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- A conformer with the open cavity exists 1.5 kcal/mol above the global minimum conformer with the collapsed cavity.
- To confirm this idea, a receptor **3** ( $R_1=R_2=Me$ ) was prepared from  $\alpha$ -methyl alanine. CPK modeling study on **3** suggest that the low energy conformer of **3** has the structure similar to that of **1** except the substitution Me for H on binding surface of **1**. As a result, methyl groups of alanine in **3** place on the expected binding surface. Subsequent binding studies revealed that **3** is unable to bind peptides. Although the subtle conformational changes of receptors by substituents of receptors cannot be ignored, this implies that the steric effects between Me in receptors (**2** and **3**) and peptides play an important role in receptor's peptide-binding ability.<sup>9</sup>
- NOE study on complex of **1** and N-Ac-(D)Ser-NHtBu support partially the proposed structure of complex as shown in Scheme 2. Although many expected NOE signals between protons in the complex were not observed, a NOE signal was found between the acetyl protons of N-Ac-(D)Ser-NHMe and  $\alpha$ -protons of  $\gamma$ -lactams in **1** which are placed on the convex surface of **1**. This observation is partially in accord with the binding mode of **1** emerged from binding studies.
- Further support on this notion comes from the observation of the intermolecular self-complexation properties of **1** and **2**. Within 1~10 mM concentration range, **1** shows moderate self-complexation properties although **2** shows no self-complexation. This suggests that Me groups in **2** prevent the self-complexation because of the steric hindrances between them.

## Alternate Organic and Inorganic Molecular Layers Assembled by Electrostatic Attraction

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Ultrathin films formed by electrostatic attraction of macromolecules of opposite charge have received considerable attention in recent years.<sup>1-17</sup> Specifically, in 1991 Decher and Hong<sup>1</sup> reported a technique of constructing multilayer assemblies by alternating adsorption of anionic and cationic bipolar amphiphiles on charged surfaces. Later they extended the concept to multipolar compounds such as polyelectrolytes.<sup>2,3</sup> In 1994, Keller *et al.*<sup>6</sup> applied the technique to sequential layering of structurally well-defined, two dimensional colloidal inorganic polyanions with a variety of oligomeric and polymeric cations.

When a multilayered film is prepared using bipolar cations and anions that have two identical charges at each end, the bipolar molecules are usually assumed to align perpendicularly with respect to the substrate underneath.<sup>1</sup> Based on a small angle X-ray scattergram, Decher and Hong<sup>2</sup> concluded that the bipolar anion should not be tilted

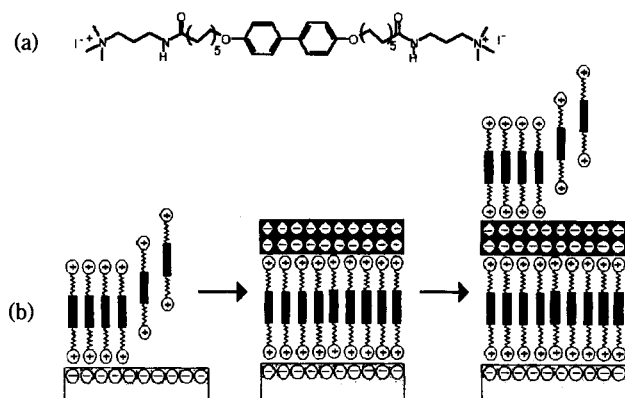
from the layer normal when a multilayered film was formed between bipolar anionic amphiphiles and polymeric cations such as poly-4-vinylbenzyl-(*N,N*-diethyl, *N*-methyl) ammonium ion.

We hope to report that alternating multilayered film can be also assembled between organic and inorganic molecules. As observed using ellipsometry, UV absorption spectroscopy, and quartz crystal microbalance (QCM) measurements, organic bipolar cations appeared to adopt a rather flat stance when they formed multilayered films with the inorganic colloidal polyanions,  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>.

