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INTERMOLECULAR CHARGE TRANSFER IN LANGMUIR-BLODGETT FILMS: FORMATION OF MIXED AND ALTERNATE-LAYER LB FILMS OF QUINHYDRONE AND TTF-TCNQ DERIVATIVES

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Abstract

Intra- and interlayer charge transfer properties were examined in the mixed and the alternate-layer Langmuir-Blodgett (LB) films of 2-methyl-5-octadecyl-1,4-dihydroxybenzene ($C_{18}HQ$) and 2-methyl-5-octadecyl-1,4-benzoquinone ($C_{18}Q$), which is an example of the "neutral" charge transfer complex, and 2-hexadecyl-3-heptadecyl-6,7-dimethyltetrathiafulvalene ($C_{16}C_{17}DMTTF$) and 2-octadecyl-7,7,8,8-tetracyanoquinodimethane ($C_{18}TCNQ$) for the "ionic" complex. In the former case, intermolecular charge transfer took place in both types of LB films. The charge transfer band between $C_{18}HQ$ and $C_{18}Q$ appeared at 590 nm even for the bilayer film. The charge transferred state should be accompanied by hydrogen bonding, although the IR spectra revealed that a certain amount of non-hydrogen bonded C=O group exists in the film. The 1:1 mixture of $C_{16}C_{17}DMTTF$ and $C_{18}TCNQ$ gave an ionic charge transfer complex in the form of mixed LB films. UV-visible and IR spectra revealed the strong complex formation during the film-forming process. On the other hand, the charge transfer interaction between the adjacent layer of the interleaved LB films essentially did not take place.

Keywords: Langmuir-Blodgett films, charge transfer complex, alternate-layer LB films, quinhydrones

INTRODUCTION

Intermolecular charge transfer phenomena in the Langmuir-Blodgett (LB) films have the potential for the application in the field of microelectronics and photonics. A number of conducting LB films using charge transfer complexes aiming at fabricating thin film electronic devices have been reported.[1] In the charge transfer complexes, electrons are transferred from donor to acceptor molecules to form conduction bands to exhibit high electrical conductivity. Most of the film-forming materials so far used for the conducting LB films are amphiphilic donor or amphiphilic acceptor complexes with unsubstituted counter part. Among these LB films, highly conducting thin films with metallic electron transport properties have been obtained.[2] The conducting LB films composed of amphiphilic donor and amphiphilic acceptor are rare, probably due to the difficulty in the synthesis of these complicated molecules. However, to take advantage of the molecular-manipulation technique of the LB method, it is preferable to bear hydrophobic long chain(s) in each molecule. Such molecules may form monolayers (with the aid of a matrix molecule if necessary) and can be incorporated at the desired sites in a multilayer to form interleaved LB films. For example, alternate head-to-head, tail-to-tail structure of donor and acceptor molecule will be easily obtained. Although the photo-induced electron transfer in the interleaved LB films has been extensively studied in connection with photosynthetic center,[3] the studies on the "static" intermolecular charge transfer between adjacent donor and acceptor layers in the interleaved LB film are limited.[4] Large second harmonic generation (SHG) effect through interlayer charge transfer is also expected in the LB film with noncentrosymmetric structure. Bjørnholm et al. already reported the SHG from the alternate-layer LB films of long-chain donors and long-chain acceptors.[5]

In this paper, we will describe the formation of mixed and alternate-layer LB films of amphiphilic donors and amphiphilic acceptors and examine intra- and interlayer charge transfer properties. Schematic views of a mixed and an alternate-layer LB films are shown in Figure 1. We adopted two kinds of donor-acceptor systems: 2-methyl-5-octadecyl-1,4-dihydroxybenzene ($C_{18}HQ$) and 2-methyl-5-octadecyl-1,4-benzoquinone ($C_{18}Q$) for an example of "neutral" charge transfer complex and 2-hexadecyl-3-heptadecyl-6,7-dimetyltetrathiafulvalene ($C_{16}C_{17}DMTTF$) and 2-octadecyl-7,7,8,8-tetracyanoquinodimethane ($C_{18}TCNQ$) for an example of "ionic" charge transfer complex. Here, the charge transfer ratio between a donor and an acceptor is less than 0.5 and nearly unity for the "neutral" and the "ionic" complex, respectively.

