Unique Monolayer Assembly of Squarylium Dye with Short Alkyl Chains

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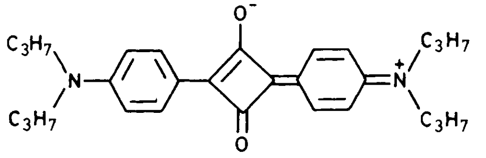
The first J-aggregates of squarylium dyes with short alkyl chains have been observed on water surfaces, the films obtained under higher surface pressure having an unique multi-piled monolayer structure.

Bis(dialkylaminophenyl)squarylium dyes are known to be highly sensitive organic photoconductors for xerography,[1] but there is little information[2] on the relationship between the molecular structure of the dyes and their photosensitivity. We have synthesized various squarylium dyes with different substituents and evaluated their photosensitivities.[3] Particular combinations of substituents were found to produce a high xerographic photosensitivity. In organic photoconductors for xerographic use, photosensitive dyes are generally dispersed in binder polymers with no control over the orientation of the dye molecules. The Langmuir–Blodgett (LB) technique allows the formation of uniform ultra thin films with orienta-



(1)

$C_{19}H_{39}CO_2H$
(2)

tional control, but only a few reports[4,5] on LB films of squarylium dyes have been described by other investigators and so far there has been no report on the formation of J-aggregates.

In the present work, we have studied the influence of alkyl chain lengths on the monolayer structure of squarylium dyes. During spectroscopic investigation of monolayer structures of squarylium dyes under different surface pressures, we found that J-aggregates of squarylium dyes with short alkyl chains are formed on the water surface and the films obtained under higher surface pressures have an unique multi-piled monolayer structure, which is different from the supermonomolecular structure[5] formed by the 'squeezing out' mechanism.

2-(4-dipropylaminophenyl)-4-(4-dipropyliminocyclohexa-2,5-dienylidene)-3-oxocyclobut-1-enolate (**1**) was prepared by a procedure described in the literature[6] and identified by i.r. and visible spectroscopy and elemental analysis. Icosanoic acid (**2**) was purchased from Sigma and used without further purification. Surface pressure(π)-area (A) isotherms were measured using a Wilhemy type film balance (Kyowa Kaimen Kagaku Ltd.) for the aqueous subphase containing 2.5×10^{-4} M $CdCl_2$ and 3×10^{-5} M $KHCO_3$ at pH 6.3 and 5 °C. Chloroform of spectral grade was used as the spreading solvent. The absorption spectra of monolayers on the water surface were measured through an optical fibre using an Otsuka–Denshi (MCPD-100) spectrometer. Visible and i.r. spectra data [Hitachi (U-3400), JEOL (JIR-100)] and X-ray diffraction data [JEOL (DX-GO-S)] were obtained. π–A isotherms (Figure 1) for a monolayer of pure (**1**) and a mixed monolayer of (**1**) and (**2**) in a molar ratio of 1:1 exhibit a characteristic phase transition at a surface pressure of about 20 mN/m, which suggests the existence of two stable condensed states. The first condensed state of the mixed monolayer is formed below the transition pressure, while the second is formed beyond it. The area occupied by a dye molecule in the first and second condensed states of the mixed monolayer was estimated to be about 77 or 23 Å^2, respectively, assuming the area per molecule of (**2**) to be 19 Å^2. Recently, the formation of a bilayer structure by the 'squeezing out' mechanism has been reported for a surface active dye and fatty acid mixed system. If the second condensed phase in the (**1**)–(**2**) mixed monolayer is formed by this mechanism, the area per dye molecule should be zero. On the contrary, the above result (23 Å^2) indicates that the dye molecules are not 'squeezed out' but retained in the mixed monolayer in some manner.

The absorption spectrum for the dye in $CHCl_3$ has a sharp peak at 638 nm (Figure 2). This peak is shifted to 760 nm in the spectra of monolayers of pure (**1**) and the (**1**)—(**2**) mixture on the water surface at 5 °C, suggesting the formation of J-aggregates of (**1**) in the monolayer. The J-band absorbance of the mixed monolayer at 30 mN/m was about twice as large as that at 15 mN/m.

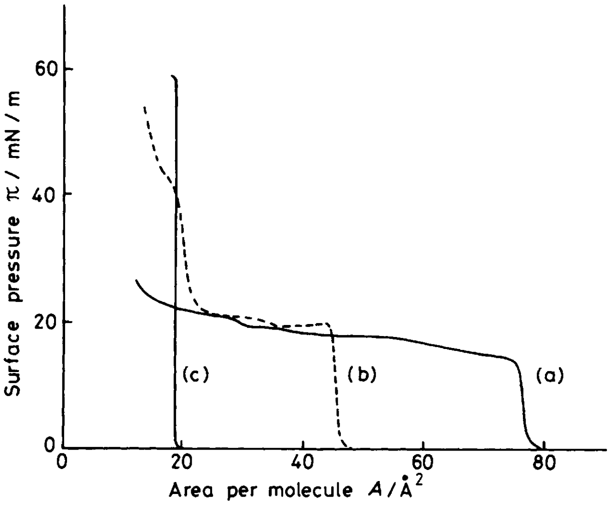


Figure 1. π–A isotherms for monolayers of (a) pure (**1**), (b) mixed (**1**) and (**2**) (1:1), and (c) pure (**2**).

