

Acidichromism in the Mixed Langmuir-Blodgett Films of Stearic Acid with a Carbazole-containing Schiff Base

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A new Schiff base containing carbazole group (CzSB) was synthesized. Although the compound can not form stable monolayer at air/water interface itself, it does form stable monolayers by mixing with stearic acids as verified from the surface pressure-area measurements. The mixed monolayers can be deposited by vertical dipping method. UV Spectroscopic studies of the mixed LB films reveal a broadening and red shift of the absorption spectra compared to those of CzSB in the ethanol solution, which confirms the formation of organized aggregates of the compounds in the mixed LB films. An ordered LB film was obtained as confirmed by using low-angle X-ray diffraction. The mixed LB film shows acidichromism, that is, the colors of the LB films can be reversibly changed upon exposing to HCl and NH₃ gas alternatively. On the basis of FT-IR measurement, it is proposed that the protonation of the imine group in the compound is the reason for the acidichromism.

Keywords Schiff bases, carbazole derivative, mixed LB films, acidichromism

Introduction

Reversible color changes upon external or internal stimulations have been attracting much attention due to their utility as functional materials. For example, photochromism describes the color changes induced by photoirradiation and can be used as photo-recording materials. So far, reversible color changes induced by various stimulations such as photochromism,¹ electrochromism,² thermochromism³ have been widely investigated. Langmuir-Blodgett (LB) films, closely resembles nature

biomembranes,⁴ are one of the most fascinating molecular films and have potential uses in nanoscience and technology and future molecular devices.⁵ Similarly, color changes induced by various stimulations have been investigated in the LB films. Acidichromism describes the color changes induced by the pH variation.⁶ Acidichromism is less investigated in the LB films compared with the photo- and thermochromism. Schiff bases are a class of important compounds⁷ in which photochromisms and thermochromisms have been widely investigated. In the course of study on the properties of Schiff bases, it has been found that some Schiff bases containing heteroaromatic rings such as carbazole show an acidichromism, that is, the colors of the compounds can be changed by pH variation. Although the compound itself can not form stable monolayer, a stable LB film containing the compounds can be fabricated by mixing with stearic acids and the color changes are obvious by exposing the film to HCl and NH₃ gas alternatively. The properties of mixed monolayers of the compound with stearic acid and acidichromism were investigated through the surface pressure-area (π -A) isotherms, UV-vis spectra, fluorescence spectra, X-ray diffraction and FT-IR spectra.

Experimental

Materials

According to a literature method,⁸ the compound

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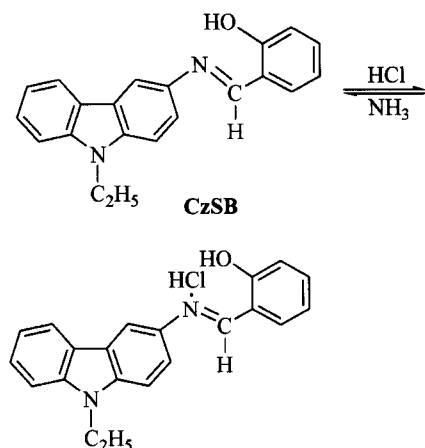
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(Scheme 1, abbreviated as **CzSB**) was synthesized by the condensation of the 3-amino-9-ethylcarbazole (Aldrich) and salicyl aldehyde (Tokyo Kasei, Japan) in ethanol. An equimolar mixture of the two compounds was refluxed in ethanol solution with a droplet of acetic acid for 4 h, cooled to room temperature to cause the formation of saffron yellow crystal. After filtration the crystal was collected and recrystallized twice from ethanol.

CzSB M. p. 105–106 °C; ¹H NMR (CDCl₃, 300 MHz) δ: 1.45 (t, *J* = 7.14 Hz, 3H), 4.43 (q, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.22 Hz, 1H), 7.24–7.29 (m, 1H), 7.43–7.51 (m, 6H), 8.08 (s, 1H), 8.12 (d, *J* = 7.68 Hz, 1H), 8.81 (s, 1H), 13.7 (s, 1H); Anal. calcd for C₂₁H₁₈N₂O: C 80.23, H 5.77, N 8.91; found C 80.26, H 5.73, N 8.77.