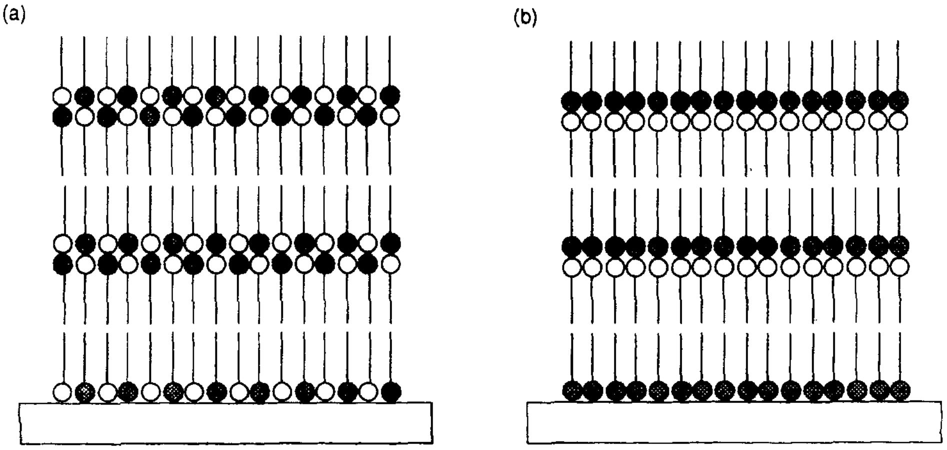
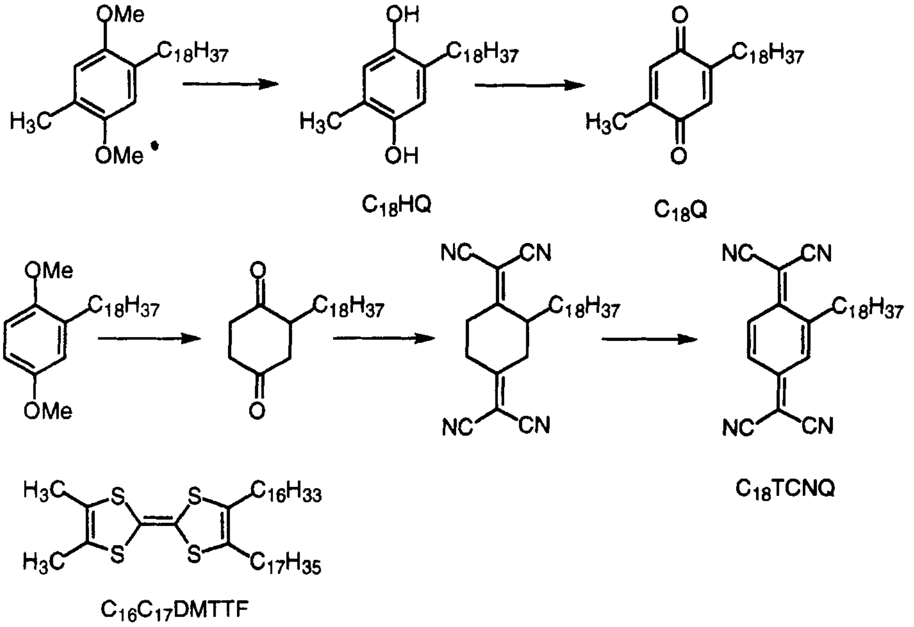


FIGURE 1. Molecular organisation of mixed (a) and alternate-layer (b) LB films.

EXPERIMENTAL

$C_{16}C_{17}$DMTTF was prepared according to the literature.[6] C_{18}HQ, C_{18}Q and C_{18}TCNQ were synthesised from the corresponding alkyl substituted 1,4-dimethoxybenzene derivatives as described in Scheme 1.



