Supramolecular Assemblies and Molecular Recognition of Amphiphilic Schiff Bases with Barbituric Acid in Organized Molecular Films

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A bolaform Schiff base, *N*,*N*′-bis(salicylidene)-1,10-decanediamine (BSC10), has been synthesized and its interfacial hydrogen bond formation or molecular recognition with barbituric acid was investigated in comparison with that of a single chain Schiff base, 2-hydroxybenzaldehyde-octadecylamine (HBOA). It has been found that while HBOA formed a monolayer at the air/water interface, the bolaform Schiff base formed a multilayer film with ordered layer structure on water surface. When the Schiff bases were spread on the subphase containing barbituric acid, both of the Schiff bases could form hydrogen bonds with barbituric acid in situ in the spreading films. As a result, an increase of the molecular areas in the isotherms was observed. The in situ H-bonded films could be transferred onto solid substrates, and the transferred multilayer films were characterized by various methods such as UV−vis and FT-IR spectrosopies. Spectral changes were observed for the films deposited from the barbituric acid subphase, which supported the hydrogen bond formation between the Schiff bases and barbituric acid. By measuring the MS-TOF of the deposited films dissolved in CHCl₃ solution, it was concluded that a 2:1 complex of HBOA with barbituric acid and a 1:2 complex of BSC10 with barbituric acid were formed. On the other hand, when the multilayer films of both Schiff bases were immersed in an aqueous solution of barbituric acid, a similar molecular recognition through the hydrogen bond occurred. A clear conformational change of the alkyl spacer in the bolaform Schiff base was observed during the complex formation with the barbituric acid.

Introduction

Molecular assembly and molecular recognition through a noncovalent intermolecular action is one of the central topics in supramolecular chemistry.[1] Various kinds of molecular interactions such as hydrogen bonds,[2−4] hydrophobic interaction,[5−8] π−π stacking,[9] and electrostatic interaction[10−13] are widely used to assemble the ordered supramolecular structures. The hydrogen bond, as an important class of molecular interactions, is particularly useful in constructing artificial molecular assemblies due to its directionality and strong matching between different molecules. Air/water interface provided a crucial environment for different molecules to react with each other, and many supramolecular assemblies were fabricated through the interaction at the air/water interface.[14−17] In addition, a lot of systems showing molecular recognition properties, such as crown ether[18−20] and calixarene,[21−24] have been widely investigated. Molecular recognition through hydrogen bonding is one of the most attractive topics in supramolecular systems, and excellent work has been done by Ariga, Kunitake, et al. at the air/water interface.[25−28] In this paper, we report a new molecular recognition system at the air/water interface, which is based on the hydrogen bonding between Schiff base and barbituric acid.

Schiff bases are one of the important classes of organic compounds and have extensive applications in biological function materials,[29−31] polymer ultraviolet stabilizers,[32,33] and laser dyes[34] as well as molecular switches in logic or memory circuits.[35] So far, two important properties of Schiff bases are

widely involved, especially for those Schiff bases from salicylaldehyde. One is trans−cis isomerization[36] or photochromism,[37] and some organized molecular films of these photochromic derivatives are reported.[38] The other is the coordination properties. As a ligand, Schiff bases could form coordination compounds with various metal ions.[39] The photochromic properties of Schiff bases are closely related to the intramolecular hydrogen bonding, while the coordinative properties intensely depend on the coordination of the imine and hydroxyl groups with the metal ions. Besides these two properties, Schiff bases from salicylaldehyde were reported to form hydrogen bonds with barbituric acid in solution.[40,41] By taking advantage of the Langmuir and Langmuir−Blodgett (LB) techniques,[42,43] we have investigated the interaction between Schiff bases and barbituric acid in the interfacial molecular films in detail. The bolaform Schiff base was designed for two reasons. First, bolaform amphiphiles can form different kinds of conformations at the air/water interface.[44−46] Although various kinds of conformations have been suggested and investigated, a clear spectroscopic characterization on the conformations, particularly the U-shape conformation, has not been experimentally clarified. Second, barbituric acid has multiple sites for hydrogen bonding; a stable supramolecular assembly is expected with bolaform Schiff bases because the latter could be assumed as a tweezers for barbituric acid. In comparison, we have simultaneously investigated the interfacial hydrogen bonding of a typical amphiphilic Schiff base with barbituric acid. Molecular recognition through the hydrogen bond was observed for the Schiff bases both in situ in the spreading film and ex situ in transferred multilayers. An obvious

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conformational change of the alkyl spacer in the bolaform Schiff base was observed during the hydrogen bonding formation.

The interfacial hydrogen bonding behaviors of the Schiff bases with barbituric acid were investigated by $\pi-A$ isotherm measurement, UV–vis and Fourier transform infrared (FT-IR) characterization of the transferred multilayer films, and atomic force microscopic (AFM) measurements.

Experimental Section

Materials. Salicylaldehyde, octadecylamine, and 1,10-diaminodecane were purchased from Aldrich Chemicals and used without further purification. Barbituric acid (abbreviated as BA) was obtained from Acros and used as received. The two Schiff base compounds were synthesized by the condensation of the corresponding amines with salicylaldehyde according to the literature method.[47] The corresponding Schiff bases, *N,N'*-bis-(salicylidene)-1,10-decanediamine (abbreviated as BSC10) and 2-hydroxybenzaldehyde-octadecylamine (abbreviated as HBOA) were obtained after recrystallization twice from an absolute ethanol. The analysis data are as follows.

N,N'-Bis(salicylidene)-1,10-decanediamine (BSC10): mp 55–56 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.29 (m, 12H), 1.62 (t, 4H); 3.57 (t, 4H); 6.87 (t, 4H); 7.31 (t, 2H); 7.43 (d, 2H); 8.56 (s, 2H); 13.67 (s, 2H). Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75%; H, 8.48%; N, 7.36%. Found: C, 75.64%; H, 8.47%; N, 7.38%.

2-Hydroxybenzaldehyde-octadecylamine (HBOA): mp 43–44 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 0.92 (t, 3H), 1.28 (m, 28H); 1.38 (t, 2H); 1.72 (t, 2H); 3.62 (t, 2H); 6.91 (t, 1H); 7.03 (d, 1H); 7.28 (d, 1H); 7.35 (t, 1H); 8.35 (s, 1H); 13.65 (s, 1H). Anal. Calcd for $C_{25}H_{43}NO$: C, 80.37%; H, 11.60%; N, 3.75%. Found: C, 80.51%; H, 11.62%; N, 3.83%.

