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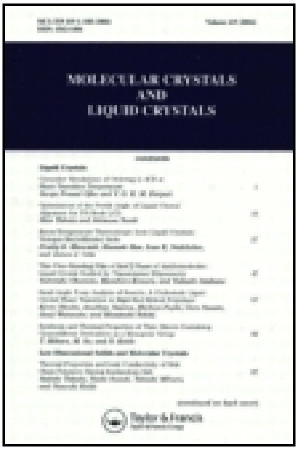

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Molecular Orientations and Photoconductivity in LB Films

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MOLECULAR ORIENTATIONS AND PHOTOCONDUCTIVITY IN LB FILMS

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Abstract N-Docosylquinolium-TCNQ was synthesized and the π-A isotherm of the molecule was obtained. The TCNQ anion radical is particulary interesting because it gives a good electrical conductivity as for the organic materials. The π-A isotherm of the N-docosylquinolium-TCNQ exhibited a break at the surface pressure of 30mN/m. The limiting area per molecule calculated at the surface pressure of 30mN/m is 68Å^2 and that at 45mN/m was 32Å^2. The orientation and arrangement of the TCNQ anion radical fabricated on a glass surface at each surface pressure were studied with polarization technique. The LB film layered at 30mN/m shows dichroic behavior with respect to the direction of dipping. The photoconductivities of the quinolium-TCNQ LB films fabricated at 30 and 45mN/m were 3.9×10^{-9}S/cm and 2.84×10^{-8}S/cm, respectively. The difference in photoconductivity may result from the molecular orientations which are deduced on the ground of the optical properties and polarization results.

INTRODUCTION

Attempt to control electric and optical signals at molecular level has been made last decade.[1~9] The size of control unit is reduced and processing time is decreased. Demands for more functions naturally make the microprocessors bulky. Therefore, thin films with many fuctional groups are required to meet both demands. Highly

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organized assemblies, which perform multiple functions, will be formed, if molecular distributions and orientations are controlled. The Langmuir-Blodgett methods has advantages in controlling the molecular distribution,[1~9] and thickness of film.[1~9] However, desired molecular orientation of chromophores is somewhat difficult to obtain. Molecular orientation of chromophores in LB monolayer was studied by various spectroscopic methods.[1~9] Polarized absorption study of LB films is the most popular method in determining dichroism. The molecules which lie flat on the surface with random orientation of long axis did not show dichroism unless an incident beam at an oblique angle to the substrate.[1] Some chromophore layered on a substrate with uniaxial orientation.[3] Bird et al. tried polarization study of 3,3-dioctadecyl-9-ethylthiacarbocyanine$^+$ aggregate, which show all chromophore axis lie parallel to the gypsum a-axis with a short axis vertical to the gypsum face.[4] Nakahara and Fukuda prepared films with anthraquinone derivatives and azobenzene derivatives with horizontal lifting methods.[5] Dichroic ratio of 1.2~1.4 at normal incidence with respect to the direction of monolayer compression was obtained for 1- and 1,4-substituted anthraquinones. Möbius et al. tried to understand the orientations of monolayer on water surface and galss plates. Porphyrin, cyanine and azo dyes were used.[6] The second harmonic generation(SHG) in LB film became popular. There are still many problems to be solved in improving SHG. Incident angle of polarized fundamental light and SH intensity are attached when N-acyl-p-nitroaniline and its homologous amphiphile, p-alkylamino phenylacetic acid are used in Y-type film.[10] The SH inensity study was also performed for polymerized non-linear optical LB films based on 2-(21-docosenyl)amiono-5-nitropyridine. Rather smooth angular dependency on SH intensity was obtained.[11]

In this paper, angular dependences of UV-visible absorption spectra, obtained from Z-type LB film of N-docosylquinolium-TCNQ, with respect to the polarization plane and incident angle are presented. The molecular arrangement and orientation are compared between the LB films layered at the surface pressure of 30mN/m and 45mN/m. Conductivity and photoconductivity are measured and compared for the LB films, obtained at two surface pressure, on the basis of molecular orientations and order of the films.

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EXPERIMENTALS

Materials

N-Docosylquinolium-TCNQ was prepared by N-alkylquinolium bromide and LiTCNQ as described earlier.[ref] Its purity was confirmed by NMR and elemental analysis. We used arachidic acid purchased from the Tokyo Kasei Co.

