FORMATIONS OF ORGANIC SEMICONDUCTORS: BISTROPYLIUM IONS LINKED BY HETEROCYCLIC MOIETIES AS COMPONENTS OF CHARGE TRANSFER COMPLEX

Kazuaki Ito[+] and Katsuhiro Saito*

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho,
Showa-ku, Nagoya 466, Japan
[+] Department of Material Science and Engineering, Faculty of Engineering,
Yamagata University, Yonezawa 992, Japan

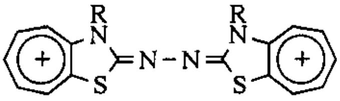
Abstract Bistropylium ions linked by heterocyclic moieties were synthesized to measure their reduction potentials of -0.47 ~ -0.42 V vs. SCE. Charge transfer complexes between these bistropylium ions and radical anion of TCNQ showed conductivities of $7.7X10^{-4}$ ~ $7.7X10^{-5}$ Scm^{-1}, indicating that they can be classified as semiconductors.

The research on the organic conductors of charge transfer complexes seems to be one of the most progressive field of the recent organic chemistry.[1] It is known that the redox potentials of donors and acceptors were important factor to determine the conductivity. In the case of the typical organic conductors, TTF (tetrathiafulvalene)-TCNQ (tetracyanoquinodimethane) systems, the differences between the first oxidation potentials of donors (E_1^{ox} (D)) and the first reduction potentials of acceptors (E_1^{red} (A)) are in a range from 0.34 to -0.02 V.[1a] On the other hand, it is known that complexes between several cations and TCNQ radical anion usually exhibit low conductivities as a result of complete charge transfers.[2] *N*-Methylphenazinum (NMP), which has a higher reduction potential as compared with those of other cations is an exceptional cation.[2a] The salts between NMP and TCNQ radical anion has properties as an organic metal. However, tropylium ion, whose reduction potential is close to that of NMP, is known to undergo a reaction with TCNQ radical anion without generating any complexes.[3]

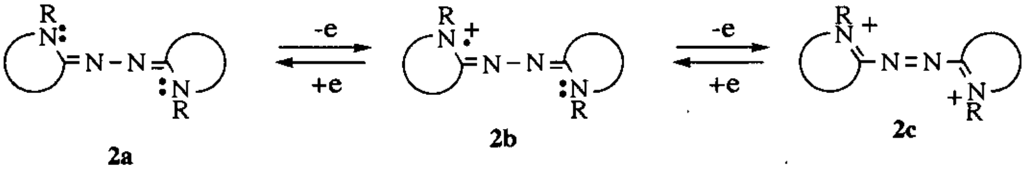
Recently, a formation of highly conductive TCNQ radical anion salts with tropylium ions having variable substituents was reported.[4] Very recently, we documented a synthesis of organic semiconductors composed of tropylium ions fused with heterocyclic systems.[5]

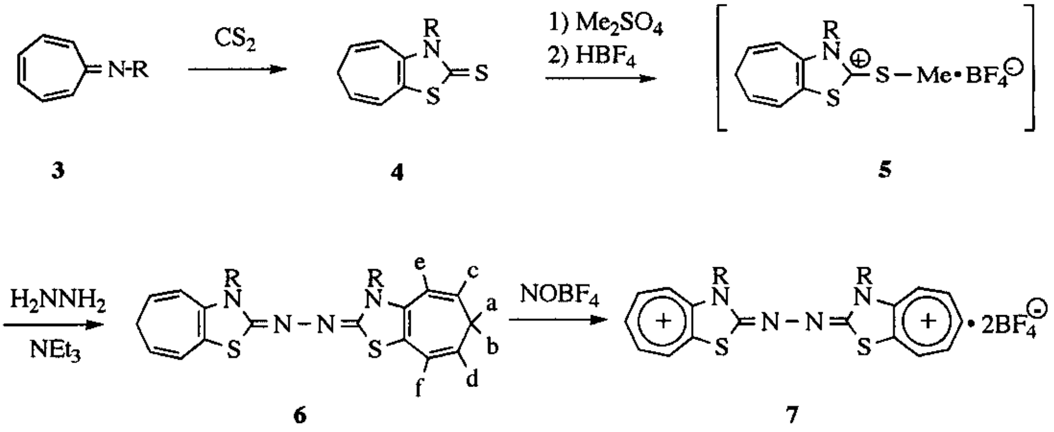
As a series of our researches on the organic conductors we investigated the synthesis of charge transfer complexes between TCNQ radical anion and bistropylium ions linked by heterocyclic components. Here the results will be discussed.

