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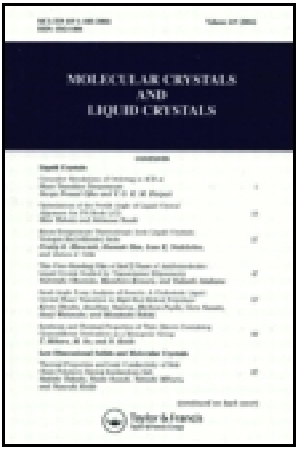

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A New LB Film Forming Molecule Containing Both an Electro- and Photoactive Part

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A NEW LB FILM FORMING MOLECULE CONTAINING BOTH AN ELECTRO- AND PHOTOACTIVE PART

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Abstract LB multilayers of the amphiphilic unsymmetrical disulphide S-(2-azobenzenethio)-11-mercaptoundecanoic acid (AMU) have been prepared and investigated by spectroscopic methods. A reversible photochromic switch can be observed upon film irradiation.

Keywords: photochromic, Langmuir-Blodgett film, ultrathin films, azobenzene, mercapto-alkanoic acids

INTRODUCTION

There is a continued interest in photochromic ultrathin organic films with prospects for applications such as optical data storage or photochemical switching of film properties. As constituents of such films, molecules containing an azobenzene[1], spiropyran[2] or salicylidenaniline[3] moiety have been reported. One problem is to cope with the demand for enough free volume in the closely packed films. This could be managed by controlling the area per molecule by the use of a polymeric counterion[4] or by the incorporation of the photochromic molecules into a film forming cyclodextrin derivative[5]. Fujishima et al.[6] were able to show that in a photochromic LB film of an azobenzene derivative, the azo-function can be reduced electrochemically.

The next step is to introduce additional functional units into the photochromic molecules giving rise to, e.g. conductive films. Kawabata et al.[7] reported a reversible switch of the lateral conductivity in an LB film by use of

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an azobenzene unit. In this work, we employed the combination of an azobenzene unit with a disulphide bridge of which the latter should be electrochemically cleavable and may further provide the possibility for creating semiconducting e.g. (capped) CdS nanoparticles within the film.

EXPERIMENTAL

S-(2-Azobenzenethio)-11-mercapto-undecanoic acid (AMU), Fig. 1, was synthesised as follows. Addition of thioacetic acid to 10-undecenoic acid yielded 11-acetylthio-undecanoic acid, which was hydrolised in aqueous alkaline solution to 11-mercapto-undecanoic acid, which in turn afforded the desired product upon reaction with azobenzene-2-sulfenyl-bromide.

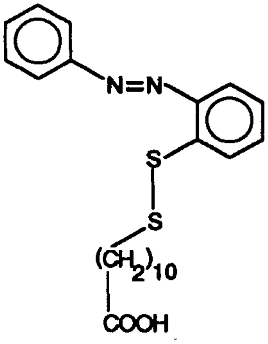

FIGURE 1 Chemical structure of AMU (trans isomer).

Chromatography on a silica gel column gave a pure product which was characterised by its ^1H NMR spectrum. AMU was dissolved in chloroform, which was used as the spreading solvent in a concentration of ca. 1 mg/ml and the solution was kept in the dark. This turned out to be essential for obtaining stable monolayers. The LB films were prepared on a commercial LB trough (Lauda FW1) using a subphase containing polyethylenimine (5 mg/l), the pH being adjusted to 6 with hydrochloric acid. The temperature of the subphase was 4°C. Deposition of monolayers at a constant surface

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pressure of 10 mN/m yielded Y-type LB films with the transfer ratios being 0,85 for downstroke and 1,0 for upstroke, with both staying constant over many dipping cycles (tested up to 50 monolayers).

For surface plasmon resonance (SPR) experiments, evaporated silver films (40 nm - 45 nm thickness) on BK-7 glass substrates were used. The SPR setup was in the configuration of Kretschmann[8] using a p-polarized HeNe laser (632,8 nm). The angular resolution was 0,02°.

Polarization dependent Fourier transform infrared (FTIR) spectra were recorded with a Bruker spectrometer (113v) in connection with a wire grid polarisator. As substrates, Si(111) single crystals for transmission and silver films (200 nm thickness) on Si(111) for grazing incidence experiments were employed.

Optical absorption spectra were measured with a two beam spectrometer (Perkin-Elmer, Lambda 2). For this purpose, monolayers were deposited on silanized (by application of a chloroform solution of hexamethyldisilazane) Suprasil glass substrates. Film irradiation was performed using a UV lamp (Hanau, Fluotest; 4 W) 1 cm distance from the surface for 30 seconds.

