Electroabsorption of Amphiphilic Tetrathiafulvalene Derivatives / 7,7,8,8-Tetracyano-2,3,5,6-tetrafluoroquinodimethane Systems in Langmuir-Blodgett Films

Tohru Nakamura,* Reiko Azumi, Hiroaki Tachibana, and Mutsuyoshi Matsumoto
Department of Molecular Engineering, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305

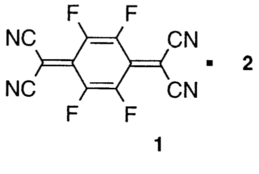
(Received November 9, 1995)

External electric field effects on the electronic structures of charge transfer salts were examined for the first time in Langmuir-Blodgett films. Significant electroabsorption signals arising primarily from the first Stark effect were obtained for the films of amphiphilic tetrathiafulvalene derivatives / 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane 1 : 1 salts.

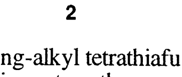
Organic charge transfer (CT) complexes have been receiving considerable attention from the viewpoint of elucidating the physical processes involved in CT reaction as well as applying CT complexes to electroactive and photoactive materials.[1] It is well known that tetrathiafulvalene (TTF) / chloranil system undergoes a neutral-ionic transition under appropriate conditions.[2] At lower temperatures, the compound is in an ionic state (degree of charge transfer ρ is more than 0.5), while above the critical temperature the compound is in a neutral state ($\rho < 0.5$). The materials of this kind, if the transition is controlled by other external stimuli such as electric and magnetic field, are promising as switching elements.

Electroabsorption of organic compounds has been investigated in many areas.[3] This spectroscopy detects the change in absorption spectrum when external electric field is applied. In other words, this technique can monitor the change in electronic structure of CT compounds caused by the change in ρ. To facilitate the measurements of electroabsorption spectra, the molecules should be arranged in an ordered manner, which can be realized using the Langmuir-Blodgett (LB) technique. Actually, electroabsorption spectroscopy has been used to study the electronic properties and the orientation of chromophores in the LB films.[4] In particular, external electric field effects on photo-induced electron transfer process from cyanine dyes to viologens have recently been observed.[5]

In this paper, we will report for the first time on the external electric field effects on the electronic state of CT salts based on TTF and 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives in LB films.



1



2

1 or 2	R^1	R^2
a	$C_{16}H_{33}$	H
b	$C_{16}H_{33}$	S $C_{16}H_{33}$

Long-alkyl tetrathiafulvalene derivatives **2a**, **b** were prepared according to the reported procedures and with slight modifications.[6] The developed reaction of lithium TTF with *p*-toluenesulfonic acid cetyl thioester gave the desired TTF derivatives **2a** with monoalkyl chain in good to moderate yields in a one-pot way.

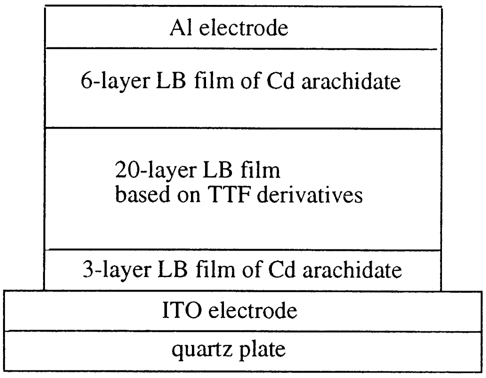


Figure 1. Fabrication of the samples.

Next, tetrathiafulvalene derivatives **2a**, **b** obtained were mixed with quinoid such as TCNQ or 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (F_4TCNQ). In the case of F_4TCNQ, the corresponding 1 : 1 salts **1** were formed as deep blue green crystals in organic solvents such as dichloromethane and chloroform. The ratio of TTF **2** and F_4TCNQ in the salts was confirmed by elemental analyses.[7] In the case of TCNQ, however, the complexation with TTF **2** did not occur at ambient condition.[8]

The fabrication of the samples studied is shown in Figure 1. The neutral TTF **2b** or CT salts **1a**, **b** were deposited as 20-layer LB films at 15 - 16 mN/m on indium thin oxide (ITO) electrodes by using a horizontal lifting method. For the TTF **2** / TCNQ systems, equimixtures of component solutions were used as spreading solutions. The LB films of cadmium arachidate were used as insulating barriers at the top and bottom of the active layers. After transfer of the LB films, aluminium semitransparent (Al) film was vacuum-evaporated to form upper electrodes. Resistances over a few mega ohm were observed between the ITO and Al electrodes for all samples.