Considering that tropylium ions behave as electron acceptors,[4,5] it seems important to deminish the reduction potentials of tropylium ions to avoid the reaction with TCNQ radical anion. Bistropylium ions linked with heterocyclic systems containing an azine linkage such as **1** are considered to have deminished



1

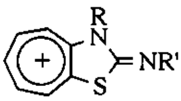




$\xrightarrow{TCNQ^{\bullet -}\,Li^+}$ Complex

8

a: R=*p*-MeOC$_6$H$_4$
b: R=*p*-MeC$_6$H$_4$
c: R=*p*-ClC$_6$H$_4$
d: R=*p*-BrC$_6$H$_4$



9

potentials because of the electron donating nature of the attached azine system through the azine-azo redox system (**2**).

Bistropylium ion systems (**7**) were synthesized as follows. Thiazoline-2-thions (**4**) were synthesized by the addition reactions of 2,4,6-cycloheptatrien-1-imines (**3**) with carbon disulfide according to a literature.[6] A mixture of **4** and dimethyl sulfate was heated at 100 °C for 10 min and then 42% HBF_4 aqueous solution was added at 0 °C. The reactions of the resulted products (**5**) with hydazine in the presence of triethylamine afforded biscycloheptatrienes (**6**) in 20 ~ 40 % yields.[7] Subsequent eliminations of hydride ions from **6** using nitrosonium tetrafluoroborate ($NOBF_4$) yielded the fluoroborates of bistropylium ion derivatives (**7**) in 70 ~ 90% yields.[4]

The structural elucidations of **6** and **7** were accomplished on the basis of their spectral properties and were confirmed by the comparisons of them to those of the analogous compounds. The ir spectra showed the characteristic absorptions of C=N bonds at *ca.* 1610 cm^{-1}. The ^1H nmr spectra well resembled to the analogous compounds[5,6] and were compatible to the structures. The first reduction potentials (E_1^{red} = -0.42 ~ -0.47 V vs. SCE) of **7** measured by cyclic voltammetry were lower than those of the tropylium ions fused with heterocyclic systems such as **9** (E_1^{red}= -0.15 ~ -0.38 V).[5] The lower reduction potentials of **7** can be attributed to the existence of the azine system.[8]

Charge transfer complexes (**8**) between **7** and TCNQ radical anion were prepared as follows. A mixture of boiling ethanol solutions of **7** and a boiling ethanol solution of TCNQ radical anion gave the complexes (**8**).[5]

In the uv-visible spectra of **8** in methanol, the absorption bands at 836, 740, 678, and 400 nm were assigned to the absorptions due to the TCNQ radical anion.[3] The nitrile stretching frequencies of **8** were lower than that of completely charge transfered TCNQ radical anion litium salt (2195 cm^{-1}) indicating that **8** composed mixed stacks in their crystals.[9] The conductivites of **8** were *ca.* 10^{-4} ~ 10^{-5} Scm^{-1} indicating that **8** can be considered to belong to a semiconductor.[1b] As compared with the corresponding complexes of the monotropylium ions (**9**) a slight improvement in conductivities are observed.[5] One reason for this is considered to be attributable to the expansion of the conjugated systems in **8**.

Reduction Potentials of Cations (**7**) and Properties of Salts (**8**)

Cation	E_1^{red} a)	Complex Salt		
R		ν_{CN}/cm^{-1}	σ/Scm^{-1} b)	Cation:TCNQ
C_6H_4(*p*-OMe)	-0.46	2180	$1.9X10^{-5}$	1 : 1.5
C_6H_4(*p*-Me)	-0.47	2180	$7.7X10^{-4}$	1 : 1
C_6H_4(*p*-Cl)	-0.43	2180	$9.2X10^{-4}$	1 : 1.1
C_6H_4(*p*-Br)	-0.42	2178	$7.7X10^{-5}$	1 : 1.2

a) V vs. SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode

b) Measured at room temperature as compressed pellets

AKNOWLEDGEMENT

The authors are indebited to professor Yoshiro Yamashita of Institute for Molecular Sience for his frutifull suggestions and measurements of cyclic voltammetries and electron condctivities.

EXPERIMENTAL

Melting points were measured with a Yanagimoto Micro Melting Point Apparatus and were uncorrected. Nmr spectra were taken with Hitachi R-90 or Varian XL-200 spectrometer with tetramethylsilane as an internal standard. Ir spectra were measured with JASCO FT/IR 5300 or Horiba FT-200 spectrophotometer. Uv-vis spectra were measured with Hitachi 228A spectrophotometer. Mass spectra were taken with Hitachi M-2000S or JEOL AX-350 spectrometer. Only typical experiments are mentioned below.

