

## Physical characterization of organic-inorganic hybrid charge transfer complexes

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**Abstract** : It was confirmed experimentally that a certain chemical reaction occurs in alkyl TCNQ-CuI mixed Langmuir films prepared on pure-water surfaces. The degree of charge transfer was estimated at  $\sim 1$ . The UV-visible and IR absorption spectra of mixed LB films will be discussed with variation of molar mixing ratios, although no such frequency shift of vibrational modes with different molar mixing ratios were observed. We did not find any significant structural differences among several molar mixing ratios of  $C_{15}$ TCNQ-CuI mixed LB films, except the change in molecular orientation of TCNQ chromophore and alkyl chain part.

**Keywords** : Langmuir-Blodgett, infrared spectra, ultraviolet spectra

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### 1. Introduction

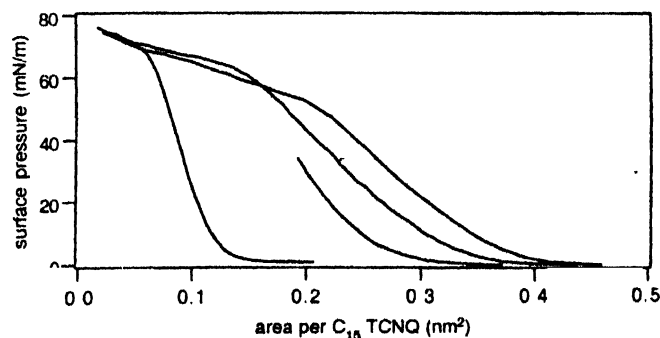
In fabricating organic-inorganic hybrid charge transfer complexes that may have functional electric and magnetic properties depending on their structural and geometrical configurations deposited by Langmuir-Blodgett (LB) technique is a unique method. In earlier occasion, we already reported preparation and physical and structural characterization of Langmuir-Blodgett (LB) films based on pure 2-dodecyl-7, 7, 8, 8-tetracyanoquinodimethane ( $C_{12}$ TCNQ) and 1 : 5  $C_{12}$ TCNQ : CuI mixed film [1] and pure 2-pentadecyl-TCNQ ( $C_{15}$ TCNQ) and 1 : 10  $C_{15}$ TCNQ : CuI mixed film [2,3]. In this work, we are going to report a relative variation of molecular orientation depending on molar mixing ratio of  $C_{15}$ TCNQ : CuI mixed film.

### 2. Experimental

$C_{15}$ TCNQ and CuI were purchased from the Japanese Research Institute for Photosensitizing Dyes, Co. and Wako Pure Chemical Industries, Ltd., respectively, and used without further purification. These materials were mixed with the molar ratio of 1 : 5, 1 : 10 and 1 : 10 for preparing mixed Langmuir (L) and LB films. Other experimental and analysis procedures were the same as those described in the previous report [1-3].

### 3. Results and discussion

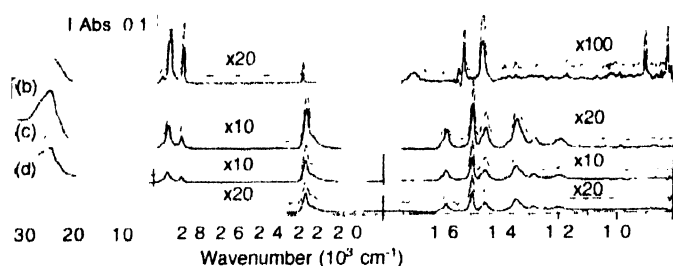
A drastic change of the surface pressure ( $\pi$ )-area (A) isotherms of  $C_{15}$ TCNQ-CuI mixtures were noticed in compare to  $\pi$ -A isotherm of pure  $C_{15}$ TCNQ (Figure 1). Besides, the limiting area increased with the increase of molar mixing ratio (Figure 1) and also increased with the increase of alkyl chain length [2]. In compare to the  $\pi$ -A isotherms and electronic absorption spectra observed for pure and CuI-mixed L films of  $C_{15}$ TCNQ, we can suggest that a definite CT reactions occur at the air-water interface in the mixed case [4,5]. Two distinct absorption bands are identified at  $ca. 25 \times 10^3$  and  $ca. 13 \times 10^3$   $cm^{-1}$  for the mixed films those similar to earlier reports [1-3], while only a band at  $ca. 28 \times 10^3$   $cm^{-1}$  was observed for the pure films. The appearance



**Figure 1.** Surface-pressure area isotherms of pure and CuI-mixed  $C_{15}$ TCNQ. The curves are labeled by the molar mixing ratio.