SCHEME 1

Cyclic voltamograms were taken on a Yanako Polarographic Analyser P-1100 under argon using saturated calomel electrode (SCE) as a reference at a scanning rate 50 mV/s in tetrahydrofuran (THF) solution containing 0.1 M tetrabutylammonium tetrafluoroborate (TBA-BF_4). A conventional Langmuir trough (LAUDA film balance) was used for the monolayer formation and the multilayer deposition. Fused silica and CaF_2 substrates, both of which were coated with five layers of cadmium arachidate, were used for UV-visible (fused silica or CaF_2) and IR spectroscopic measurements (CaF_2). The UV-visible spectra were taken using a Perkin Elmer Lambda 19 spectrophotometer with a resolution of 6 nm. The IR spectra were recorded on a Perkin Elmer Spectrum 2000 FT-IR spectrophotometer equipped with MCT detector with a resolution of 4 cm^{-1}.

Preparation of the LB films of C_{18}HQ and C_{18}Q

Two kinds of LB films, mixed or alternate-layer, were prepared with the aid of cadmium arachidate as a matrix molecule. Each compound was dissolved in benzene at the concentration of 1 x 10^{-3} M and mixed before spreading on a water surface containing 4 x 10^{-4} M $CdCl_2$ and buffered with $KHCO_3$. The mixing ratio (donor:acceptor:arachidic acid = 1:1:2) was adopted for the formation of mixed LB films which was deposited in Y-type manner. The donor or the acceptor was mixed 1:1 with arachidic acid to form alternate-layer LB films. The first layer to be transferred was donor-containing layer (downward stroke).

Preparation of the LB films of $C_{16}C_{17}$DMTTF and C_{18}TCNQ

The mixed LB films can be deposited with arachidic acid as a matrix molecule in Y-type manner. Each compound was dissolved in benzene at the concentration of 1 x 10^{-3} M and mixed ($C_{16}C_{17}$DMTTF:C_{18}TCNQ:arachidic acid = 1:1:2) before spreading on a pure water surface. For the deposition of the alternate-layer LB films, each material was mixed 1:1 with arachidic acid. The $C_{16}C_{17}$DMTTF containing layer was first transferred (downward stroke) followed by C_{18}TCNQ containing layer (upward stroke).

RESULTS AND DISCUSSION

Redox potentials of film-forming components

The redox potentials of the film-forming materials together with those of the corresponding unsubstituted molecules measured by cyclic voltammetry are summarised in Table 1. It is possible to predict the degree of charge transfer to a certain extent from electrochemical data.[7,8] In an organic solid, the degree of charge transfer is mainly determined by the competition of two energies: I_p-E_a (the difference between the ionisation potential of the donor (I_p) and the acceptor electron affinity (E_a)) and the electrostatic Madelung energy. If the difference in the latter term between the given materials is small, we can estimate the degree of charge transfer from $\Delta E_{red/ox}$ (the difference between the oxidation potential of the donor and the reduction potential of the acceptor), which is a good measure of I_p-E_a.[8]

Due to the effect of alkyl substituent, first redox potentials ($E(1)_{1/2}$) of $C_{16}C_{17}$DMTTF and C_{18}TCNQ were shifted to the lower potential region compared with those of unsubstituted parent molecules. However, $\Delta E_{red/ox}$ value of 0.20 V is comparable to that of TTF-TCNQ ($\Delta E_{red/ox}$ = 0.19 V, charge transfer ratio of the complex is 0.59), indicating that the donor-acceptor system is within the region where "ionic" charge transfer is expected.[7]

In the case of C_{18}HQ and C_{18}Q, the $E(1)_{1/2}$ value was also shifted to lower potential region compared to corresponding unsubstituted molecules. The charge transfer complex between 1,4-dihydroxybenzene and 1,4-benzoquinone is well known as quinhydrone. The charge transfer ratio of this complex is estimated to be 0.2 - 0.3.[9,10]

As the molecular structures closely correlate to each other, substitution with alkyl groups will give the same degree of perturbation on HOMO level of $C_{18}HQ$ and LUMO level of $C_{18}Q$.[11] As a result, the HOMO-LUMO gap in the amphiphilic quinhydrone is expected to be almost the same as that of the unsubstituted quinhydrone. Consequently, "neutral" charge transfer interactions as in the case of quinhydrone will occur in the LB films.