RESULTS AND DISCUSSION

Pressure-area isotherm of AMU

Figure 2 shows the pressure-area isotherm of compound AMU at 4°C on a subphase containing polyethylenimine. Under these conditions a stable monolayer was obtained; the collaps pressure was determined to be 22 mN/m. The extrapolated area per molecule of 33 Å^2 is in accordance with space filled molecular models, assuming that the azobenzene units limit the molecular packing.

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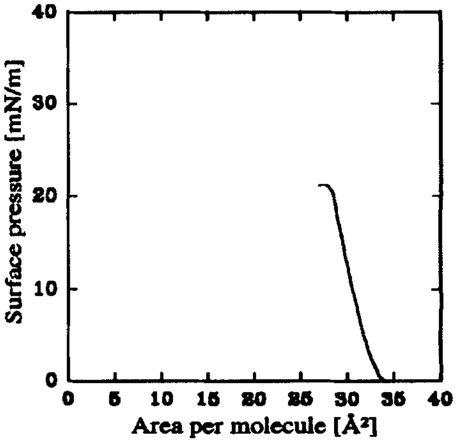

FIGURE 2 Surface pressure-area isotherm of AMU, 4°C.

Surface plasmon resonance (SPR)

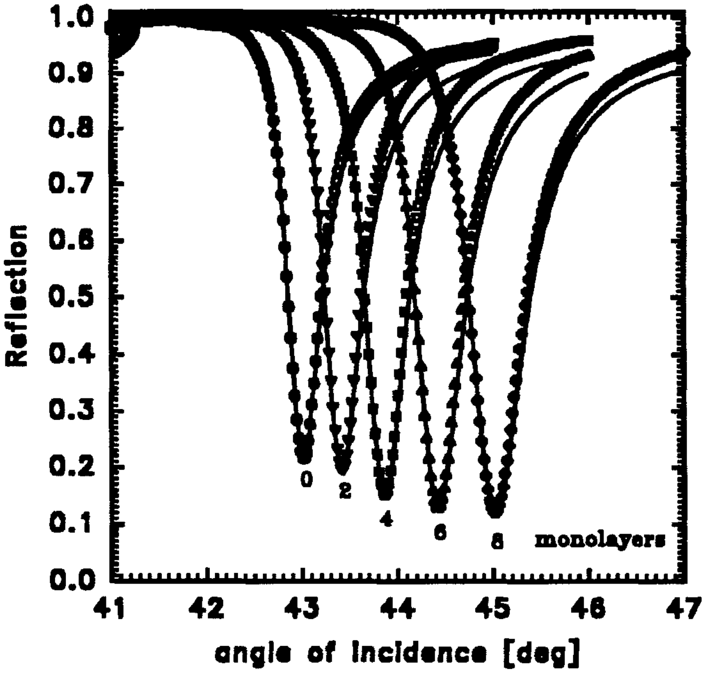

FIGURE 3 Reflected intensity (symbols) for uncoated silver and with 2,4,6 and 8 monolayers of AMU. Full lines represent curves calculated with the Fresnel equation.

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In Figure 3, the angle dependent reflected (normalized) intensity of the uncoated silver film and with 2,4,6 and 8 layers of AMU, respectively, is shown (symbols). The angle of incidence was calibrated using the total reflection angle of a silver free part on the glass substrate. The solid lines were obtained by fitting the theoretical curves (resulting from the exact Fresnel equation[9]) to the measured data. The best fit was obtained with the following values for the silver film: Thickness = 416Å ±6,5%, optical constants $\varepsilon' = -16,9$ and $\varepsilon'' = 0,532$. Table 1 summarises the measured resonance shifts and fitted values for the LB layers.

TABLE 1 SPR results for LB multilayers of AMU

Number of monolayers	2	4	6	8
Shift of resonance minimum	0,42°	0,86°	1,42°	2,02°
Refractive index n	1,581	1,581	1,581	1,581
Thickness of LB film [Å]	40	79	121	160
Thickness per monolayer [Å]	20,0	19,8	20,2	20,0

It should be noted that there is a highly linear dependence of LB film thickness on the number of transfered monolayers. The monolayer thickness of 20 Å can be visualised by molecular models assuming a nearly flat lying azobenzene unit and a tilt angle of the aliphatic C_{10} chain not greater than ca. 30° (with respect to the surface normal).

Polarization dependent FTIR spectroscopy

In the transmission and grazing incidence FTIR spectrum (in both cases 10 monolayers AMU), the symmetrical und asymmetrical CH_2 stretch vibration could be observed at 2855 cm^{-1} and 2925 cm^{-1}, respectively. The intensities of these vibrations were used to determine the tilt angle of the aliphatic chain with respect to the normal of the substrate following a method developed by Umemura et al.[10]. This tilt

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angle was calculated to be 20,7°, which is in accordance with the monolayer thickness obtained by the SPR experiment.

