In-Plane Anisotropy in Mixed Langmuir–Blodgett Films of Triphenylene Derivatives and 2,4,7-Trinitro-9-fluorenone

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Monolayers and Langmuir–Blodgett (LB) films of 2,3,6,7,10,11-hexaalkoxytriphenylenes (C*n*OTP; *n* denotes the number of carbon atoms per alkyl chain substituent; $n=3$—6) and their charge transfer (CT) complexes with 2,4,7-trinitro-9-fluorenone (TNF) were studied. It was found that the surface pressure applicable for the deposition of LB film increases as the length of alkyl chain of the peripheral substituents decreases. Polarized UV-vis and infrared spectra for the LB films of the CT complexes can be explained consistently with the following model of molecular assembly: The long axes of one-dimensionally stacked molecular columns are preferentially oriented along the dipping direction in the LB films. Marked in-plane dichroism was observed for the LB films of the CT complexes while the LB film of C*n*OTP without TNF showed only a little dichroism.

Langmuir–Blodgett (LB) technique is recognized as an effective method to obtain ultrathin organic films with highly regulated molecular orientation. Typically, as in the case of the LB films of fatty acids, the regulation of molecular orientation is achieved on the water surface in the form of monolayer, being afforded by the amphiphilicity and self-organizing character of sample compounds. Then, the monolayer is transferred onto a solid support, the molecular orientation being mostly retained, to yield an LB film with controlled molecular orientation with respect to the surface normal of the substrate. In many previous studies, functional molecules for LB film materials have been designed along the strategy of giving amphiphilicity to the molecules by attaching appropriate long alkyl chains and/or hydrophilic groups.

Meanwhile, it has recently become well-known that LB films of some dyes and polymers exhibit in-plane anisotropy.[1—16)] In most cases, anisotropic orientation of molecules occurs with respect to the dipping direction. This type of anisotropy is thought to be induced by a flow of monolayers on the water surface during the vertical dipping process, accompanied by the alignment of the long axis of molecular assemblies or the main chain of polymers, along the dipping direction.[2,4d)] The degree of in-plane alignment has often been conveniently evaluated by measuring dichroic ratios in polarized absorption spectra. This phenomenon provides us a possibility of obtaining LB films with highly controlled molecular orientation with respect not only to the surface normal of substrates but also to the dipping direction. In many cases, however, dichroic ratios are of the order of 2 or 3 for as-deposited LB films. In order to obtain higher ordering of molecules, it is required that the idea of molecular design for such anisotropic LB films should be more sufficiently established.

Previously, the present authors reported that the LB films of copper tetrakis(alkoxycarbonyl)phthalocyanines show extremely high in-plane dichroism, which is caused by the highly preferential orientation of the stacking axis of phthalocyanine assemblies parallel to the dipping direction.[15)] Dichroic ratios for those as-deposited LB films exceed 5 when relatively short alkyl chains are employed as the substituents. It is also notable that the LB films of the phthalocyanine derivatives can successfully be prepared with good monolayer stability and transfer ratios, though their symmetric molecular structures can hardly be thought as typical amphiphiles. In these cases, the mutual interaction between the aromatic macrocycles provides close packing of the molecules in the monolayer, and the short alkyl chains furnish the monolayers with appropriate fluidity to let the deposition smooth and to produce the high in-plane ordering.[15d)]

On the other hand, some disk-shaped molecules called discotic liquid crystals (DLCs) are known to form one-dimensionally stacked molecular assemblies in bulk, showing columnar mesophases. Such molecules have typical structures with a planar aromatic core and some flexible side chains, such as some benzenehexaalkanoates,[17)] 2,3,6,7,10,11-hexaalkoxytriphenylenes,[18)] and peripherally substituted phthalocyanines.[19,20)]

Several studies on monolayers of DLCs exemplify two typical ways of molecular orientation, i.e., 'lie flat' and 'edge on' arrangement of the planar cores on the water surface.[21—25)] Some triphenylene (TP) derivatives have been deposited as LB films, and the 'edge on' structure was suggested.[22,25b,25c)] Deposited LB films of some other DLCs have also been studied.[16,25c)] However, only a few experimental results concerning the in-plane anisotropy have appeared.[16)]