Chloroform and ethanol were purchased from Beijing Chemicals and distilled before use. DMSO-d_6 was of analytical grade and obtained from Beijing Chemicals. Pure water (18 MΩ cm) was obtained from the Milli-Q system and used in all cases.

Procedures. The spreading films and the deposited multilayer films were performed using a KSV minitrough (KSV instruments, Helsinki, Finland). Schiff bases were spread on water surface or the subphase containing 1.0 mM BA. After waiting 20 min for the evaporation of chloroform, surface pressure–area ($\pi-A$) isotherms were recorded with a compression speed of 5.0 mm/min at 20.0 ± 0.2 °C. The Langmuir–Blodgett films were prepared by the vertical dipping method at a constant speed of 2.0 mm/min on the quartz or CaF$_2$ plates for UV–vis and FT-IR spectra, respectively. In the case of AFM measurement, one layer of spreading films was deposited onto a freshly cleaved mica surface. UV–vis and FT-IR spectra of the multilayer films were obtained by a JASCO UV-530 and a JASCO FT/IR-660 plus spectrophotometer, respectively. AFM images were recorded using a tapping mode (Nanoscope IIIa multimode system, Digital Instruments, Santa Barbara, CA) with silicon nitride cantilever probes. All AFM images were shown in the height mode without any image processing except flattening. The elemental analysis was carried out with the Flash EA Carlo-Erba-1106 Thermo-Quest. ^{1}H NMR spectra were obtained on an ARX400 (Bruker) NMR spectrometer in DMSO-d_6 or CDCl$_3$ with TMS as an internal standard. Melting points were measured with an XT$_4$-100$_x$ microscope apparatus and uncorrected. MALDI-TOF mass spectra (MS) were determined with BI-FLEXIII.

Results and Discussion

Spreading Films of Schiff Bases on Water and Aqueous BA Subphases. Figure 2 shows the surface pressure–area
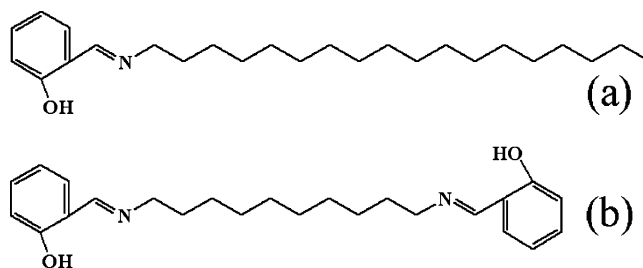

Figure 1. Chemical structures of HBOA (a) and BSC10 (b).

isotherms of HBOA and BSC10 spreading films on pure water surface and the aqueous subphase containing 1.0 mM BA. The isotherm of HBOA monolayer on water surface shows the onset of the surface pressure at 0.36 nm^2/molecule and experiences a plateau region upon compression to 16 mN/m or 0.18 nm^2/molecule. After the plateau region, the surface pressure increases steeply from 0.09 nm^2/molecule. The extrapolated molecular areas from the linear part of the isotherm before and after the plateau region were 0.28 and 0.085 nm^2/molecule, respectively. On the basis of the CPK (Corey–Pauling–Kolton) model, it can be suggested that HBOA formed a monolayer at the beginning and collapsed from the plateau region. When BA was added to the subphase, an isotherm without any plateau region was obtained. The limiting area from the linear region of the isotherm was 0.25 nm^2/molecule. This indicated that a stable monolayer was formed in the presence of BA subphase. The significant difference in the shape of the isotherm and the disappearance of the plateau region suggested that there existed some interactions between HBOA and barbituric acid.

The bolaform Schiff base BSC10 formed different spreading films. On pure water surface, an isotherm without any plateau region was obtained. The extrapolated molecular area of the isotherm was only 0.03 nm^2/molecule. When BSC10 was spread on the subphase of BA, although an increase in the molecular area was observed, the molecular area was still too small to be regarded as a true monolayer. The isotherm showed a hysteresis in the compression–expansion process. However, the compression isotherms from different experimental batches could be reproduced. This suggested that BSC10 formed some regular structures on both water surface and the subphase containing BA. Previously, we have observed that some bolaamphiphilic diacids, even with longer alkyl spacer, formed multilayer films on water surface.[14b] Lahav et al. have also confirmed that some bolaamphiphilic diacids or diols formed multilayer films with several molecular thickness or three-dimensional architecture at the air/water interface using the GIXD method.[15,48] To confirm the multilayer structure of the BSC10 and BSC10/BA films, we have measured the X-ray diffraction of the deposited films at 20 mN/m. Four and three diffraction peaks were observed for BSC10 and BSC10/BA films, respectively (see Supporting Information S1). On the basis of Bragg's equation, layer distances of 2.28 and 3.59 nm were obtained for the BSC10 and BSC10/BA films, respectively, indicating that regular multilayer structures were formed for the both films. The larger distance of BSC10/BA film indicated the complex formation between BSC10 and BA.

Characterization of Transferred Multilayer Films. *UV–Vis Spectra of Transferred Films.* Schiff base has characteristic UV–vis and FT-IR absorption. We used the UV–vis and FT-IR spectra to study the interaction between the Schiff base derivatives and barbituric acid by measuring the corresponding spectra of the multilayer films deposited on solid substrates.

