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Orientation Control of Quinacridone Derivatives with Long Alkyl Chains in Langmuir-Blodgett Films

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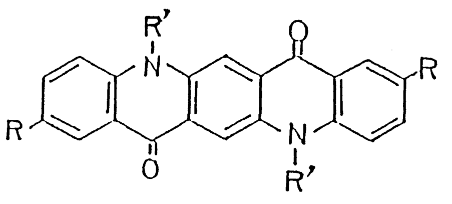
By introducing four alkyl chains to quinacridone, the soluble derivatives can be spread as monolayers on water surface and their surface pressure – area isotherms were found to depend significantly on the temperature and the alkyl chain length. Different orientations and packings were realized, depending on the alkyl substituents.

Polyheterocyclic compounds which are interesting for functional pigments are almost insoluble in usual organic solvents. By introducing long alkyl chains to chromophores, the soluble derivatives can be obtained and spread as monolayers on water surface. Quinacridones are well known chemically stable pigments which are expected to have photovoltaic functions.$^{1)}$ In this work, quinacridone derivatives with four alkyl chains are newly synthesized and used for the Langmuir-Blodgett films to control the orientation and packing of the chromophores.

2,9-Dialkylquinacridones were still scarcely soluble in organic solvents because of the intermolecular hydrogen bonding. 2,5,9,12-Tetraalkylquinacridones (Fig.1) were obtained by N-alkylation of 2,9-dialkylquinacridones with alkyl halides in the presence of a phase transfer catalyst, as reported previously.$^{2)}$ Tetraalkylquinacridones with the same alkyl chains ($C_{12}NC_{12}$) and with the hetero-length of chains ($C_{18}NC_8$) were synthesized and purified by column chromatography on silica gel and by recrystallization from ethanol solutions. Their structures were identified using ^{1}H-NMR, visible and IR spectroscopies together with elemental analysis.



(Abbr.)	R	R'	mp
$C_{18}NC_8$	$C_{18}H_{37}$	C_8H_{17}	98 °C
$C_{12}NC_{12}$	$C_{12}H_{25}$	$C_{12}H_{25}$	100 °C

Fig.1. Long-chain quinacridone derivatives used in this work.

The monolayers were spread on the distilled water from benzene solutions and surface pressure (π) – area (A)

