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Molecular arrangement and photochemistry of a bolaamphiphilic anthracene derivative in Langmuir–Blodgett film

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Abstract

Molecular arrangement and photochemical reactions have been investigated in the Langmuir–Blodgett (LB) films of a novel bolaamphiphilic anthracene derivative (BISANS) in comparison with those of one-headed amphiphilic anthracene derivative (ANS). It has been found that ANS forms a stable monolayer at the air/water interface, while BISANS undergoes aggregation processes to form crystal film on the water surface, as evidenced from the surface pressure (π)–area (A) isotherm, scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. UV–VIS spectra reveal that both the H-aggregation and the J-aggregation exist in the deposited LB films of bolaamphiphilic BISANS; while only J-aggregation is formed in the LB film of ANS. The content of the H-aggregation in the LB films depends on the transfer surface pressure. The orientation of anthracyl chromophores has an effect on the photoreaction in the LB films. When both the ANS and the BISANS LB films were irradiated with UV light (365 nm), photodimerization took place predominantly in nitrogen atmosphere, while photooxidation occurred preferentially in air. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bolaamphiphile; Air/water interface; Monolayer; Photodimerization

1. Introduction

Ordered supramolecular assemblies based on functional molecules and photochemical reactions have been attracting considerable interest in recent years [1]. Monolayer and Langmuir–Blodgett (LB) techniques are among the most effective ways in controlling the molecular orientations and packing at a molecular level [2,3]. Various kinds of photochemical reactions have been investigated in the organized monolayers and LB films, and many interesting features have been revealed [4–8]. However, all these researches are concerned with either polymer monolayers or the monolayers prepared from typical amphiphiles, i.e. the molecules consist of one hydrophilic head group and one hydrophobic tail. Compared to huge amounts of investigations on typical amphiphiles, fewer are devoted to the bolaamphiphiles, in particular, chemical reactions in the ordered molecular assemblies based on bolaamphiphiles. Bolaamphiphile describes a class of amphiphiles where two polar head groups are linked by one or two hydrophobic chains [9–11]. The original interest in bolaamphiphiles may stem from their possibility to form unique monolayer lipid membranes (MLM), which is a model membrane of archaebacteria that can survive in rather crucial conditions such as higher temperature and higher salty concentration [12–17]. Another interest in the bolaamphiphiles is their possibility to form various conformations at the air/water interface, i.e. U-shaped, stretched and flat conformations [18–20]. In this paper, a novel kind of bolaamphiphile containing anthracene moiety was synthesized and the molecular assembly and photoreaction in LB films have been investigated in comparison with those of the one-head long chain derivative. The structures of compounds used in this work are shown in Fig. 1.

Anthracene is a planar aromatic compound and the photoreactivity has been investigated for over a century. Interest in anthracene is stemmed from the excellent spectroscopic and photoreactive properties. This is the reason that we select the anthracene moiety as a probe to detect the assembly and photoreaction features in organized molecular thin films of the bolaamphiphile. Although there are a lot of reports on the assemblies and photoreactions, electron transfer and energy transfer properties of amphiphilic anthracene derivatives [21–25] and also there are reports on the properties of bola-type anthracene derivative in solution [26], this is the first report on the bolaamphiphilic anthracene derivative in the organized LB films.

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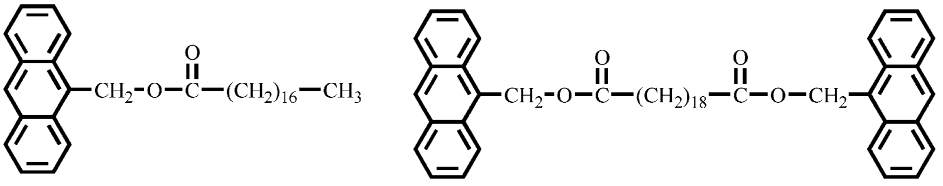

ANS

BISANS

Fig. 1. Structures and abbreviations of the two compounds used in the work.

2. Experimental

2.1. Materials

1,20-Octadecanedicarboxylic acid and 9-anthracenemethanol were purchased from Tokyo Kasei and used without further purification. All the solvents used for synthesis were dried over molecular sieves. A general procedure for the synthesis of the one-head and bola-type anthracene derivatives is as follows: a solution of organic acid in $SOCl_2$ was heated to reflux for 7 h. The excess $SOCl_2$ was removed by azeotropic distillation with dry benzene to give the corresponding acyl chloride. To a stirred toluene solution of 9-anthracenemethanol and dry pyridine, a solution of acyl chloride in toluene was added dropwise within 1 h. Then, the solution was stirred at room temperature for 48 h. The solvent was removed by a rotary evaporator and the residue was washed with water and dried. The yellow crystals were obtained after recrystallization from $CHCl_3$/acetone twice.