Scheme 1 Compounds used in the work and a proposed mechanism for the acidichromism



Procedures

The measurements of surface pressure-area (π -A) isotherms and the multilayer depositions were carried out on a KSV1100 minitrough (KSV instruments, Helsinki, Finland) at 20 °C. Monolayer at the air/water interface was prepared by spreading a chloroform solution (1×10^{-3} mol/L) onto water surface by a microsyringe. Millipore Q water was from the Institute of semiconductors (Beijing, CAS). After the chloroform was evaporated (10 min), the monolayer was compressed with a compression rate of 5 mm/min. Multilayer films were built up depositing the film at 20 mN/m with a down and upward dipping

speed of 10 mm/min. The UV-vis absorption spectra were measured on a JASCO UV-530 system. Fluorescence spectra were recorded using a HitachiF-450 system. FT-IR spectra were performed with a Bio-Rad system. Low-angle X-ray diffraction measurements were performed on a Hitachi Natural D/Max-RB X-ray diffractometer (Japan) with a Cu K α radiation.

Results and discussion

Surface pressure-area (π -A) isotherms

When pure compound **CzSB** was spread from a chloroform solution onto water surface and compressed continuously at a rate of 5 mm/min, surface pressure was detected. The molecular area where the surface pressure begins to appear is found at low area (less than 0.05 nm²/molecule). The significantly smaller area per molecule clearly indicates that pure compound does not form a true monolayer. Mixing **CzSB** with stearic acid (**SA**) results in highly stable and compressible monolayers that can be easily transferred onto solid substrates with a good transfer ratio. Fig. 1 shows the π -A isotherms of mixed monolayers of **CzSB** with **SA** in different molar ratios on pure water subphase at 20 °C, where the concentration of stearic acid was taken as a standard. With increasing molar fraction of **CzSB** in the mixed films, the molecular areas increase. From the corresponding molar ratio of **CzSB** and the limiting area of the mixed films, the molecular area of **CzSB** in them can be estimated as 0.18, 0.063, 0.042, 0.023 and 0.01 nm²/molecule for 1/9, 3/7, 5/5, 7/3 and 8/2 (**CzSB**/**SA**), respectively. These molecular areas are much smaller than the minimum area of **CzSB** from the CPK model (*ca.* 0.25 nm²/molecule), suggesting the stacking and aggregation of **CzSB** molecules. This phenomenon is similar to the case of mixed film of anthracene and **SA**.⁹

Characterization of the LB films

UV-vis absorption spectra

Fig. 2 shows the absorption spectra of **CzSB** in ethanol and in the mixed LB films with **SA**. The solution absorption spectrum shows three sets of absorption bands, 330–400 nm, 287 nm and 227 nm.¹⁰ In the mixed LB film (**CzSB**/**SA** = 7/3), the absorption bands are ob-

served at 350–420 nm, 304 nm and 234 nm, respectively. The broadened and red shifted bands indicate the formation of J-like aggregates in the LB multilayers. In the LB films with other ratios of **CzSB** with **SA**, the same results were obtained.

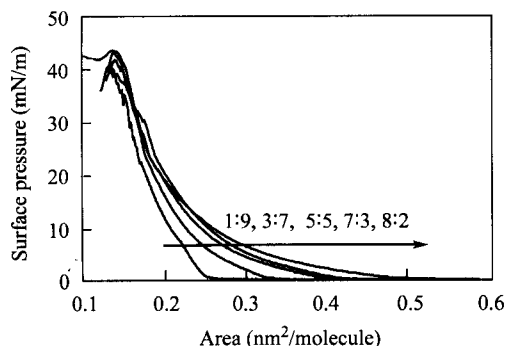


Fig. 1 Surface pressure-area isotherms of mixed monolayers of **CzSB** with **SA** in different molar ratios on pure water sub-phase at 20 °C.

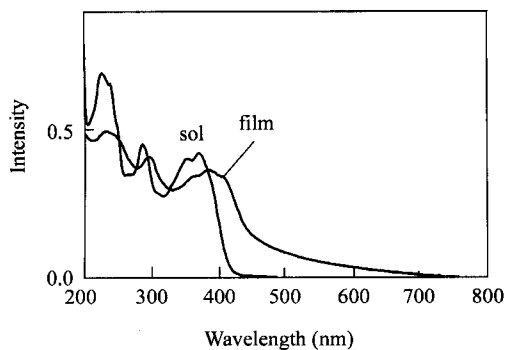


Fig. 2 UV-vis absorption spectra of **CzSB** in ethanol and in the mixed LB films with **SA** at a molar ratio of 7:3.