### Experimental

Cationic bola-amphiphile (Bola), (see Figure 1(a)), and  $\alpha$ -zirconium phosphate (ZrP) were synthesized and purified following the procedure reported in the literature.<sup>1,18</sup> All other chemicals were reagent grade and used as received unless specified. Aqueous solutions were prepared by using tri-

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**Figure 1.** (a) Structure of cationic Bola molecule. (b) Schematic diagram of multilayer formation.

ply distilled water whose resistivity was greater than 18.0 M $\Omega$ ·cm. To prepare an aqueous ZrP solution, 100 mg of ZrP was added in 10 mL of 0.1 M tetrabutyl ammonium hydroxide. After stirring for one day, 100 mL of water was added and stirred for one week.

Alternate layers of Bola and ZrP were anchored on either quartz or silicon wafer substrates. Initially, the substrates were sonicated in a H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (7:3) solution at 65 °C for 90 min and subsequently in a H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>/NH<sub>3</sub> (5:1:1) solution at 65 °C for 90 min. By these treatments, very acidic silanol groups are formed on the substrate surfaces so as to be negatively charged upon deprotonation. After carefully washing with deionized water, the substrates were immersed in an aqueous 0.1%(w/w) Bola solution for 20 min. The substrates were washed with water three times, each time by immersing them into water for 2 min, and subjected to a strong nitrogen gas jet. Thereafter, the substrates were immersed in an aqueous ZrP solution for 20 min, washed with water, and dried with nitrogen. These processes were repeated to obtain multilayered alternating films. A schematic diagram of the multilayer formation is drawn in Figure 1(b). The films prepared on quartz and silicon wafer were subjected to UV/VIS absorption and ellipsometric measurements, respectively.

UV/VIS spectra were taken with an HP 8452A Diode Array spectrophotometer. When taking polarized spectra, the incident angle was set at 45° with respect to the surface normal of quartz substrate. The thickness of multilayered film on silicon wafer was determined with a Gaertner Model L 116C and a Rudolph Model AutoEl-II optical ellipsometer, both of which were equipped with a 632.8 nm line of He/Ne laser incident upon the sample at 60° and 70°, respectively.

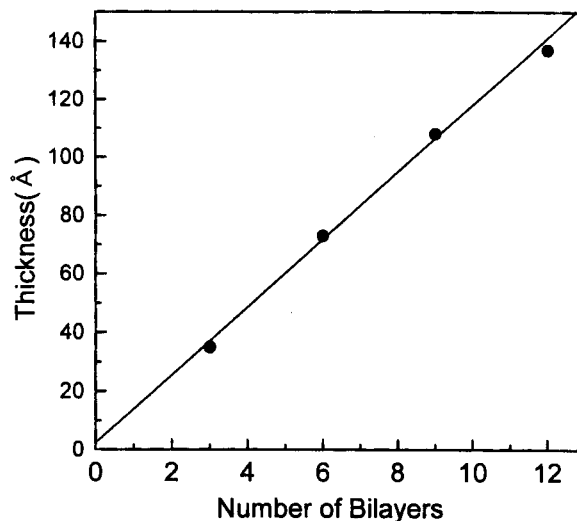
Separately, formation of multilayer film on gold was examined ex-situ with a quartz crystal microbalance; the apparatus consisted of a frequency counter (Fluke PM6681), an oscillator (in house customized), and a 10 MHz Au-coated AT-cut quartz crystal (International Crystal). One side of the crystal was masked with silicon glue to reduce the shunt effect. Just before the experiment, the quartz crystal was cleaned with a H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (3:1) solution, rinsed with deionized water and ethanol, and dried with a N<sub>2</sub> gas jet. The crystal was then dipped into a 5 mM 2-amino-

ethanethiol/HCl solution in ethanol for 6 hrs. By this treatment, 2-aminoethanethiol is chemisorbed on the gold surface by forming Au-S bonds, and the gold surface becomes positively charged upon protonation of the amino group. After washing with excess ethanol, the crystal was immersed consecutively into solutions (3 mg/mL) of poly(vinylsulfate, potassium salt) and poly(allylamine hydrochloride) for 20 min. These processes were repeated five times (in the interim the crystal was washed with excess water and dried under nitrogen). Subsequently, the crystal was immersed into ZrP and Bola solutions consecutively for 20 min or 2 hr. In each step, the frequency changes were monitored with respect to the initial frequency of the crystal.

