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CONDUCTING LANGMUIR-BLODGETT FILMS OF 1:2 CHARGE TRANSFER COMPLEX, N-DOCOSYLPYRIDINIUM-$(TCNQ)_2$

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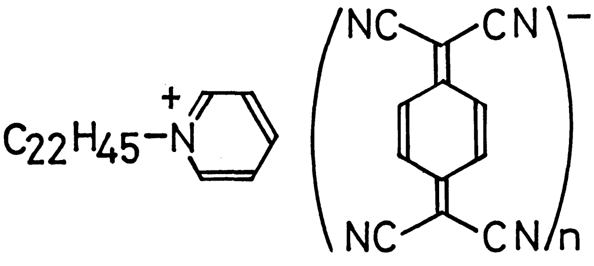
The bulk conductivity, 10^{-2} S cm^{-1}, in the lateral direction of the Langmuir-Blodgett films has been achieved using the amphiphilic 1:2 charge transfer complex, N-docosylpyridinium-$(TCNQ)_2$, without any doping or further treatments. These films are stable for at least two months in air at room temperature.

The Langmuir-Blodgett (LB) method is one of the most powerful tools to obtain a desired arrangement of organic molecules. Especially, the advantage of using this method is the feasibility of realizing close contact of hydrophilic and/or hydrophobic groups. However, there are only a few studies intending to apply this method to charge transfer complexes in order to obtain conducting materials.[1-5]

The LB film of N-docosylpyridinium-TCNQ (**1**) 1:1 charge transfer complex[1] has two types of lateral packing which depends upon the subphase temperature.[2] The conductivity is 3×10^{-5} S cm^{-1} for films prepared at room temperature (290 K), whereas it is 7×10^{-7} S cm^{-1} for those prepared at lower temperatures (276-278 K). With I_2 doping, the film, supposedly prepared at room temperature by Ruaudel-Teixier et al., is converted into a ternary system, N-docosylpyridinium-TCNQ-I_3.[1,3-5] High conductivity is obtained by partial oxidation of $TCNQ^-$ and reorganization of the multilayer structure caused by I_3^-. The conductivity is estimated to be 0.1 S cm^{-1} by neglecting the insulating portion which occupies ca. 90% of the system. The conductivity of the monolayer of a ternary complex on the glycerin subphase is estimated to be 0.5 S cm^{-1} by employing the same calculations.[5]



1 : n = 1
2 : n = 2

Recently we have demonstrated the feasibility of attaining high conductivity without I_2 doping by employing TMTTF-octadecylTCNQ 1:1 charge transfer complex.[6] The alternative method to attain high

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conductivity is to work with 1:2 complex which is also expected to realize partially oxidized state of TCNQ$^-$.$^{7)}$

This paper presents the first example where conducting 1:2 charge transfer complex, N-docosylpyridinium-(TCNQ)$_2$ (**2**), is appropriately organized in the forms of a monolayer on the glycerin subphase and a built-up multilayer on a solid substrate by means of the LB method without I$_2$ doping or further treatments.

1:1 complex **1** was synthesized as previously described.$^{2)}$ 1:2 complex **2** was obtained by mixing **1** and TCNQ in hot acetonitrile. The IR spectrum of **2** (KBr disk) showed a broad band centered at ca. 3200 cm^{-1}, which is assigned to charge transfer transition within the TCNQ column, whereas the spectrum of **1** exhibited the characteristics of an insulator.$^{8)}$ Benzene-acetonitrile (1/1) was used as a spreading solvent. The conductivity-area (σ-A) isotherm on the glycerin subphase was obtained simultaneously with the surface pressure-area (π-A) isotherm at a barrier speed of 8×10^{-4} nm^2 complex^{-1} s^{-1} at 298 K.$^{6)}$ The monolayers of **1** and **2** were deposited as Y type films at 25 mN m^{-1} onto glass slides coated with three monolayers of cadmium eicosanoate from the pure water and the aqueous subphase containing $CdCl_2$ (4.0×10^{-4} mol dm^{-3}) and $KHCO_3$ (5.0×10^{-5} mol dm^{-3}, pH=6.0), respectively,$^{9)}$ at 290 K. The IR spectrum of 32 layered sample of **2** on CaF_2 was almost identical with that of the powder. AC conductivities of LB films were measured using the method of Sugi

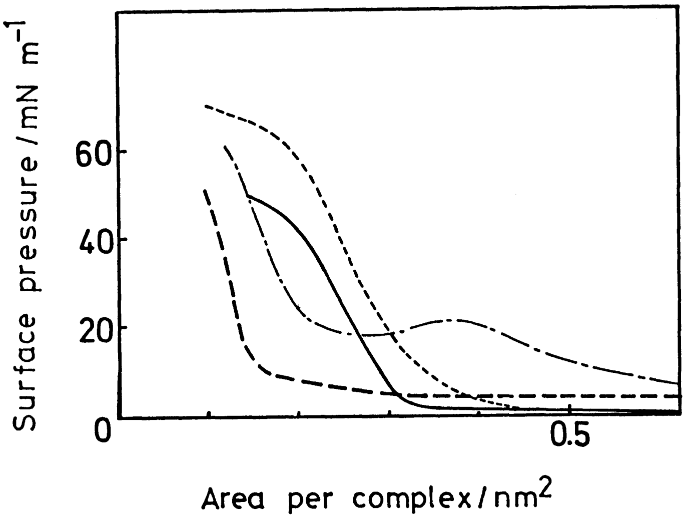

Fig. 1. Surface pressure-area isotherms of 1 and 2;
(— — —): 1 on the glycerin subphase,
(—·—): 1 on the pure water subphase,
(———): 2 on the glycerin subphase,
(······): 2 on the aqueous subphase containing Cd^{2+}.