Figure 3 shows the UV–vis spectra of the BSC10 and HBOA films deposited from water subphase and the subphase contain-
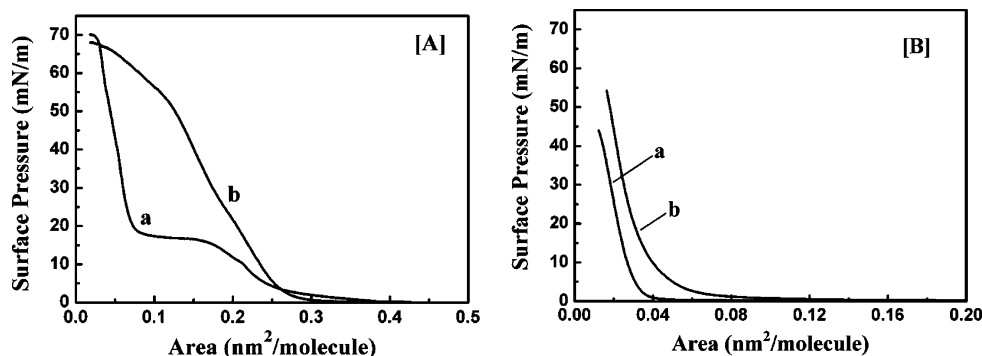
Figure 2. Surface pressure−area isotherms of HBOA (A) and BSC10 (B) on pure water subphase (a) and subphase of 1.0 mM BA (b), respectively, at 20 °C.
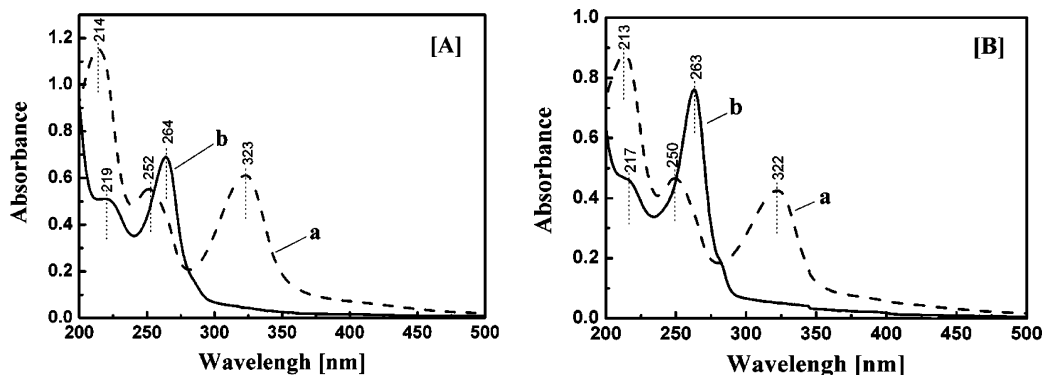

Figure 3. UV−vis spectra of BSC10 (A) and HBOA (B) multilayer films deposited from pure water subphase (a) and subphase of 1.0 mM BA (b).
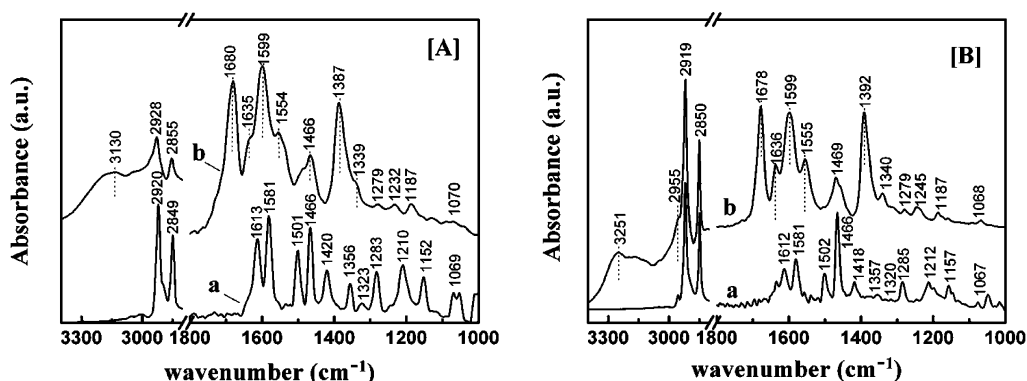

Figure 4. FT-IR spectra of BSC10 (A) and HBOA (B) multilayer films on pure water subphase (a) and subphase of 1.0 mM BA (b).

ing BA. The UV−vis spectrum of the BSC10 film from water surface showed three strong absorption peaks at 214, 252, and 323 nm. The former two bands can be ascribed to the localized absorption of the aromatic rings, while the peak at 323 nm can be assigned to the charge transfer band. When the film was deposited from the BA subphase, a great change in the absorption spectra was observed. The charge transfer band disappeared completely, and the other two bands showed a shift to 219 and 264 nm, respectively. The disappearance of the charge transfer band at 323 nm indicated the disruption of the conjugated imine band and suggested that the interaction between BSC10 and BA occurred at the imine group of BSC10. A similar change of UV−vis spectra was also observed for HBOA films, indicating a similar interaction between HBOA and BA.

FT-IR Spectra of Transferred Films. FT-IR spectroscopy is a powerful technique to detect the vibration changes during molecular interaction. This method is expected to be useful to those systems with hydrogen bonding. Figure 4 shows the FT-

IR spectra of the deposited LB films from water and aqueous subphase containing BA.

In the region of $1800-1000$ cm^{-1}, which is sensitive to the hydrogen bonding and the stretching of the aromatic rings, many strong vibrations peaks are observed. For the films deposited from water surface, strong vibrations were observed at 1613 and 1283 cm^{-1} for BSC10 films and were observed at 1612 and 1285 cm^{-1} for HBOA films. These two bands can be assigned to the C=N and C−O stretching vibrations, respectively. Another strong band at 1466 cm^{-1} was also observed for both films, which can be assigned to the CH$_2$ scissoring vibration.

Significant spectral changes were observed for the films deposited from the BA subphase. Typical changes are included in two parts. The first change is the new bands that appeared at 3130, 1680, and 1554 cm^{-1} for BSC10 films. The bands at 3130 and 1554 cm^{-1} can be assigned to the H-bonded N−H stretching and deformation vibration bands, respectively. The band at 1680 cm^{-1} can be assigned to the C=O stretching vibration from

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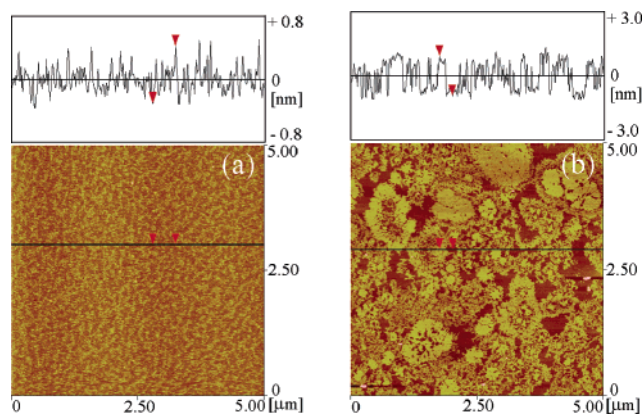*J. Phys. Chem. B, Vol. 109, No. 7, 2005* **2535**

Figure 5. AFM images of one-layer BSC10 LB films from pure water (a) and 1.0 mM aqueous BA subphase (b) at a surface pressure of 5 mN/m.

the barbituric acid which has intermolecular hydrogen bonding. Another change is that the C=N band at around 1613 cm^{-1} in the Schiff base films shifted to 1635 cm^{-1} when spread on BA subphase, which suggested a C=N stretching mode of the cis isomer.[49] All these FT-IR spectral changes clearly indicated hydrogen bonding formation between the Schiff bases and barbituric acid.

