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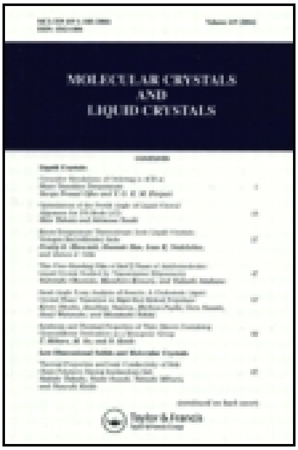

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Mono- and Multilayers of Novel Molecular Complex of Thiophene Derivative with Long-Chain TCNQ

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MONO- AND MULTILAYERS OF NOVEL MOLECULAR COMPLEX OF THIOPHENE DERIVATIVE WITH LONG-CHAIN TCNQ

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Abstract Electronic structures of the 2,5-dihydrothiophene derivatives were characterized by UPS spectra together with crystallographic analysis. A novel complex between the thiophene derivative and C_{18}TCNQ was obtained and the multilayer of the complex was prepared. Electrical conductivities with respect to the parallel and perpendicular direction to the film plane have been studied to the film structures.

INTRODUCTION

In a series of researches on functional molecules containing chalcogens and on their molecular organized thin films, previously electronic structures of oligothiophenes with 3 – 8 thiophene rings were revealed by ultraviolet photoelectron spectroscopy (UPS) together with the calculated geometrical optimization,[1] and the rod-like oligothiophenes were found to be well incorporated in the mixed monolayers with fatty acids.[2] Recently, 2,5-bis(diarylmethylene)-2,5-dihydro-thiophene, furan, selenophene and N-methylpyrole analogues were synthesized by Ishii et al.[3] On the other hand, one of them, 2,5-bis(di-2-thienylmethylene)-2,5-dihydrothiophene was also obtained by G.Hieber et al.[4] The 2,5-dimethylene-2,5-dihydrothiophene derivatives have been attractive materials for the amphoteric properties of electron donating and accepting in dependence on the substituents at the exocyclic double bonds. In this work, effects of the substituted aryl-groups on the electronic structures of the 2,5-dihydrothiophene and selenophene derivatives (Fig.1) have been investi-

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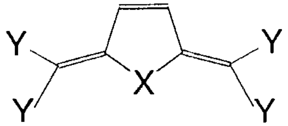
gated by UPS spectra of the vacuum-deposited films together with crystallographic analysis of the single crystals. Furthermore, complex formation between 2,5-bis(diarylmethylene)-2,5-dihydrothiophenes and octadecyl tetracyanoquinodimethane (C_{18}TCNQ) has been examined by UV-visible and NMR spectra, and the multilayer of the complex was prepared. Electrical conductivities with respect to the parallel and perpendicular directions to the film plane have been studied in relation to the film structures.

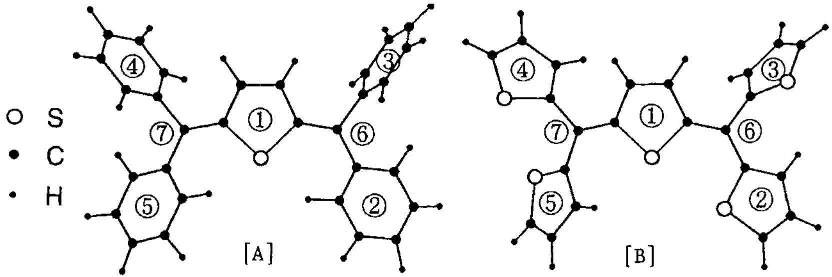


[1] X = S, Y = phenyl
[2] X = S, Y = thienyl
[3] X = Se, Y = phenyl
[4] X = Se, Y = thienyl

Fig.1. 2,5-Dihydro-thiophene and selenophene derivatives.