Absorption spectra of the samples were obtained using a JASCO HSSP-1 spectrophotometer. The absorption maximum of TTF **2b** in the LB films is positioned at 320 nm (31300 cm^{-1}) and those of the CT salts at around 390 and 680 nm (25600 and 14700 cm^{-1}), which can be assigned to superpositions of the local excitations of anionic F_4TCNQ[9] and cationic TTF[10] (Figure 2 (a)). The electroabsorption of the samples was measured at 1f and 2f modes.[11] Changes in optical absorption resulting from the application of electric field were detected using a lock-in technique. No significant electroabsorption was observed for the samples without active layers.

Significant 1f electroabsorption was observed in the LB film of CT salt **1a** as shown in Figure 2 (b). Similar results were obtained for **1b**. These signals are considered to primarily arise from the electronic structures of CT salts **1** since the signals for

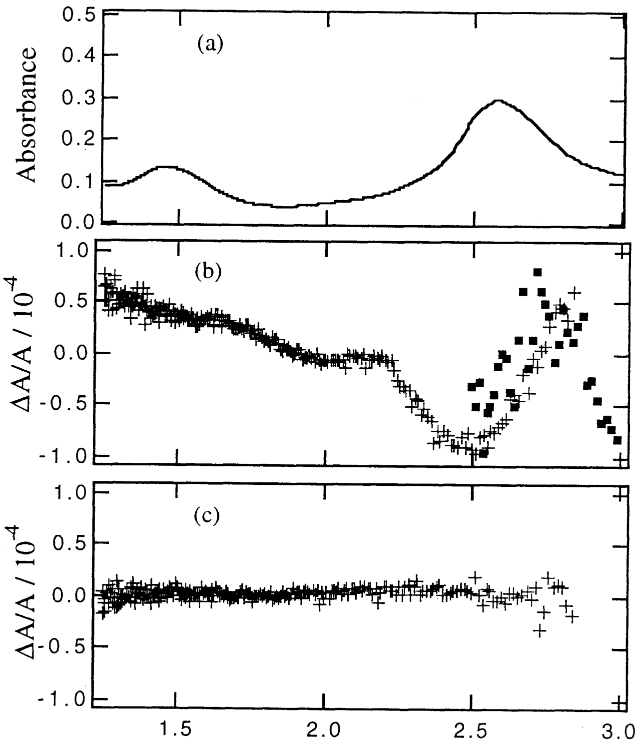


Figure 2. Electroabsorption of CT salt **1a**; (a) absorption spectrum, (b) 1f electroabsorption spectrum at 10^6 V/cm, (c) 2f electroabsorption spectrum at 10^6 V/cm (+ : using a tungsten lamp, ■ : using a deuterium lamp).

the LB films of neutral TTF **2b** were very weak.

The signals in the 1f electroabsorption spectra are mainly due to the first Stark effect. This is confirmed by the following observations: (1) when the direction of the applied electric field was reversed, the sign of the absorption intensity, ΔA/A, changed, (2) the signal intensities were directly proportional to the applied electric field, (3) 2f electroabsorption intensities of the CT salts **1** were very weak as shown in Figure 2 (c), and (4) the spectral shape of 1f electroabsorption is qualitatively the same with that of the differential absorption spectrum. These results indicate that the electric dipole moments originating from the donor-acceptor arrangements of CT salts **1** have fixed directions with respect to the normal of the LB films. This is in a sense understandable since the LB films were transferred by the horizontal lifting method which gives polar structures if reorganization of the LB film structures does not take place. We do not claim that the film structure should be preserved during the film transfer. What we suggest is that the LB films transferred by the horizontal lifting method have chances of remaining polar structures, though perturbed when a kind of reorganization occurs. The overall picture would be that ρ in CT salts **1** in the LB films are perturbed by the applied electric field.