The present work is motivated by an expectation of obtaining LB films of DLC materials or their analogues with high in-plane ordering. This idea seems reasonable, considering that the in-plane ordering of molecules in LB films may arise from the elongated shape of molecular assemblies (i.e. one-dimensional stackmer) and the fluidity of monolayers.[2,4d,15b,15d)] In this paper, we report the properties of monolayers and LB films of the charge transfer (CT) complexes of hexaalkoxytriphenylenes (C*n*OTP; *n* denotes the number of carbon atoms per alkyl chain substituent; n=3—6) and 2,4,7-trinitro-9-fluorenone (TNF). The structures of the compounds are shown in Fig. 1. It will be shown that the involvement of TNF in the monolayer strongly affects the dichroic properties of the LB films as well as the monolayer properties. Spectroscopic study for LB films of C3OTP–TNF CT complex will be presented, exemplifying highly anisotropic molecular orientation.

Experimental

Material Preparation. The four CnOTPs (n=3—6) were synthesized according to a literature method,[27] and identified by ^{1}H NMR (400 MHz) and elemental analysis.

C3OTP. Anal. Found: C, 74.9; H, 8.3%. Calcd for $C_{36}H_{48}O_6$: C, 75.0; H, 8.4%. ^{1}H NMR ($CDCl_3$) δ=1.1 (t, CH_3, 18H), 2.0 (m, CH_2, 12H), 4.2 (t, OCH_2, 12H), 7.8 (s, ArH, 6H).

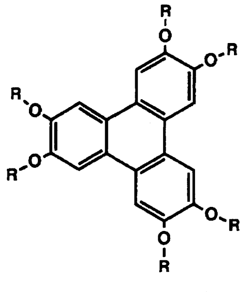
C4OTP. Anal. Found: C, 76.3; H, 9.1%. Calcd for $C_{42}H_{60}O_6$: C, 76.3; H, 9.2%. ^{1}H NMR ($CDCl_3$) δ=1.0 (t, CH_3, 18H), 1.6 (m, CH_2, 12H), 1.9 (m, CH_2, 12H), 4.2 (t, OCH_2, 12H), 7.8 (s, ArH, 6H).

C5OTP. Anal. Found: C, 77.3; H, 9.7%. Calcd for $C_{48}H_{72}O_6$: C, 77.4; H, 9.7%. ^{1}H NMR ($CDCl_3$) δ=1.0 (t, CH_3, 18H), 1.4—1.6 (m, CH_2, 24H), 2.0 (m, CH_2, 12H), 4.2 (t, OCH_2, 12H), 7.8 (s, ArH, 6H).

C6OTP. Anal. Found: C, 77.9; H, 10.3%. Calcd for $C_{54}H_{84}O_6$: C, 78.2; H, 10.2%. ^{1}H NMR ($CDCl_3$) δ=0.9 (t, CH_3, 18H), 1.4—1.6 (m, CH_2, 36H), 1.9 (m, CH_2, 12H), 4.2 (t, OCH_2, 12H), 7.8 (s, ArH, 6H).

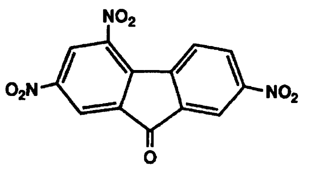
TNF was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification.

Experiments on Monolayers and Multilayers. All the experiments on monolayers and multilayers were performed with a commercial LB trough system (KSV 5000LB). CnOTP and TNF were dissolved in benzene at various mixing ratios of 4 : 1, 2 : 1, 1 : 1, and 1 : 3, and spread onto pure water surface to form monolayers. The temperature of the water subphase was controlled at 20 °C. Quartz plates ($38\times12\times1$ mm^3) were rendered hydrophobic by immersing them into a chloroform solution of dimethyldichlorosilane, washed successively with chloroform and hexane, and then used as substrates, unless otherwise mentioned. LB films were deposited by a conventional vertical dipping method at a dipping velocity of 30 mm min^{-1}.



R = -C_nH_{2n+1} (n=3-6)

2,3,6,7,10,11-Hexaalkoxytriphenylene (CnOTP)



2,4,7-Trinitro-9-fluorenone (TNF)

Fig. 1. Structural formulas of the sample compounds.

