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Langmuir Monolayers of Azobenzene Derivative with a Urea Head Group

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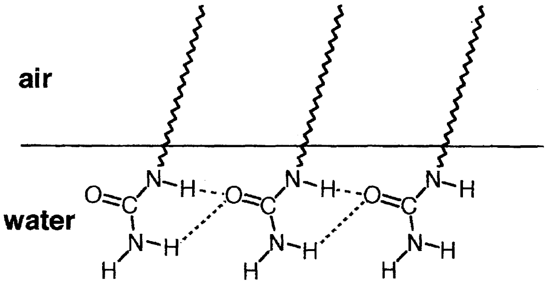
An azobenzene (Az) containing amphiphile having a urea head group [*N*-(10-{4-[(4-hexylphenyl)azo]phenoxy})-decylurea (6Az10-Urea)] was synthesized for the first time, and the spreading behavior, morphology, absorption spectral features, and photoreactivity of this amphiphile at the air–water interface was examined. The features of this monolayer were argued in comparison with those of a carboxylic acid derivative of the homologous structure. Polymer-like stable stable monolayers were formed form 6Az10-Urea both in the *trans* and *cis* forms of the Az unit, possibly indicating the formation of intermolecular bifurcated NH···O=C hydrogen bonds of urea heads. Unlike monolayers of simple long alkylureas, the present monolayer did not show a thermal phase transition within the temperature region examined (10—35 °C). In the *trans*-6Az10-Urea monolayer, the Az unit formed tilted aggregates. In this aggregation state, the *trans*-to-*cis* photoisomerization in the 6Az10-Urea monolayer was completely hindered despite the fact that the monolayer was more expanded than that of a corresponding carboxylic acid derivative in which the photoisomerization proceeded.

Langmuir monolayers and Langmuir–Blodgett (LB) films of azobenzene (Az) containing amphiphiles have attracted extensive attention in recent years. These two-dimensional molecular assemblies provide vast varieties of fascinating light-triggered functions, such as information storage,[1—3] photomechanical response,[4,5] alignment control of liquid crystals,[6,7] conductivity control,[8] morphological inductions,[9—12] and polymerization control.[13] With respect to the molecular design for single-chain amphiphiles, various types of hydrophilic head groups have been employed, for instance, carboxylic acid,[1,2,11,12,14—17] sulfonic acid,[10] alcohol,[17] amine,[17,18] ammonium,[18,19] and pyridinium.[8,21] The utilization of the hydrophilic polymer chain[3—7,9,13,22—24] and ion complexation with a polyelectrolyte[10,18—20] are also subjects of great interest for the preparation of stable LB films, which frequently show an efficient *trans*/*cis* photoisomerization.

Adam found in 1922 that Langmuir monolayers of long-chain urea derivatives show a unique polymorphism having two forms of packing states, depending on the temperature.[25,26] According to Glazer and Alexander,[27] in the α form (high temperature form, 0.20—0.21 nm^2 per molecule) the urea head groups align vertically with no hydrogen bonding between them, and the alkyl chains are fully extended close-packed and vertical. On the other hand, in the β form (low temperature form, 0.25—0.27 nm^2) the urea groups are more horizontal with two hydrogen bonds between the oxygen atom of one molecule and the two nitrogen atoms of a neighbor (see Scheme 1); also, the alkyl chains are tilted at an angle of 45° [27] or 35° [28] to the vertical. This peculiar polymorphism in a matter of continuing research in recent years.[28—31]

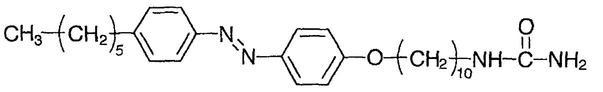


Scheme 1.

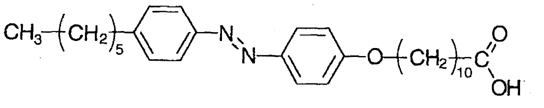
Since the photoisomerization behavior of the Az unit in Langmuir films and LB films is strongly dependent on the molecular packing state, it seemed of great interest to undertake an exploration which combines the functionalities of Az and urea within a molecule. In this paper we report on the synthesis and fundamental characteristics of monolayers composed of a urea containing the Az derivative (6Az10-Urea), in comparison with that of a carboxylic acid derivative of homologous structure (6Az10-COOH). It has been found that there are marked contrasts between these two types of monolayers with respect to packing state, morphology, and photoreactivity, as revealed by surface pressure-area isotherms, Brewster angle microscopy, and UV-visible absorption spectroscopy. The molecular structure of the Az-containing amphiphiles used in this study is indicated in Chart 1.

Experimental

1. Materials. The solvents used for Langmuir film spreading and spectroscopic measurements were of spectroscopic garde (Uvasol, Ciba-Merck). 1,1,1,3,3,3-hexaflouro-2-propanol (HFIP)



6Az10-Urea



6Az10-COOH

Chart 1.

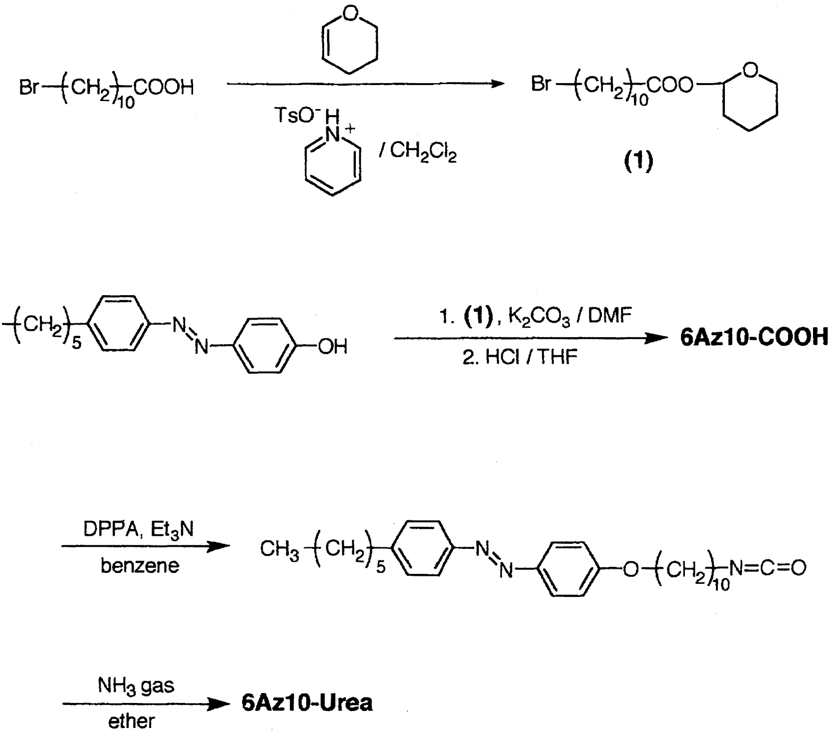
was purchased from Tokyo Kasei Kogyo and used without further purification.