9-Anthracenemethyl stearate (ANS) was obtained from 9-anthracenemethanol and stearyl chloride as a yellow crystal. Mp: 56.5–58.0°C, ^1H NMR ($CDCl_3$) δ: 0.89 (t, $-CH_3$, 3H); 1.25–1.6 (m, $-(CH_2-)_{16}$, 32H); 2.35 (t, $-OCOCH_2-$, 2H); 6.15 (s, $-CH_2O-$,2H); 8.03 (d, 2H, $J = 8.25$Hz); 8.33 (d, 2H, $J = 8.79$ Hz); 8.53 (s, 1H).

1,20-Bis(9-anthracenemethyl)octadecanedicarboxylate (BISANS) was from 9-anthracenemethanol and 1,20-octadecyldioyl dichloride as a yellow crystal. Mp: 62.0–63.0°C, ^1H NMR ($CDCl_3$) δ: 1.23 (m, 28H); 1.62 (m, 4H); 2.37 (t, 4H); 6.17 (s, $-CH_2O-$, 4H); 7.31–7.23 (m, 8H); 8.06 (d, $J = 8.31$ Hz, 4H); 8.32 (d, 4H, $J = 8.79$ Hz); 8.53 (s, 2H).

2.2. Surface pressure (π)–area (A) isotherm and LB film deposition

π–A isotherm measurements were conducted in a KSV minitrough (KSV 1100, Helsinki, Finland). Ten minutes after the samples had been spread on the air/water interface, the isotherms were recorded at a compression speed of 5 mm/min. The temperature of the subphase was kept at 20°C. The LB films were fabricated by a vertical dipping method on KSV minitrough at a downward and upward speed of 5 mm/min. Hydrophobic glass substrates were used for low-angle X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. Hydrophobic optically polished quartz and CaF_2 plates were used for UV–VIS and fluorescence spectroscopy, and for IR spectra, respectively.

2.3. Photoreaction in the deposited LB films

Photochemical reactions in the LB films were performed under UV irradiation (365 nm, Mercury lamp) in air or in N_2 atmosphere. The spectral changes were monitored at various time intervals by stopping the reaction. For investigation on the photoreaction in N_2 atmosphere, samples were sealed in a designed quartz cell under the purge of N_2 in the system. UV spectra were recorded on a JASCO UV-530 and fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. FT-IR spectra were measured using a Bio-Rad system. XRD was measured by a Hitachi Natural D/Max-RB diffractometer. SEM was performed on a JSM35C (JEOL). All the experiments were performed at room temperature.

3. Results and discussion

3.1. Spreading properties of the compounds at the air/water interface

Fig. 2 shows the π–A isotherms of the spreading films of ANS and BISANS on air/water interface. The

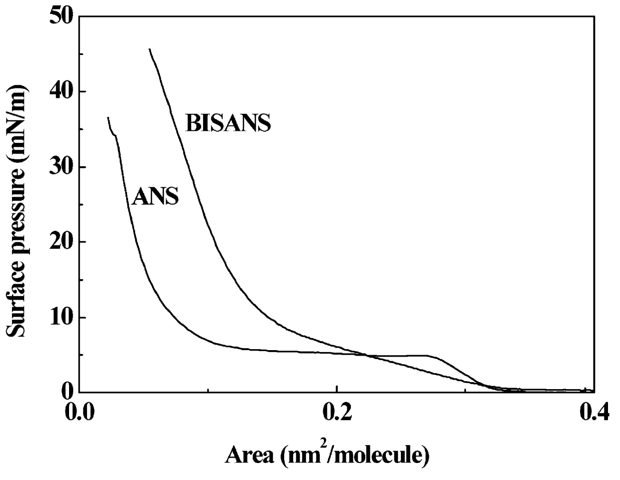

Fig. 2. π–A isotherms of the Langmuir film of ANS and BISANS at the air/water interface at 20°C.