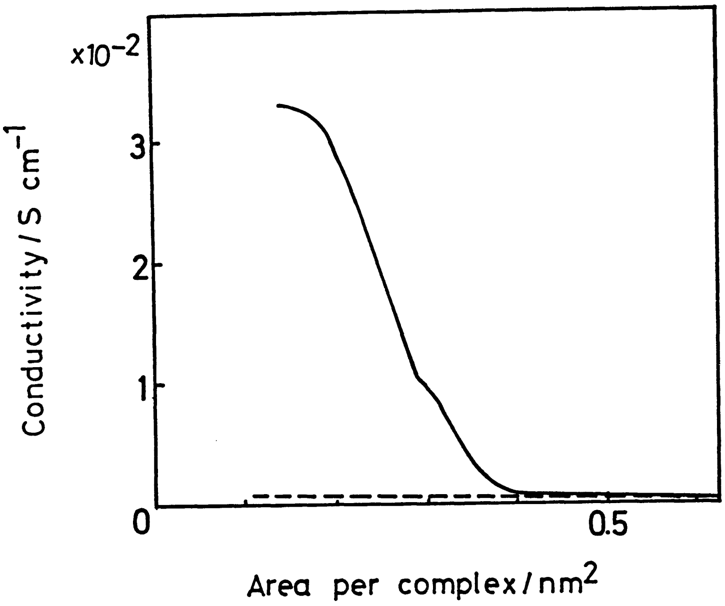

Fig. 2. Conductivity-area isotherms of 1 and 2 on the glycerin subphase; (— — —): 1, (———): 2.

et al.[10)] The gap cell was formed by use of silver paste (Dotite D-550). The bulk conductivities in the lateral direction for 16 and 32 layered samples and those in the normal direction for 3-9 layered samples were obtained by assuming that the thickness of the monolayer of **2** is identical with that of **1** (4.9 nm).[2)]

Figure 1 shows the π-A isotherms of **1** on the glycerin and the pure water subphases, and those of **2** on the glycerin subphase and the aqueous subphase containing Cd^{2+}. Each complex exhibited a smaller limiting area per complex on the glycerin subphase than on the aqueous subphase. This is probably due to the slight miscibility of the complexes with glycerin.[5)] The limiting area of **2** on the aqueous subphase containing Cd^{2+} is almost identical with that on the pure water subphase, which is larger than the limiting area of **1** on the pure water subphase. This fact indicates that the limiting area of **2** is governed by the bulky acceptor of **2**.

The σ-A isotherms of **1** and **2** on the glycerin subphase, which were measured simultaneously with the corresponding π-A isotherms in Fig. 1, are shown in Fig. 2. The conductivity of **1** was below the limit of detection ($< 10^{-3}$ S cm^{-1}). However, the bulk conductivity of **2** increased with a decrease in area per complex, and reached the maximum value of ca. 3×10^{-2} S cm^{-1}. The area per complex where a significant value of the conductivity is observed (ca. 0.4 nm^2) is larger than that where surface pressure begins to rise (ca. 0.3 nm^2). This suggests that the conductivity measurement is, in some cases, more sensitive to the lateral arrangement of molecules than the surface pressure measurement.

The bulk conductivities of the compaction samples, the monolayers on the glycerin subphase, and the built-up multilayers are summarized in Table 1. The segregated columnar structure with partially oxidized state of $TCNQ^-$ present in **2** is reflected in the fact that the conductivities of **2** are higher than those of **1** by several orders except for the conductivity in the normal direction of the LB film. Moreover, conductivities in the lateral direction of the monolayer on the glycerin subphase and the LB film of **2** are higher than that of the compaction sample as is the case with **1**.[2)] This proves that the monolayers at gas-liquid interfaces and the trasfer of them onto solid substrates are useful for assembling the segregated column of TCNQ extensively in the planes parallel to the film surface.

The bulk conductivities in the lateral direction of **2** in the forms of the monolayer on the glycerin subphase and the LB film are almost the same. This

Table 1. Bulk conductivities in the three systems[a)]

	Compaction	Monolayer on the glycerin subphase[b)]	LB film //[b)]	 ⊥[c)]
1	6.1×10^{-10}	—— d)	3×10^{-5}	$\approx 10^{-14}$
2	2.4×10^{-6}	2×10^{-2} e)	1×10^{-2}	$\approx 10^{-13}$

a) S cm^{-1}. b) Conductivity in the lateral direction.
c) Conductivity in the normal direction.
d) Below the limit of detection. e) At 25 mN m^{-1}.

strongly suggests that the lateral stacking of conducting portion in the LB film deposited from the aqueous subphase containing Cd^{2+} is identifiable with that on the glycerin subphase, although the water and the glycerin are quite different in many aspects, for example, affinity to hydrophilic portion, viscosity, and surface tension.

The net conductivity of the LB film of **2** in the lateral direction is estimated to be ca. 0.1 S cm^{-1} according to the calculation employed by Barraud et al.[4] This is comparable with the value of I_2-doped 1:1 complex.[1,4] The film is stable for at least two months at room temperature in air probably due to the absence of any volatile component.

Quite low conductivities of the LB films in the normal direction are originated from the insulating portions, each separating the adjacent conducting planes.

The application of the LB method to a charge transfer complex, N-docosylpyridinium-$(TCNQ)_2$, has enabled us to obtain stable thin films of high conductivity without any doping. The results obtained strongly suggest the utility of the LB method in constructing the molecular assemblies with metallic conductivity and other aimed functions.

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