The Az compound having a urea head group was synthesized from a carboxylic acid derivative through a conversion to isocyanate,[32] followed by a reaction with ammonia gas.[33] The synthetic strategy is shown in Scheme 2. The identification of synthesized materials was performed using the following equipments. The melting point was measured with a Yanaco MP-S3 melting-point apparatus, and are uncorrected. ^{1}H NMR spectra were recorded on a Brucker AC-200 spectrometer using Me_4Si as the internal standard. IR spectra were taken on a JASCO FT/IR-300. Elemental analysis was performed on a Yanaco MT-5 CHN CORDER.

2-Tetrahydropyranyl 11-Bromoundecanoate. A mixture of 11-bromoundecanoic acid (10.0 g, 37.7 mmol) and 3,4-dihydro-2*H*-pyrane (3.62 g, 37.7 mmol) in dichloromethane (20 ml) was prepared and pyridinium *p*-toluenesulfonate (0.95 g, 3.80 mmol) was added at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and at room temperature for an additional 2 h. After washing with 4% $NaHCO_3$ aqueous solution, water, and brine, the solution was dried over anhydrous $MgSO_4$. The solvent was evaporated and the product was obtained as an oily material. Yield: 12.8 g (ca. 100%).

11-{4-[(4-Hexylphenyl)azo]phenoxy}undecanoic Acid (6Az10-COOH). To a mixed solution of 4-[(4-hexylphenyl)azo]-phenol (7.50 g. 26.2 mmol) and 2-tetrahydropyranyl 11-bromoundecanoate (13.92 g, 39.9 mmol) in dry *N*,*N*-dimetylformamide (50 ml), K_2CO_3 (3.95 g, 47.9 mmol), and a catalytic amount of KI were added and stirred at 70 °C for 2 d. The reaction mixture was extracted with ether and washed with water. After evaporation of the organic solvent, tetrahydrofuran (100 ml) and concentrated HCl (10 ml) were added. The solution was stirred for 40 min at room temperature. After extraction with chloroform, the organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was recrystallized from hexane–ethyl acetate. Yield: 10.6 g (85%), mp 102—106 °C. IR (KBr) 3300—2400 (ν_{OH}), 1709 ($\nu_{C=O}$), 1249 (ν_{C-O-C}), 842 cm^{-1} (δ_{CH}, *p*-Ph); ^{1}H NMR ($CDCl_3$, 50 °C) δ = 0.89 (3H, t, J = 7 Hz, CH_3–), 1.32—1.85 (24 H, m, –CH_2–), 2.35 (2H, t, J = 7 Hz, –$\underline{CH_2}$–COOH), 2.67 (2H, t, J = 7 Hz, –$\underline{CH_2}$–Ph), 4.03 (2H, t, J = 7 Hz, –O–CH_2–), 6.99 (2H, d, J = 9 Hz, Ph–H), 7.29 (2H, d, J=9 Hz, Ph–H), 7.77–7.90 (4H, m, Ph–H). Found: C, 72.35; H, 9.25; N, 11.53%. Calcd for $C_{29}H_{44}N_4O_2$: C, 72.50; H, 9.17; N, 11.67%.

***N*-(10-{4-[(4-Hexylphenyl)azo]phenoxy})decylurea (6Az-10-Urea).** To a solution of 6Az10-COOH (3.00 g, 6.44 mmol) in dry benzene (80 ml) were added diphenylphosphoryl azide (DPPA) (2.13 g, 9.66 mmol) and triethylamine (975 mg, 9.66 mmol). After stirring at refluxing temperature for 4 h, the solvent was evaporated. To the residue was added ether (80 ml), and dry ammonia gas was passed into the solution for 1 h at room temperature. After the pale-yellow solid was precipitated, the mixture was vigorously stirred overnight. The solid was filtered off and recrystallized from chloroform. Yield: 1.99 g (64%), mp 145—148 °C. IR (KBr) 3415, 3344 (ν_{NH}), 1636 ($\nu_{C=O}$), 1561 (δ_{NH}), 1246 (ν_{C-O-C}), and 842 cm^{-1} (δ_{CH}, *p*-Ph); ^{1}H NMR ($CDCl_3$, 50 °C) δ = 0.89 (3H, t, J = 7



Scheme 2.

Hz, CH_3–), 1.31—1.85 (24H, m, –CH_2–), 2.66 (2H, t, J = 8 Hz, –$\underline{CH_2}$–Ph), 3.12 (2H, q, J = 7 Hz, –$\underline{CH_2}$–NH–), 4.02 (2H, t, J = 7 Hz, –O–CH_2–), 4.40 (2H, bs, –NH_2), 4.68 (1H, bs, –NH–), 6.96 (2H, d, J = 7 Hz, Ph–H), 7.27 (2H, d, J = 7 Hz, Ph–H), and 7.75—7.88 (4H, m, Ph–H). Found: C, 72.35; H, 9.25; N, 11.53%. Calcd for $C_{29}H_{44}N_4O_2$: C, 72.50; H, 9.17; N, 11.67%.

2. Methods. The spreading behavior of Az-containing monolayers was evaluated with a Lauda FW1 film balance in subdued red light. Unless stated otherwise, pure water (Milli-Q grade, 18 $\mathrm{M\Omega\,cm^{-1}}$, pH = 5.8) was filled in the trough. After evaporation of the solvent, the monolayer was compressed at a speed of 20 $\mathrm{cm^2\,min^{-1}}$, and the surface pressure was recorded versus the molecular area. The temperature of the subphase was controlled by water circulation using a Yamato–Komatsu CTE-22W at an accuracy of ±0.5 °C.

Brewster angle microscopic observations were achieved with a NLE-EMM633 (Nippon Laser Electronics) equipped with a 10 mW He–Ne laser. The obtained images were recorded on video tape, and appropriate snap shots were printed.