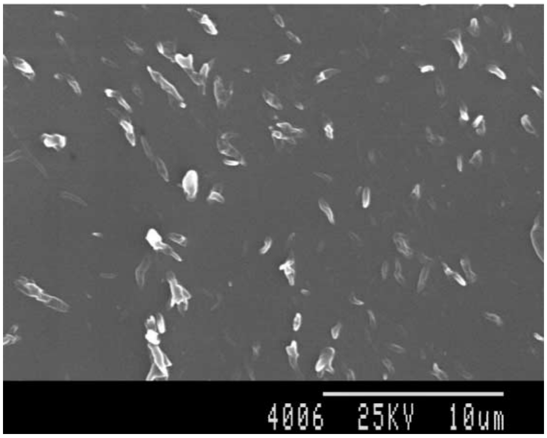

Fig. 3. SEM of BISANS LB film deposited at 5 mN/m.

isotherm of ANS displays a plateau in the range of 0.27–0.1 nm^2/molecule, followed by a steep increase in the surface pressure. From the CPK model, the size of anthracene moiety can be estimated to be 11.9 nm × 7.4 nm × 0.34 nm. It is reasonable to regard that compound ANS formed a monolayer at lower surface pressures and the plateau region is a transition from the monolayer to the collapsed film. On the other hand, the isotherm of the bola-type derivative, BISANS, condensed after a slow increase in the surface pressure to about 10 mN/m. The extrapolating area from the condensed region is 0.16 nm^2/molecule, which is so small that it cannot be regarded as a monolayer. This implies that multilayer film may form at this region. In order to verify this deduction, SEM of the film transferred on glass (deposited at 5 mN/m) was taken, as shown in Fig. 3. Rod-like aggregates were observed in the BISANS LB film, while no aggregates were observed for that of ANS. This indicates that strong interactions between the hydrophobic anthracyl groups and long alkyl chain caused such multilayer formation of BISANS. Such kind of multilayer formation or crystallization on water surface is reported in the case of α,ω-alkanediols [27].

3.2. LB films fabrication and spectroscopic studies

In order to investigate the influence of surface pressure on the molecular orientations, we transferred the films at different surface pressures using the vertical dipping method. Both the films were deposited with unity transfer ratio. The deposited LB films were characterized by the absorption spectra, fluorescence spectra and XRD, respectively.

Fig. 4 shows the absorption spectra of one layer LB film of BISANS and ANS deposited at various surface pressures. In comparison, a spectrum of the corresponding compound in methanol solution is also shown. Both BISANS and ANS show the same absorption peaks at 254, 346, 364 and 384 nm in methanol solution. These spectral features are typical of anthracene moiety. The band at 254 nm can be assigned to the ^1B_b, while the other three bands to the structured ^1L_a band [28]. In the deposited LB film of ANS, the ^1B_b absorption peak is observed at 261 nm (Fig. 4b), which is 7 nm red-shifted in comparison to that in the solution. This indicates that the anthracene chromophores of ANS in LB film take a head to tail orientation or J-aggregation. In the LB films of BISANS, split of ^1B_b band is observed at 251 and 261 nm (Fig. 4a). This split is characteristic of the LB film of bola-type derivative because no split was observed in either the LB film of ANS or in solution. Compared to the ^1B_b band in solution, the blue shift of the peak at 251 nm corresponds to the H-aggregation of the chromophores, while the red shift of the peak at 261 nm corresponds to the J-aggregation. Such kind of peak splitting can be attributed to the interaction between the two anthryl chromophores, indicating that chromophores take Λ-aggregation or the existence of both H-aggregation and J-aggregation.[1] It is interesting to note that the ratio of the peaks at 251 and 261 nm changes with increasing surface pressure. The higher the surface pressure, the stronger is the intensity of the peak at 251 nm. This indicates that higher surface pressure favors the formation of such H-aggregation.