Small-angle X-ray diffraction of the mixed LB films

Further details concerning the multilayer structure of the mixed LB films were obtained by low-angle X-ray diffraction measurements. X-ray diffraction (XRD) patterns of the mixed LB films (40 layers) with different molar ratios, taken using Cu K α radiation with $\lambda = 0.15418$ nm, revealed a high degree of long range order of diffraction, as shown in Fig. 3. In the case of these systems, d-spacing of 5.022, 5.101 and 4.891 nm were obtained for the mixed LB films in the molar ratios of **CzSB** to **SA** 3:7, 5:5 and 7:3. The d-spacing of the mixed films initially increases with increasing molar concentration of **CzSB**. However, when molar fraction of **CzSB** is large

than 0.5, the d-spacing diminished. In addition, in the case of **CzSB/SA** = 7/3, the number of diffraction peaks decreased and the peak broadened. This indicates that small amount of **CzSB** can help the arrangement of stearic acid molecules, while larger amount of **CzSB** make the alkyl chain tilted and the film less ordered.

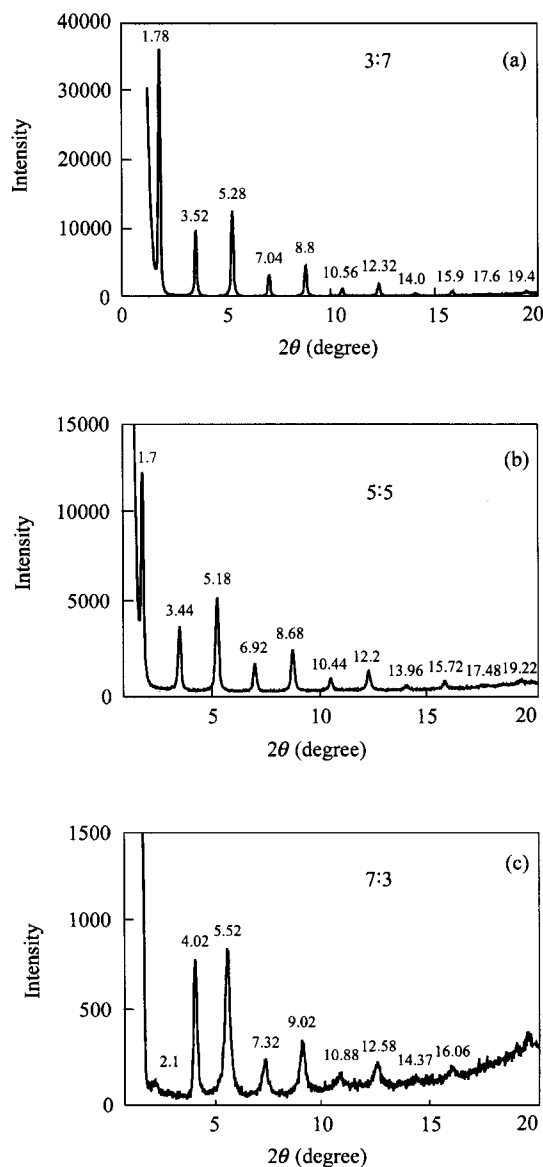


Fig. 3 XRD patterns of the mixed LB films of **CzSB** with **SA** in different molar ratios (a) 3:7; (b) 5:5; (c) 7:3.

Acidichromism of the mixed LB films

Interestingly, new property was found for the transferred LB film of **CzSB** mixed with **SA**. When the film was exposed to HCl gas, significant color change was ob-

served. The film turned from yellow into jacinth immediately. Such an obvious color change can be clearly monitored by UV-vis spectra, as shown in Fig. 4. Significant change in the spectra is the appearance of a new peak at 460 nm. The jacinth-colored film is stable in the air. By exposing the film to NH_3 gas, however, the jacinth color disappeared immediately and the film returned to its original color. Spectral measurement confirmed that the absorption spectrum of the film recovered to its original one, as shown in Fig. 4. In addition, such kind of color change can be repeated many times by exposing the film to HCl and NH_3 gases, alternatively. For a 10-layer LB film, 15 cycles were realized.