TABLE I Redox Potentials (V) of electron donor and acceptor molecules.[a)]

Molecule	$E(1)_{1/2}$	$E(2)_{1/2}$
	$C_{16}C_{17}DMTTF$-$C_{18}TCNQ$ System	
$C_{16}C_{17}$DMTTF	0.52	0.72
TTF	0.54	0.78
C_{18}TCNQ	0.32	- 0.40
TCNQ	0.35	- 0.41
	$C_{18}HQ$-$C_{18}Q$ System	
C_{18}HQ	1.13[b)]	—
1,4-dihydroxybenzene	> 1.3[c)]	—
C_{18}Q	-0.57	—[d)]
1,4-benzoquinone	-0.47	—[d)]

a) Measured at a scan rate 50 $mVsec^{-1}$ using Pt vs. SCE in 0.1 M $TBA{\bullet}BF_4$ / THF. b) Irreversible process. c) No oxidation peak below 1.3 V. d) Could not be determined due to the chemical reaction.

LB films of $C_{18}HQ$ and $C_{18}Q$

In recent years, quinhydrone and its derivatives have attracted much attention from the view point of cooperative proton-electron transfer phenomena arising from the charge transfer state accompanied by hydrogen bonding.[10,12] The hydrogen-bonding ability should have the advantage of taking place intermolecular charge transfer in the LB multilayer, because the donor and the acceptor can be fixed through hydrogen bonding at appropriate sites for charge transfer .

Figure 2 shows the UV-visible spectra of 16-layer mixed and alternate-layer LB films of $C_{18}HQ$ and $C_{18}Q$. Two distinct absorption bands were observed at around 260 and 590 nm, which are the local excitation band of the quinone moiety and the intermolecular charge transfer band, respectively. The peak intensity of these bands increased linearly with the number of layers.

It is clear from the charge transfer band observed at around 590 nm that intermolecular charge transfer takes place in both mixed and alternate layer LB films. The position of the charge transfer band is almost the same as that of quinhydrone (600 nm),[11] indicating that the HOMO-LUMO gap is not affected by the substitution of alkyl groups and that the charge transfer ratio should be around 0.2-0.3 in the amphiphilic quinhydrone as discussed above. The charge transfer band already appeared for the bilayer films and the peak position did not change significantly with an increase in the number of layers or with the deposition manner (mixed or alternate-layer). On the other hand, the local excitation band of the quinone moiety appeared at 254 and 268 nm in the mixed and alternate-layer LB films, respectively. This peak appears at 257 nm in chloroform solution of $C_{18}Q$ (1 x 10^{-4} M, not shown). The band appeared almost the same position in the mixed LB films as that in solution and showed a red-shift in the alternate-layer LB films. These results suggest that the molecules form J-like aggregates in the alternate-layer LB films.