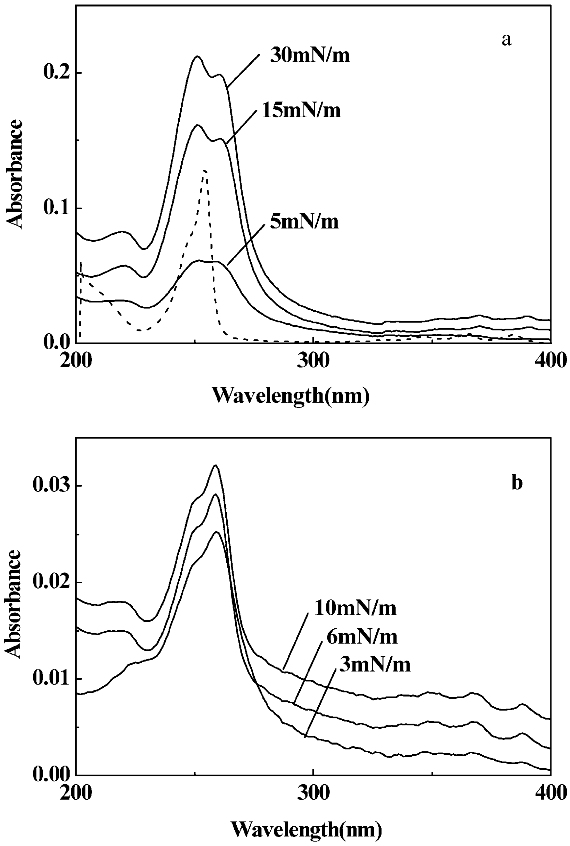

Fig. 4. UV–VIS absorption spectra of (a) BISANS and (b) ANS LB films deposited at various surface pressures and in methanol solution (dotted line).

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[1] Λ-aggregation of the chromophores can also be considered. Spectroscopically, the Λ-aggregation can be regarded as the combination of H-aggregation and J-aggregation. In order to describe easily, we refer the red-shifted band to J-aggregation and blue-shifted band to H-aggregation.

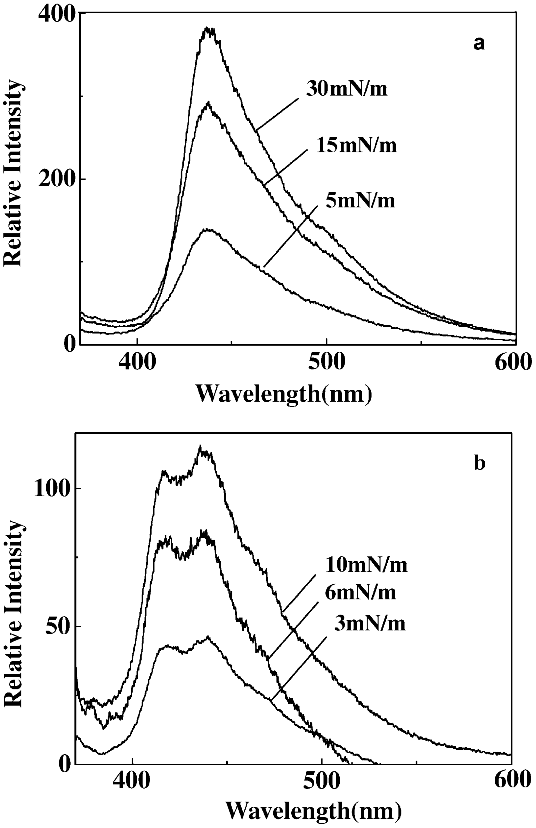

Fig. 5. Fluorescence emission spectra of the LB films of (a) BISANS and (b) ANS deposited at various surface pressures ($\lambda_{exc} = 350$ nm).

Although the same fluorescence spectra were obtained for the two compounds in methanol solution, different fluorescence spectra are observed for the compounds in LB films. Fig. 5 shows the fluorescence spectra of the LB films of ANS and BISANS deposited at various surface pressures. In the LB film of ANS (Fig. 5b), two monomer emission peaks are observed around 420 and 440 nm. The fluorescence spectra of BISANS in LB films are obviously different from those of ANS or in solution, where only a strong emission band is observed at 436 nm (Fig. 5a). With the surface pressure of the film deposition increased, both ANS and BISANS LB films show the increase in the intensity of the emission band. In addition, a shoulder band appeared at around 502 nm at higher surface pressure for BISANS LB film. In the UV spectra of the LB films of BISANS deposited at higher surface pressure, strong H-aggregation band was observed. Therefore, it is regarded that this emission band at 502 nm is consistent with the H-aggregation, i.e. a close-packed array of the chromophores at higher deposited surface pressure in the BISANS LB film.

Further evidence of the conformation of the bola-type films is from the low-angle XRD measurement, as shown in Fig. 6. While no diffraction peak is observed for ANS LB film, three diffraction peaks are observed for a 40-layer BISANS LB film deposited at 15 mN/m. The 2θ values of these peaks are found at 5.8, 8.8 and 11.8°, respectively.