UV-visible absorption spectra for the floating monolayer were taken on a spectrometric system comprising a photodiode-array detector (MCPD-2000, Ohtsuka Electronics) assembled with a deuterium/halogen lamp (MC-2530, Ohtsuka Electronics), and a processing computer.

Light irradiation was performed with a 150 W Hg–Xe lamp (San-ei UV Supercure-230S). The 365 nm line was selected using a combination of Toshiba optical filters, UV-35/UV-D36A. The light intensity was estimated with an optical power meter (Advantest TQ-8210).

Results and Discussion

1. Surface Pressure–Area Isotherms. Sruface pressure–area (π–A) curves of 6Az10-Urea monolayer in the *trans* form obtained at temperatures ranging 10—35 °C are shown in Fig. 1. We anticipated a temperature-dependent characteristic in the spreading behavior of this amphiphile, taking into account the behavior of hexadecyl- and octadecylurea, as stated in the introductory section. As shown in the figure, however, no appreciable thermal transition was observed for the 6Az10-Urea monolayer. The limiting area per Az unit of 6Az10-Urea, which was estimated by extrapolating the steepest slope to zero pressure, was almost constant within the range of 0.30—0.35 $\mathrm{nm^2}$ at all temperatures examined. We assume at the moment that this insensitivity to the temperature change stems from the strong π stacking interaction among the Az units, which impairs any rupturing of hydrogen bonds.

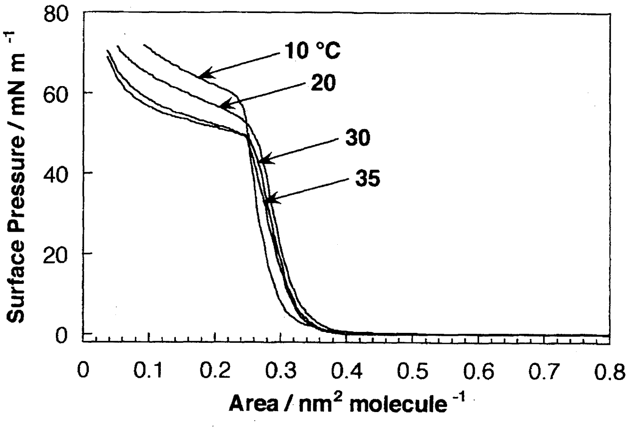


Fig. 1. The surface pressure-area isotherms of 6Az10-Urea monolayer on pure water at various temperatures.

In the above context, all measurements performed hereinafter were commonly achieved at 20 °C. Figure 2 shows the π–A isotherms of monolayers comprising 6Az10-Urea (solid line) and 6Az10-COOH (dashed line). For both materials, the monolayer was spread in the *trans* form (a), and in the photoequilibrated state with irradiation of 365 nm light (b, *cis* form content of exceeding 90%). A monolayer in this photostationary state is simply called a *cis*-Az monolayer for simplicity in this paper. The notations A—H correspond to the positions of the BAM observation shown in Figs. 3, 4, 5, and 6.

The 6Az10-COOH monolayer in the *trans* form gave a limiting area of 0.25 $\mathrm{nm^2}$; also, the collapse pressure was observed at 50 $\mathrm{mN\,m^{-1}}$ (Fig. 2a). The molecular occupying area is in agreement with expected cross section of an Az unit oriented perpendicular to the surface plane. On the other hand, limiting area of a 6Az10-Urea monolayer is considerably larger (0.32 $\mathrm{nm^2}$) with a collapse pressure on the same level. In appearance, the shape of the π–A isotherm of the 6Az10-Urea monolayer is very similar to that of the monolayer of a homologous polymeric material, a poly(vi-

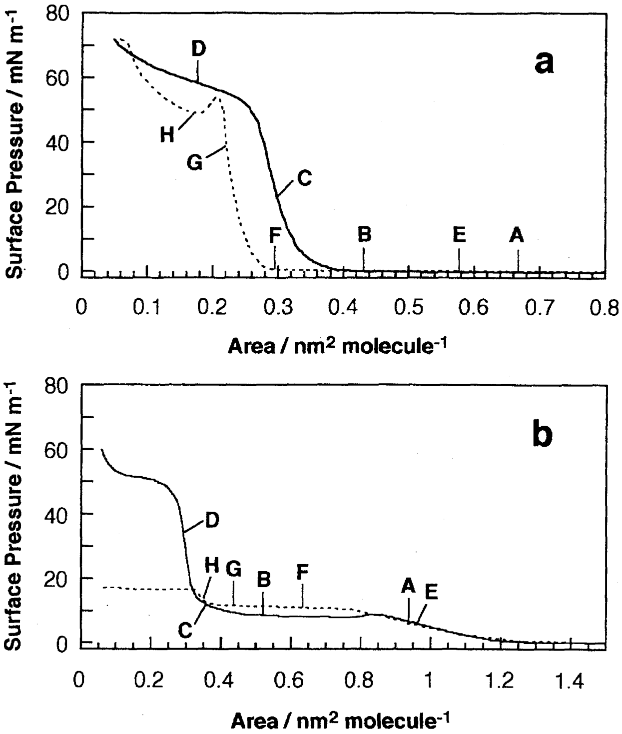


Fig. 2. The surface pressure-area isotherms of Az containing amphiphiles in the *trans* (a) and in the UV (365 nm) light equilibrated *cis* form (b) on pure water at 20 °C. The solid and dashed lines indicates the isotherms of 6Az10-Urea and 6Az10-COOH monolayer, respectively. The notations A—H indicate the conditions for BAM observation shown in Figs. 3, 4, 5, and 6, A—D, and E—H corresponding to observations of 6Az10-Urea and 6Az10-COOH, respectively.