On the other hand, obvious changes are also observed for the vibrations that originated from the alkyl chain or spacer. The stretching vibration bands of the alkyl spacer appeared at 2920 and 2849 cm^{-1} for BSC10 film, and at 2919, 2850, and 2955 cm^{-1} for HBOA film. The band at 2955 cm^{-1} can be assigned to the antisymmetric vibration of CH$_3$, which was only observed in the HBOA films due to the existence of the end CH$_3$ group. The vibration bands at 2920 and 2849 cm^{-1} can be assigned to the antisymmetric and symmetric CH$_2$ vibration, respectively. It is well-known that the frequencies of the bands due to the CH$_2$ antisymmetric and symmetric modes of the alkyl chain usually appear at 2915 and 2850 cm^{-1}, corresponding to highly ordered hydrocarbon chains with an all-trans conformation.[50,51] All of the CH$_2$ antisymmetric vibration in the present case appeared at a relatively higher frequency, indicating the existence of gauche conformation in the film.[52] Upon interacting with BA, packing of the alkyl chain or spacer changed differently for the two Schiff base molecules. For HBOA films, no obvious change of the CH$_2$ stretching vibration was observed, while there was a slight shift in the CH$_2$ scissor vibration from 1466 to 1469 cm^{-1}. In the case of BSC10 film, the antisymmetric and symmetric vibration peaks shifted from 2920 and 2849 cm^{-1} to 2928 and 2855 cm^{-1}, respectively. The increases in the frequencies of the two bands indicate the increment of gauche conformation into the alkyl spacer. In the present case, a relative larger CH$_2$ vibration was observed, indicating the existence of more gauche conformation in the films.

AFM Measurements of Transferred Films. To get further insight into the interaction between the two Schiff bases and BA, one layer of the spreading films of the Schiff bases on both water and the BA subphase were transferred onto the newly cleaved mica and their surface morphologies were measured with atomic force microscopy (AFM).

The BSC10 LB film deposited from the water surface showed dotlike domains (Figure 5a), and the surface is rather rough. When spread on BA subphase, great changes in the surface domains are observed. Lotuslike domains, which have a clear boundary, are observed for the film deposited at a large scale. The height profile of the film indicated a thickness of 1.8 nm. However, a sublayer of the film could be seen in the picture

with larger magnification. This indicated that a multilayer film was essentially formed when BSC10 was spread on water or BA subphase. The clear image change indicated the interaction between BSC10 and BA.

For HBOA, there exists a plateau region in the $\pi-A$ isotherm. Therefore, we have transferred the films at the surface pressures below and above the plateau region. One-layer HBOA LB film deposited from the water surface at a surface pressure of 5 mN/m showed the dotted domains in AFM pictures. Interestingly, these dotted domains tended to align into a ribbon (Figure 6a), which might be due to the packing of the Schiff base group. For the film transferred at a surface pressure over the plateau region, some large ribbon structures with a width of approximately 210 ± 10 nm appeared, as shown in Figure 6b. The height of the ribbon (9.7 ± 0.2 nm) was much larger in comparison with the molecular length of HBOA. This indicated that, upon compression over the plateau region, HBOA formed a multilayer film, which is in accordance with the $\pi-A$ isotherm. On the other hand, when HBOA was spread on the BA subphase, plank-like morphology with a clear boundary was observed. When the surface pressure increased to 25 mN/m, domains with a similar shape appeared but the height of the domains changed, as shown in Figure 6d. However, the height profiles showed that the thickness of HBOA/BA film was 3.2 ± 0.1 nm, which is very close to the molecular length of HBOA, indicating a complex monolayer formation between HBOA and BA at the air/water interface.

MS-TOF Measurements of the Transferred Films. From the above discussion, it is clear that both HBOA and BSC10 can react with BA through intermolecular hydrogen bonding. To get further insight into the structure of the supramolecular assemblies, we measured the MALDI-TOF mass spectra by dissolving the transferred films into CHCl$_3$ solution, as shown in Figure 7. BSC10 film deposited from subphase of BA shows a peak at 637.0, which is assignable to the protonated complex between BSC10 and BA at a ratio of 1:2. On the other hand, in the spectrum of dissolved solution from HBOA/BA film, a weak peak is observed at 876.6, which could be ascribed to the complex between HBOA and BA at a ratio of 2:1. These data clearly indicated that 2:1 and 1:2 complexes of HBOA and BSC10 with BA were formed, respectively.[53] Such a complex mode can be regarded as related to the molecular structures of the Schiff bases, which is illustrated in Scheme 1.

For the BSC10/BA films, BSC10 molecule, having two Schiff base headgroups, can act as a tweezers and two BA molecules are embedded in the BSC10 molecule. In this case, the alkyl spacer curved at the air/water interface and the two BA molecules formed intermolecular hydrogen bonding and were encapsulated under the alkyl chain.

A similar 1:2 complex formation between BSC10 and BA was also observed in the solution from ^{1}H NMR spectra measurement (Supporting Information S3). While in the solution, the complex was in a random way; it was orderly arranged in the LB film.