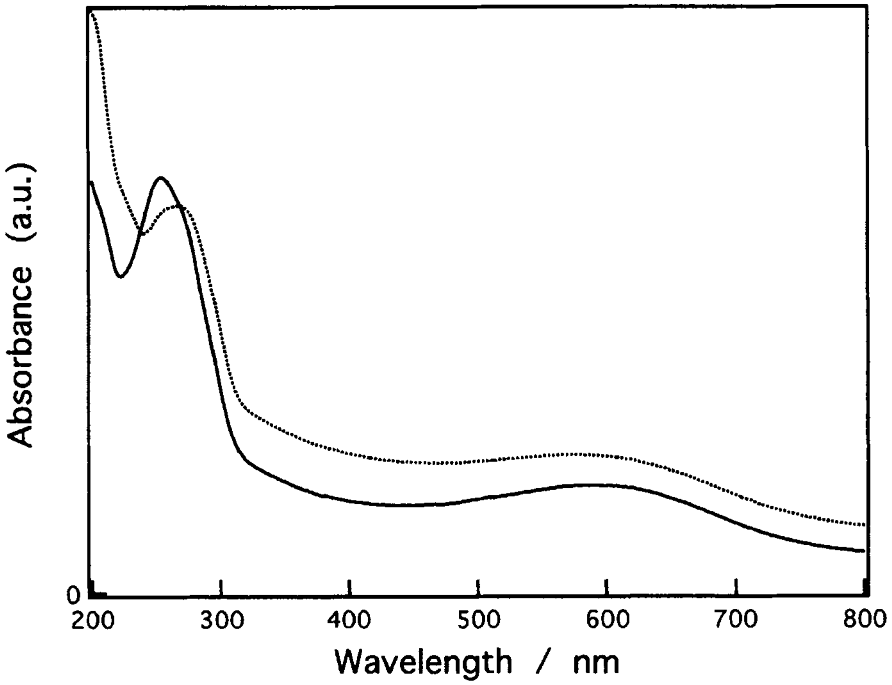


FIGURE 2. UV-visible spectra of 16-layer sample of the mixed (solid line) and the alternate-layer (dotted line) LB films of $C_{18}HQ$ and $C_{18}Q$.

The IR spectra of mixed and alternate-layer LB films are shown in Figure 3. As we used a matrix material, the spectra contain that of cadmium arachidate. In the transmission spectrum of an LB film of 5-layer cadmium arachidate on CaF_2, peaks appeared at 1542, 1473, 1463 and 1421 cm^{-1}. The peaks at 1473 and 1463 cm^{-1} are the CH_2 scissoring bands, splitting because the hydrocarbon chains are packed in the orthorhombic subcell in LB films.[13] The corresponding peak appeared at around 1470 cm^{-1} in both mixed and alternate-layer LB films. However, the peak is overlapped with that of phenyl ring, which prevents determining the packing manner of the alkyl chains in the present LB films.

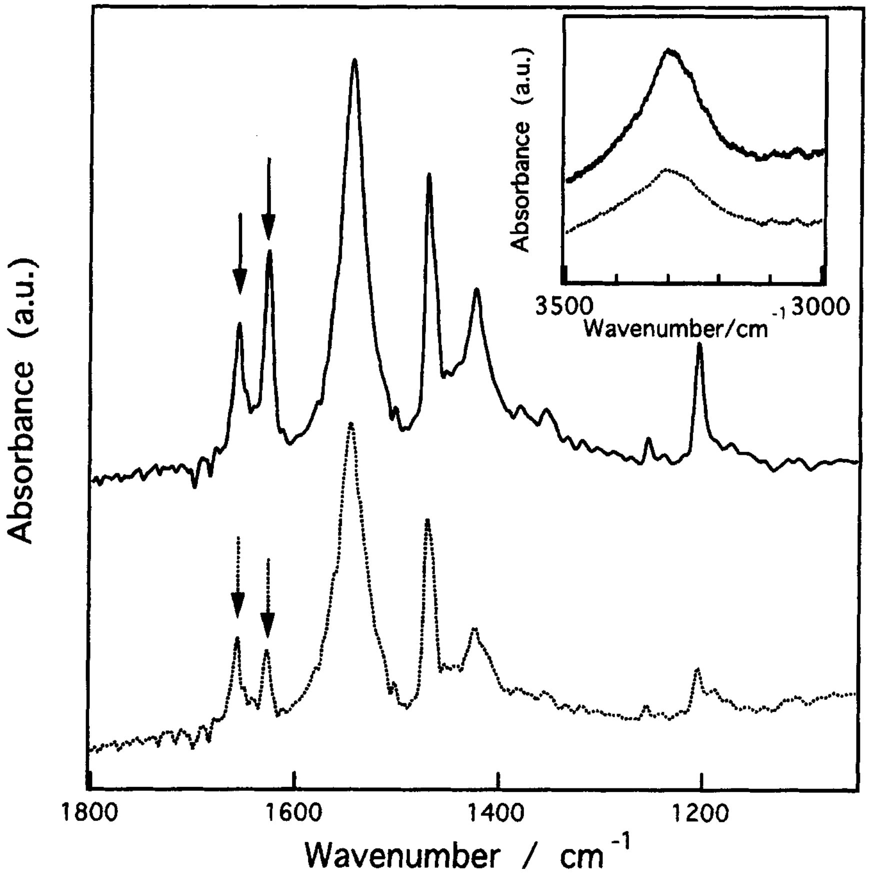


FIGURE 3. IR spectra of 16-layer sample of mixed (solid line) and alternate-layer (dotted line) LB films of $C_{18}HQ$ and $C_{18}Q$. The peaks at higher wavenumber region are indicated in the inset. The peaks indicated by arrows are those of C=O stretching band of quinone moiety (see text).