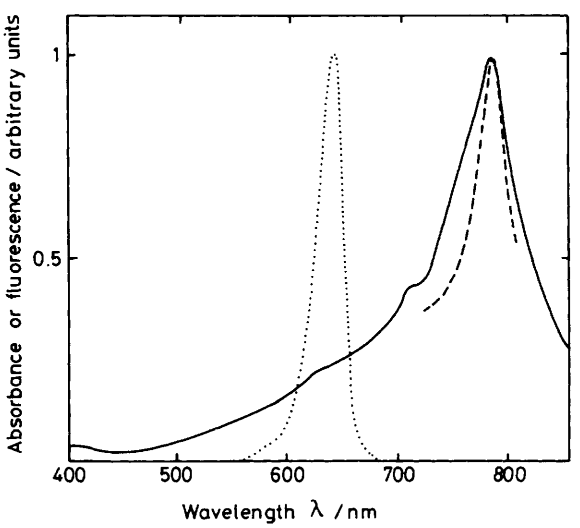


Figure 2. Absorption (———) and fluorescence (– – –) spectra of a mixed multilayer of (**1**) and (**2**) (1:1 molar ratio). Absorption spectrum of (**1**) in $CHCl_3$ solution (· · · · · ·).

These results suggest that in the second condensed phase at higher surface pressure, the dye molecules in the mixed monolayer have a multi-piled structure.

Mixed monolayers of (**1**) and (**2**) (1:1) could be transferred successively at 30 mN/m to a glass slide by either the conventional LB or the horizontal lifting technique.[7] The LB technique gave typical Y-type film with a transfer ratio of about 1.0. As shown in Figure 2, the u.v.–visible spectrum of a mixed film deposited on a glass slide at 5 °C and 30 mN/m retains a sharp absorption at 770 nm and exhibits a fluorescence band with a small Stokes shift of 5 nm, characteristic of J-aggregates. However, an LB film of pure (**1**) deposited at 15 mN/m showed an absorption band around 670 nm, which suggests that J-aggregates in the monolayer under lower surface pressure are labile and easily disappear during the dipping process. LB deposition of the mixed film at 15 mN/m with the J-aggregates intact was also difficult, but the horizontal lifting technique allowed the mixed monolayer of

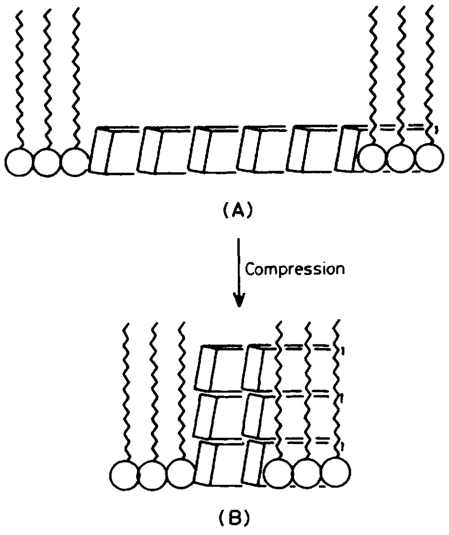


Figure 3. Model for the formation of triple-layered J-aggregates in a mixed film.

(**1**) and (**2**) to be transferred to a glass slide, retaining the J-band even at the lower surface pressure.

Molecular models indicate that the squarylium dye molecule is approximated by a rectangular block with dimensions of about 19 × 8 × 4 Å. The area per dye molecule in the first condensed state (77 Å^2) corresponds to the side area of the molecular model along the long axis. It suggests that the molecular plane of (**1**) stands almost vertically with its long axis parallel to the surface. In the second condensed state, there is another orientational possibility in which the long axis is perpendicular to the substrate, but this orientation was excluded by spectroscopic examination of the deposited film. The direction of the transition moment for the J-band in visible spectra is considered to be parallel to the long axis and that for the C=O stretching band in i.r. spectra perpendicular to it. The dependency of these two absorbances on the incident angle in the respective polarized spectra showed that molecular orientation is the same irrespective of the deposition pressure.

A value for the long spacing of 55.6 Å was obtained by X-ray diffraction for the mixed films deposited at 30 mN/m, identical to that for the built up film of pure Cd-icosanoate. If the mixed monolayer obtained under higher surface pressure has a bilayer structure formed by the 'squeezing out' mechanism, there should be two long spacing values corresponding to two different distances between Cd-containing planes, but only one value was obtained from the X-ray measurements. This result indicates that head-to-head and tail-to-tail arrangements of (**2**) are formed in the mixed films and that the dye aggregates with a multi-piled structure are included in each layer.

From the results of π–A isotherms, spectroscopic measurements, and X-ray diffraction, it can be deduced that at lower surface pressure the mixed monolayer with structure (A) (Figure 3) is formed and, as the surface pressure increases, the monolayer of J-aggregates of (**1**) initially formed on the water surface undergoes a transition resulting in a multi-piled layer as in structure (B), which is characterized as a mixed film composed of a triple layer of J-aggregates of the squarylium dye with a fatty acid monolayer. This unique multi-piled structure of (**1**) may be stabilized by the surrounding Cd-icosanoate monolayer, since the thickness of the triple layer of dye molecules with approximately vertical orientation of the short axes is comparable with the molecular length of Cd-icosanoate.

Electronic devices made from LB films of surface active functional dyes generally have the drawback that electrons cannot move efficiently in the vertical direction to a substrate due to insulative layers of long alkyl chains, despite easy lateral movement through interactions between adjacent chromophores in the LB film. This new type of monolayer assembly in an LB film may have applications in countering this problem in the development of highly efficient electronic devices.

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