Molecular Recognition in Preformed Molecular Films. We have found that the molecular recognition between the Schiff bases and barbituric acid occurred not only in situ at the air/water interface but also ex situ between the preformed Schiff base films and barbituric acid at the solid/liquid interface. This was due to the fact that there are many "holes" in the preformed Schiff base films, as observed from the AFM measurement. Such a process can be monitored by UV−vis and FT-IR spectra, and the results can aid in further understanding the molecular recognition process between the Schiff bases and barbituric acid.
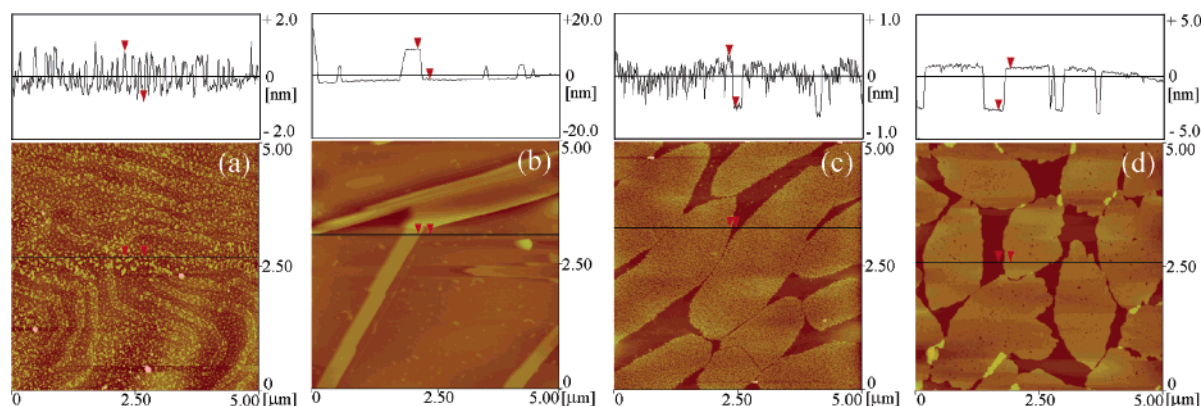
Figure 6. AFM images of one-layer HBOA LB films from pure water at surface pressures of 5 (a) and 25 mN/m (b), respectively, and from 1.0 mM aqueous BA subphase at surface pressures of 5 (c) and 25 mN/m (d), respectively.
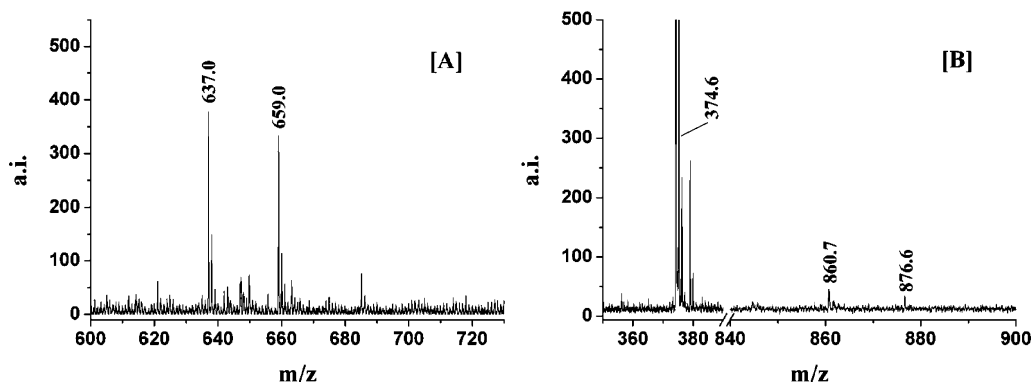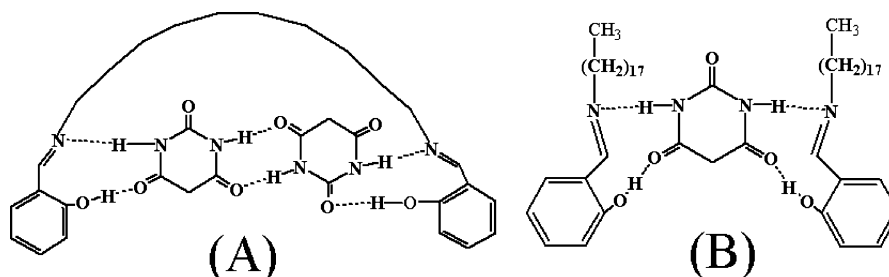

Figure 7. Mass spectra of BSC10 (A) and HBOA (B) multilayer films on subphase of 1.0 mM BA.

SCHEME 1: Schematic Illustration of Structures of BSC10/BA (A) and HBOA/BA (B) Complexes

UV Spectra of BSC10 and HBOA Films in BA Solution. Figure 8 shows the UV−vis spectral changes of the BSC10 and HBOA films after immersion into the BA solution at different time intervals.

With increasing time, the UV spectra changed in a similar manner. The charge transfer band decreased while the bands at shorter wavelength increased. Such spectral changes are essentially the same as those in situ at the air/water interface, suggesting that H-bonding has also occurred ex situ in the preformed films. Such a process can be further analyzed by plotting the change of the optical density of the band at 322 nm as a function of immersion time, as shown in Figure 8C,D. It is interesting to find that the plots are different for the two Schiff base films. There existed two processes in the case of BSC10 film. Before and after immersion for 35 min, the slope of the plot changed clearly. Two reasons can be considered: one is due to the partial dissolution of the BSC10/BA films into the solution. We have found that, after a long-time immersion of the BSC10 film into aqueous BA solution, the film peeled off. The other reason may be due to the different complex formation in the case of BSC10 with BA. To confirm this, we measured the MS-TOF for the BSC10 film immersed

into the aqueous BA solution before and after the point (Supporting Information S4). It was found that, before the turning point of the absorbance, 1:1 and 1:2 complexes of BSC10 and BA both formed. After the point, 1:2 complexes existed predominantly. It seems that, at the initial time of immersing, a 1:1 complex was dynamically formed. Due to the larger excess of BA in solution, the interaction can be continued and the more stable 1:2 complex of BSC10 and BA finally formed. In case of HBOA, because of the weak interaction and loose connection in a continuous process, a smooth plot was obtained. These data are in good agreement with the case of in situ molecular recognition.

FT-IR Spectra of BSC10 and HBOA Films in BA Solution. To further verify the wedging process of BA into the preformed films, ex situ FT-IR spectra of BSC10 and HBOA films immersed in BA (10.0 mM) solution were also measured, as shown in Figure 9A,B. Figure 9C,D shows the changes of CH_2 stretching vibration of HBOA and BSC10 films immersed in aqueous BA solution as a function of immersion time.

A clear change of the vibration bands was observed in the region of $1800-1000$ cm^{-1}. Taking HBOA as an example, at the beginning, the main vibration bands were observed at 1612,