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of the intra-molecular transition band at  $ca. 13 \times 10^3 \text{ cm}^{-1}$  band due to characteristic absorption of anionic TCNQ [4,5], indicates the presence of TCNQ anions in the mixed L films. The charge transfer band [4,5]  $ca.$  at  $11 \times 10^3 \text{ cm}^{-1}$  were observed in electronic absorption spectra of CuI-mixed  $C_{15}$ TCNQ LB films (Figure 2).



**Figure 2.** Polarized absorption spectra observed for a 10-layered LB film of pure  $C_{15}$ TCNQ and that for a 56-layered LB film of the  $C_{15}$ TCNQ-CuI mixtures. The angle of incidence is  $45^\circ$ . The solid and dotted lines represent the spectra observed with  $p$ - and  $s$ -polarized light, and  $s$ -polarized light, respectively. Curves (a) for pure  $C_{15}$ TCNQ, (b) 1 : 5, (c) 1 : 10 and (d) 1 : 20  $C_{15}$ TCNQ-CuI mixture

The observed magnitudes of the Red shifts, those implied for CT weakens the bond alternation of the  $\pi$ -conjugating system in the TCNQ anion, are 50, 26, 22 and  $98 \text{ cm}^{-1}$ , respectively, for the  $b_{1u}\nu_{20}$  ( $C=C$ ),  $b_{2u}\nu_{34}$  ( $C=C$ ),  $b_{1u}\nu_{19}$  ( $C\equiv N$ ) and  $b_{2u}\nu_{33}$  ( $C\equiv N$ ) modes [4] in all the mixed films studied,  $ca.$  irrespective of molar mixing ratio (Figure 2) and alkyl chain length [1-3]. Those observed shifts in our case in compare to those reported for the alkaline TCNQ salts [6,7] can suggest us about the averaged charge on the TCNQ moiety, *i.e.* the CT degree, in the mixed films can be estimated at  $-1$ .

By denoting the long, short, and normal axes of the TCNQ molecular plane as  $x$ ,  $y$ , and  $z$ , respectively and for the alkyl chain parts, the averaged direction of  $\nu_s(\text{CH}_2)$  and  $\nu_a(\text{CH}_2)$  transition dipoles are respectively denoted by  $u$  and  $v$  [8,9], we will discuss below a relative molecular orientation of TCNQ chromophore and alkyl chain part. In this analysis, the all-*trans* conformation is assumed for the alkyl chains as the lowest-order approximation, *i.e.* the long axis of the chain is assumed to be orthogonal to  $u$  and  $v$ .

The average of the squared direction cosine of  $k$  ( $=x, y, z, u$ , or  $v$ ) with respect to the surface normal of the substrate,  $\langle I_k^2 \rangle$ , can be estimated by applying Chollet model [8,9] to the corresponding vibration modes. The assignments of these modes done in ref. [1] are adopted.

For pure films (Figure 2(a)),  $\langle I_z^2 \rangle$  ( $\psi$ ) was estimated at 0.4 ( $50^\circ$ ) from the anisotropic behavior of the  $833 \text{ cm}^{-1}$  band. From those of the  $908$  ( $b_{2u}$ -like) and  $1530 \text{ cm}^{-1}$  band,  $\langle I_y^2 \rangle$  ( $\phi$ ) was estimated at 0.1 ( $71^\circ$ ). Consequently,  $\langle I_x^2 \rangle$  ( $=1 - \langle I_y^2 \rangle - \langle I_z^2 \rangle$ ) ( $\theta$ ) of those films was estimated at 0.5 ( $45^\circ$ ). These orientation parameters are almost irrespective of  $n$ . On the contrary, longer