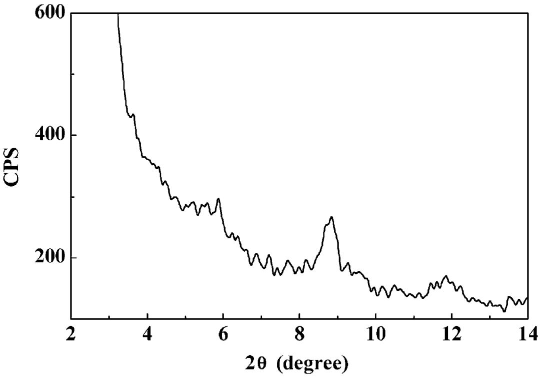

Fig. 6. XRD pattern of the LB film of BISANS (40 layers deposited at 15 mN/m).

Because of the coexistence of the H- and J-aggregation, the diffraction peaks are rather blunt. According to the Bragg's equation ($2d \sin\theta = n\lambda$), the long spacing d of LB film of BISANS is calculated to be 3.0 nm. The value is smaller than 4.0 nm, which is estimated from CPK model, suggesting that molecules of BISANS take a stretched conformation but the

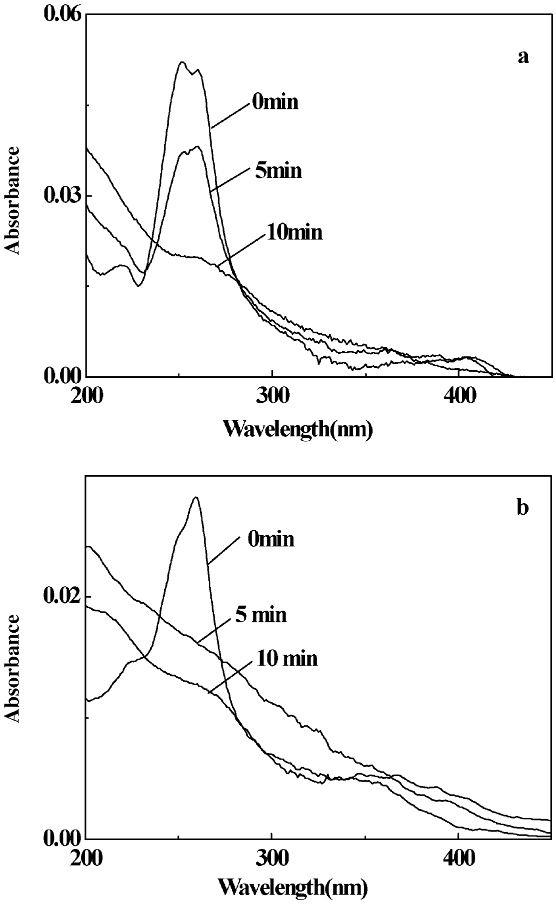

Fig. 7. UV–VIS absorption spectra of (a) BISANS and (b) ANS LB films deposited at 5 mN/m before and after UV irradiation for different time in air.

alkyl chain in the film is rather tilted. Stretching vibration of CH_2 is very sensitive to the packing of alkyl chains [29,30]. FT-IR spectra of the LB films showed the asymmetric and symmetric vibrations at 2920 and 2850 cm^{-1} (see Fig. 10), suggesting that the alkyl chains stacked tilted in the LB films, supporting the above XRD data.

3.3. Spectroscopic studies of the photoreaction in the LB films

3.3.1. UV–VIS spectra

Anthracene can undergo topochemical photodimerization upon irradiation and also photooxidation in the presence of oxygen. The dramatic changes in the UV–VIS absorption spectra of the one-layer LB films of both ANS and BISANS deposited at 5 mN/m upon irradiation in air and in N_2 atmosphere are presented in Figs. 7 and 8, respectively. Upon UV irradiation in air, the absorption of anthracene moiety dropped rapidly and almost disappeared within 10 min irradiation, as shown in Fig. 7. However, much slower reduction in absorbance of anthryl chromophores is observed when the LB films of ANS and BISANS were irradiated in N_2 atmosphere. Both ANS and BISANS LB films show the absorption peak around 261 nm after 50 min irradiation (Fig. 8). Continuous irradiation does not cause further changes in the UV spectra. It is worth noting that for BISANS LB film, the peak at 251 nm decreases more rapidly than the peak at 261 nm upon irradiation. Because the peak at 251 nm is ascribed to the H-aggregation, it is suggested that H-aggregation favor the photodimerization.