RESULTS AND DISCUSSION

Crystal structures of the 2,5-dihydrothiophene derivatives were analyzed using a Enraf Nonius diffractometer with Mo-K_{α} radiation. Details of the crystal data shall be reported elsewhere.[5] Figure 2 shows the skeleton structures of 2,5-bis(diphenylmethylene)- [1] and 2,5-bis-(dithienylmethylene)-2,5-dihydrothiophenes [2] projected in the a-c plane and the b-c plane respectively. And also the dihedral angles between the central thiophene ring and the substituted phenyl or thienyl rings together with the relative electron density of each HOMO are indicated. In both cases, the substituted aryl-groups are twisted largely out of the plane of the ring ① in the order of the rings ②, ⑤, ④ and ③. The electron density is scarcely found in the ring ③ with the largest



	[A] ①	[A] ②	[A] ③	[A] ④	[A] ⑤	[A] ⑥	[A] ⑦	[B] ①	[B] ②	[B] ③	[B] ④	[B] ⑤	[B] ⑥	[B] ⑦
Dihedral angle (°)	-	26.1	75.2	56.1	38.4	-	-	-	14.6	68.7	48.8	40.2	-	-
Electron density (%)	43	12	1	4	11	15	15	37	15	3	5	16	12	12

Fig.2. Skeleton structures of [A] 2,5-bis(diphenylmethylene)- and [B] 2,5-bis(dithienylmethylene)-2,5-dihydrothiophenes, and the dihedral angles between the central and the substituted rings together with the relative electron density.

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angle of the twisting. In comparison with the substituted thienyl groups, the phenyl groups with larger steric hinderance have greater torsion and less electron density except for the ring ⑤. Therefore, the electron is localized in the central thiophene ring substituted with the phenyl groups rather than that with the thienyl groups. This fact seems to reflect on the electronic spectra of the solution, in which the absorption maximum is a shorter wavelength of 414 nm for the former in comparison with 472 nm for the latter.

The UPS measurements were carried out using an angle-resolving photoelectron spectrometer combined with a plane-grating monochrometer at the beam line BL8L2 of a UVSOR storage ring at the Institute for Molecular Science. Sample films of 30 → 50 nm thickness were prepared on a polished molybdenum substrate by in situ vacuum deposition. Photoelectron spectra were measured for electrons emitted normal to the sample surface (θ = 0°) with an incident angle α = 50° of the light beam (hν = 45 eV).

Figure 3 shows the UPS spectra of 2,5-bis(diphenylmethylene)-2,5-dihydrothiophene [1] and dihydroselenophene [3], as compared with that

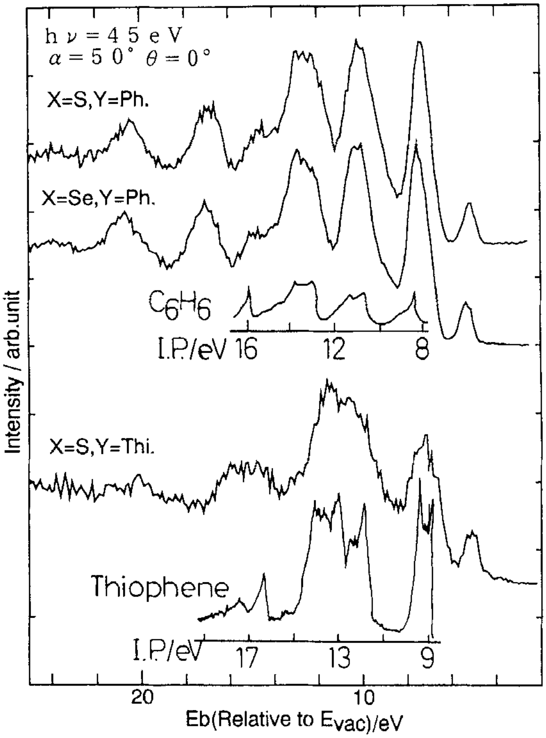

Fig.3. UPS spectra of 2,5-bis(diphenylmethylene)-dihydrothiophene [1], dihydroselenophene [3] and 2,5-bis(dithienylmethylene)-2,5-dihydrothiophene [2], as compared with those of benzene and thiophene.