UV-visible absorption spectroscopy

Figure 4 shows a comparison between the absorption spectrum of an AMU solution in acetonitrile (1,8 µM) and an LB film consisting of 8 monolayers (on each side of the glass substrate). For the LB film, there is an absorption maximum at 324 nm attributed to the π-π^* transition of the azo function (trans form)[11]. This peak occurs at the same wavelength even for 2 monolayers; in the solution spectrum it is found at 318 nm. The absence of a more pronounced shift demonstrates that there is only slight evidence for J-aggregation (i.e., the molecular transition dipole moments are not rigidly oriented with respect to each other).

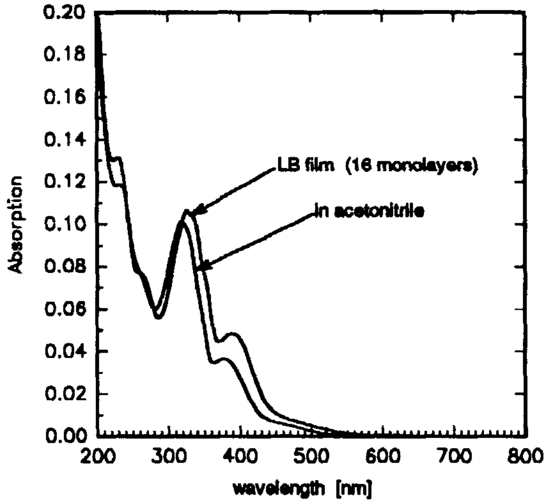

FIGURE 4 Absorption spectra of an LB film and acetonitrile solution of AMU.

The dependence of film absorption at 324 nm on the number of transfered monolayers is shown in Figure 5 for 4,8,16 and 24 layers (on each side of the glass substrate).

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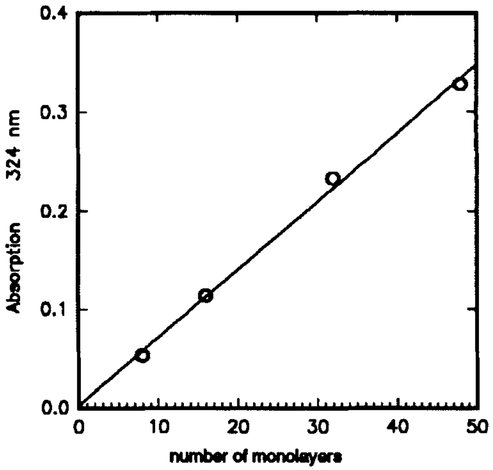

FIGURE 5 Absorption at 324 nm against number of transfered LB monolayers.

This (nearly) linear relationship corresponds well to the SPR results, showing constant growth of the film. For the purpose of studying the photochromic behaviour, an LB film (8 monolayers on each side of the substrate) was irradiated with light of the wavelength 366 nm. Figure 6 shows the absorption spectrum before and after irradiation.

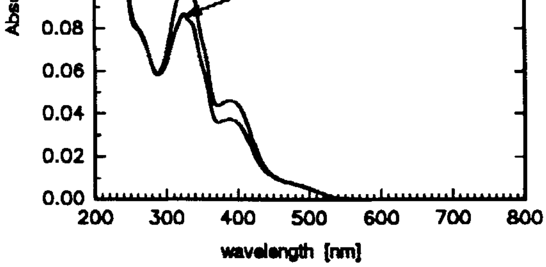

FIGURE 6 Absorption spectrum of an LB film before and after irradiation with 366 nm.

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The observed decrease in absorption at 324 nm was 15% of the value prior to irradiation. After irradiation, the original spectrum was regained by thermal back isomerization after two hours in the dark. After 10 switching cycles in a film, only negligible changes in the spectrum could be observed, demonstrating the reversibility of the photoisomerization. 2 hours for back iso-merization should be a sufficient time span to investigate the (e.g. electrochemical) properties of the two "states" of the film. The possibility of photoisomerization can be rationalized by the end standing azo unit (within the molecule AMU) to which is given enough free volume for the conformational change to occur. No additional part of the molecule has to be moved within the film as it is the case with, for example, molecules containing the azobenzene unit between two alkyl chain parts.

CONCLUSIONS

We have demonstrated the possibility of building up Y-type LB multilayers of the new film forming asymmetrical disulphide AMU. Monolayer thickness could be determined by the SPR experiment and correlated with the results of FTIR measurements. UV-visible spectra reveal a photochromic switch upon film irradiation near the absorption peak of the azo group (π-π^*-transition of the trans isomer). This was shown to be reversible and without apparent destruction of the structural integrity of the film.

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