Spectroscopy and X-Ray Diffraction. Polarized UV-vis absorption spectra were measured on a Hitachi U-3500 spectrometer with Glan–Taylor prisms. The beam direction was normal to the plane of the film. Infrared spectra were recorded on an FT/IR-5M spectrometer (Japan Spectroscopic Co., Ltd.). LB films for transmission IR absorption spectroscopy and reflection-absorption spectroscopy (RAS) were prepared onto a germanium plate ($30\times25\times1$ mm^3) and onto a silver film (thickness ca. 1200 nm) evaporated on a glass plate ($76\times26\times1$ mm^3), respectively. RAS spectra were measured with a p-polarized beam of 80° incident angle. X-Ray diffraction was measured with an RAD-IIA diffractometer (Rigaku Co.) for LB films of C3OTP-TNF system (100 layers per side) deposited on hydrophobized glass plates.

Results and Discussion

Monolayer Properties. Surface pressure (π)–area (A) isotherms of the monolayers of CnOTPs and the mixed monolayers of CnOTPs and TNF are shown in Fig. 2 A—D. For the calculation of the area on the abscissa, we considered only the amount of CnOTP molecules, but not that of TNF molecules, since monolayers are not formed with TNF alone. The isotherms of CnOTPs without TNF exhibit the limiting areas of 65—83 Å^2, which are thought to be fairly reasonable values if the 'edge on' structures of the molecules in the monolayers are assumed.[22] These isotherms showed rather slow rising of the surface pressure and do not have long straight-line regions except the case of C3OTP.

Upon mixing TNF with CnOTPs, striking features of the monolayer properties were observed, such that the rising of surface pressure becomes steeper and straighter. As the mole fraction of TNF in the spreading solution was increased, the limiting area became larger (see the insets in Fig. 2). This is ascribed to the intercalation of TNF molecules into the monolayers of CnOTPs with the aid of CT interaction. The increment of limiting area was linear with the amount of TNF molecules added per one CnOTP molecule in solution at low TNF/TP ratios but showed a tendency to level off at higher molar ratios of TNF. Presumably, excess TNF molecules in the spreading solution may have sunk or dissolved into the water subphase without being involved in the formation of monolayers, especially at high ratios of TNF.

Another striking feature in Fig. 2 is the appearance of plateau region in the isotherms that occurs upon adding TNF. This type of plateau has sometimes been observed in isotherms for monolayers of some disc-like molecules which may form one-dimensionally stacked assemblies.[4e,15d] Therefore, the occurrence of the plateau may be induced by the stabilization