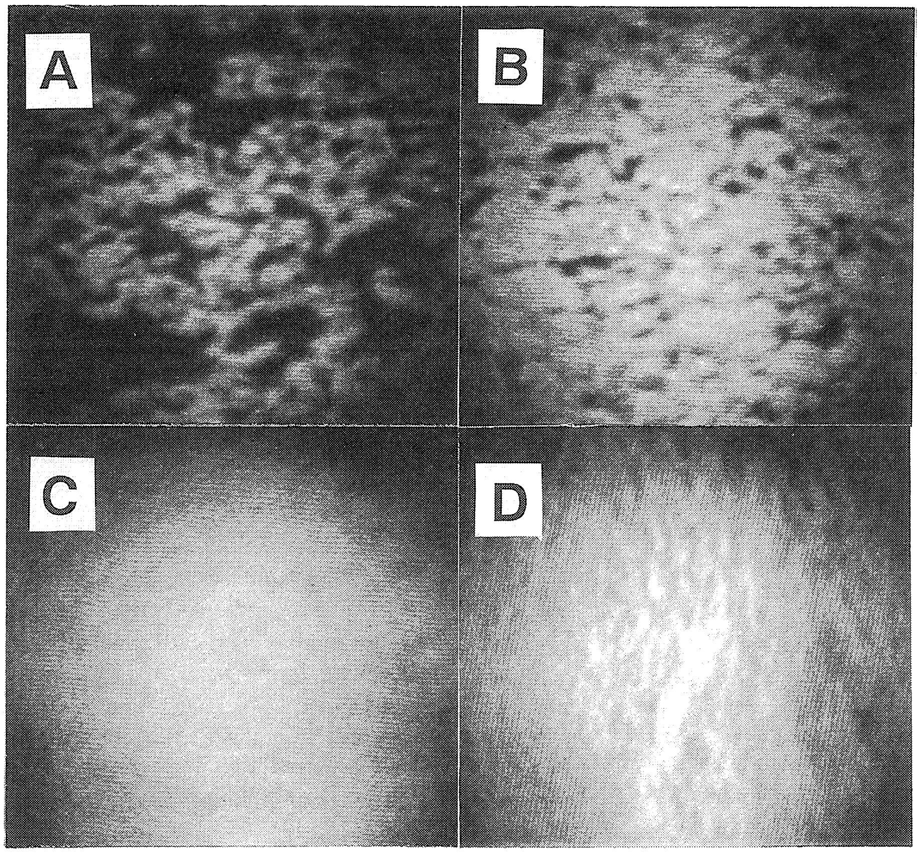


Fig. 3. BAM images of 6Az10-Urea monolayer in the *trans* Az form. The images, A—D, were taken at the positions of A—D in Fig. 2a, respectively.

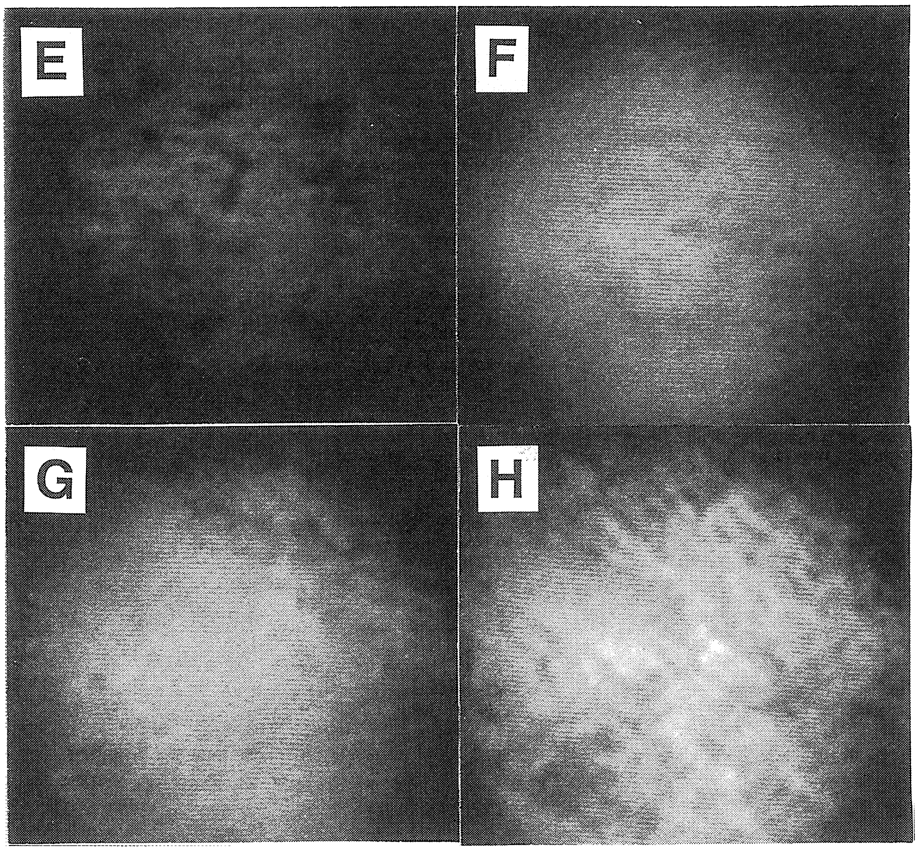


Fig. 4. BAM images of 6Az10-Urea monolayer in the *trans* Az form. The images, E—H, were taken at the positions of E—H in Fig. 2a, respectively.