It is reported that there is a strong correlation between the O-O distance forming hydrogen bond and the position of O-H stretching band.[11,14] The O-H stretching band appeared at 3297 cm^{-1} in both LB films as is indicated in the inset of Figure 3. This is almost the same position (3300 cm^{-1}) as that of 2:1 complex of 2,5-dimethyl-1,4-benzoquinone and 2,5-dimethyl-1,4-dihydroxybenzene, in which the O-O distance forming hydrogen bond is 2.818 Å.[15] The same range of O-O distance is expected in both LB films. The two peaks at 1628 and 1657 cm^{-1} indicated by arrows are hydrogen bonded and non-hydrogen bonded C=O stretching band, respectively. The intensity of the former peak is weak in the alternate-layer LB film, indicating that a relatively large amount of free quinones exist in the film. In other words, the interlayer charge transfer is not complete in the alternate-layer LB film. It is most probable that the matrix molecules occupy the neighbouring site in the adjacent layer to prevent the hydrogen bonding between quinone and hydroquinone moiety.

The non-hydrogen bonded C=O moiety is still remaining in the mixed LB film. However, we can not conclude at present that the complex formation is insufficient even in the mixed LB film. One explanation for the 1657 cm^{-1} peak in the mixed LB film is the formation of 2:1 complex as in the case of the dimethyl derivative described above, in which complex the molecules form triads (hydroquinone is sandwiched by two quinone molecules) and two carbonyl groups terminating the triad are not hydrogen bonded.[15]

LB films of $C_{16}C_{17}$DMTTF and C_{18}TCNQ

A closely related mixed LB film using 2-heptadecyl-6,7-dimetyltetrathiafulvalene (C_{17}DMTTF) and 2-hexadecyl-7,7,8,8-tetracyanoquinodimethane (C_{16}TCNQ) is already reported.[16] The relatively homogeneous LB film was obtained with a conductivity value of 0.5 S/cm. The 1:1 mixture of $C_{16}C_{17}$DMTTF and C_{18}TCNQ also gave Y-type LB films with arachidic acid. The aid of the matrix molecules was also needed to fabricate the alternate-layer LB films.

Figure 4 shows the UV-visible spectra for 16-layer LB films on CaF_2 substrate. The spectrum is dominated by the peaks arising from local excitation of TTF and TCNQ moiety in both mixed and alternate-layer LB films. These two absorption spectra showed distinct difference to each other. In shorter wavelength region, two peaks at 310 and 365 nm appeared in the alternate-layer LB films, which are at almost the same positions as that of the neutral $C_{16}C_{17}$DMTTF and the neutral C_{18}TCNQ, respectively, measured separately in the form of LB films of each molecule. These peaks were shifted to 300 and 395 nm, respectively, in the mixed LB films. The most remarkable feature in the spectrum of mixed LB film is the appearance of the new band around 630nm. This band should arise from intramolecular transitions of TTF and TCNQ ion radical moieties, which transitions appear at almost the same position and should overlap in the spectrum in Figure 4.[17,18] In addition, a charge transfer band appeared in IR region (at around 3500 cm^{-1}, not shown) only in the spectrum of mixed LB film. These spectrum features indicate that $C_{16}C_{17}$DMTTF and C_{18}TCNQ form a charge transfer complex in the mixed LB films and that charge transfer in the alternate-layer LB films essentially did not take place.