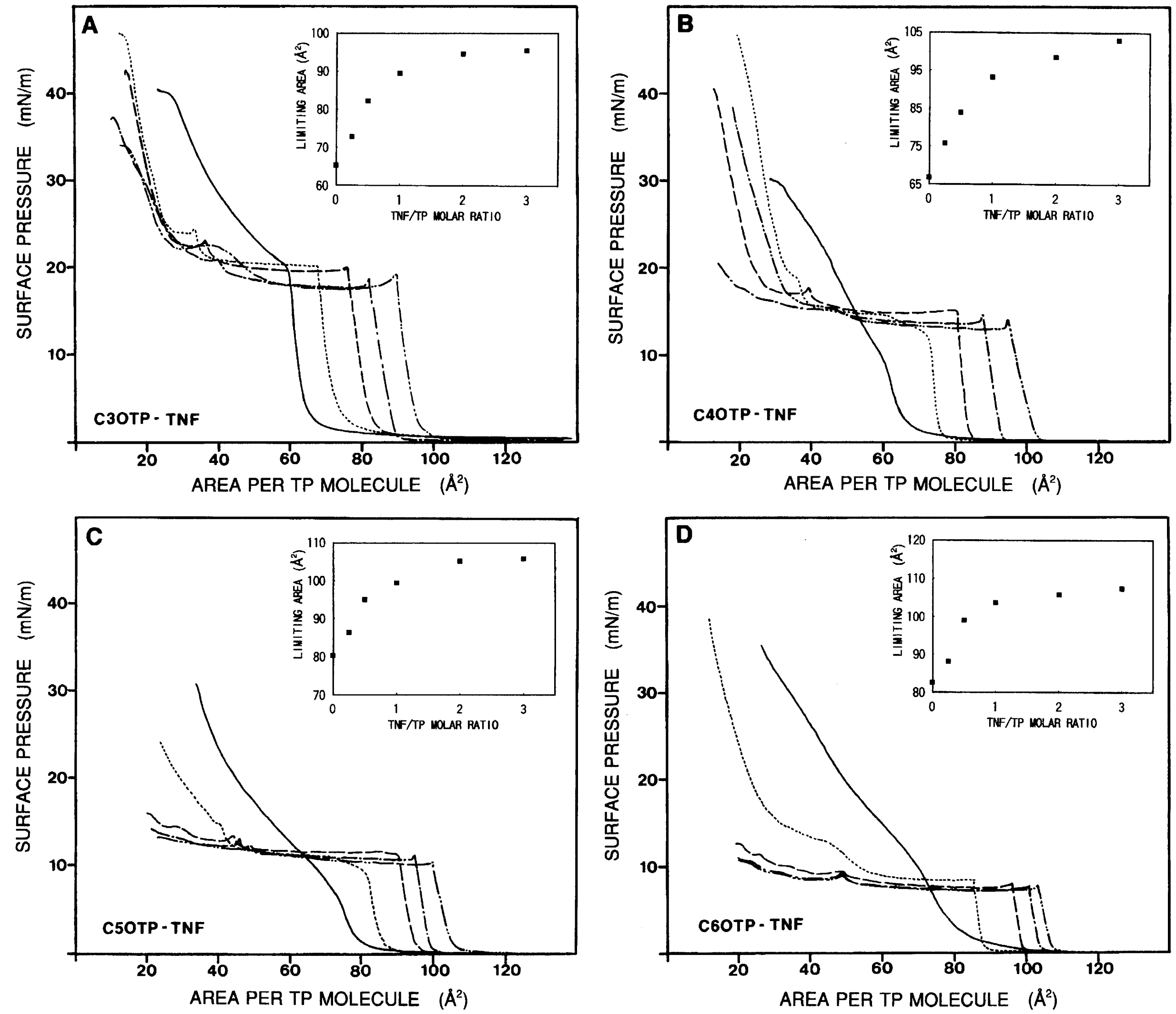


Fig. 2. Surface pressure–area isotherms (20 °C) for the monolayers of C*n*OTPs and the CT complexes with TNF in various mixing ratios in the sample solutions. (A) C3OTP–TNF, (B) C4OTP–TNF, (C) C5OTP–TNF, (D) C6OTP–TNF. —— without TNF, ···· TP : TNF=4 : 1, - - - TP : TNF=2 : 1, –·– TP : TNF=1 : 1, –··– TP : TNF=1 : 3. Insets are plots of limiting area vs. TNF/TP molar ratio.

of columnar arrangement of molecules upon the formation of mixed-stack CT complex.[26] The surface pressure at the plateau region becomes higher as the side-chain length *n* becomes shorter from 6 to 3. This type of relationship between alkyl chain length and surface pressure at the plateau can also be seen in the case of phthalocyanine derivatives in our previous study.[15d,15f] Considering that the monolayers can be stably kept and transferred as LB films only at the surface pressures below the plateau pressures, it is beneficial to employ shorter alkyl chains for this type of molecules to obtain monolayers with better transferrability, as long as the alkyl chains stay flexible and provide appropriate fluidity with the monolayers. The plateau region may be associated with conformational change of alkyl chains during the compression of the monolayer or with partial formation of double layers on the water surface.

Deposition and Characterization of LB Films. Among the samples examined, the C3OTP–TNF system was most successfully deposited as LB films, since higher surface pressures were applicable for the film deposition unlike the other systems. The monolayers made from solutions of C3OTP and TNF at various mixing ratios could be transferred onto the hydrophobized quartz plates at surface pressures between 15.5—19.0 mN m^{-1} as listed in Table 1.

Polarized UV-vis spectra of the LB films made from C3OTP–TNF mixture solutions are shown in Fig. 3 A—C, in which strong dichroism is recognized. In every case, the π–π^* absorption in the UV region is stronger with the light beam polarized perpendicular to the dipping direction than with that polarized parallel. These highly anisotropic spectra can be easily explained by assuming that the aromatic cores in the LB films are arranged with orientation nearly perpendicular to the substrate and also to the dipping direction in average,

Table 1. Deposition Conditions and Dichroic Ratios of the LB Films of C3OTP–TNF CT Complex

TP : TNF ratio	4 : 1	2 : 1	1 : 1	1 : 3
Surface pressure (mN m^{-1})	18.0	18.0	16.5	15.5
Transfer ratio	0.6—0.9	0.8—1.0	0.9—1.0	0.9—1.0
Dichroic ratio	5.1	4.6	3.1	5.2
$\lambda_{\max}$ (nm)	265	266	272	274

whereas 'lie flat' orientation can hardly be consistent with these dichroic features. The most plausible mechanism for the occurrence of the in-plane anisotropy in this case is the flow-orientation of the long axis of one-dimensional (or columnar) molecular assemblies made of TP and TNF molecules. The alignment of the molecular columns along the dipping direction may be facilitated by the fluidity of monolayers afforded by the short alkyl chains and by self-assembling nature of these molecules.