Prepration of LB films

Distilled water was purified by a Elgastat spectrum C water purification system for the LB trough. Optically polished glass plates(50mmX50mmX1mm) and ordinary glass plate(50mmX70mmX1.2mm) were cleaned in sonicator with acetone for 30 minutes and then in the sulfuric acid with potassium dichromate for 12 hours. They were throughly rinsed with distilled water and cleaned in sonicator with an ultrapure water for several times. A moving wall type deposition apparatus(Nippon Laser & Electronics, NL-LB-240S-MWA) was used for layering the films. Arachidic acid was deposited 4 layers in Y-type LB films and N-docosylquinolium-TCNQ was deposited by upward processes(Z-type LB films). The N-docosylquinolium-TCNQ monolayer was deposited at the surface pressure of 30 or 45mN/m, compression speed of 2.3cm/min and dipping speed of 5mm/min after spreading chloroform solutions at 25°C. The subphase was deionized ultrapure water(18MΩ-cm), pH 5.6.

Fabrication of electrodes

For the purpose of in-plane photoconductivity measurements, aluminium electrodes were evaporated under

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the N-docosylquinolium-TCNQ LB films. A structure of the electrodes are sandwiched type between the arachidic acid and N-docosylquinolium-TCNQ films. The gap between the electrodes and a width of electrode are 1mm and 5mm, respectively.

Measurements

The π-A isotherm was measured by a moving wall type apparatus with a compression speed of 2.3cm/min. at 25°C.

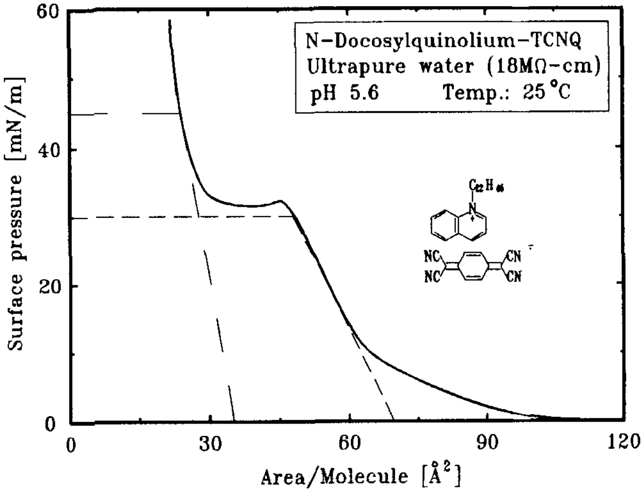

FIGURE 1. π-A isotherm of N-docosylquinolium-TCNQ

Polarized absorption spectra of films were measured with a Hewlett-Packard 8452A diode array type spectrophotometer and Melles Griot glan-thompson polarizer. The transmission characteristics of polarizer or background scattering were corrected by employing an optically polished glass plate coated with the same number of arachidic acid layers as a reference. Two angular dependences of UV/visible absorption spectra were measured by changing the incident angle(β) and polarization angle(α) as shown in FIGURE 1.

The incident angle, β, between the z-axis and the incident beam with its electric vector perpendicular to the dipping direction(y-axis) was varied by rotating an

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optically polished glass plate around the y-axis. The polarization angle, α, which is the angle between the dipping direction(y-axis) and the direction of electric vector of incident beam, was varied by rotating the polarizer at normal(β = 0°) incidence.

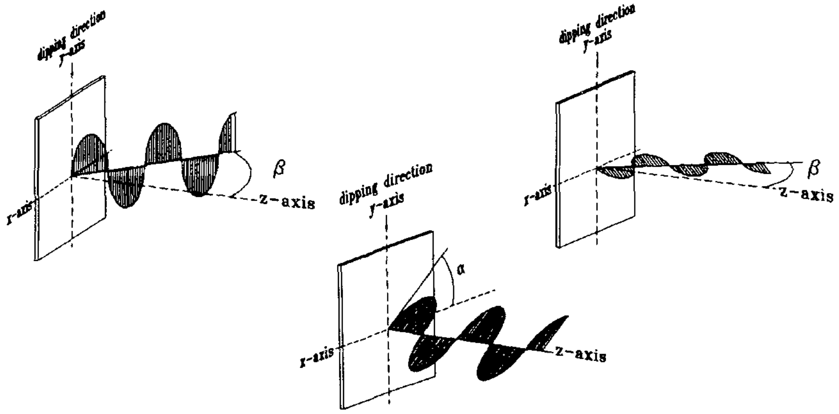

FIGURE 2. Measurements of dependences of UV/visible absorption spectra on the incident angle β and the polarization angle α

The experimental setup for the in-plane photoconductivity measurements is shown in FIGURE 2.