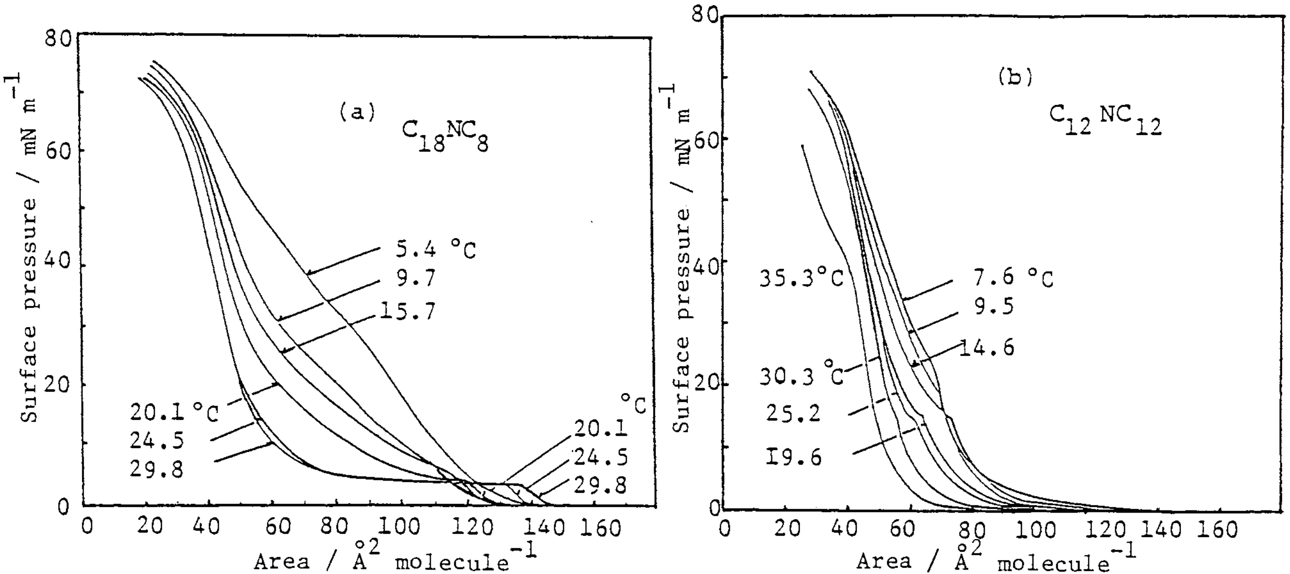


Fig.2. Temperature dependence of surface pressure – area isotherms for monolayers of (a)$C_{18}NC_8$ and (b)$C_{12}NC_{12}$.

isotherms were measured by a Lauda film balance. Figures 2(a) and 2(b) show the π – A isotherms for the monolayers of $C_{18}NC_8$ and $C_{12}NC_{12}$, respectively, at various temperatures of 5 – 30 °C. In the case of $C_{18}NC_8$, the isotherms depend strongly on the temperature of the aqueous subphase. Surface pressures begins to develop at molecular areas of 135 – 145 Å^2, where the chromophore is considered to lie flat on water surface. At lower temperatures the molecular area changes with relatively large compressibility on compression. At higher temperatures the monolayer exhibits a clear transition region from 135 Å^2 to 80 Å^2 at about 5 mN/m and further compression the film becomes rigid in the condensed state (below 60 Å^2) with small compressibility. Orientation and packing of the chromophores seem to differ on the both sides of the transition region. As the temperature increases, the limiting area ($A_{\pi\to 0}$) obtained from the condensed region was constricted to about 60 Å^2/molecule. On the other hand, for the $C_{12}NC_{12}$ the temperature dependence of the π – A isotherms is relatively small in comparison with that for $C_{18}NC_8$. The limiting area decreases from 80 Å^2 to 60 Å^2/molecule with increasing the temperature. Taking the molecular dimension of the chromophore (about 17.5 x 8 x 4 Å) into account together with four alkyl chains, the area of 60 Å^2/molecule seems to be too small.

It was difficult to obtain the multilayers successfully using a conventional LB method because of the rigidity of these monolayers. However, the multilayers were able to be prepared by a horizontal lifting method.[3]

From observation by a fluorescence microscopy (Olympus IMT-2), the monolayers transferred at higher pressures were almost homogeneous, although some voids could be detected in those monolayers at lower pressures.

Figures 3(a) and 3(b) show polarized electronic absorption spectra at 45° incidence for the multilayers (15 layers) of $C_{18}NC_8$, prepared at 4.5 and