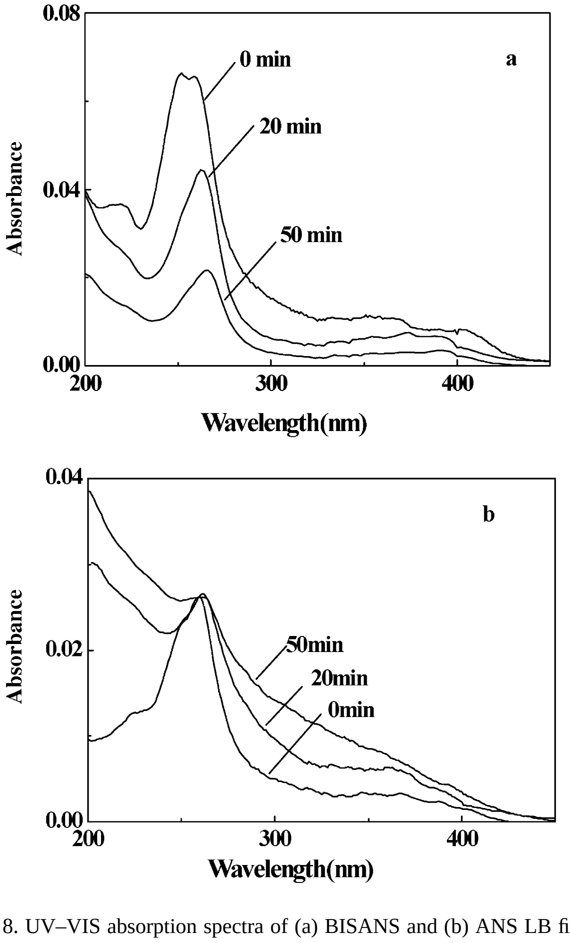

Fig. 8. UV–VIS absorption spectra of (a) BISANS and (b) ANS LB films deposited at 5 mN/m before and after UV irradiation for different time in N_2 atmosphere.

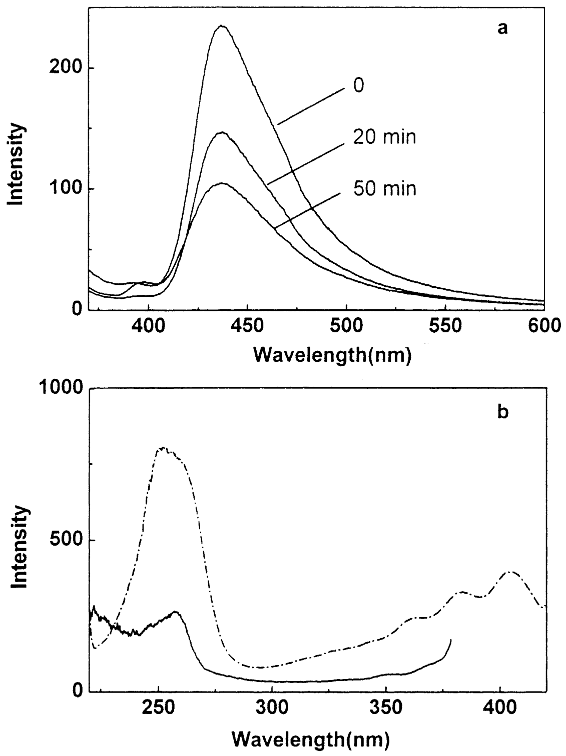

Fig. 9. (a) Fluorescence emission spectral changes of the BISANS LB film deposited at 5 mN/m in N_2 atmosphere at various irradiation stage ($\lambda_{exc} = 350$ nm); (b) Fluorescence excitation spectra of the BISANS LB film after irradiation, monitored at 390 nm (solid line) and 430 nm (dotted line).

3.3.2. Fluorescence spectra

Fluorescence spectra have also been used to detect the photochemical changes during the irradiation of the LB films. In air, the fluorescence spectra were very complicated due to the oxidation and quench. Fig. 9a shows the fluorescence spectral changes during the UV irradiation in N_2 atmosphere. It is noted that upon UV irradiation, emission band at 436 nm decreased continuously and a new band appeared at 390 nm. After irradiation for 50 min, the fluorescence peak at 390 nm becomes obvious. In order to make out the nature of this new band, we have measured the excitation spectrum of the LB film after irradiated for 50 min, as shown in Fig. 9b. When monitoring the emission at 430 nm, the excitation spectrum is similar to the absorption spectrum of the LB film before UV irradiation. On the other hand, when monitoring at 390 nm, the excitation is similar to the absorption spectrum of the LB film after UV