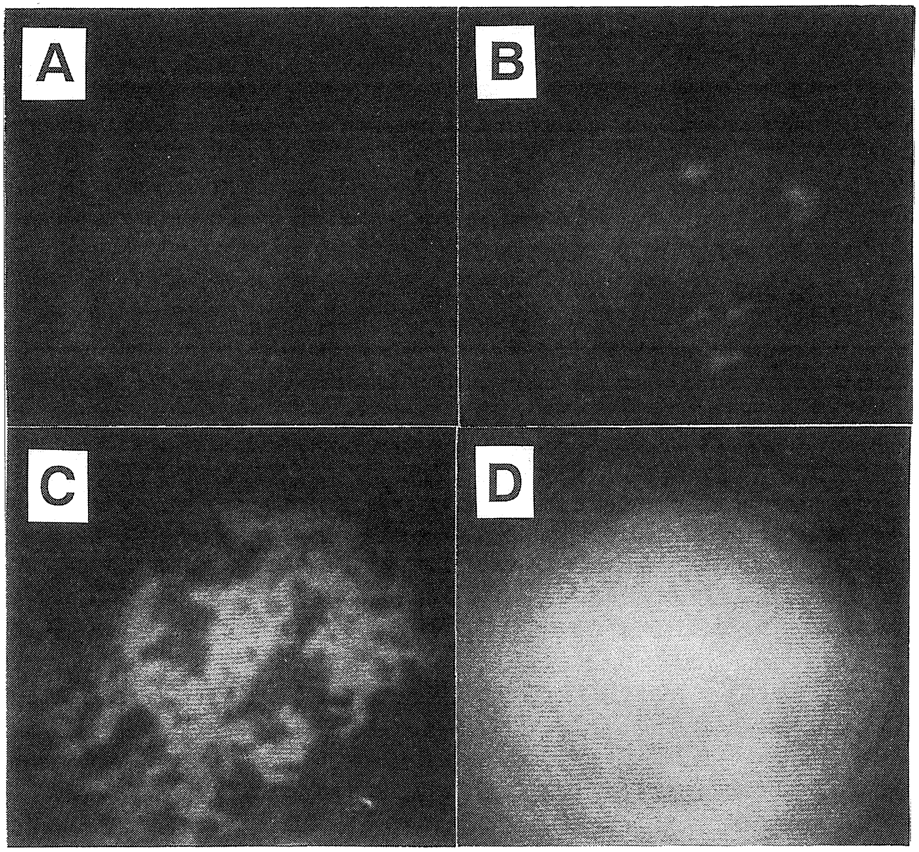


Fig. 5. BAM images of 6Az10-Urea monolayer in the *cis* Az form. The images, A—D, were taken at the positions of A—D in Fig. 2b, respectively.

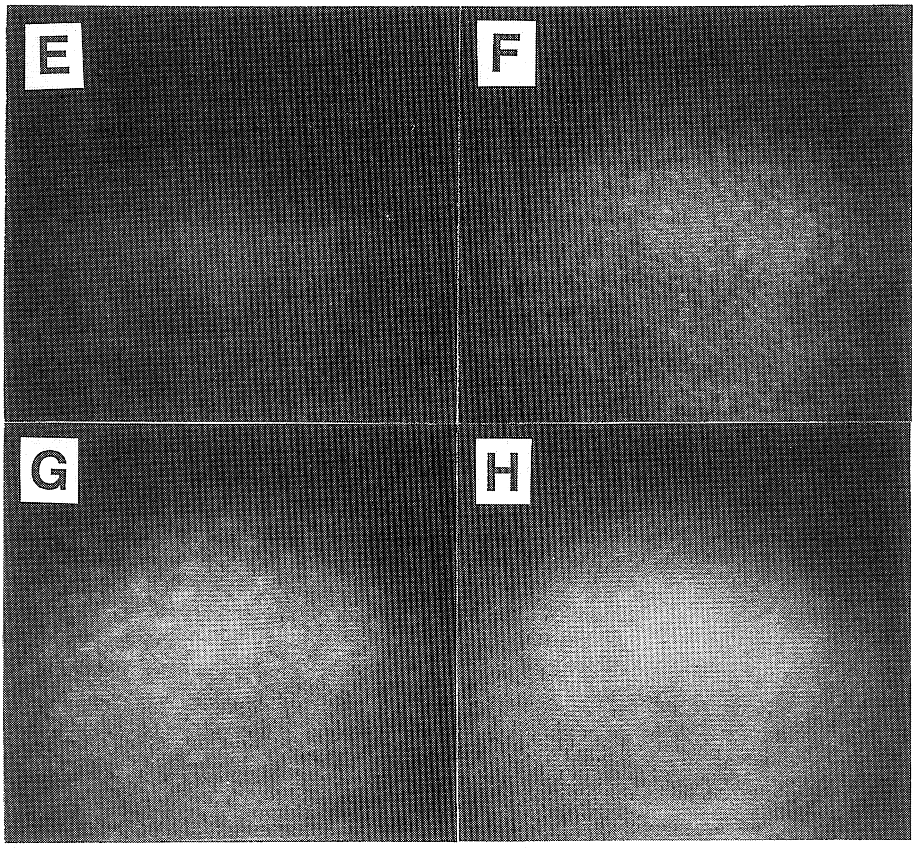


Fig. 6. BAM images of 6Az10-Urea monolayer in the *cis* Az form. The images, E—H, were taken at the positions of E—H in Fig. 2b, respectively.

nyl alcohol) derivative having the 6Az10-side chain (6Az10-PVA in Ref. 4, 0.37 nm^2) in terms of the expanded area per molecule and no sign of a pressure decrease after collapse. We are not currently able to obtain any direct evidence of hydrogen-bond formation in the 6Az10-Urea monolayer; however, such polymer-like characteristics strongly suggest the existence of firm intermolecular interactions, most probably the participation of hydrogen bonding. The expanded area of the urea-containing monolayer indicates either a molecular tilt or a disordering of the hydrocarbon chains; however, the former factor is plausible, judging from the spectroscopic data, as will be shown later.

Both monolayers gave highly expanded π–A isotherms when the Az moiety was pre-isomerized to the *cis* form before spreading (Fig. 2b). In both monolayers the surface pressure lifted off at 1.2 nm^2 per molecule. An inflection showing a compressional phase change was observed at around 0.8 nm^2 for both monolayers. After a wide plateau ranging ca. 0.8—0.4 nm^2, both isotherms exhibited a steep slope at around 0.3 nm^2. At this point, there was a marked difference in the collapse pressure. The monolayer of 6Az10-COOH collapsed at 20 mN m^{-1}, whereas that of 6Az10-Urea did so at 50 mN m^{-1}, a surprisingly high value for a *cis*-Az monolayer. This can be ascribed to enhanced mechanical stabilization due to intermolecular hydrogen bonding. It is worth noting that the collapse pressure was even higher in the urea system than that of the covalent-bonded polymeric material (6Az10-PVA), the collapse pressure being ca. 30 mN m^{-1}.[4)]

The coincidence in the molecular occupying area for the 6Az10-Urea monolayer in the *trans* and *cis* forms in the compressed state (0.32—0.33 nm^2) is somewhat strange. This may be explained either by (i) a large molecular tilt in the *trans*-6Az10-Urea monolayer which coincides incidentally with that of the *cis*-6Az10-Urea monolayer or (ii) the occurrence of the compression-induced isomerization of the *cis*-to-*trans* form of the Az chromophore. Spectroscopic data of the monolayer on the water surface obtained upon compression gave no indication of the isomerization of Az, indicating that the former explanation is plausible.

It is also to be noted that the 6Az10-COOH monolayer can also form lateral intermolecular hydrogen bonding between the neighboring carboxylic acid moieties (C=O···HO).[34)] The features observed in the urea-based monolayer imply a stronger interaction with less positional freedom through the formation of bifurcated hydrogen bonding with an adjacent molecule (Scheme 1).