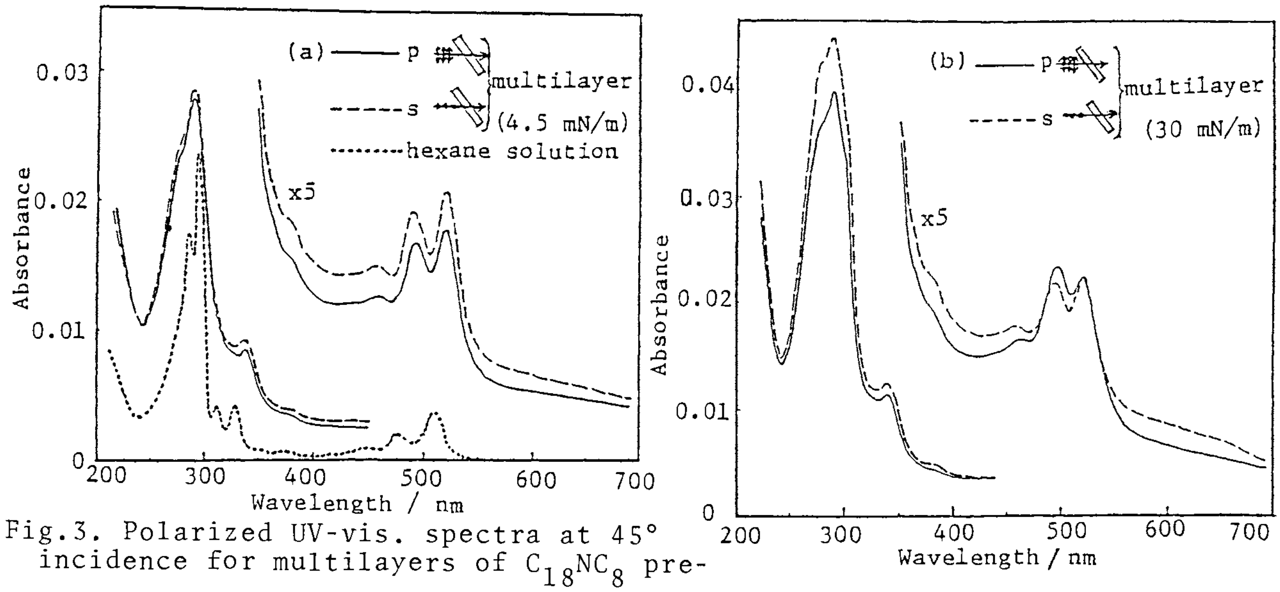


Fig.3. Polarized UV-vis. spectra at 45° incidence for multilayers of $C_{18}NC_8$ prepared at 4.5 (a) and 30 mN/m (b), as compared with the solution spectrum.

30 mNm (20 °C), which correspond to the surface pressures below and above the transition region, respectively. The solution spectrum is also shown in Fig.3(a), for comparison. Visible bands (around 500 nm) in the solution, which can be assigned to the transition moment nearly along the long axis of the chromophore, shifted to a slightly longer wavelength in the films. The intensity of the visible bands in the p-polarized spectrum is lowered for the film at 4.5 mN/m, while that is enhanced at 30 mN/m. And further, relative intensities of the visible bands for the film at 4.5 mN/m were larger than those at 30 mN/m, whereas the situation for the UV bands was reversed. These results suggest that the chromophore is oriented with the long axis rather parallel to the surface at the lower pressure and more inclined at the higher pressure.

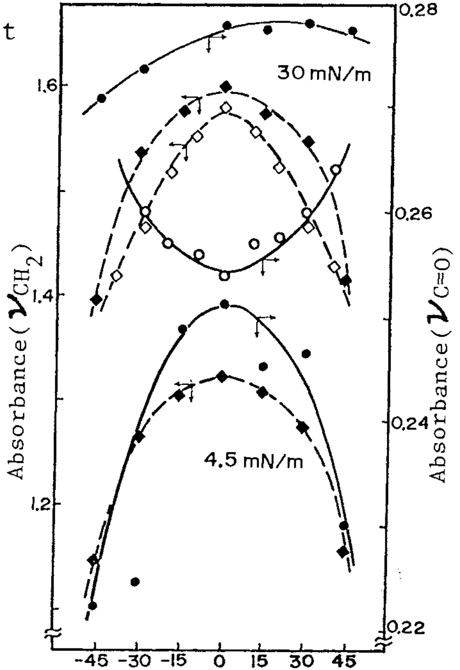


Fig.4. Dependence of IR intensities on the incident angle θ for CH_2 and quinone C=O stretching bands of $C_{18}NC_8$ (—●—, —◆—) and $C_{12}NC_{12}$ (—○—, —◇—) multilayers.