alkyl chain tilts more largely:  $\langle I_u^2 \rangle$  ( $\alpha$ )  $\approx 0.03$  ( $80^\circ$ ) and  $\langle I_v^2 \rangle$  ( $\beta$ )  $\approx 0.07$  ( $75^\circ$ ) were obtained for the  $C_{12}$  case, while  $\langle I_u^2 \rangle$   $\approx 0.10$  ( $0.2$ ) and  $\langle I_v^2 \rangle$   $\approx 0.14$  ( $0.2$ ) were obtained for the  $C_{15}$  ( $C_{18}$ ) case.

For the CuI-mixed films of  $C_{15}$ TCNQ (Figure 2(b)-(d)),  $\langle I_z^2 \rangle$  ( $\theta$ ) is estimated at 0.19 ( $64^\circ$ ) for 1 : 5 molar mixing ratio, 0.16 ( $66^\circ$ ) for 1 : 10 molar mixing ratio and 0.25 ( $60^\circ$ ) for 1 : 20 molar mixing ratio from the  $1497 \text{ cm}^{-1}$  band, although the estimations of  $\langle I_x^2 \rangle$  are not so accurate because of the overlapped  $\text{H}_2\text{O}$  and cadmium-arachidate signals, which can be positive and negative. From the  $1284 \text{ cm}^{-1}$  band,  $\langle I_y^2 \rangle$  ( $\phi$ ) is estimated at 0.55 ( $42^\circ$ ) for 1.5 molar mixing ratio, 0.63 ( $38^\circ$ ) for 1:10 molar mixing ratio and 0.66 ( $36^\circ$ ) for 1 : 20 molar mixing ratio. As for the alkyl chains,  $\langle I_u^2 \rangle$  ( $\alpha$ ) and  $\langle I_v^2 \rangle$  ( $\beta$ ) were estimated at 0.38 ( $52^\circ$ ) and 0.40 ( $51^\circ$ ), 0.41 ( $50^\circ$ ) and 0.42 ( $49^\circ$ ), and 0.54 ( $43^\circ$ ) and 0.50 ( $45^\circ$ ) for the 1 : 5, 1 : 10 and 1 : 20  $C_{15}$ TCNQ : CuI cases, respectively. For the all-*trans* alkyl chains, which are rigid rods, the sum of  $\langle I_u^2 \rangle$  and  $\langle I_v^2 \rangle$  should be less than unity. The excess of this sum over unity in the 1 : 20 case may be due to the presence of *gauche* conformation with a considerable rate.

It is observed that an interdigitated bilayer structures can be proposed by taking into the consideration of a simple geometrical model [1,10] using experimentally obtained  $\langle I_k^2 \rangle$  values and the estimated layer thicknesses for both the pure and CuI-mixed LB films for the all molar mixing of  $C_{15}$ -mixed films cases. The film structures of CuI-mixed LB films of different molar mixing ratio of  $C_{15}$ TCNQ proposed by this model are very close to each other, except change in the orientation of TNCQ chromophore and alkyl chain part.

#### 4. Conclusion

Because the changes in  $\langle I_x^2 \rangle$  and  $\langle I_y^2 \rangle$  are small and the presence of the overlapped  $\text{H}_2\text{O}$  and cadmium-arachidate signals may lead to errors in the estimation of these values, we can not imply that the variation of the mixing ratio changes the status of the coordination bonds, because the estimated CT degree of  $-1$  is irrespective to the mixing ratio. The mixing ratio of 1 : 5 seems enough for complete salt formation. For 1 : 10 and 1 : 20 cases, excess CuI must be included in the films, but it may keep its chemical status and may not react with TCNQ, *i.e.*, chemical status of TCNQ may not be changed by the variation of the mixing ratio. In addition, the tilting arrangements of the alkyl chains are changed with the variation of molar mixing ratio those are consistent with the fact that the limiting area increases with the increase of molar mixing.

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