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of 2,5-bis(dithienylmethylene)-2,5-dihydrothiophene [2], together with the spectra of benzene and thiophene for references. Irrespective of the central ring with sulphur or selenium the UPS spectra are found to be almost same. However, the spectra are significantly different with changing the substituent rings at the exocyclic double bonds from the phenyl to the thienyl groups. In both the phenyl and the thienyl substituents, the spectra are very similar to those of benzene and thiophene respectively, except for the bands at the lowest binding energies.

Furthermore, these observed UPS spectra were compared with the calculated ones which were simulated by broadening the delta function located at the MNDO orbital energies with each Gaussian function. The simulated spectra were well correspondence to the observed ones. The band at the lowest binding energy could be mainly ascribed to the electronic structures of the central dihydrothiophene ① with the double bonds ⑥ and ⑦, and the bands in the ranges of 6 — 16 eV and 20 — 22 eV were considered to be due to those of the phenyl substituents ②, ③, ④ and ⑤. And it was found that the electronic structures of dihydrothiophene substituted with thienyl groups were more delocalized around the HOMO in comparison with that having phenyl groups. Detail discussion on the UPS spectra of the dihydrothiophene and selenophene derivatives shall be reported elsewhere.[6]

From preliminary measurements of cyclic volyammograms for 2,5-bis (dithienylmethylene)-2,5-dihydrothiophene [2] and -dihydroselenophene [4], 2,5-bis(diphenylmethylene)-2,5-dihydrothiophene [1], C_{18}TCNQ in acetonitrile solutions, the oxidation and reduction potentials were obtained to be +0.21, +0.28, +0.39 and -0.23 V respectively, from the potential of the ferrocene/ferrocenium (Fc/Fc$^+$) as a standard. These potentials seem to reflect the electronic structures deduced from the UPS measurements. From these values it is considered that the dihydrothiophene substituted with thienyl groups is more favorable for the donor to the acceptor of C_{18}TCNQ rather than the other dihydro-thiophene and selenophene.

By refluxing the acetonitrile or ethanol solution of the dihydrothiophene [2] and C_{18}TCNQ (1 : 1 — 1 : 2 in the molar ratio) for six hours and cooling the solution at a room temperature, the molecular complex was precipitated as black crystals.

Figure 4 shows the electronic absorption spectrum of the complex in acetonitrile solution, as compared with those of the dihydrothiophene [2]

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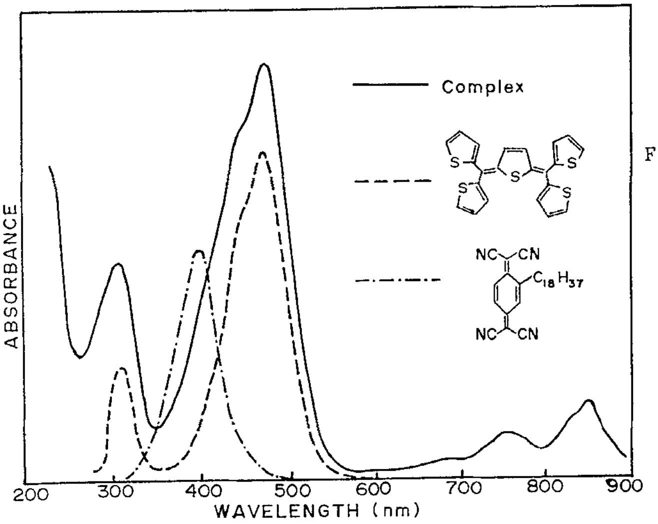

Fig.4. Electronic absorption spectrum of the dihydrothiophene [2] : C_{18}TCNQ complex in CH_3CN solution as compared with that of each constituent molecule.