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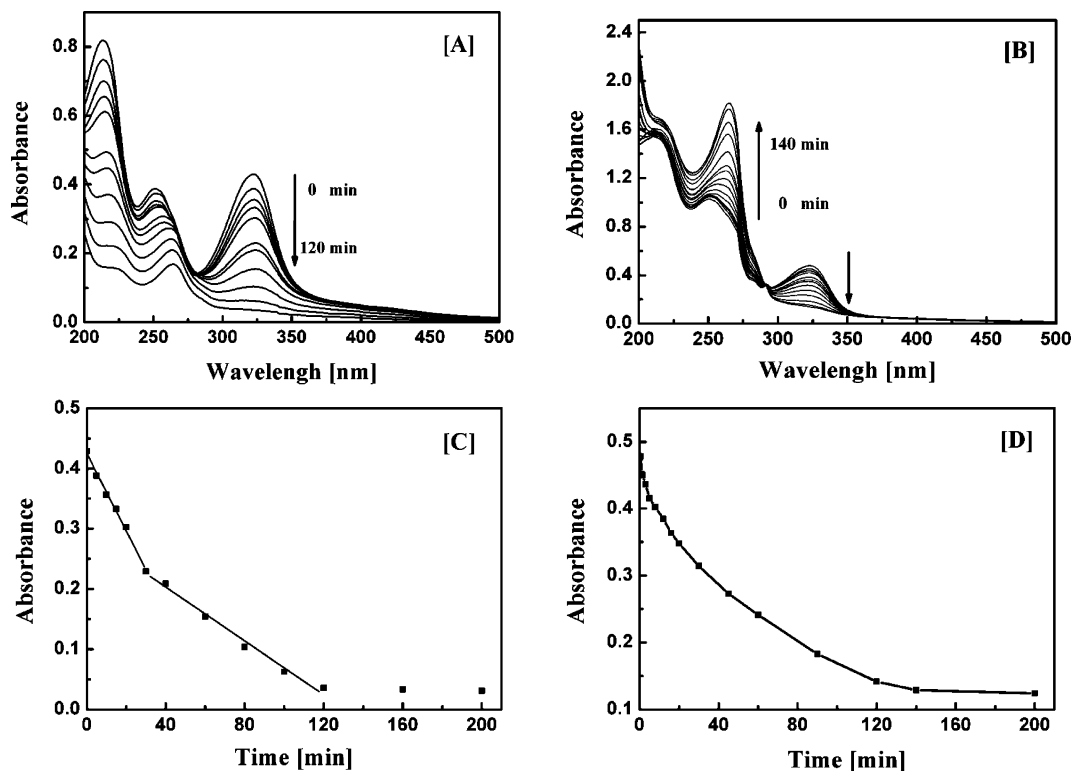*J. Phys. Chem. B, Vol. 109, No. 7, 2005* **2537**

Figure 8. Ex situ UV spectra and absorbance−time plots of BSC10 (A, C) and HBOA (B, D) multilayer films transferred at 5 mN/m on water surface immersed in 10 mM aqueous BA solution measured at different time intervals. Absorbance−time plots are the optical density of UV−vis absorbance at 322 nm against immersed time.
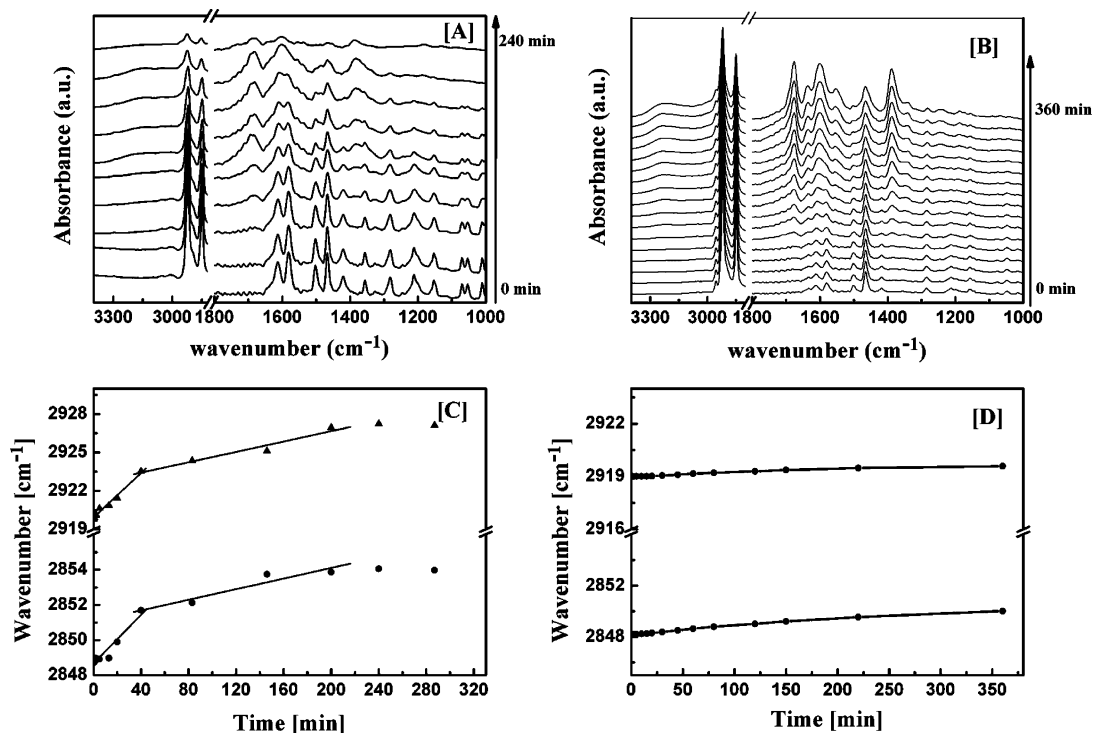

Figure 9. Ex situ FT-IR spectra and wavenumber−time plots of BSC10 (A, C) and HBOA (B, D) multilayer films transferred at 5 mN/m on water surface immersed in 10.0 mM aqueous BA solution measured at different time intervals. Wavenumber−time plot indicates the change of the CH_2 vibration as a function of immersion time.

1581, 1466, and 1285 cm^{-1}. After immersing the films in BA solution, a significant change was observed. The C=N vibration band at 1612 cm^{-1} shifted to 1636 cm^{-1}. The band at 1581 cm^{-1} disappeared, and a new band around 1392 cm^{-1} appeared. Finally, a FT-IR spectrum similar to that of the in situ deposited films was obtained. A similar case was found for the BSC10/

BA system. This indicated that molecular recognition can occur in both deposited films.

Interesting changes are observed for the packing of the alkyl chains. The situation is simple in the case of HBOA/BA films, in which the CH_2 antisymmetric and symmetric vibrations at 2919 and 2850 cm^{-1} changed slightly. However, in the case of

BSC10, significant changes of the vibration bands were observed. There are two steps in the change process of CH_2 vibration. At the beginning, the CH_2 vibrations appeared at 2920 and 2849 cm^{-1}. The bands shifted continuously to the longer wavenumber at the initial 40 min. After that turning point a slow increase of the vibration continued and at last the vibrations leveled off at the wavenumbers of 2926 and 2854 cm^{-1}. Such a great change of the vibration bands indicated clearly the change of the alkyl chain conformation from all trans to gauche. Such a conformational change in the FT-IR spectrum is in agreement with the above changes in the absorption. In the initial stage of the reaction, both 1:1 and 1:2 complexes were formed. The 1:1 complex was less stable and in which one BA molecule was suggested to be attached to one of the headgroup. Therefore, no significant changes in the alkyl conformation were observed. After a long time, a more stable 1:2 complex was formed, as shown in Scheme 1A. In this complex, the alkyl spacer took an obvious gauche conformation due to the space requirement of the H-bond. So far, the gauche conformation has been suggested to form in the LB films. Here, we presented direct experiment evidence for the change of the conformation of alkyl chains from all trans to gauche in the LB films.

