FORMATION OF ORGANIC SEMICONDUCTORS: SYNTHESIS OF CHARGE TRANSFER COMPLEXES BETWEEN TCNQ RADICAL ANION SALT AND TROPYLIUM IONS FUSED WITH HETEROCYCLIC SYSTEMS

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Abstract —— Tropylium ions fused with heterocyclic systems were synthesized to measure their reduction potentials of −0.15 to −0.37 V vs. SCE. Radical anion of TCNQ and these tropylium ions formed charge transfer complexes, which have conductivities of $\sigma=10^{-4}$–10^{-7} Scm^{-1}, suggesting that they belong to semiconductors.

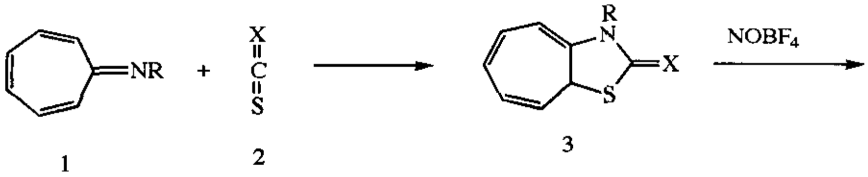
Much attention has been focused on the organic conductors of charge transfer complexes composed from electron donnors and electron acceptors.[1] G. Saito *et al.*, researched on the requirements for the formation of such organic conductors and found that the redox potentials of the components of the complexes were the most important factor to determine the conductivity.[1a,b] The differences between the first oxidation potentials of donors (E_1^{ox} (D)) and the first reduction potentials of acceptors (E_1^{red} (A)) lie in a range from 0.34 to −0.02 V in the case of TTF (*tetrathiafulvalene*)–TCNQ (*tetracyanoquinodimethane*) systems, which are known to be typical organic conductors.[1a] An exceptional one is a case of *N*-methylphenazinium ion (NMP), which forms a conductive salt with TCNQ radical anion despite of its higher reduction potential than those of other cations.[2] However, tropylium ion, whose reduction potential is close to that of NMP has been reported to undergo a reaction with TCNQ radical anion without forming any salts.[3] Previously, Y. Yamashita *et al.* reported the formation of highly conductive TCNQ radical anion salts with tropylium ions, whose reduction potentials could be controlled by introductions of several substituents.[4]

As a series of our research on the organic conductors we investigated the formation of complexes of TCNQ radical anion salt and tropylium ions fused with heterocyclic systems.

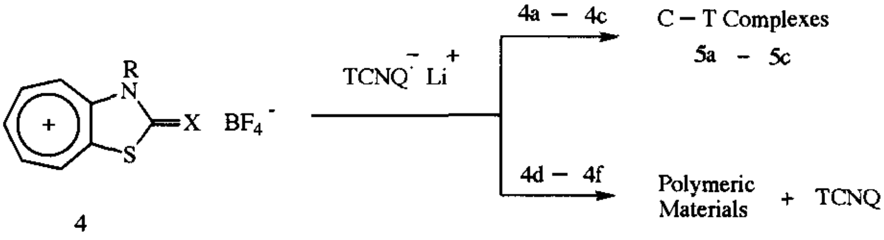
Tropylium ions (4) fused with heterocyclic systems were prepared by addition reactions of *N*-aryl-2,4,6-cycloheptatrien-1-imines (1) with heterocumulenes (2) such as carbon disulfide or isothiocyanates to afford [8+2] type adducts (3).[5] Subsequent elimination of hydride ion from 3 using $NOBF_4$ afforded the tropylium ion derivatives (4).[4]

The structures of **4** were deduced on the basis of their spectral properties as follows. In the ir spectra of **4a–c**, the characteristic absorptions for C=N bonds were observed at 1640 cm^{-1}. The absorptions of thiocarbonyl groups were observed at 1080 cm^{-1} in the ir spectra of **4d–f**. In ^1H nmr spectra, the signals of the protons on the seven-membered rings were observed at 8–9 ppm.

The first reduction potentials (E_1^{red}) of tropylium ions (**4**), measured by cyclic voltammetry, are summarized in the following table. The first reduction potential peaks of **4** were irreversible, indicating that the reduced products were fairly unstable under the measurement conditions. Introductions of NPh or NMe groups at the X position of **4** decreased the reduction potentials to −0.38 – −0.35 V, while an introduction of sulfur atom at X position scarcely changed the potentials, to −0.15 – −0.19 V.



a: R=*p*-MeC_6H_4, X=NPh
b: R=*p*-ClC_6H_4, X=NPh
c: R=*p*-MeC_6H_4, X=NMe
d: R=*p*-$OMeC_6H_4$, X=S
e: R=*p*-MeC_6H_4, X=S
f: R=*p*-ClC_6H_4, X=S



Charge transfer complexes of TCNQ radical anion (**5**) were prepared as follows. Mixing of boiling ethanol solutions of **4a–c** and TCNQ radical anion lithium salt afforded the corresponding charge transfer complexes (**5a–c**), respectively. In contrast, under the same conditions as above **4d–f** underwent reactions with TCNQ radical anion to give polymeric materials and the recovered neutral TCNQ without forming any salts. It should be noted that only the cations having higher reduction potentials underwent the reactions. This fact shows that the reduction potentials strongly affect the formation of charge transfer complexes. The reaction is considered to proceed through the complete one electron transfer from TCNQ radical anion to tropylium ions to afford the tropylium radicals and neutral TCNQ. The resulting tropylium radicals are unstable to undergo polymerization.