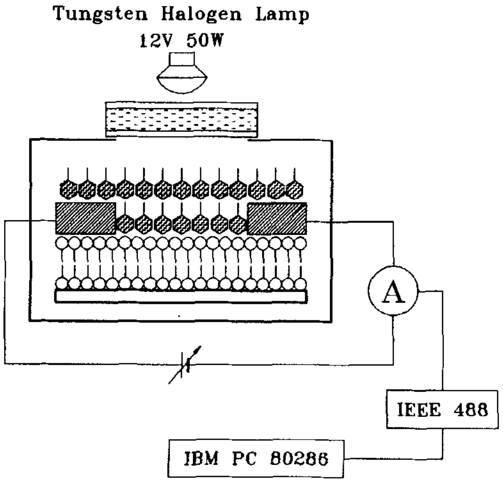

FIGURE 3. Experimental setup for the in-plane photoconductivity measurements

The LB films in a shield box were illuminated by a 50W tungsten halogen lamp through a 1.5cm water filter. In-plane photocurrent were measured under 1~10V bias(Yokogawa Electric Works) between the aluminium electrodes by an electrometer(Keithley 617 programmable electrometer) interfaced with IBM clone computer.

RESULTS AND DISCUSSIONS

There was a take-off in the π-A curve shown in FIGURE 2 for N-docosylquinolium-TCNQ at the molecular area of 120Å^2. Two phase changes shown as a large variation of surface pressure over relatively small changes in area/molecule, were observe. The calculated limiting area occupied by a molecule was 68Å^2 at the surface pressure of 30mN/m and 32Å^2 at 45mN/m. The deposition ratio was fairly low, less than 0.4, for the downstroke and the ratio reached 0.97~0.99 for the upstroke. Therefore, Z-type LB membrane was tried for N-docosylquinolium-TCNQ. The transfer ratio for arachidic acid layer ranges in 0.98 and 1.12. The calculated head group areas are 45Å^2 when the head group lies flat on a surface and 27Å^2 when the short axis of head group lies vertically. These results suggest that the TCNQ ring does not lie flat at 30mN/m. The absorption spectra of LB films deposited on optically polished glass plate at 45mN/m show higher absorption in whole spectral region, FIGURE 4. This suggests that the transfer from water surface to solid surface maintains the density of molecules. The polarized absorption spectra at normal incidence with the electrical vector parallel(s-polarized light, dotted line) and perpendicular(p-polarized light, solid line) to the dipping direction are shown in FIGURE 4.