Figure 4 shows dependence of the intensities on the incident angles for the quinone C=O stretching (1635 cm^{-1}) and the CH_2 stretching (2950 cm^{-1}) in the p-polarized IR spectra for the multilayers of $C_{18}NC_8$ and $C_{12}NC_{12}$. It has been found that the transition moments due to the quinone C=O stretching are oriented almost parallel to the surface for $C_{18}NC_8$ at least 4.5 mN/m, whereas they are nearly vertical for $C_{12}NC_{12}$ at 30 mN/m. This fact indicates the chromophore orientation with the short axis nearly parallel to the surface for $C_{18}NC_8$, and vertical for $C_{12}NC_{12}$, though the short axis of

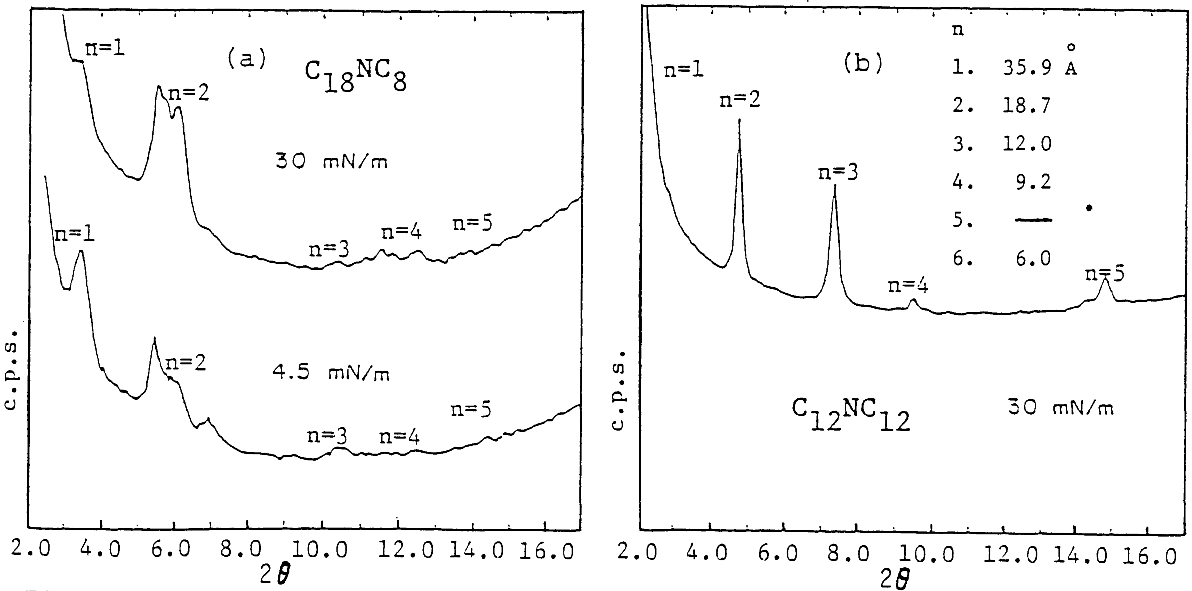


Fig.5. X-Ray diffraction for multilayers (50 layers) of $C_{18}NC_8$(a) prepared at 4.5 and 30 mN/m, and $C_{12}NC_{12}$(b) at 30 mN/m.

$C_{18}NC_8$ is somewhat inclined at the higher pressure. In any case the transition moments due to CH_2 stretching take parallel orientation to the surface, that is, the alkyl chains stand nearly vertically.

Figure 5 shows X-ray diffractions for the multilayers of $C_{18}NC_8$(a) and $C_{12}NC_{12}$(b). In the former case, the diffraction peaks were broad and difficult to be assigned to a unique series of the index. In the latter case sharp diffraction peaks gave a series of the index of d=35.9 Å, indicating that the derivative with the same alkyl chain gives a more homogeneous layered structure.

In conclusion, orientation of the quinacridone derivatives with four alkyl chains can be controlled in the multilayers, depending on the chain length of alkyl substituents. In the case of $C_{18}NC_8$, the chromophore is oriented with the short axis parallel to the surface and the long axis rather parallel at the lower pressures and on compression somewhat inclined in the films. While, for $C_{12}NC_{12}$ considering all results, i.e., the molecular area in the monolayer, the long-spacing and also the hydrophobic surface as deposited for the X-type by the horizontal lifting together, it is suggested that the molecular arrangements take the chromophore with the short axis nearly vertical and two of four alkyl chains oriented up and the other chains down. Different orientations of the quinone moiety are expected to have an influence on the electron acceptabilities in the layered molecular systems.

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