2. Brewster Angle Microscopy. The morphologies of monolayers on water in the compression process were observed by BAM, and typical images are displayed in Figs. 3, 4, 5, and 6. Figures 3 and 4 shows the images of monolayers in the *trans* form for 6Az10-Urea and 6Az10-COOH, respectively. In the same manner, Figures 5 and 6 display the data of the *cis*-monolayers for 6Az10-Urea and 6Az10-COOH, respectively. In BAM observations, the presence of the monolayer is visualized as a bright part in the image, and an exposed water surface is observed as a darker one.[35,36)]

In Fig. 3, BAM images corresponding to A—D in the π–A curve of Fig. 2a are indicated. At an area exceeding twice the limiting area (A, 0.75 nm^2), the monolayer consisted of small grain-like islands of a few hundred micrometers in size, which formed a network structure. Seemingly, the floating islands did not possess optical heterogeneity under polarized BAM observation. Upon compression, these islands were gathered without any deformation of contours until the surface pressure raised (B, 0.45 nm^2), indicating that the monolayered assembly is robust and solid-like. After a pressure lift-off (C, 0.27 nm^2), the domains were gathered to form a highly homogeneous monolayer. The collapsed film consisted of brighter stripes running perpendicular to the compressive direction (D). All of these morphological features are common to those of the material of the polymeric monolayer of 6Az10-PVA.[37)] In this way, the monolayer of 6Az10-Urea resembles that of 6Az10-PVA in nature, and in terms of the film morphology.

For the 6Az10-COOH monolayer in the *trans* form (Fig. 4, corresponding to E—H in Fig. 2a), the difference in reflectivity (contrast) between the regions of monolayer occupation and the bare water surface was rather poor. At a large area (E, 0.55 nm^2), the image also indicated a heterogeneous structure containing both film and a bare water surface. As the pressure increased (F and G), the monolayer was also gathered to form a homogeneous monolayer. Although there may be a trace of heterogeneity in the film, possibly a partial collapse, it is difficult to be resolved in the BAM observation. After the film collapse (H), the stripe morphologies grew.

The morphological features were more clearly discerned in the case of the *cis*-Az monolayers. In Fig. 5, BAM images of *cis*-6Az10-Urea corresponding to A—D in Fig. 2b are shown. In the highly expanded state of the *cis*-Az monolayers before the pressure lift-off, the contour of the monolayer domain was hardly recognized due to very low light reflectivity. Before the phase change of the monolayer near to 0.8 nm^2, the monolayer was highly homogeneous (A, 0.9 nm^2). At the start of the plateau region (B, 0.7 nm^2), the monolayer exhibited brighter portions of several ten micrometers in size. The brighter areas gradually increased upon compression to form a mosaic structure (C, 0.35 nm^2) until they occupied the entire area. In the steep region (D), a homogeneous film with high reflectivity was observed. Surface potential measurements of the floating 6Az10-PVA monolayer imply that the *cis* Az unit contacts with the water surface in the highly expanded regions, and that the compression procedure induces a normal orientation of the side chain, detaching the Az moiety from the water surface.[38)] We interpret this as meaning that in the plateau region the laid and upright Az side chains coexist. Since the BAM reflectivity is enhanced with increasing the film thickness,[35,36)] the bright portions in the mosaic structure seem to correspond to the Az side chains with a normal orientation. If this is the case, the rising motion of the side chain takes place in a cooperative fashion to form a mosaic domained structure.

In the case of the *cis*-6Az10-COOH monolayer, although the behavior was basically similar to that of the urea compound, clear differences in the domain morphology in the plateau region were observed. For this monolayer, bright circular domains with ca. 30 μm diameters appeared in the plateau region (F, 0.65 nm^2), which increased in size and number upon further compression (G, 0.45 nm^2). Just before the collapse, the bright parts covered the entire area of the monolayer.

3. UV-visible Absorption Spectroscopy. Figure 7 displays the transmission UV-visible absorption spectra of the 6Az10-Urea (a) and 6Az10-COOH (b) monolayer taken at the air–water interface, together with those observed in chloroform. The spectra of monolayers on the water surface of each series involve measurements at 0, (0.50, and 0.30 nm^2 for 6Az10-Urea and 6Az10-COOH, respectively), 10, and 50 mN m^{-1}. Comparisons of the spectra for the two monolayers can be argued concerning three issues: First, the peak position of the π–π* band attributed to the long axis transition ($\lambda_{\max}$); second, the spectral shape in terms of the half width and vibrational structures; and third, the absorption ratio of the π–π* band of the short-axis transition (peaking below 250 nm) relative to the long-axis transition (300—400 nm) ($A_{\text{short}}/A_{\text{long}}$).The former two issues can be measures of the aggregation state of the Az chromophore, and the final parameter provides information concerning the molecular orientations with respect to the water surface plane. In Fig. 8, the two parameters $\lambda_{\max}$ (a) and $A_{\text{short}}/A_{\text{long}}$ (b) are plotted as a function of the surface pressure.

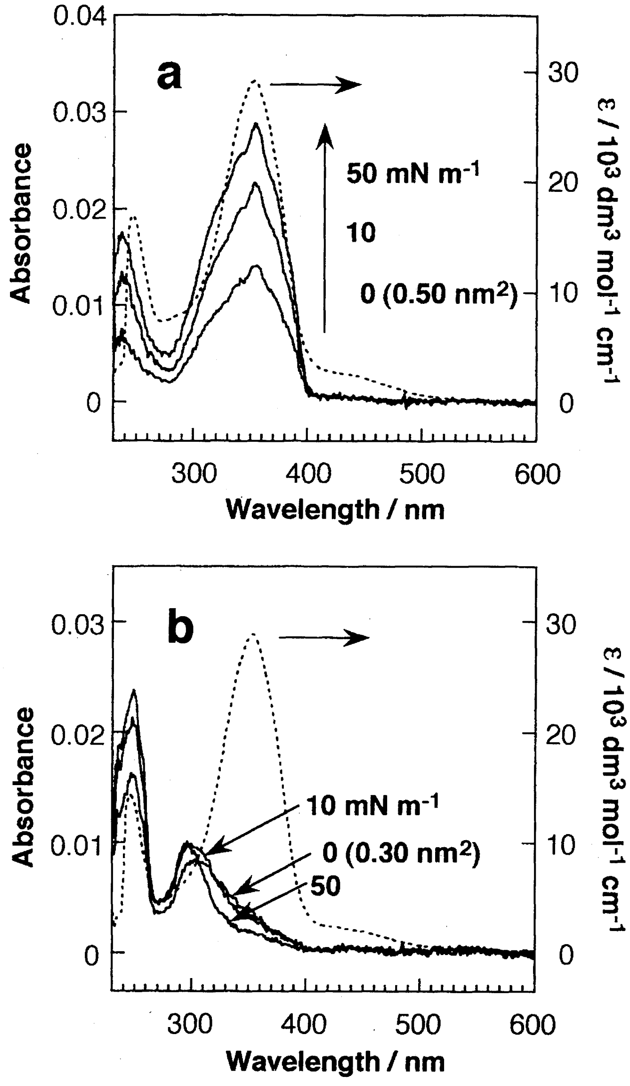


Fig. 7. UV-visible absorption spectra of 6Az10-Urea (a), and 6Az10-COOH (b). The solid lines are the spectra taken on the pure water surface at varied surface pressures. This figure also involves the spectrum taken in chloroform as indicated by a dotted line.