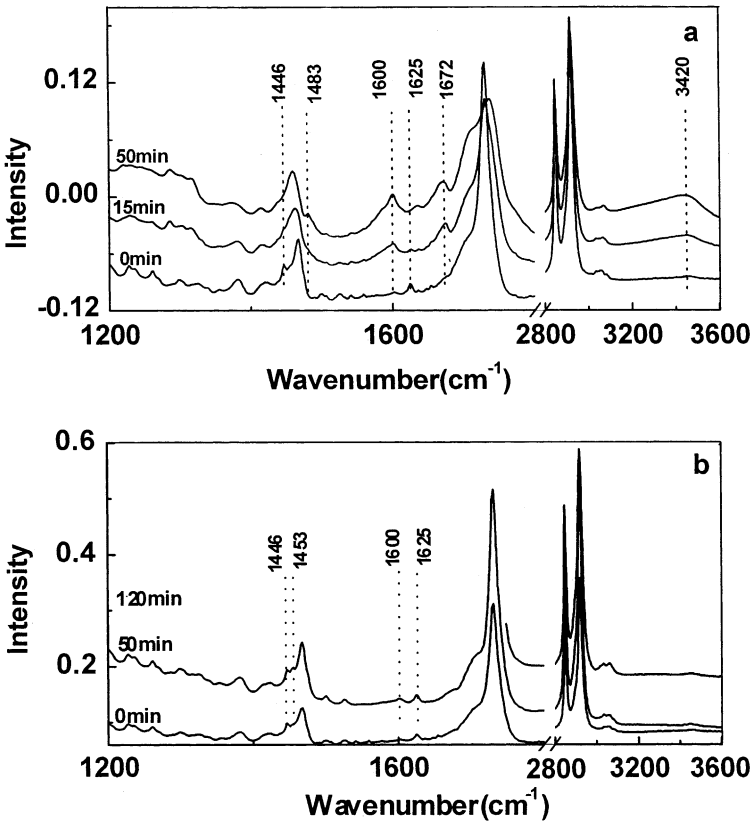

Fig. 10. FT-IR spectra of the BISANS LB films at various irradiation stage in (a) air and (b) N_2 atmosphere.

irradiation. Therefore, the emission band at 390 nm originate from photoproduced dimer. Similar phenomenon was observed in the case of ANS, where a new band was also detected at 390 nm after 50 min irradiation.

3.3.3. FT-IR spectra

The photooxidation and photodimerization in the BISANS LB films upon irradiation at 365 nm in air or in N_2 atmosphere are clearly confirmed from the FT-IR spectra measurements of the deposited LB films. Fig. 10 shows the FT-IR spectra of the deposited LB films of BISANS upon irradiation in air and in N_2 atmosphere, respectively. In the region of 1000–1800 cm^{-1}, main vibration bands are observed at 1107, 1163, 1446, 1463, 1625 and 1730 cm^{-1} before irradiation. When it was irradiated in air for 50 min, a significant vibration at 3420 cm^{-1} is appeared in the region of 2800–3800 cm^{-1}, which can be assigned to the –OH stretching vibration (Fig. 10a). Another important feature in the FT-IR spectra of the LB film upon irradiation is the appearance of strong vibration bands at 1483, 1600, 1672 cm^{-1} and the disappearance of the bands at 1446 and 1625 cm^{-1}. The two strong vibration bands at 1600 and 1672 cm^{-1} can be assigned to the C=C vibration of benzene ring and C=O stretching of anthraquinone respectively, suggesting that photoirradiation of the BISANS LB film in air leads to an anthraquinone product. The anthraquinone is produced through the endoperoxide [31]. When the LB film of BISANS was irradiated in N_2 atmosphere, photodimerization occur within 120 min irradiation, which can be confirmed from the disappearance of the band at 1446 cm^{-1} and appearance at 1453 cm^{-1} (Fig. 10b). They have been assigned to the aromatic C–H stretch at the position 10 of anthracene. In the photoreaction of the LB film in N_2 atmosphere, some weak vibrations due to the photooxidation, as in air, were also observed. This may be attributed to the slight oxygen adsorbed in the LB film.