In the visible region (450—700 nm), on the other hand, peaks of CT absorption[28] are apparently observed only in the spectra polarized parallel to the dipping direction (see the insets in Fig. 3), indicating that the transition moments of the CT absorption should be oriented along the dipping direction. It has been reported that, in 3-dimensional bulk, the molecules of TP and TNF form cofacial 'mixed-stack' CT columns; the term 'mixed-stack' means that the molecules of TP and TNF are admixed in a column.[26] In this kind of CT complex, the transition moment of CT absorption is known to be parallel to the stacking axis.[28,29] Therefore, the orientation of the transition moment of the TP–TNF CT absorption along the dipping direction should be consistent with the orientation of the stacking axis of the molecular columns along the dipping direction, as stated above.

Dichroic ratios (DR's) for the LB films of C3OTP–TNF series are listed in Table 1 together with the wavelengths at which the DR's were determined; DR's are the ratios of absorbance between the spectra polarized perpendicular (S_{ppd}) and parallel (S_{prl}) to the dipping direction at $\lambda_{\max}$ of S_{ppd}. The DR's were ranged between 2.4 and 5.2, without clear correlation with the mixing ratios of TP and TNF. The dichroic properties may be not simply affected by the mixing ratios but more importantly by such other subtle conditions as the surface pressure. However, the existence of TNF (i.e., the formation of CT complex) is essential for the occurrence of strong dichroism, since an LB film of C3OTP without TNF showed only negligible dichroism (dichroic ratio 1.09 at 278 nm, Fig. 4).

Polarized IR absorption spectra (transmission) of an LB film (100 layers on each side) prepared from the C3OTP–TNF 1 : 3 solution also revealed the anisotropic character (Fig. 5). In the spectra polarized perpendicular and parallel to the dipping direction (S_{ppd} and S_{prl}), the absorption peaks attributable to aromatic C=C breathing and stretching of C–O–C (from TP, 1262 cm^{-1}), N–O (from TNF, 1342 and 1520 cm^{-1}), and C=O (from TNF, 1731 cm^{-1}) are much more intense in S_{ppd} than in S_{prl}, while the difference at the alkyl C–H stretching region (2800—3000 cm^{-1}) is negligible. In contrast, the two peaks seen in the region of aromatic C–H out-of-plane bending (731 and 840 cm^{-1}) is stronger in S_{prl} than in S_{ppd}. It is known that the transition moment of aromatic C–H out-of-plane bending occurs perpendicularly to the aromatic plane, while most of the other transition moments are thought to lie within the molecular plane. Therefore, the IR spectra are in line with the orientation of the aromatic cores in the LB films discussed above from the UV-vis spectra.

RAS spectrum of an LB film made from the C3OTP : TNF 1 : 3 solution (20 layers) on an evaporated silver film is shown in Fig. 6. Because RAS dominantly detects the vibrational transition whose moment is oriented perpendicularly to the film plane, preferential molecular orientation with respect to the surface normal can be recognized by comparing the RAS spectra with the transmission absorption spectra.[30] A distinct difference is the lack of the out-of-plane bending peaks at 731 and 840 cm^{-1} in the RAS spectrum (Fig. 6), confirming an 'edge on' structure of the aromatic cores. If the molecular orientation were in a 'lie flat' structure, the transition moments of the bending mode should be perpendicular to the film plane to result in the appearance of the two peaks in the RAS spectrum.