The properties of 5 are summarized in the Table. It is known that there is a linear correlation between the nitrile stretching frequencies of TCNQ complex in ir spectra and the degree of charge transfer from the donnor to TCNQ.[6] However, the frequencies of all these complexes (5) are lower than those of completely charge-transfered TCNQ radical anion lithium salt (2195 cm^{-1}), indicating that the nitrile stretching frequencies are not linearly correlated with the degrees of charge transfer in the present case.[7] The electronical conductivities of these salts (10^{-4} - 10^{-7} Scm^{-1})[4] show that these salts belong to semiconductor, though their conductivities are relatively low. These low conductivities are considered to be the result of the interference of stacking caused by the existence of aryl groups on the heterocyclic moieties.

Reduction Potentials of Cations (4) and Properties of Salts (5)

	Cations (4)		E_1^{red} *)	Salts (5)	
	R	X		$\nu_{C N}$/cm^{-1}	σ/Scm^{-1} **)
	tropylium cation		-0.16	-	-
a	C_6H_4(*p*-Me)	NPh	-0.37	2177	3.1×10^{-4}
b	C_6H_4(*p*-Cl)	NPh	-0.38	2179	2.8×10^{-7}
c	C_6H_4(*p*-Me)	NMe	-0.35	2179	7.6×10^{-6}
d	C_6H_4(*p*-OMe)	S	-0.19	-	-
e	C_6H_4(*p*-Me)	S	-0.18	-	-
f	C_6H_4(*p*-Cl)	S	-0.15	-	-

*) V vs SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode, 100 mv/s.

**) Measured at room temperature as compressed pellets

ACKNOWLEDGEMENT

We are indebted to Professor Yoshiro Yamashita of Institute for Molecular Science for his measurements of cyclic voltammetries and electron conductivities.

EXPERIMENTAL

General procedure of the preparation of tropylium ions (4). To a suspension of 3 (1.0 mmol) in acetonitrile (3.0 ml) was slowly added a solution of nitorosonium tetrafluoroborate (350 mg, 3.0 mmol) in acetonitrile (5.0 ml) at 0°C for 15 min. The solution was poured into ether (200 ml) with stirring at room temperature. The precipitate formed was filtered and washed with ether. The tropylium ions were used for the next step without further purifications. ^{1}H Nmr spectra of only stable cations were measured.

4a: 98% yield. mp 210°C (decomp.). Ir (KBr): 1645, 1583, 1460, 1066 cm^{-1}.

4b: 87% yield. Oil. Ir (oil): 1641, 1589, 1485, 1458, 1203, 1086 cm^{-1}. ^{1}H Nmr (MeCN-d_3) δ: 7.00–7.85 (m, 9H), 8.15–8.40 (m, 4H), 8.68 (m, 1H).

4c: 95% yield. Oil. Ir (oil): 1651, 1543, 1512, 1450, 1327, 1251, 1070 cm^{-1}. ^{1}H Nmr (MeCN-d_3) δ: 2.56(s. 3H), 3.30 (s, 3H), 7.50–7.76 (m, 4H), 8.20 (m, 1H), 8.70–8.80 (m, 3H), 9.40 (m, 1H).

4d: 83% yield. mp 210°C. Ir (KBr): 1637, 1510, 1230, 1084 $^{-1}$.

4e: 83% yield. mp 200°C. Ir (KBr): 1655, 1456, 1230, 1080 cm^{-1}.

4f: 64% yield. mp 220°C. Ir (KBr): 1637, 1452, 1231, 1084 cm^{-1}. ^{1}H Nmr (MeCN-d_3) δ: 7.46–7.85 (m, 4H), 7.90 (m, 1H), 8.50–8.70 (m, 3H), 9.05 (m, 1H).

General procedure of the preparation of complexes (5). To a boiling solution of TCNQ radical anion lithium salt (2.5 mmol) in ethanol (5.0 ml) was added a boiling solution of tropylium ion derivatives (4) (1.0 mmol) in a 1:1 mixed solvent of acetonitrile and ethanol (10 ml). The mixture was allowed to stand at room temperature overnight. The black precipitate formed was filtered`and washed with ethanol.

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   It was reported that when charge-transfer complexes of TCNQ radical anions make mixed stacks in their crystals, no linear correlations can be detected between the nitrile stretching frequencies in the ir spectra and the degrees of charge transfer.[7]
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Received, 10th August, 1994