and C_{18}TCNQ solutions. The complex formation has been confirmed by appearance of the 743 nm and 847 nm bands due to the TCNQ radical anion accompanied with a significant decrease in absorbance of the 395 nm band ascribed to the neutral TCNQ, though the 473 nm band for the dihydrothiophene [2] is retained. In the ^{1}H-NMR spectrum of the complex in the CD_3CN solution, the signals of 14-H due to the dihydrothiophene at the lower magnetic field, 6-H due to the radical anion and neutral TCNQ moieties at 2.5 — 6.0 ppm, and 74-H due to the hydrocarbons at the higher field below 1.5 ppm were observed. From these spectra, it has been found that the complex is constituted of the dihydrothiophene cation and both the radical anion and neutral C_{18}TCNQ (the dihydrothiophene : C_{18}TCNQ = 1 : 2 in the molar ratio).

The monolayer of the complex was spread from the mixed solvent of ethanol and hexane in a volume ratio of 4 : 1 onto the distilled water or the aqueous subphase containing 10^{-5} M LiTCNQ. Surface pressure (π) — area (A) isotherms were measured with a Lauda film balance at 15 °C. As shown in Fig.5, the π — A isotherm of the complex differs clearly from that of C_{18}TCNQ alone or a simple mixture of C_{18}TCNQ and the dihydrothiophene. The complex gives a typical condensed monolayer on the distilled water with the limiting area of about 60 $Å^2$/molecule. On the other hand, when the monolayer of the complex is spread on the aqueous subphase containing LiTCNQ (10^{-5}M), it exhibits an expanded region in

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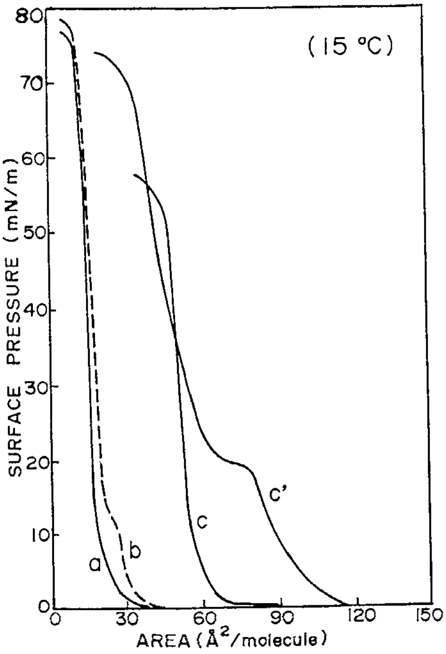

Fig.5. Surface pressure — area isotherms for monolayers of C_{18}TCNQ (a), the mixture of the dihydrothiophene [2] and C_{18}TCNQ (b), and the complex (c), spread on distilled water, as compared with that on the aqueous subphase with 10^{-5}M LiTCNQ (c').

the range of 70 – 110 Å^2 molecule, probably because of incorporation of TCNQ anion from the subphase, which is squeezed out on compression above 20 mN/m and the stable condensed film of the complex is formed with higher collapse pressure.

These monolayers of the complex can be transferred onto solid plates at 30 mN/m by the horizontal lifting method,[7] but the conventional Langmuir-Blodgett method was unsuitable because of the rigidity of the complex monolayer. From observation with a fluorescence microscopy for the deposited films on quartz plates, it has been found that the more homogeneous film of the complex can be obtained from the spread monolayer on the aqueous LiTCNQ subphase in comparison with that on the distilled water.

In Fig.6, the film thickness measured by an optical interference method is plotted against the number of the layers, from which the value of 49 Å per layer was obtained. This is considered to be reasonable for the molecular length of a pair of C_{18}TCNQ (32 Å) anchored on the dihydrothiophene molecule (16 Å), as shown in schematically in the insert of Fig.6. This molecular arrangement corresponds approximately to the area obtained by the π – A isotherm.