## Results and Discussion

Figure 2 shows ellipsometric thickness versus the number of Bola/ZrP bilayers on the silicon substrate. The data correspond to multilayers with ZrP at the outermost layer. Since the true refractive indices were unknown, we assumed the film refractive index to be 1.54 in analyzing the ellipsometry data.<sup>6</sup> The thickness is seen to increase linearly with the number of bilayers. This indicates that alternating layers can be assembled stepwise between organic and inorganic molecules. From the slope, a growth step per bilayer is estimated to be 11.5 Å. On the other hand, the regression line drawn in Figure 2 has an intercept at 2.5 Å. This may be due to hydroxide ions present on the silicon substrate and/or tetrabutyl ammonium (TBA) ions present on the outermost ZrP layer. Referring to the standard bond lengths and van der Waals radii, the diameter of a single TBA ion is estimated to be *ca.* 11 Å so that the number of TBA ions on the outermost ZrP layer is supposed quite low, however.

According to the X-ray crystallographic data,<sup>19</sup> ZrP crystal has a layered structure, in which zirconium ions are bridged on a plane with phosphate groups, and its interlayer distance is 7.6 Å. Assuming that ZrP forms alternating multilayers with Bola in a fully exfoliated single layered configuration with the same thickness as that in ZrP crystal,

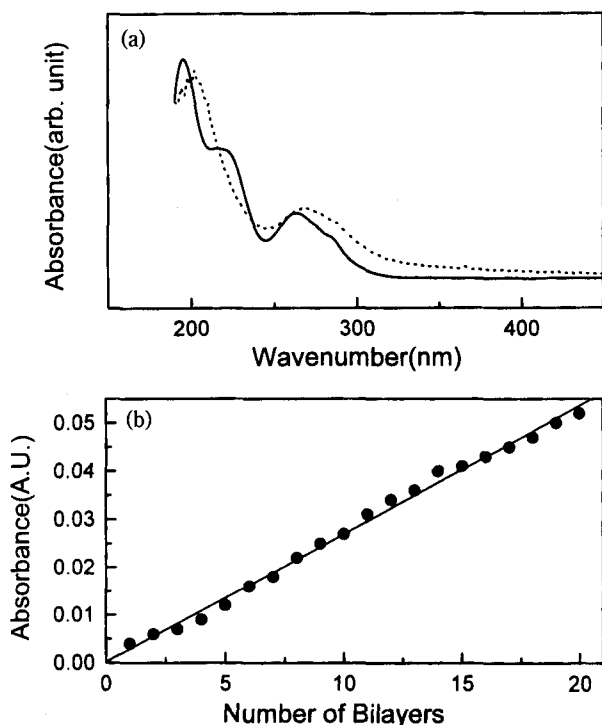


**Figure 2.** Ellipsometric thickness versus the number of bilayers formed from Bola and ZrP on silicon substrate.

each Bola layer in alternating multilayers is estimated to be  $\sim 3.9$  Å thick. If the ZrP layer consists of not a single but several exfoliated pieces, the actual thickness per Bola layer will be somewhat greater than 3.9 Å. Nonetheless, recalling the molecular modelling calculation<sup>1</sup> that the length of the Bola molecule is *ca.* 52.6 Å, the ellipsometry measurement suggests that Bola molecules should lie flat with respect to the ZrP layer rather than having a perpendicular stance.

It is worthwhile to know that the thickness of the Bola layer is measured to be 8 Å when the Bola layer is the outermost layer (considering that certain amounts of TBA and  $I^-$  ions are present on the outermost ZrP and Bola layers, respectively, the thickness of the outermost Bola layer may have to be corrected to 9-10 Å). Present observation implies that upon depositing ZrP on a Bola layer, Bola molecules interact with two ZrP layers, above and below the Bola layer, resulting in a decrease in the thickness of Bola layer. This contrasts with the usual assumption<sup>1</sup> that bipolar amphiphiles are aligned normal to the underlying substrate (Figure 1(b) is drawn referring to the usual assumption).