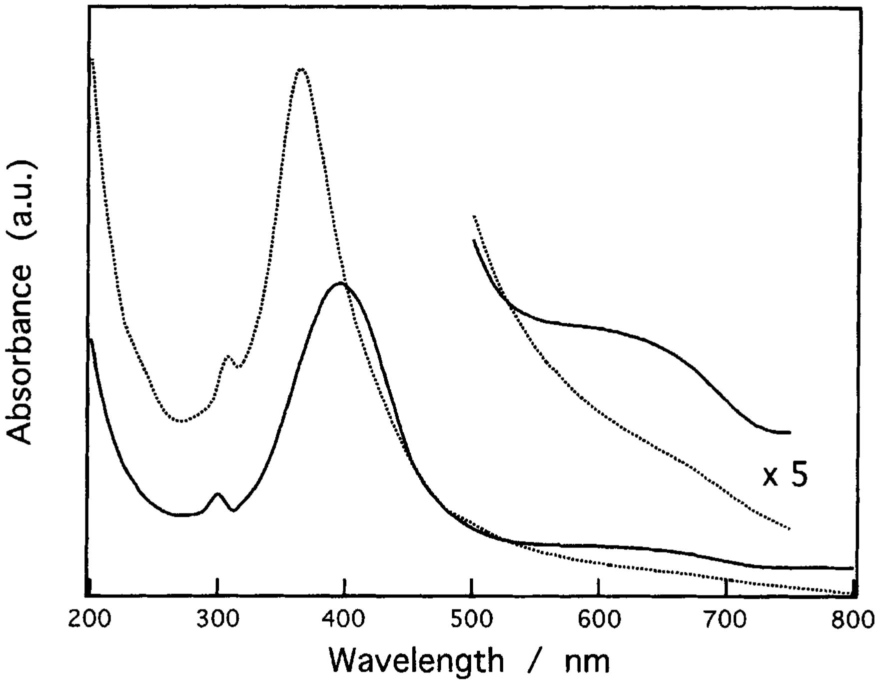


FIGURE 4. UV-visible spectra of 16-layer sample of the mixed (solid line) and alternate-layer (dotted line) LB films of $C_{16}C_{17}$DMTTF and C_{18}TCNQ.

The charge transfer interaction in the LB films was examined from the IR spectra shown in Figure 5. As we used the matrix material, the spectra contains the peaks from arachidic acid which appeared at 1704 and 1471 cm^{-1}. Relatively strong absorption bands were observed at 1571 and around 1300 cm^{-1} only in the spectrum of mixed LB film. These bands should be attributed to the a_g modes of TTF and TCNQ moieties, which become IR active due to the electron-molecular vibration (EMV) coupling.[19] This is the further evidence of the strong charge transfer interactions in the mixed LB films.

The charge transfer ratio can be estimated from the position of CN stretching band.[20] The CN stretching band appeared at 2179 cm^{-1} in the mixed LB film, which is almost the same position as that of C_{10}TCNQ (2-decyl-7,7,8,8-tetracyanoquinodimethane) in the LB film of BEDO-TTF (bisethylenedioxytetrathiafulvalene)-C_{10}TCNQ complex, in which the charge on C_{10}TCNQ transferred from BEDO-TTF is close to unity.[2a] The peak due to the neutral C_{18}TCNQ, which appears at 2222 cm^{-1}, could not be detected (or was very weak depending on sample) in the spectrum. Although the further investigation should be necessary before determining the exact value of the charge transfer ratio, these results strongly suggest the "ionic" state of the complex in the mixed LB films.

The CN stretching band appeared at two different position in the alternate-layer LB film. The peak at 2223 cm^{-1} apparently shows that a significant amount of neutral TCNQ species remain in the LB film. Another CN stretching band was observed at almost the same position as that of the mixed LB film, indicating that a certain amount of charge transfer complexes formed in the alternate-layer LB films. The estimation of the ratio between neutral and charge-transferred TCNQ species in the LB film is difficult because the intensity of CN stretching band of the latter species should be strongly enhanced due to the EMV coupling. The amount of charge transferred TCNQ species in the alternate-layer LB film will be smaller than that expected from the intensity of CN stretching band, which fact should be the reason why the bands attributed to ion radical species as well as the charge transfer band could not be detected in the spectrum of the alternate-layer LB film. However, the peak position of the CN stretching band of charge transferred species indicates that $C_{16}C_{17}$DMTTF and C_{18}TCNQ form an "ionic" complex in the alternate-layer LB film.