For 6Az10-Urea, compression of the monolayer did not change the spectral shape, except for proportional absorption enhancements to the increase in the lateral density; $\lambda_{\max}$ po-

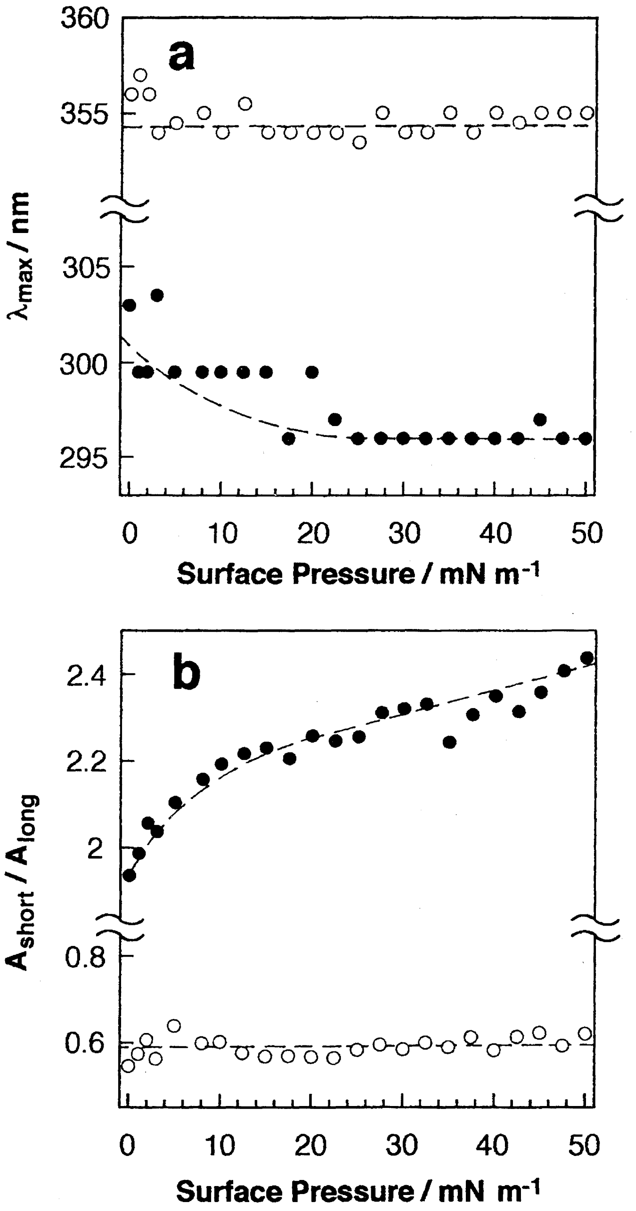


Fig. 8. $\lambda_{\max}$ (a) and $A_{\text{short}}/A_{\text{long}}$ (b) as a function of surface pressure. For definition of these parameters, see the text. Open and filled circles correspond to the data of 6Az10-Urea and 6Az10-COOH monolayer, respectively.

sitioned at 355±2 nm, which was perfectly invariable with the surface pressure. As for the spectral shape, the different features for the monolayer can be admitted in comparison with that in solution. The π–π* band attributed to the long-axis transition was broadened, the half width being 80 nm (c.f. 60 nm in chloroform), and the vibrational structure was clearly observed. Both features imply aggregation of the Az chromophore. The value of $A_{\text{short}}/A_{\text{long}}$ (0.6±0.05) was constant at all pressures (Fig. 8a). Such small values, comparable to that in solution indicate that the Az chromophores in the monolayer, are tilted from the surface normal. This is in reasonable agreement with the larger limiting area of 6Az10-Urea in the *trans* form (see Fig. 2a). Although the position of $\lambda_{\max}$, itself, was closed to that in chloroform (352 nm), this coincidence should be ascribed to the tilted aggregation in the 6Az10-Urea monolayer.

In contrast, the 6Az10-COOH monolayer gave spectra having completely different features (Fig. 7b). Upon compression, $\lambda_{\max}$ showed hypsochromic shifts from 303 nm at zero pressure to 296 nm at 40 mN m^{-1} (Fig. 8a). Concomitantly, $A_{\text{short}}/A_{\text{long}}$ increased from 1.9 to 2.4 in the same process (Fig. 8b). These results imply that Az chromophores are forced to orient more perpendicular to the water surface by the application of surface pressure. Thus far, these pressure-induced spectral changes are often observed in monolayers of various types of Az containing amphiphiles including low molecular mass[14,18] and polymeric materials.[7] It can thus be inferred that the spectral features and the assembled state of 6Az10-Urea monolayer that are already firmly fixed before compression are quite exceptional.

Direct evidence of the participation of hydrogen bonding in the floating monolayer is currently difficult to obtain. Therefore, a hydrogen bond breaking reagent (HFIP) was added to the subphase and the spectral behavior was followed. HFIP is a powerful proton donor in hydrogen bond formation, and is used as a good solvent for dissolving oligopeptides.[39] Figure 9 indicates the UV-visible absorption spectra of the 6Az10-Urea monolayer at 30 mN m^{-1} in the presence of HFIP in the subphase at various concentrations. The spectral shape showed large changes with increasing concentration of HFIP. The spectral shape inherent to this monolayer was maintained at 1.0×10^{-3} mol dm^{-3} (dashed line), but this band was almost completely replaced by a hypsochromic new band peaking at 310 nm at 1.0×10^{-2} mol dm^{-3} (solid line). At a concentration of 5.0×10^{-3} mol dm^{-3}, the spectrum possessed both features, having dual peaks (dotted line). This hypsochromic shift with the addition of HFIP is attributable to destruction of the intermolecular hydrogen bonds in the 6Az10-Urea monolayer. The peak position of this monolayer with a sufficient HFIP in the subphase was close to that of 6Az10-COOH.