With the IR spectra, it may also be discussed whether or not TNF molecules take any preferential orientation with respect to the rotation around the stacking axis of the molecular column in the LB film. Particularly, it should be noted that the RAS spectrum does not differ qualitatively from the transmission spectra except the out-of-plane bending peaks discussed above, as contrasted with the case of typical amphiphiles such as cadmium stearate.[30] This observation suggests that the molecular orientation of TNF is not distinctly regulated with respect to the rotation around the stacking axis. Since TNF is not amphiphilic in nature, it may not be reasonable to expect a fixed orientation in which, for example, the direction of the C=O bond stands upright or lies along the surface of the plate. However, the C=O stretching peak (1731 cm^{-1}) in the RAS spectrum is smaller compared with that in the transmission spectra. The ratio of the peak area (in absorbance) of 1731 cm^{-1} to that of 1342 cm^{-1} (N–O stretching) is 0.17 in the RAS spectrum but 0.56 in the transmission spec-

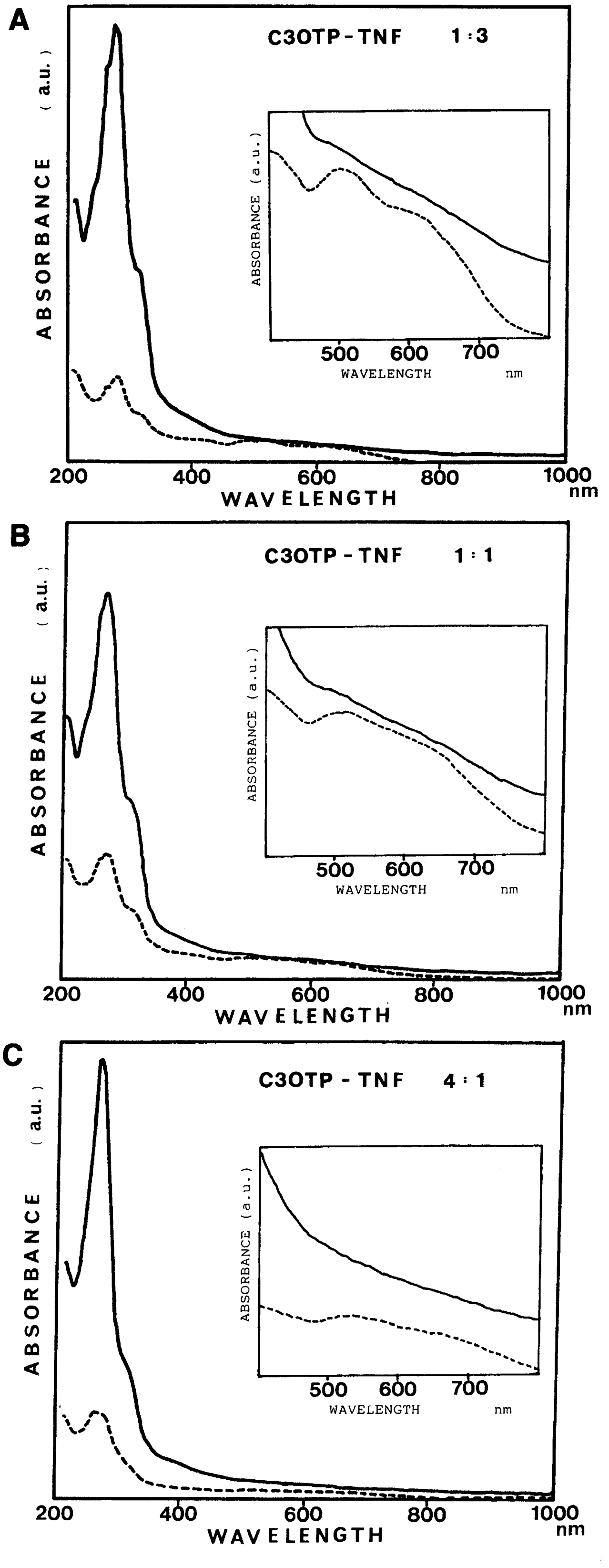


Fig. 3. Polarized UV-vis absorption spectra of the LB films (50 layers per side) of C3OTP–TNF CT complex at the ratios of (A) TP : TNF=1 : 3, (B) TP : TNF=1 : 1, and (C) TP : TNF=4 : 1, polarized perpendicular (—) and parallel (····) to the dipping direction.