The solid line in Figure 3(a) represents the UV/VIS spectrum of a bola-amphiphile aqueous solution. The peak at 263 nm can be attributed to the  $\pi\pi^*$  electron transition of the biphenyl group in a Bola molecule.<sup>20</sup> The dotted line in Figure 3(a) shows the UV/VIS spectral pattern of 20 alternating bilayers anchored on a quartz substrate, with ZrP at the outermost layer. The UV absorption peak appears at 268 nm with a slightly broadened bandwidth. Figure 3(b)



**Figure 3.** (a) UV/VIS spectra of Bola in aqueous solution (solid line) and 20 bilayered film of Bola and ZrP anchored on quartz substrate (dotted line). (b) UV absorbance versus the number of bilayers formed with Bola and ZrP anchored on quartz substrate. Absorbance in (b) corresponds to the peak height in absorbance unit (A.U.) at 268 nm.

shows UV absorbance versus the number of bilayers. The absorbance varies linearly with the number of bilayers, in agreement with the ellipsometry data.

It is also informative to refer to the effect of small ionic salt on the growth of Bola/ZrP multilayers. Two different cases were examined, one with a Bola solution in 0.1 M NaCl and the other with a Bola solution in 0.5 M NaCl. Once again, alternate multilayers were assembled readily in the presence of NaCl. However, according to the ellipsometry data, the growth step of the Bola/ZrP pair was found to increase from 11.5 Å to 15.3 Å in 0.1 M NaCl and to 18.3 Å in 0.5 M NaCl. The UV absorption peak was located at 263 nm for both films, about 5 nm lower than that of the film prepared in the absence of NaCl. Nonetheless, the UV absorbance increased linearly along with the number of bilayers. The absorbances per bilayer for the films prepared in 0.1 and 0.5 M NaCl, respectively, were 1.4-1.7 times greater than that observed for the film prepared in the absence of NaCl.

We have attempted to estimate the orientation of the biphenyl moiety in the Bola/ZrP film based on the polarized UV spectra obtained at a 45° incidence angle. The estimation was made by referring to the optoelectric equations reported by Vandevyver *et al.*<sup>21</sup> The infinite dilution hypothesis was applied, and the  $\pi\pi^*$  transition dipole was assumed to be directed along the long molecular axis of the biphenyl group.<sup>20</sup> The refractive indices of quartz and Bola layer were taken to be 1.47 and 1.54, respectively.<sup>6,21</sup> On this basis, the average tilt angle of the biphenyl moiety with respect to the substrate normal was computed to be  $\sim 59^\circ$ . Anticipated from the ellipsometry data, the biphenyl ring of the Bola molecule should adopt a rather parallel orientation. Considering that the long molecular axis of the biphenyl moiety is *ca.* 12.6 Å (based on standard bond lengths), the tilt angle estimated here dictates that the biphenyl moiety contributes to each Bola layer by *ca.* 6.3 Å in thickness (this value is about 2 Å larger than that estimated from the ellipsometry data). For the films prepared in the presence of 0.1 and 0.5 M NaCl, the average tilt angles of the biphenyl moiety were estimated to be  $\sim 62^\circ$  and  $\sim 65^\circ$ , respectively, with respect to the substrate normal. The biphenyl moiety of the Bola molecule seems therefore to adopt a slightly more parallel stance when Bola molecules are adsorbed on the ZrP layer in the presence of NaCl.

Assuming that the thickness of the ZrP layer is 7.6 Å, the thickness of each Bola layer should be 7.7 and 10.7 Å, respectively, for multilayers prepared in 0.1 and 0.5 M NaCl (if the ZrP layer consists of not a single but several exfoliated pieces, the actual thicknesses per Bola layer will be somewhat greater than these values). The absorbance ratio of the three different films is not consonant with their thickness ratio. Since the orientation of the biphenyl moiety is not affected greatly by the presence of NaCl, this may imply that in the presence of NaCl the side chains bonded to the biphenyl moiety should be coiled up so as to assume a more perpendicular stance with respect to the ZrP layers. This finding may also imply that more Bola molecules should be bound to the ZrP layer in the presence of NaCl (*vide infra*). A similar salt effect has been reported for polyelectrolyte systems.<sup>22</sup> Although it has been claimed that the growth step is proportional to the squared ionic strength of

the adsorbing solution,<sup>22</sup> the Bola/ZrP system seemed not to work in that way.