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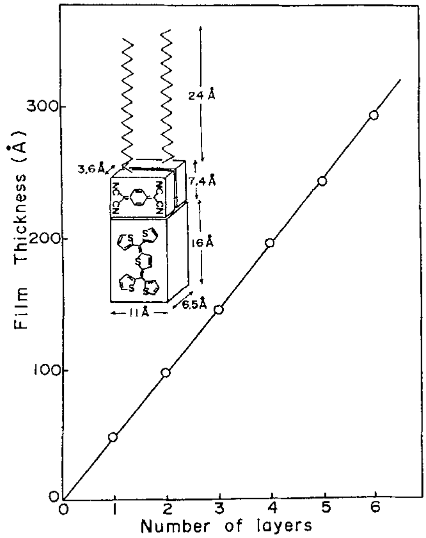
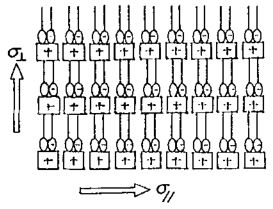


Fig.6. Film thickness of the complex multilayer plotted against the number of layers, together with the speculated complex structure in the film (in the insert).

Table 1. Anisotropic conductivities for the multilayer of the complex between the dihydrothiophene [2] and C_{18}TCNQ.



Conductivity σ (S cm^{-1})		Subphase
σ⊥	1.0 x 10^{-14}	distilled water
σ//	8.9 x10^{-8} ~ 8.3 x 10^{-9}	
σ//	1.1 x 10^{-7}	10^{-5}M LiTCNQ

The electrical conductivities for the multilayers of the complex, deposited on aluminium electrodes arranged in a surface cell and a sandwich cell, were measured in the directions parallel ($\sigma_{//}$) and perpendicular ($\sigma_{\perp}$) to the film plane, respectively. The conductance was obtained by analyzing Lissajous's figure taken at 10 mHz and 150 mV.[8] A good linear relationship between the lateral conductivity ($\sigma_{//}$) and the gap width (1 — 5 mm) was held. The values of conductivities in air for the multilayers of the complex are listed in Table 1. The normal conductivity was 1.0 x 10^{-14} S cm^{-1}, while the lateral one falled in the range of 8.9 x 10^{-8} — 8.3 x 10^{-9} S cm^{-1} from the monolayers spread on the distilled water. The latter value increased up to 1.1 x 10^{-7} S cm^{-1} with the aqueous LiTCNQ subphase. It is noted that the lateral conductivity is closely related with the film homogeneity improved by adding the TCNQ salt into the aqueous subphase. Thus, it has been found that the multilayer of the novel molecular complex of the dihydrothiophene substituted with thienyl groups [2] and C_{18}TCNQ (1 : 2) exhibits the remarkably anisotropic conductivity, that is, the lateral conductivity is about 10^7 times larger than the normal one. Further spectroscopic characterizations for the multilayers of the complex are in progress, and also other complex formations between the selenophene analogues and C_{18}TCNQ are under examination.

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REFERENCES

1. H. Fujimoto, U. Nagashima, H. Inokuchi, K. Seki, Y. Cao, H. Nakahara, J. Nakayama, M. Hoshino and K. Fukuda, J. Chem. Phys., 92, 4077 (1990).
2. H.Nakahara, J. Nakayama, M. Hoshino and K. Fukuda, Thin Solid Films, 160, 87 (1988).
3. A. Ishii, Y. Horikawa, I. Takaki, J. Shibata, J. Nakayama, M. Hoshino, Tetrahedron Lett., 32, 4313 (1991).
4. G. Hieber, M. Hanack, K. Wurst and J. Strahle, Chem. Ber., 124, 1597 (1991).
5. C. Nakano, K. Kamiya, H. Inokuchi, H. Nakahara, J. Nakayama, A. Ishii, M. Hoshino and K. Fukuda, to be published elsewhere.
6. K. Kamiya, U. Nagashima, C. Nakano, H. Inokuchi, H. Nakahara, J. Nakayama, A. Ishii, M. Hoshino and K. Fukuda, to be published elsewhere.
7. H. Nakahara and K. Fukuda, J. Colloid Interface Sci., 69, 24 (1979).
8. M. Sugi, T. Fukui and S. Iizima, Appl. Phys. Lett., 27, 559 (1975).

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