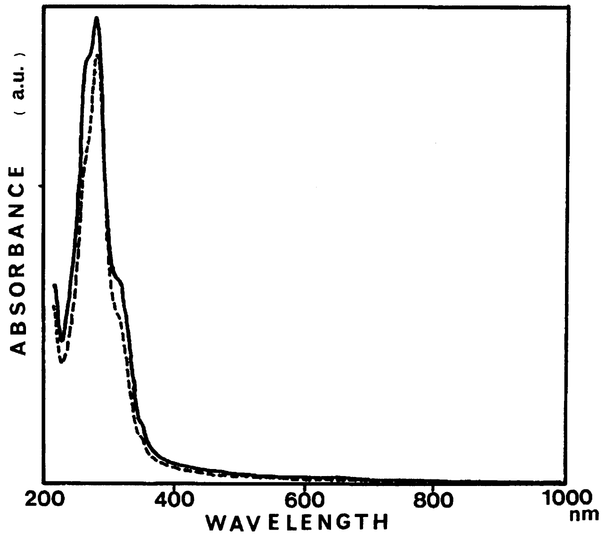


Fig. 4. Polarized UV-vis absorption spectra of the LB film (30 layers per side, deposited at 15 mN m^{-1}) of C3OTP without TNF polarized perpendicular (—) and parallel (····) to the dipping direction.

trum (S_{ppd}). Thus, the TNF molecules in the LB film possibly take a statistically preferential orientation in which the direction of the C=O bond tends to lie along the film plane.

X-Ray diffraction patterns (Cu $K\alpha$-ray) for C3OTP–TNF LB films are shown in Fig. 7, and the d-spacings calculated with the Bragg's formula are listed in Table 2. Only one diffraction peak was observed for the C3OTP : TNF=4 : 1 and 2 : 1 samples, whereas two more peaks were observed for the other samples with excess TNF. Diffraction peaks corresponding to the spacings of 3—4 Å expected for intermolecular distances within a column are absent in any case, confirming that the stacking axis of the discotic column lies along the plane of the substrate. The d-spacings in Table 2 suggest the presence of two different column structures. In one of them, the diameter varies depending on the mixing ratio. The other structure which corresponds to the d-spacings at 7.35 and 14.77 Å in the 1 : 1 and 1 : 3 samples might be attributable to the CT complex of TP and TNF at a fixed mixing ratio. However, details of the structures are still unknown.

Conclusions

Although TNF does not form a monolayer on water without TP derivatives, the formation of CT complexes of C*n*OTP with TNF considerably affected the properties of the monolayers and the LB films, especially the dichroic properties. Strong dichroism was observed only with the LB films prepared from solution of C*n*OTP admixed with TNF, even at a molar ratio of TNF as low as TP : TNF=4 : 1. It was shown from the spectroscopy and the X-ray diffraction that the planes of aromatic cores in the LB films of C3OTP–TNF CT complex are

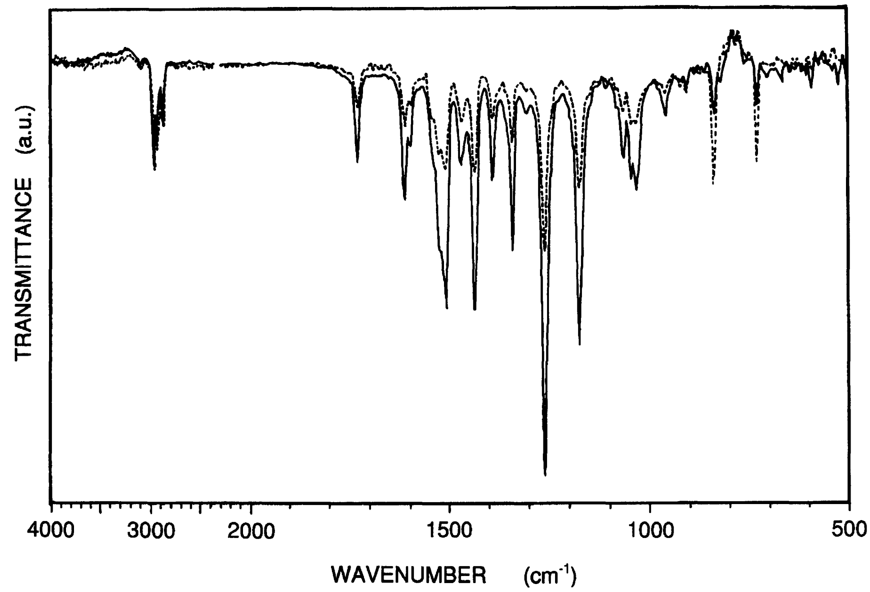


Fig. 5. Polarized infrared spectra (transmission) of the LB film of C3OTP–TNF (1 : 3) CT complex polarized perpendicular (—) and parallel (····) to the dipping direction.