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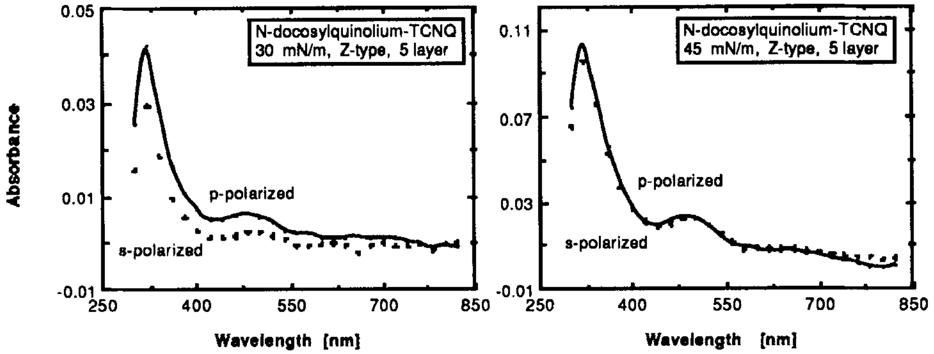
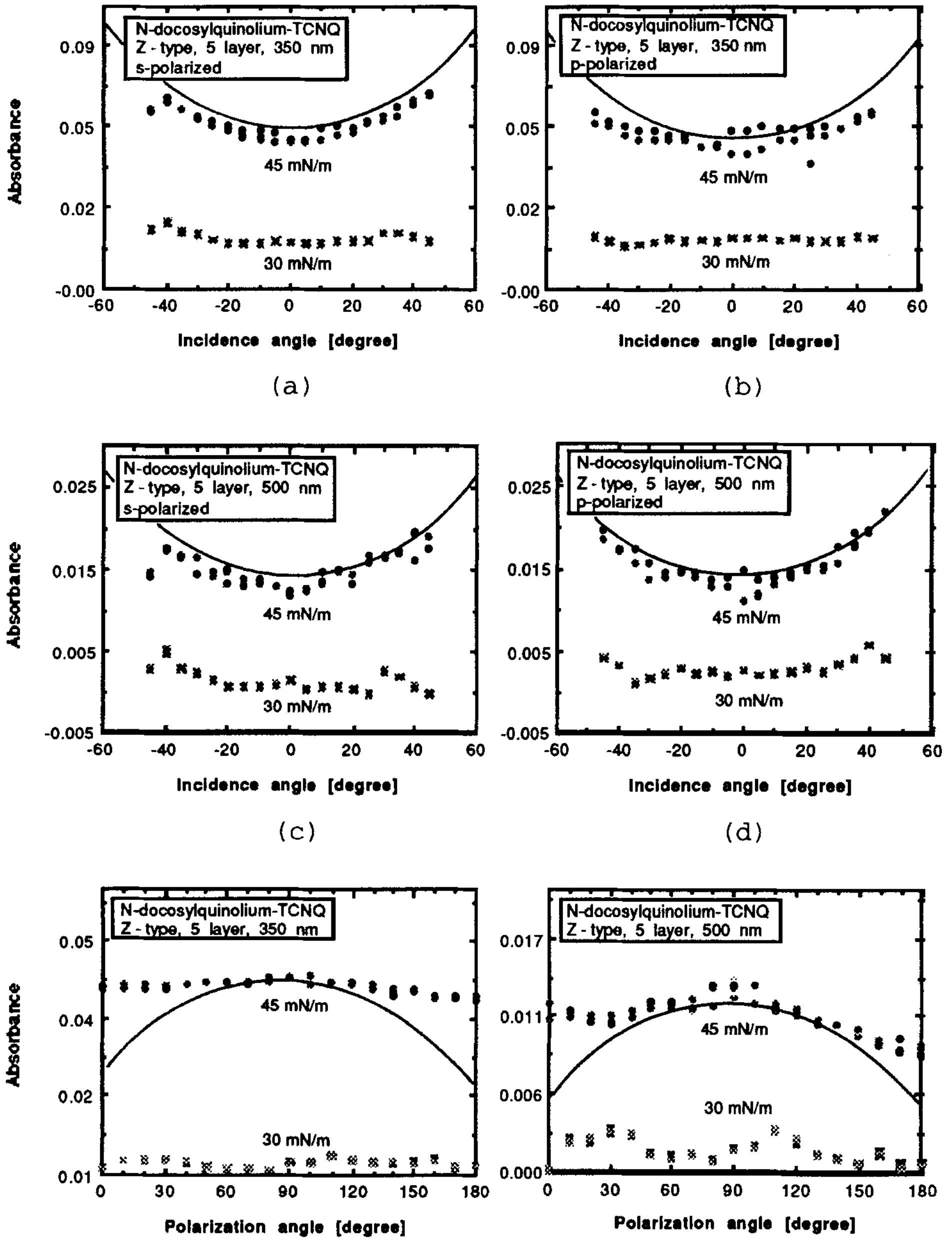


FIGURE 4. Polarized absorption spectra at normal incidence with electric vector parallel (dotted line) and perpendicular(solid line) to the dipping direction for N-docosylquinolium-TCNQ deposited 5 layers on one side of a optically polished glass plate

The N-docosylquinolium-TCNQ was deposited 5 layers with Z-type on on-side of optically polished surface. The p-polarized light was absorbed more strongly at 350nm and 500nm than that of s-polarized one. The dichroic ratio(A_p/A_s) observed at normal incidence at 350 and 500nm were in the range of 1.5 and 2.5 for the LB films fabricated at 30mN/m. Surprisingly, the dichroic ratios got low value, 1~1.1 for the LB films fabricated at 45mN/m. These results clearly indicate that the transition moment of absorbances at 350 and 500nm were not randomly distributed on the film plane. A preferential distribution of transition moments are perpendicular to the dipping direction. The only plausible explanation for the decrease in dichroic ratio for the LB films layered at 45mN/m is that the absorptivity decreases for the molecules packed perpendicularly to the dipping direction as the angle ϕ becomes smaller at high surface pressure. However, the relative absoptivity of the TCNQ's which lie in different orientation and presumably flat on the surface is high. The dichroic ratio becomes small, although the molecular packing got tighter.

The distribution of transition moment in LB films was studied by the angular dependences of polarized absorption on the incident angle β and the polarization angle α, as shown in FIGURE 5.