4. Conclusions

Molecular arrangement and photochemical reactions have been investigated in the LB films of a novel BISANS in comparison with those of ANS. Spreading of BISANS undergo aggregation to form crystal film at air/water interface, while ANS form a stable monolayer. In the ANS LB films, the anthracyl chromophores form J-aggregates independent of the surface pressure, while H-aggregates and J-aggregates coexisted in BISANS LB film. With the increase in surface pressure, the content of H-aggregates increases. Upon UV irradiation (365 nm), the photooxidation occurs dominantly in air, while photodimerization predominates in N_2 atmosphere.

Acknowledgements

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References

[1] V. Ramamurthy, Photochemistry in Organized and Constrained Media, VCH publisher, Weinheim, 1991.

[2] G.L.J. Gains, Insoluble Monolayers at Liquid–Gas Interfaces, Wiley, New York, 1972.

[3] A. Ulman, An Introduction to Ultrathin Organic Films, Academic Press, Boston, 1991.

[4] J. Zhao, K. Abe, H. Akiyama, Z.F. Liu, F. Nakanishi, Langmuir 15 (1999) 2543.

[5] M. Fujimaki, S. Kawahara, Y. Matsuzawa, E. Kurita, Y. Hayashi, K. Ichimura, Langmuir 14 (1998) 4495.

[6] L.A. Lucia, K. Wyrozebski, L.H. Chen, C. Geiger, D.G. Whitten, Langmuir 14 (1998) 3663.

[7] A. Ahluwalia, R. Piolanti, D. De Rossi, A. Fissi, Langmuir 13 (1997) 5909.

[8] K. Balashev, I. Panaiottor, J.E. Proust, Langmuir 13 (1997) 5373.

[9] J.H. Fuhrhop, D. Fritsch, Acc. Chem. Res. 19 (1986) 130.

[10] J.H. Fuhrhop, J. Mathieu, Angew. Chem. Int. Ed. Engl. 23 (1984) 100.

[11] G.H. Escamilla, G.R. Newkome, Angew. Chem. Int. Ed. Engl. 33 (1994) 1937.

[12] A. Gliozzi, A. Relini, in: Handbook of Nonmedical Applications of Liposomes, CRC Press, Tokyo, 1995.

[13] A. Relini, D. Cassinadri, Q. Fan, A. Gulik, R. Mirghani, A. Gliozzi, Biophys. J. 71 (1996) 1789.

[14] J.H. Fuhrhop, H.H. David, J. Mathieu, U. Liman, H.J. Winter, E.J. Boekema, Am. Chem. Soc. 108 (1986) 1785.

[15] J.H. Fuhrhop, U. Liman, V.J. Koesling, Am. Chem. Soc. 110 (1988) 6840.

[16] J. Kim, D.H. Thompson, Langmuir 8 (1992) 637.

[17] P. Nostro, G. Briganti, S.W.J. Chen, Colloid Interface Sci. 142 (1991) 214.

[18] N.K. Adam, G. Jessop, Proc. R. Soc., London, Ser A. 112 (1926) 376.

[19] H. Matuo, D.K. Rice, D.M. Balthasar, D.A. Cadenhead, Chem. Phys. Lipids 30 (1982) 367.

[20] V. Vögel, D. Möbius, Thin Solid Films 132 (1985) 205.

[21] N. Tamai, T. Yamazaki, I.J. Yamazaki, Phys. Chem. 91 (1987) 841.

[22] T. Lawai, S. Scheib, M.P. Cava, R.M. Metzger, Langmuir 13 (1997) 5627.

[23] M.I. Sluch, I.D.W. Samuel, A. Beeby, M.C. Petty, Langmuir 14 (1998) 3343.

[24] A. Vaes, M. Van der Auweraer, P. Bosmans, F.C. De Schryver, J. Phys. Chem. B 102 (1998) 5451.

[25] M.A. Fox, M.D. Wooten, Langmuir 13 (1997) 7099.

[26] H. Bouas-Laurent, A. Castellan, J.P. Desvergne, Pure Appl. Chem. 52 (1980) 2633.

[27] R. Popovitz-Biro, J. Majewski, L. Margulis, S. Cohen, L. Leiserowitz, M. Lahav, J. Phys. Chem. 98 (1994) 4970.

[28] H.B. Klevens, J.R. Platt, J. Chem. Phys. 17 (1949) 470.

[29] D. Allara, R.G. Nuzzo, Langmuir 1 (1985) 52.

[30] S.C. Chang, I. Chao, Y.T. Yao, J. Am. Chem. Soc. 116 (1994) 6792.

[31] R. Dabestani, K.J. Ellis, M.E. Sigman, J. Photochem. Photobiol. A: Chem. 86 (1995) 231.