In addition, it is noticed that the final wavenumber of the CH_2 antisymmetric vibration in the ex situ reacted BSC10/BA film appeared at 2926 cm^{-1}, while that in the in situ H-bonded film at 2928 cm^{-1}. This indicated that the in situ formed BSC10/BA complex has more gauche conformation than that of ex situ formed one. This can be easily explained by the more free space at the air/water interface than that in the preformed films.

It should be further noted that when we tried a similar reaction of BSC10 cast film with BA, we found that, although a similar H-bond could occur between BSC10 and BA, no significant conformational changes happened as in the LB films of BSC10 (Supporting Information S5). This indicated that the H-bond in the LB film proceeded in an ordered way.

Conclusion

Both an amphiphilic long chain and a bolaform Schiff base can be spread on water surface to form stable monolayer and multilayer films respectively at the air/water interface. When they were spread on the subphase containing barbituric acid, in situ molecular recognition through the hydrogen bond occurred. As a result, a 2:1 complex was formed for the single chain Schiff base with barbituric acid, while a 1:2 complex was formed for the bolaamphiphilic Schiff base through the hydrogen bonding. Upon interaction with barbituric acid, while the packing of the alkyl chain did not change much for the single chain molecule, great change was found for the bolaform Schiff base. A gauche conformation was predominantly obtained when the bolaamphiphilic Schiff base films interacted with barbituric acid. We provided a new hydrogen bonding system at the air/water interface. In addition, a continuous conformational change of the alkyl spacer was clearly shown experimentally in the LB film.

Supporting Information Available: XPS spectra of BSC10 LB films from BA subphase, ^1H NMR spectroscopic titration of barbituric acid with BSC10 in DMSO-d_6, ex situ FT-IR spectra of BSC10 cast film immersed in BA solution measured at different time intervals. Mass spectra of BSC10 film immersed in BA solution measured before and after the turning point. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: Weinheim, 1995. (b) Lehn, J.-M. *Science* **2002**, *295*, 2400. (c) Lehn, J.-M. *Angew. Chem., Int. Ed.* **1990**, *29*, 1304.

(2) Craig, S.; Wilcox, J. C.; Adrian, J.; Thomas, H.; Webb, F.; Zawacki, J. *J. Am. Chem. Soc.* **1992**, *114*, 10189.

(3) David, K. S.; François, D. *Chem. Commun.* **1998**, 2501.

(4) Zimmerman, S. C.; Wang, Y.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 2172.

(5) Jullien, L.; Canceill, J.; Valeur, B.; Bardez, E.; Lefavre, J.-P.; Lehn, L.-M.; Marchi-Artzner, V.; Pansu, R. *J. Am. Chem. Soc.* **1996**, *11*, 5432.

(6) Chen, H.; Ogo, S.; Fish, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4993.

(7) Gerhard, W. *Angew. Chem., Int. Ed.* **1994**, *33*, 803.

(8) Ariga, K.; Sakai, D.; Terasaka, Y.; Tsuji, H.; Kikuchi, J. *Thin Solid Films* **2001**, *393*, 291.

(9) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681 and references therein.

(10) Fish, R. H.; Jaouen, G. *Organometallics* **2003**, *22*, 2166.

(11) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2002**, *124*, 6604.

(12) Sommer, R. D.; Rheingold, A. L.; Goshe, A. J.; Bosnich, B. *J. Am. Chem. Soc.* **2001**, *123*, 3940.

(13) Nabeshima, T.; Yoshihira, Y.; Saiki, T.; Akine, S.; Horn, E. *J. Am. Chem. Soc.* **2003**, *125*, 28.

(14) (a) Liu, M. H.; Kira, A.; Nakahara, H. *Langmuir* **1997**, *13*, 4807. (b) Lu, Q.; Luo, Y. H.; Li, L., Liu, M. H. *Langmuir* **2003**, *19*, 285.

(15) Weissbuch, I.; Baxter, P. N. W.; Cohen, S.; Cohen, H.; Kjaer, K.; Lahav, M.; Leizerowitz, L. *J. Am. Chem. Soc.* **1998**, *120*, 4850.

(16) (a) Yuan, J.; Liu, M. *J. Am. Chem. Soc.* **2003**, *125*, 5051. (b) Zhai, X.; Zhang, L.; Liu, M. *J. Phys. Chem. B* **2004**, *108*, 7180.

(17) Wilde, J. N.; Nagel, J.; Petty, M. C. *Thin Solid Films* **1998**, *31*, 726.

(18) Liu, C.; Walter, D.; Neuhauser, D.; Baer, R. *J. Am. Chem. Soc.* **2003**, *125*, 13936.

(19) Heiney, P. A.; Stetzer, M. R.; Mindyuk, O. Y.; DiMasi, E.; McGhie, A. R.; Liu, H.; Smith, A. B. *J. Phys. Chem. B* **1999**, *103*, 6206.

(20) Badis, M.; Tomaszkiewicz, I.; Joly, J.-P.; Rogalska, E. *Langmuir* **2004**, *20*, 6259.

(21) Brewster, R. E.; Shuker, S. B. *J. Am. Chem. Soc.* **2002**, *124*, 7902.

(22) Credi, A.; Dumas, S.; Silvi, S.; Venturi, M.; Arduini, A.; Pochini, A.; Secchi, A. *J. Org. Chem.* **2004**, *69*, 5881.

(23) Liu, F.; Lu, G. Y.; He, W. J.; Liu, M. H.; Zhu, L. G. *Thin Solid Films* **2004**, *468*, 244.

(24) Ito, K.; Noike, M.; Kida, A.; Ohba, Y. *J. Org. Chem.* **2002**, *67*, 7519.

(25) Ariga, K.; Kunitake, T. *Acc. Chem. Res.* **1998**, *31*, 371 and references therein.