4. UV Light Irradiation. UV light was directly irradiated onto the monolayer in the *trans* form, and the photoisomerization behavior was followed by UV-visible absorption spectroscopy. The UV-visible absorption spectra with UV light illumination is presented in Fig. 10 for monolayers of 6Az10-Urea (a) and 6Az10-COOH (b). To our surprise, photoisomerization of the Az unit in the urea-containing monolayer was completely hindered, even under very low surface pressure conditions, (2 mN m^{-1} (a)). Irradiation exceeding 5 J cm^{-2} did not induce any spectral changes. On the other hand, the *trans*-to-*cis* photoisomerization proceeded in the 6Az10-COOH monolayer despite the fact that the limiting area of the 6Az10-COOH monolayer is smaller (Fig. 2a). In the case, the light energy required to reach an photostationary state was 1 J cm^{-2}. The striking hindrance of photoreaction in the 6Az10-Urea monolayer leads to a decisive conclusion that the characteristic structured band peaking at 355 nm can be attributed to a firm aggregated state. The *cis* to *trans* photoisomerization proceeded upon visible light (436 nm) irradiation (data not shown). However, once it was isomerized to the *trans* form, the photoreaction was completely suppressed.

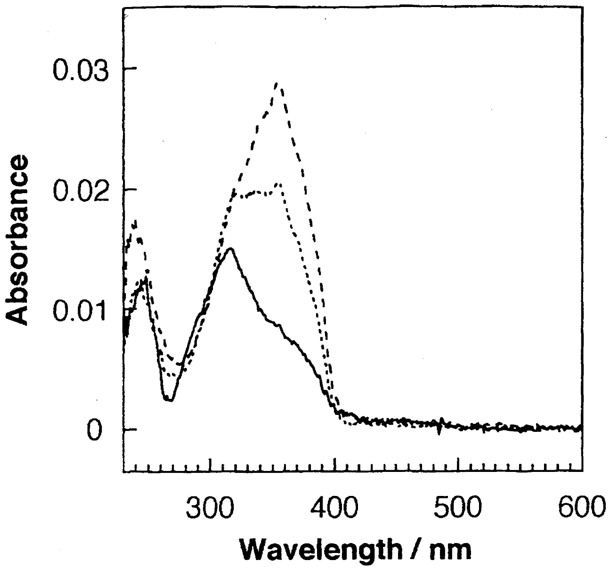


Fig. 9. UV-visible absorption spectra of 6Az10-Urea monolayer on the water surface at 30 mN m^{-1} and 20 °C in the presence of HFIP. The concentrations of HFIP were 1.0×10^{-3} (dashed line), 5.0×10^{-3} (dotted line), and 1.0×10^{-2} (solid line) mol dm^{-3}, respectively.

Summary

In this work, an azobenzene-containing amphiphile with a urea head group was first synthesized, and the spreading behavior of its monolayer at the air–water interface, morphological and spectral features, and photoreactivity were investigated. Possibly due to the participation of bifurcated hydrogen bonds bridging the adjacent urea heads, a polymer-like stable monolayer is formed both in the *trans* and *cis* form of Az unit. The most curious result observed with the urea-containing monolayer was that the *trans* to *cis* photoisomerization is thoroughly impaired in the tiled molecular array of the monolayer. We are not yet able to give clear explanations concerning this, or to elucidate the assembled structure of 6Az10-Urea on the water surface. Any future investigation should involve structural justifications of the head group by infrared spectroscopy of a deposited film, and system-

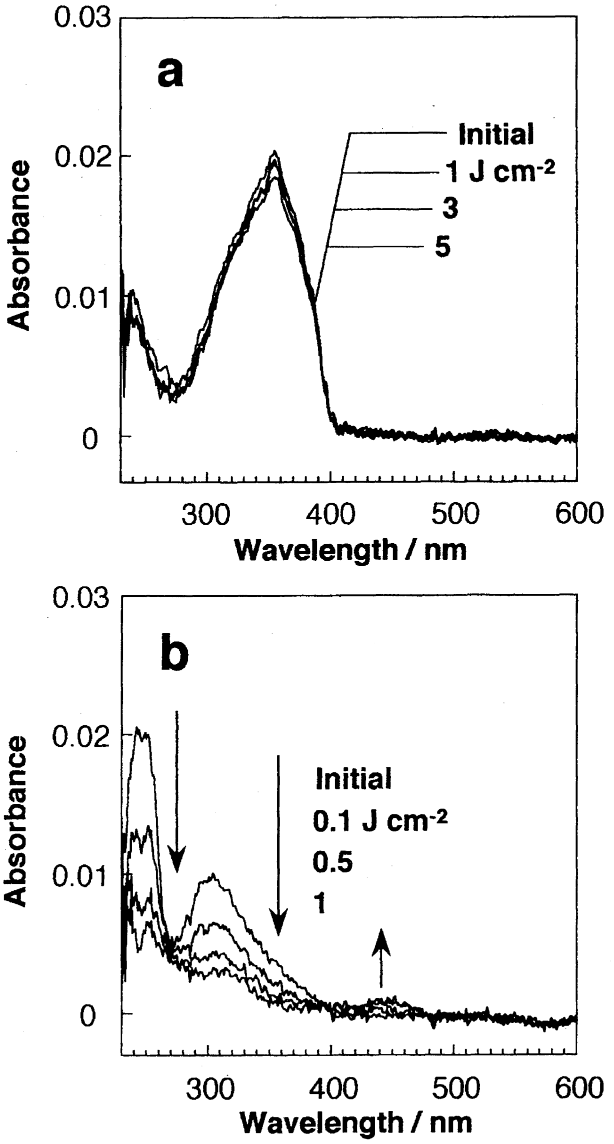


Fig. 10. Changes in UV-visible absorption spectra of 6Az10-Urea (a) and 6Az10-COOH (b) monolayer on the water surface at a constant surface pressure of 2 mN m^{-1} and 20 °C under irradiation of UV (365 nm) light at an intensity of 0.5 mW cm^{-2}.

atic explorations with urea amphiphiles of varied molecular structure. Work in this regard is now in progress.

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