We have mentioned previously that the thickness of the Bola layer assumes ca. 8 Å when the Bola molecules are at the outermost layer. It is noteworthy that the thickness of the outermost Bola layer increases enormously when alternating multilayers are formed in the presence of NaCl. Namely, the ellipsometric thicknesses of the outermost Bola layer are measured to be 32 and 38 Å, respectively, when films are prepared in 0.1 and 0.5 M NaCl (considering that certain amounts of TBA and I<sup>-</sup>/Cl<sup>-</sup> ions may be present on the outermost ZrP and Bola layers, respectively, 1-2 Å has to be added to the above values). This suggests that upon incorporation of small ionic species, the Bola molecules take a near perpendicular stance, but the molecules lie down considerably as ZrP is anchored onto them (the amount of NaCl which may be incorporated inside the Bola layer is, in fact, too low to be detectable with XPS measurement). The exact role of NaCl is uncertain, but the salt is supposed to screen the electrostatic repulsion between the ionic groups on the chains of Bola molecules.

In order to obtain more concrete evidence on the growth of Bola/ZrP multilayers, we have made QCM measurements on a gold coated quartz plate.<sup>23</sup> The increase in mass was barely dependent on the dipping time between 20 min and 2 hr. However, the mass varied linearly with the number of layers, in agreement with the ellipsometry and UV absorbance data. Namely, taking the roughness factor of the gold surface to be 1.3 (inferred from a separate AFM measurement), the mass increases per Bola and per ZrP layers were measured, respectively, to be 169(±40) and 177(±40) ng/cm<sup>2</sup> in the absence of NaCl. On the other hand, in the presence of 0.1 M NaCl, the mass increase per Bola layer was measured to be 238(±40) ng/cm<sup>2</sup> while the amount of ZrP anchoring on Bola was measured to be 203(±40) ng/cm<sup>2</sup>. QCM measurement indicates clearly that more Bola molecules should be bound to the ZrP layer in the presence of NaCl. It is remarkable that the QCM data is consonant with the UV absorbance data that about 40% more Bola molecules should be bound on the ZrP layer in 0.1 M NaCl solution.

Referring to the standard bond lengths and van der Waals radii, the QCM mass increase per fully exploited single ZrP layer is estimated to be 196 ng/cm<sup>2</sup>. In case when Bola molecules are close-packed with their molecular axes aligned perpendicularly with respect to the ZrP layer, the amount per Bola layer is expected to be 350 ng/cm<sup>2</sup>. On this ground, the actual surface coverage of ZrP on the Bola layer is estimated to be ca. 90% when the Bola layer is assembled in the absence of NaCl but the ZrP coverage increases near to 100% when the underlying Bola layer is assembled in the presence of NaCl. In contrast, the amount of Bola actually assembled, in the absence of NaCl, on the ZrP layer is estimated to be ~50% of that expected for a close-packed perpendicular orientation. The amount seems to increase up to ~70% when the assembly is performed in the presence of 0.1 M NaCl. These smaller amounts of Bola may reflect that the density of negative charge on a ZrP layer is not substantial due to its rather weak electrolytic property. On the other hand, supposing that two negative charges are available per ZrP unit such that one neg-

ative charge is directed above and the other charge is directed below the ZrP layer as well as that the surface area per ZrP unit is 24 Å<sup>2</sup>, in a full coverage limit each Bola molecule may be assumed to occupy the areas of two ZrP units. In that case, the mass increase per Bola layer is expected to be 277 ng/cm<sup>2</sup>. On this ground, the amount of Bola actually assembled, in the absence of NaCl, on the ZrP layer should correspond to a 60% coverage while the amount measured in the presence of NaCl would be close to 85%. Considering the size mismatch between the Bola and ZrP molecules, lots of small positive ions are supposed also to reside simultaneously on the ZrP layers to maintain the overall charge balance. Nonetheless, exact structure of the multilayer formed via an electrostatic interaction is still a matter of conjecture. Further studies seem necessary to understand the detailed mechanism of the multilayer formation between the Bola and ZrP molecules.