(26) Koyano, H.; Bissel, P.; Yoshihara, K.; Ariga, K.; Kunitake, T. *Langmuir* **1997**, *13*, 5426.

(27) Marchi-Artzner, V.; Artzner, F.; Karthaus, O.; Shimomura, M.; Ariga, K.; Kunitake, T.; Lehn, J.-M. *Langmuir* **1998**, *14*, 5164.

(28) Ariga, K.; Kamino, A.; Cha, X.; Kunitake, T. *Langmuir* **1999**, *15*, 3875.

(29) Rousso, L.; Friedman, N.; Sheves, M.; Ottolenghi, M. *Biochemistry* **1995**, *34*, 12059.

(30) Bassov, T.; Sheves, M. *Biochemistry* **1986**, *25*, 5249.

(31) Lanyi, J. K. *Biochim. Biophys. Acta* **1993**, *1183*, 241.

(32) Das, K.; Sarkar, N.; Ghosh, A. K.; Majumdar, D.; Nath, D. N.; Bhattacharya, K. *J. Phys. Chem.* **1994**, *98*, 9126.

(33) Fores, M.; Duran, M.; Sola, M. *J. Phys. Chem. A* **1999**, *103*, 4525.

(34) Acuna, A. U.; Amat Guerri, F.; Costela, A.; Douhal, A.; Figuera, J. M.; Florido, F.; Sastre, R. *Chem. Phys. Lett.* **1991**, *187*, 98.

(35) Nishiya, T.; Yamauchi, S.; Hirota, N.; Baba, M.; Hanazaki, I. *J. Phys. Chem.* **1986**, *90*, 5730.

(36) (a) Nonella, M. *J. Phys. Chem. B* **2000**, *104*, 11379. (b) Ralph, M. P.; Robert, H. K. *J. Am. Chem. Soc.* **1976**, *98*, 4174. (c) Ralph, S.; Becker, K. F. *J. Am. Chem. Soc.* **1985**, *107*, 1477. (d) Guido, J. M.; Dormans, G. C.; Groenenboom, W. C. A.; Van, D.; Henk, M. B. *J. Am. Chem. Soc.* **1988**, *110*, 1406. (e) Ben-Nun, M.; Martinez, T. J. *J. Phys. Chem. A* **1998**, *102*, 9607. (f) Tajkhorshid, E.; Paizs, B.; Suhai, S. *J. Phys. Chem. B* **1999**, *103*, 4518.

(37) (a) Chen, Y.; Zeng, D. X. *J. Org. Chem.* **2004**, *69*, 5037. (b) Asuka, O.; Atsuya, M.; Tatsuo, A. *J. Photochem. Photobiol., A—Chem.* **2004**, *162*,

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473. (c) Eugene, H.; Aliki, R.; Ambroziak, K.; Dziembowska, T.; Mavridis, I. M. *J. Photochem. Photobiol., A—Chem.* **2004**, *162*, 521 (d) Grabowska, A.; Kownacki, K.; Karpiuk, J.; Dobrin, S.; Kaczmarek, Ł *Chem. Phys. Lett.* **1997**, *267*, 132. (e) Zhao, J.; Zhao, B.; Liu, J.; Xu, W.; Wang, Z. *Spectrochim. Acta, Part A—Mol. Biomol. Spectrosc.* **2001**, *57*, 149.

(38) Kawamura, S.; Tsutsui, T.; Saito, S.; Murao, Y.; Kina, K. *J. Am. Chem. Soc.* **1988**, *110*, 509.

(39) (a) Silva, A. R.; Freitas, M. M. A.; Freire, C.; de Castro, B.; Figueiredo, J. L. *Langmuir* **2002**, *18*, 8017. (b) Epstein, D. M.; Choudhary, S.; Churchill, M. R.; Keil, K. M.; Eliseev, A. V.; Morrow, J. R. *Inorg. Chem.* **2001**, *40*, 1591. (c) Aruna, D.; Hemakanthi, G. *Chem. Phys. Lett.* **2003**, *371*, 458. (d) Hemakanthi, G.; Dhathathreyan, A.; Möbius, D. *Colloid Surf., A—Physicochem. Eng. Asp.* **2002**, *198*, 443. (e) Hemakanthi, G.; Balachandran, U. N.; Aruna, D. *Chem. Phys. Lett.* **2001**, *341*, 407. (f) Nagel, J.; Oertel, U. *Thin Solid Films* **1998**, 327.

(40) Park, M.; Kim, Y. *Thin Solid Films* **2000**, *363*, 156.

(41) Kim, Y.; Chung, C. *Synth. Met.* **2001**, *117*, 301.

(42) Roberts, G. G. *Langmuir-Blodgett Films*; Plenum Press: New York, 1990.

(43) Ulman, A. *An Introduction to Ultrathin Organic Films, from Langmuir to Self-Assembly*; Academic Press: Boston, MA, 1991.

(44) (a) Yamaguchi, K.; Moriya, A.; Kinoshita, M. *Biochim. Biophys. Acta* **1989**, *1003*, 151. (b) Yamaguchi, K.; Sakamoto, Y.; Moriya, A.; Yamada, K.; Higuchi, T.; Kinoshita, M. *J. Am. Chem. Soc.* **1990**, *112*, 3188.

(45) Fuhrhop, J. H.; Krull, M.; Schulz, A.; Moebius, D. *Langmuir* **1990**, *6*, 497.

(46) Liu, M. H.; Cai, J. F. *Langmuir* **2000**, *16*, 2899.

(47) Lacroix, P. G.; Di Bella, S.; Ledoux, I. *Chem. Mater.* **1996**, *8*, 541.

(48) Weissbuch, I.; Guo, S.; Edgar, R.; Cohen, S.; Howes, P.; Kjaer, K.; Lahav, M.; Leizerowitz, L. *Adv. Mater.* **1998**, *10*, 117.

(49) Lewis, J. W.; Sandorfy, C. *Can. J. Chem.* **1982**, *60*, 1720.

(50) Ueno, K.; Matell, A. E. *J. Phys. Chem.* **1955**, *59*, 998.

(51) Synder, B. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.

(52) Snyder, R. G.; Ou, S. L.; Krimm, S. *Spectrochim. Acta, Part A—Mol. Biomol. Spectrosc.* **1978**, *34*, 395.

(53) Considering the fact that during the MS-TOF measurement rearrangement of complex of the host and guest might occur in this dissolution process, we have measured the XPS of BSC10/BA film and confirmed a 1:2 complex formation using the atom ratio percent, which can be seen in Supporting Information S2.