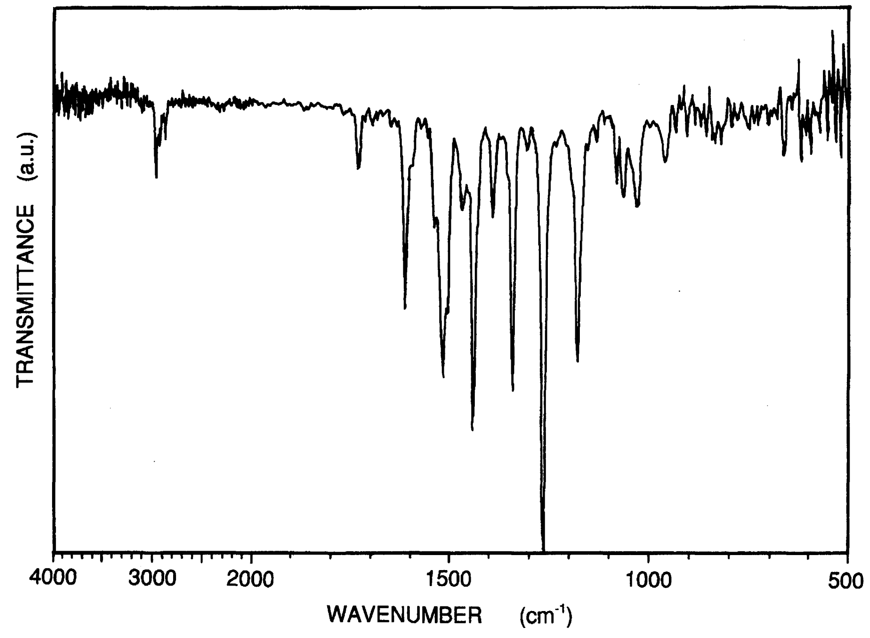


Fig. 6. Infrared RAS spectrum for the LB film (20 layers on Ag film) of C3OTP–TNF (1 : 3) CT complex. The dipping direction was set parallel to the plane of polarization of the beam. A very similar spectrum was obtained when the dipping direction was set perpendicular to the plane of polarization.

nearly perpendicular to the plane of the substrate and also to the dipping direction, in average.

The LB film materials studied here provide a new type of molecules different from classical amphiphilic molecules such as long-chain fatty acids. This study has shown that the shorter side chain gives the higher surface pressure applicable for the deposition of the LB films, resulting in fairly well deposition and highly anisotropic orientation of the molecules. Thus, a long alkyl chain is not necessarily a prerequisite for this type of molecules to obtain LB films with high molecular ordering. In the present LB films, the interaction between the aromatic cores, instead of the interaction between long alkyl chains, brings about the close packing of molecules as reported for the LB films of phthalocyanine derivatives.[15d)] Moreover, the short alkyl chains provide the monolayer with appropriate fluidity, which we call 'softening effect'. In conclusion, the present work exemplifies a new style of molecular design of LB film material that differs from the classical style of molecules

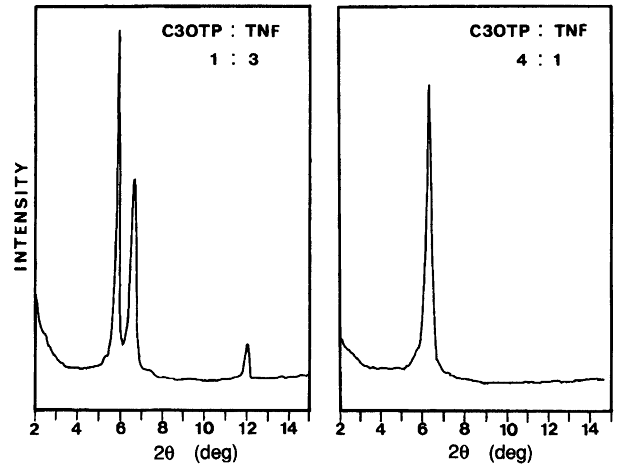


Fig. 7. Examples of X-ray diffraction pattern of C3OTP -TNF LB films.

Table 2. d-Spacings Calculated from the X-Ray Diffraction Peaks for the LB Films of C3OTP–TNF CT Complex

TP : TNF ratio	4 : 1	2 : 1	1 : 1	1 : 3
d-spacing (Å)			14.77	14.77
	13.95	13.57	13.34	13.12
			7.35	7.35

with long alkyl chains and polar head groups.

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