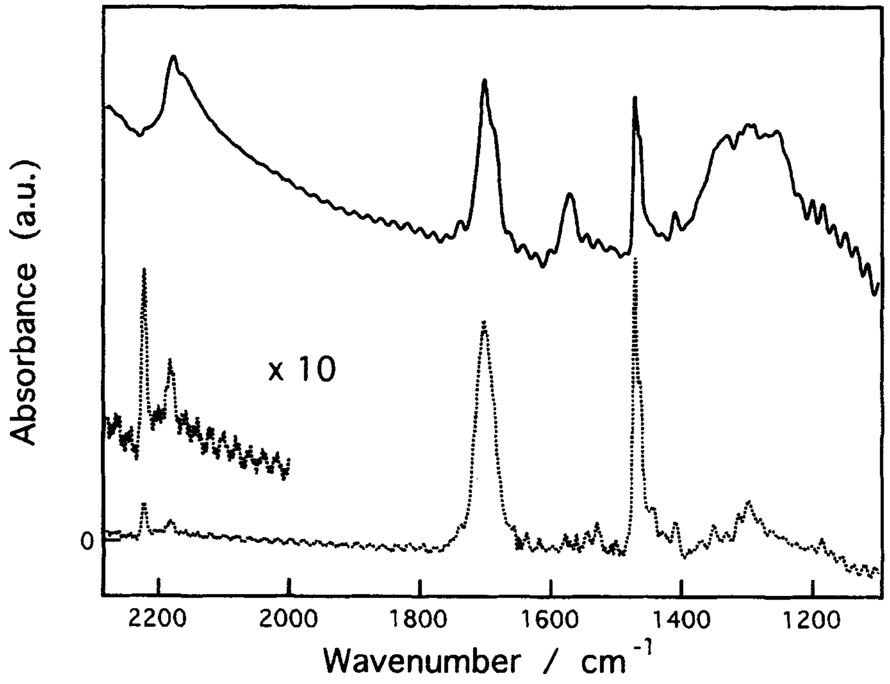


FIGURE 5. IR spectra of 16-layer sample of the mixed (solid line) and the alternate-layer (dotted line) LB films of $C_{16}C_{17}$DMTTF and C_{18}TCNQ.

The origin of the "ionic" complex in the alternate-layer LB film is not clear at present; we can not conclude that the interlayer charge transfer took place in the alternate-layer LB films. It is known that the intermixing between adjacent layers occurs during the film deposition process of the alternate-layers of hydrogenous and duterated n-docosanoic acid.[21] The formation of "ionic" complex *via* intralayer charge transfer may take place in alternate-layer LB film through such intermixing process, although the amount of the charge-transferred species is small as described above.

The inter-layer charge transfer in alternate-layer LB film should be essentially prohibited. The matrix molecule may prevent the interlayer charge transfer between $C_{16}C_{17}$DMTTF and C_{18}TCNQ as in the case of the quinhydrone LB films. However, the charge transfer basically does not occur in the former case even though stronger charge transfer interactions are expected compared to the latter. One explanation is that these strong donor molecules and acceptor molecules tend to form small crystallites in each layer due to the strong intermolecular interactions. Indeed, the formation of small crystallites in the monolayers and the LB films of 2-alkyl-TCNQ derivatives has been already reported.[22] Once such small crystallites formed at the air-water interface and transferred onto a substrate, the interlayer charge transfer should be suppressed because excess energy is needed to destroy the crystal to form a charge transfer complex with molecules at the adjacent layer.

CONCLUSION

We have demonstrated the intermolecular charge transfer phenomena which take place either intra- or interlayer in the LB films. The charge transfer interactions readily occur in the mixed LB films during the film-forming process even though each component molecules were mixed in a solution just before spreading onto a water surface. On the other hand, the formation of small crystallites within a layer due to strong intermolecular interaction may prevent the interlayer charge transfer between the adjacent layer of interleaved LB films. Further molecular engineering technique in supramolecular chemistry should be needed to arrange the molecules favourable for the charge transfer. Relatively high degree of formation of quinhydrone *via* interlayer charge transfer in the C_{18}HQ-C_{18}Q alternate-layer LB films suggests that the intermolecular hydrogen bonding is one of the most promising driving forces for this purpose.

From the application point of view, charge transfer complexes in the interleaved LB films have a noncentrosymmetric structure which is favourable for SHG. The degree of charge transfer is an important factor determining the magnitude of SHG effect, which could be controlled by changing the donor- or acceptor-ability of each molecule forming interleaved LB films. Studies on this line are now in progress.

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