CHEMISTRY LETTERS, pp. 323-324, 1986.

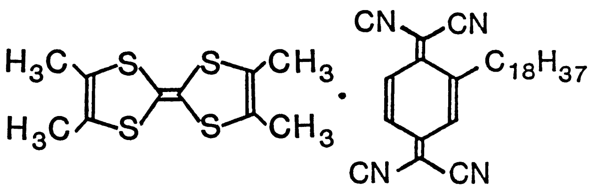
CONDUCTING MONOLAYER OF SIMPLE CHARGE TRANSFER COMPLEX ON A GLYCERIN SUBPHASE

Takayoshi NAKAMURA,* Fumio TAKEI,[††] Motoo TANAKA, Mutsuyoshi MATSUMOTO, Tatsuo SEKIGUCHI, Eiichiro MANDA, Yasujiro KAWABATA, and Gunzi SAITO[†]
National Chemical Laboratory for Industry, Yatabe, Ibaraki 305
[†]The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

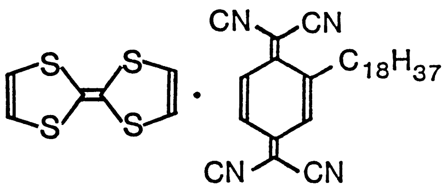
The amphiphilic simple charge transfer complexes, TMTTF-octadecylTCNQ (**1**) and TTF-octadecylTCNQ, were synthesized. The conductivities of the monolayers were measured on a glycerin subphase. The complex **1** showed the conductivity of the order of 1 S cm^{-1}, the highest value reported so far for the organic monolayer system.

The Langmuir-Blodgett (LB) film of a charge transfer complex has received increasing attention as a thin conducting membrane with highly anisotropic layered structure. Recently, the conducting LB film of N-docosylpyridinium-TCNQ doped with iodine has been reported by Ruaudel-Teixier et al.[1)] By changing the subphase from water to glycerin, the conductivity of as high as 0.5 S cm^{-1} was obtained for the monolayer of the analogous iodine doped complex.[2)] We wish to report herein the conductivities of monolayers of the amphiphilic simple charge transfer complexes **1** and **2** on a glycerin subphase.

The synthesis of octadecyl-TCNQ (**3**) was achieved by the Birch reduction (Na/NH_3-THF) of 1,4-dimethoxy-2-octadecylbenzene, followed by Knoevenagel condensation ($CH_2(CN)_2$, $AcONH_4$/AcOH-PhH) and oxidation (Br_2, $Et_3N/CHCl_3$), according to the method of Dieckmann et al.[3)] The complex of TTF or TMTTF with **3** was prepared in a hot benzene-hexane solution. Both of these complexes exhibited a broad band centered at 2000 - 3000 cm^{-1} in IR spectra (KBr disk), which is attributed to charge transfer transition within the segregated columns. The conductivities of compaction samples for **1** and **2** were 1.2×10^{-2} and 2.3×10^{-3} S cm^{-1}, respectively. Each complex dissolved in a benzene-acetonitrile(1:9) solution was spread onto a glycerin subphase. The surface pressure-area (π-A) and



1



2

[††]On leave of absence from Fujitsu Laboratory Ltd., Atsugi-shi, Kanagawa 243-01.

and conductivity-area (σ-A) isotherms were measured at a barrier speed 8×10^{-4} nm^2 $molecule^{-1}$ s^{-1}. The conductivity of the monolayer on a glycerin subphase was measured as follows. A couple of planar platinum electrodes (width: 2 cm, gap distance: 1 cm) was immersed into just below the surface of the glycerin subphase. AC voltage (f = 1 kHz, V = 10 V) was applied between the two electrodes, and the resultant inphase current was measured using lock-in amplifier.

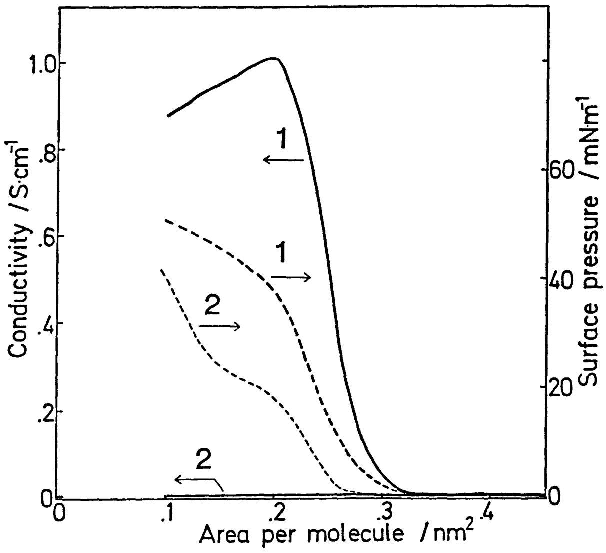


Fig. 1. σ-A and π-A isotherms of charge transfer complexes 1 and 2 on a glycerin subphase at 25 °C.

The results are shown in Fig. 1. Quite low conductivities (less than 10^{-3} S cm^{-1}) of **2** suggest an unfavorable orientation of the donor and the acceptor or some decomposition of the complex during or before the measurements. These problems were solved by employing, instead of TTF, its tetramethyl derivative. In case of **1**, the conductivity of the film up to 1 S cm^{-1} was attained, assuming the thickness of the monolayer 4 nm. This conductivity is the highest value as far as we are aware for the monolayer system. The conductivities of this monolayer higher than that of a compaction sample, in spite of the presence of the insulating long alkyl chain, result from the ordered structure of the film with close segregated stacking of the charge transfer complex. In addition, the σ-A isotherm showed the similar pattern with the corresponding π-A isotherm. This macroscopic relationship between the mechanical and the electrical properties is qualitatively explained from the microscopic ordering of molecules induced by the mechanical compression, which presumably results in the columnar structure of the charge transfer complex.

The highly conductive monolayer such as **1** on glycerin will provide a simple model of organic conductor in two-dimensional molecular assembly. The studies on monolayers of **1** at air-water interface and on multilayers are in progress.

We are grateful to Drs. T. Ishiguro, M. Saito, M. Sugi, and S. Iizima, Electrotechnical Laboratory, for informative comments and helpful discussion. We also acknowledge Prof. K. Fukuda and Dr. H. Nakahara, Saitama University, for valuable comments.

References

1) A. Ruaudel-Teixier, M. Vandevyver, and A. Barraud, Mol. Cryst. Liq. Cryst., 120, 319 (1985).
2) A. Barraud and P. Lesieur, 2nd International Conference on Langmuir-Blodgett films (Schenectady, New York, 1985), A-14; A. Barraud and P. Leisieur, Thin Solid Films, in press.
3) J. Diekmann, W. R. Hertler, and R. E. Benson, J. Org. Chem., 28, 2719 (1963).

(Received December 10, 1985)