In summary, it is found that alternating multilayers can be assembled stepwise with organic and inorganic molecules, Bola and ZrP, by virtue of electrostatic interaction. Since the growth step per Bola/ZrP bilayer was measured to be 11.5 Å, the Bola molecules appeared to adopt a nearly parallel orientation with respect to the ZrP layers. When alternating multilayers were formed with Bola in 0.1 and 0.5 M NaCl solution, the growth steps per bilayer were increased up to 15.3 and 18.3 Å, respectively. Nonetheless, the orientation of the biphenyl moiety was not susceptible to the presence of NaCl. Accordingly, the side chains bonded to the biphenyl moiety in Bola seemed to coil up with respect to the biphenyl group as small ionic species were incorporated into the Bola layer.

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## Li Ionic Salt Doped Polyaniline as Positive Electrode in Lithium Secondary Batteries

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Lithium secondary batteries generally have high energy density and are one of most actively developed ones. Lithium secondary batteries are the important applications of electroconductive polymers. More than fifteen years have passed since the possibility of using conductive polymers as electrode materials for secondary batteries was first demonstrated. Various conductive polymers have been studied on their electrochemical properties. Among the conductive polymers, polyaniline and polypyrrole are expected to be good materials for secondary batteries since they are stable and have good electrochemical properties. Especially, polyaniline has been described as the most stable conducting polymer and can be used as the cathode material of lithium secondary batteries.<sup>1,2</sup> However, there are still some problems to be solved. In a Li/conductive polymer battery, the theoretical energy density depends on the concentration and doping method of the dopant in the electrolyte solution as well as the specific capacities of the positive electrodes.

The characteristics of Li/polyaniline secondary batteries compared with conventional lithium secondary batteries have been explained as follows: longer cyclic life, less self-discharging, durable to over discharging, low cost for manufacture and thin thickness. If it is possible to more thoroughly dope the conducting polymers and if a solid polymer electrolyte is applied, the battery can be made lighter or with a higher energy density per unit of weight.

However, the general demerits of commercialized lithium secondary batteries, including lithium polymer secondary batteries, are that the size and the storage capacity of batteries is limited and small. Since the current density of Li/conducting polymer secondary batteries is small, these are only used the power source of the back-up and small elec-

tronic machines. And the manufacturing cost for the other conducting polymer except polyaniline is expensive up to the present. In the case of using the polymer doped perchlorate, it is known that this battery has an explosive problem.

Since the secondary batteries using the polyaniline doped with acid as the cathode have an any problem, the characteristics of polyaniline films, which are doped Li ionic salt, as cathode was investigated in this research. We have tried to find out the factor that affects polyaniline's electrochemical properties as electrodes, which can possibly contribute in developing new conducting polymer electrodes with higher capacity and longer cycle life.

### Experimental

The detailed synthetic procedure was already reported by MacDiarmid *et al.*<sup>3</sup> We synthesized low molecular weight polyaniline (LMW-PANI) using more oxidant than stoichiometric need at room temperature (28 °C). And the synthesis of intermediate molecular weight polyaniline (IMW-PANI) was proceeded at 0 °C. The rest of the steps was same. The free standing films were constructed with different molecular weight polyaniline solution, and we used solution casting method. The ionic salt doping solution of polyaniline films was 1M LiPF<sub>6</sub>, EC (ethylene carbonate)+DMC (dimethyl carbonate) (2:1 in volume ratio) solution. The four-point method was used to measure the D. C. conductivity. Cyclic voltammetry of the cell was performed from 1 V to 4.5 V vs. Li anode at 1 mV/s scan rate.

The electrochemical cell was fabricated as follows. A cathode was made of polyaniline films (1 cm<sup>2</sup>, 10.6 mg