The signals of 1f electroabsorption spectra of the LB films of TTF **2** / TCNQ systems were much smaller than those of the CT salts **1**. Taking into account that the TTF **2** / TCNQ systems have lower values of ρ which is assumed by the fact that no complexation reaction occurred in solutions, the results suggest that the significant signal intensities of 1f electroabsorption spectra of the LB films of **1** are due to higher values of ρ as well as the fixed preferential direction of the electric dipole moment. We are currently investigating the mechanism involved in the electroabsorption in the LB films of TTF derivatives/TCNQ derivatives systems.

We are indebted to Prof. Y. Tokura of The University of Tokyo and Dr. R. Katoh of our institue for stimulating discussions on the electric field effects.

References and Notes

1 *"Semiconductors and Semimetals,"* ed by E. Conwell, Academic Press, INC., Boston (1988), Vol. 27; *"Extended Linear Chain Compounds,"* ed by J. S. Miller, Plenum, New York (1983).

2 Y. Tokura, T. Koda, G. Saito, and T. Mitani, *J. Phys. Soc. Jpn.*, **53**, 4445 (1984).

3 For example; N. Ohta, S. Okazaki, and I. Yamazaki, *Chem. Phys. Lett.*, **229**, 394 (1994); W. Stampor, J. Kalinowski, and P. Di Marco, *Chem. Phys.*, **134**, 385 (1989).

4 S. Nishikawa, Y. Tokura, T. Koda, and K. Iriyama, *Jpn. J. Appl. Phys.*, **25**, L701 (1986); L. M. Blinov, N. V. Dubinin, L. V. Mikhnev, and S. G. Yudin, *Thin Solid Films*, **120**, 161 (1984); H. Bücher and H. Kuhn, *Z. Naturforsch.*, **25b**, 1323 (1970); H. Bücher, J. Wiegand, B. B. Snavely, K. H. Beck, and H. Kuhn, *Chem. Phys. Lett.*, **3**, 508 (1969).

5 N. Ohta, S. Okazaki, T. Itoh, and I. Yamazaki presented at Symposium on Photochemistry, Fukuoka (1995), Abstr., I A311.

6 N. Svenstrup and J. Becher, *Synthesis*, **1995**, 215; M. R. Bryce, G. J. Marshallsay, and A. J. Moore, *J. Org. Chem.*, **57**, 4859 (1992); D. C. Green, *J. Org. Chem.*, **44**, 1476 (1979); M. Narita and C. U. Pittman, Jr., *Synthesis*, **1976**, 489.

7 **1a**: Anal. Found: C, 55.23; H, 4.56; N, 7.62%. Calcd for $C_{34}H_{36}F_4N_4S_5$ (737.010): C, 55.41; H, 4.92; N, 7.60%. **1b**: Anal. Found: C, 60.23; H, 6.43; N, 5.48%. Calcd for $C_{50}H_{68}F_4N_4S_6$ (993.506): C, 60.45; H, 6.90; N, 5.64%.

8 The adjacent sulfur of TTF would decrease donor ability. For the electrochemical half-wave potentials on complexation between TTF and TCNQ derivatives, see: G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, **53**, 2141 (1980).

9 Absorption bands of TCNQ anion were reported. For the metal TCNQ such as AgTCNQ or CuTCNQ, see: T. O. Poehler, R. S. Potember, R. Hoffman, and R. C. Benson, *Mol. Cryst. Liq. Cryst.* **107**, 91 (1984). For the *N*-alkylquinolium TCNQ complexes, see: *Chem. Abs.* **117**, 258813e (1992), D. M. Shin, B. C. Shon, K. H. Choi, J. S. Kim, and D. Y. Kang, *Chongi Hakhoe Nonmunchi*, **41**, 753 (1992).

10 For the absorption bands of TTF cations, see: J. B. Torrance, A. B. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, *Phys. Rev. B*, **19**, 730 (1979).

11 At 1f mode, the in-phase signals are detected at the same frequency with that of the applied electric field, and at 2f mode the signals are monitored at twice the frequency of the applied electric field.