(a) (b)

(c) (d)

(e) (f)

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FIGURE 5. Angular dependence polarized UV / visible absorption of N-docosylquinolium-TCNQ LB films. (a)~(d): incidence angle dependences of absorbances at 350 and 500 nm for N-docosylquinolium-TCNQ deposited 5 layers on one side of a optically polished glass plate, (e)~(f): polarization angle dependences of absorbances at 350 and 500nm for N-docosylquinolium-TCNQ deposited 5 layers on one side of a optically polished glass plate.

A minimum absorption was observed at $\beta = 0^{\circ}$ in all cases, and the angular dependences were almost symmetrical, FIGURE 5. The absorption at $\beta = 0^{\circ}$ can be compared with LB films of alloxazine derivatives.[12] The dependences of absorbances at 350 and 500nm on the polarization angle observed at normal incidences are shown in FIGURE 5. A minimum was found at $\alpha = 90^{\circ}$ for the absorbance spectra obtained at 350 and 500nm.

The orientation angle are claculated from the following equations which which are derived by taking a distribution of transition moments of TCNQ in built-up films into accounts.

$$A(\alpha) = \frac{\iint \sin^2\phi \, \cos^2(\alpha-\theta) \, \sin\phi \, d\theta d\phi}{\iint \sin\phi \, d\theta d\phi} \qquad (1)$$

$$A(\beta) = \frac{\iint (\cos\phi \, \sin\beta + \sin\phi \, \sin\theta \, \cos\beta)^2 \, \sin\phi \, d\theta d\phi}{\iint \sin\phi \, d\theta d\phi} \qquad (2)$$

The solid lines in FIGURE 5 are best-fit ones from Equation (1) and (2) employing the β values as the incident angle and the following distribution of θ and ϕ values, Table 1.

TABLE 1. The orientation angle, ϕ and θ, obtained by linear regression analysis from dependences of absorbance at 350 and 500 nm on the incidence

angle and polarization angle for N-docosylquinolium-TCNQ deposited 5 layers on one side of a optically polished glass plate.

wavelength	polarization	orientation angle (ϕ & θ)
350 nm	p	$-10^{\circ} \leq \phi \leq 21^{\circ}$
		$2.86^{\circ} \leq \theta \leq 52.3^{\circ}$
	s	$-17^{\circ} \leq \phi \leq 83.6^{\circ}$
		$56^{\circ} \leq \theta \leq 88.6^{\circ}$
500 nm	p	$24.7^{\circ} \leq \phi \leq 45.3^{\circ}$
		$13.9^{\circ} \leq \theta \leq 82^{\circ}$
	s	$5^{\circ} \leq \phi \leq 82^{\circ}$
		$-11^{\circ} \leq \theta \leq 88^{\circ}$

The values indicate that the projection of dipole moments are fairly broadly distributed in the film plane. The ϕ values obtained with p-polarization indicate that the dipole moments are oriented with tilted angle from the film plane. However the ϕ values obtained with s-polarization suggest that the dipole moments have rather random orientation which supports the small dichroic ratio obtained for 45mN/m film. No correlations have made for the LB films layered at 30mN/m. The 350 and 500nm transitions are resulted from localized excitation in TCNQ anion radical and trasition moments are in the direction of long axis.[13]

We learned that the molecular arrangements and orientations of the films are fairly sensitive to the surface pressure applied. The molecular orientations are more ordered for the films that transfered at 45mN/m. The resistivity observed for LB films are in the same order as the $Li^{+}TCNQ^{-}$ which gives resistivity of $5X10^{-6}S/cm$.[14] The dark conductivities measured are $2.2X10^{-6}S/cm$ for the film layered at 30mN/m and $6.7X10^{-6}S/cm$ for the film layered at

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45mN/m. The photoconductivities measured for the films at 30mN/m and 45mN/m are 3.9×10^{-9}S/cm and 2.8×10^{-8}S/cm, respectively. The observed value of in-plane conductivity was higher that those reported for LB films of merocyanine derivatives and arachidate (1:2), chlorophyll-a, 1,3-didodecylalloxazine up to by order of 1.[15,16] It was, however, more photoresistant than porphyrin IX dimethylester and N-docosylpyridinium-TCNQ by two to three orders of magnitude.[17,18] The LB films fabricated at 45mN/m gave low dichroic ratio which might result from defects in packing, and the defects eventually gave lower value in phtoconductivity than N-docosylpyridinium-TCNQ.

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