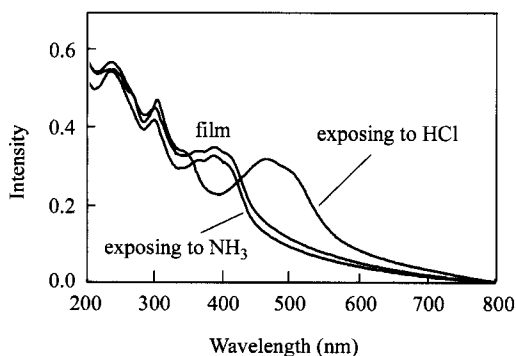


Fig. 4 UV-vis spectral changes of the mixed LB films of **CzSB** with **SA** at molar ratio of 7:3 upon exposing to HCl and consecutive to NH_3 gases.

It has also been checked for such color change in ethanol solution of **CzSB**. It was found that similar color change appeared after adding hydrochloric acid solution. But the Schiff base was unstable in acidic condition. The compound would gradually decompose to the raw material with increasing amounts of hydrochloric acid. In the LB film, the compound is relatively stable.

Such color change can be verified further by fluorescence spectra. Fig. 5 shows the emission spectra of **CzSB** in ethanol and in the LB film mixed with **SA** at a molar ratio of 7:3. In ethanol, the fluorescence emission can be observed at 520 nm. A comparative study of the LB film and the solution emission spectra shows the band slightly shifted in the mixed film. When the film was exposed to HCl gas, two weak emission bands were observed at 520 nm and 615 nm, respectively. Considering the above UV-vis spectra, it can be suggested that the broad emission band at 615 nm could be regarded as due to jacinth-colored species. The fact that the emission at 520 nm did not

disappear completely indicates that there exists equilibrium between **CzSB** and jacinth-colored species.

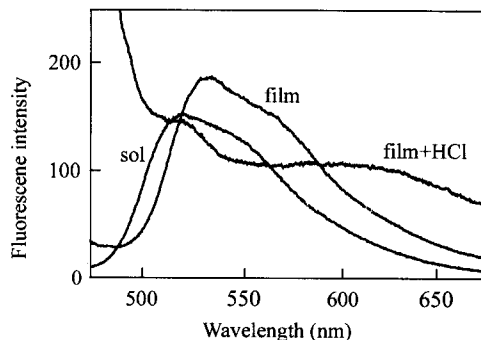


Fig. 5 Fluorescence spectra of **CzSB** in ethanol and in the LB film mixed with **SA** at molar ratio of 7:3.

Nature of the color changes

FT-IR spectroscopy

Such color changes were not only observed in the film, but also observed in the solid state. In the mixed LB films the vibration bands from stearic acid would interfere the FT-IR spectra. We have verified this acidichromism using the KBr palette. Fig. 6 shows the FT-IR spectra of the KBr pallet of **CzSB** before and after exposing to HCl gas. For the pallet before exposing to HCl, FT-IR spectrum shows the main vibration bands at 1630, 1613, 1593, 1490, 1482, 1473 and 1453 cm^{-1} . The band at 1613 and 1630 cm^{-1} could be assigned to the vibration of $\text{C}=\text{N}$ and their combination with the aromatic ring. Significant changes were observed at these bands after exposing to HCl. The most important changes in the IR spectra is that the stretching vibration of $\text{C}=\text{N}$ moiety at 1630 cm^{-1} disappeared, while a new peak at 1645 cm^{-1} appeared, which can be assigned to the stretching vibration of $\text{C}=\text{NH}^+$. These changes indicate that **CzSB** formed a HCl additive upon expose to HCl gas, as shown in Scheme 1. It is regarded that the formation of such kind of the HCl additive is the reason for the acidichromism.

Conclusion

A new Schiff base containing carbazole chromophore was synthesized. Although the compound can not form monolayer itself, it did form stable monolayers with **SA**.

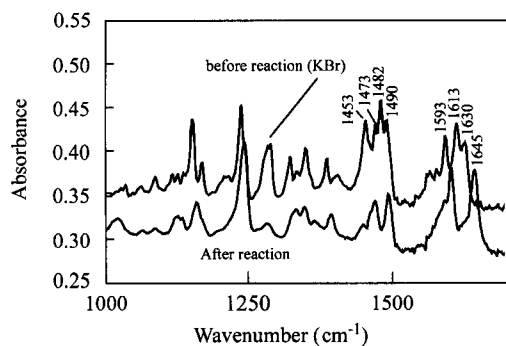


Fig. 6 FT-IR spectra of CzSB in KBr pallet before and after exposing to HCl gas.

The mixed monolayer can be fabricated into ordered LB films. The mixed LB films showed an acidichromism, *i. e.*, colors are changed upon exposing to HCl and NH₃ gas, respectively.

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