloporphyrin molecules with axial ligands (i.e. coordination reaction, Chapter 3) but also detection of the photo-induced reaction on metalloporphyrins (Chapter 4). Besides, FM-AFM with high sensitivity could be attainable to reveal interfacial liquid structures together with weekly adsorbed molecules onto surfaces. The solvent sensitive liquid structures were shown due to presence or absence of hydrogen bonds at the liquid-solid interfaces (Chapter 5).

Chapter 3 described the adsorption behavior of CoTPP face-on to the mica surface with electrostatic interactions at the interfaces and detection of the single CoTPP molecules. In addition, reversible two states of CoTPP with different heights were further identified, which was derived from presence or absence of a solvent molecule as a coordination ligand. These results suggested FM-AFM measurements in liquids could be applied to detection of adsorbed single molecules together with another interacting molecules and analyses of various chemical reactions.

In Chapter 4, real-time imaging of photo-induced chemical reactions was demonstrated by FM-AFM. Upon the visible light irradiation, the protrusions of PtTPP in presence of anthracene were changed to those with larger dimension relative to the original state

due to the transformation of anthracene to anthraquinone on adsorbed PtTPP. These distinct features derived from detection of reaction products also observed in images of PtTPP single molecules. These results revealed FM-AFM methods could attain real-time single molecular imaging of chemical reactions together with products in liquids.

As shown in Chapter 3 and 4, detection of molecules at liquid-solid interfaces plays very important roles in elucidation of chemical reactions at molecule level. In the case of probing a molecule, it is required to prevent adsorbed molecules related to the reaction from elimination so that precise measurements are carried out. In Chapter 5, two-dimensional Δf distribution was acquired over SA (110) surface in pure TES and SA saturated 1-decanol in comparison with hexadecane. In the case of TES and hexadecane without substituents to form hydrogen bonds, two-dimensional Δf distribution represented a checkerboard-like structure with different layer-to-layer spacing due to not only the molecular dimension but also the extent of packing. On the other hand, Δf distribution in saturated 1-decanol with OH groups showed only the first and uniform layer with weakly corrugated feature. This characteristic structure would be attributable to weak hydrogen bonds between OH groups of SA and 1-decanol molecules. These distinct features indicated the presence of adsorbed 1-decanol molecules onto the SA surface. Thus, AFM measurements at liquid-solid interfaces could enable to not only elucidate liquid structures but also detect adsorbed molecules leading to application for detection of components in interfacial chemical reactions.

As summarized above, probing single molecules at liquid-solid interfaces under various conditions was carried out using advanced FM-AFM with high resolution. These results provided new and fundamental insights into interfacial phenomena including chemical reactions under liquid environments relative to spectroscopic measurements. In order to give further progress of FM-AFM analyses, improvement of experimental systems could be required. As demonstrated in this study, active species, metalloporphyrins were stabilized by electrostatic interactions, which could

provoke the movement of probing targets and prevention of accurate measurements. In addition, the metal center acts as not only an adsorption site but also an active site. The division of these two functions to discrete sites makes experimental systems simple and interpretation easy. To achieve these improvements, for instance, introduction of anchor-substituent-terminated ligands to stabilize active molecules with covalent bonds would be required. These improvements would also enable to control the alignment of target molecules and conduct measurements even in presence of molecules with strong electronic interactions (such as hexylamine in this study) to interrupt adsorption onto surfaces. In the future study addressing the experimental improvement as described above, probing single molecules at liquid-solid interfaces will be expected to be applied to versatile conditions or various reactions using more advanced FM-AFM.

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