*General Procedure of the Preparation of Biscycloheptatriene Systems (**6**).* A suspension of **4** (7.0 mmol) in dimethyl sulfate (16 ml) was heated at 100 °C for 10 min. After heating, the mixture was cooled to 0°C in an ice bath, and then 42% HBF_4 aqueous solution (8.5 ml) was slowly added at 0°C. The resulted mixture was poured into water, extracted with ether ,and then the organic layer was dried over anhydrous sodium sulfate. Removal of the solvent gave a dark brown oil, which was then dissolved into methanol (20 ml). To the solution was slowly added a solution of hydrazine monohydrate (0.25 g, 5.0 mmol) and triethylamine (0.80 g, 8.0 mmol) in methanol (5.0 ml) at room temperature. After stirring for 2 h the solvent was removed to give a brown residue, which was separated with column chromatography on silica gel to give **6**.

6a: Pale yellow oil. 37% yield. Hrms: m/z 538.1496. Calcd for $C_{30}H_{26}N_4O_2S_2$: m/z 538.1496. Ms m/z (rel intensity): 538 (M^+, 13), 327 (17), 259 (23), 211 (49), 196 (16), 133 (100). Ir (oil): 1601, 1576, 1510, 1402, 1346, 1248, 1030 cm^{-1}. ^1H Nmr ($CDCl_3$) δ : 2.30 (t, H_a and H_b, 4H), 3.72 (s, Me, 6H), 4.90-5.29 (m, H_c and H_d, 4H), 5.75 (d, H_e, 2H), 6.14 (d, H_f, 2H), 6.75-7.30 (m, aromatic protons, 8H). Coupling constants in Hz; $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.9$, $J_{ce}=9.8$, $J_{df}=9.2$. ^{13}C Nmr ($CDCl_3$) δ : 27.8, 55.5, 114.4, 115.6, 118.0, 118.9, 119.3, 121.9, 128.9, 130.4, 138.5, 158.6, 159.3.

6b: Pale yellow crystals. 11% yield. mp 232-234° C (decomp.). Hrms: m/z 506.1626. Calcd for $C_{30}H_{26}N_4S_2$: m/z 506.1598. Ms m/z (rel intensity): 506 (M^+, 100), 387 (4), 311 (46), 253 (73). Ir (KBr): 1607, 1576, 1508, 1397, 1334, 1167 cm^{-1}. ^1H Nmr ($CDCl_3$) δ : 2.38 (s, Me, 6H), 2.39 (t, H_a and H_b, 4H), 5.01-5.39 (m, H_c and H_d, 4H), 5.85 (d, H_e, 2H), 6.24 (d, H_f, 2H), 7.23-7.42 (m, aromatic protons, 8H). Coupling constants in Hz; $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.8$, $J_{ce}=9.6$, $J_{df}=9.4$. ^{13}C Nmr ($CDCl_3$) δ : 21.1, 27.7, 115.6, 118.1, 118.9, 119.0, 121.8, 127.3, 129.6, 134.9, 137.1, 138.3, 159.1.

6c: Pale yellow oil. 37% yield. Hrms: m/z 546.0518. Calcd for $C_{28}H_{20}N_4Cl_2S_2$: m/z 546.0505. Ms m/z (rel intensity): 548 (M^+, 73), 546 (M^+, 84), 331 (53), 275 (27), 274 (72), 273 (100). Ir (KBr): 1605, 1570, 1489, 1397, 1341, 1086 cm^{-1}. ^1H Nmr ($CDCl_3$) δ : 2.45 (t, H_a and H_b, 4H), 5.08-5.49 (m, H_c and H_d, 4H), 5.88 (d, H_e, 2H), 6.30 (d, H_f, 2H), 7.25-7.57 (m, aromatic protons, 8H). Coupling constants in Hz; $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.8$, $J_{ce}=9.9$, $J_{df}=9.3$. ^{13}C Nmr ($CDCl_3$) δ : 27.8, 116.4, 118.7, 119.5, 121.7, 128.8, 129.1, 132.8, 136.0, 137.6, 158.9.

6d: Pale yellow crystals. 20% yield. mp 156-160° C (decomp.). Hrms: m/z 633.9483. Calcd for $C_{28}H_{20}N_4Br_2S_2$: m/z 633.9495. Ms m/z (rel intensity): 634 (M^+, 91), 547 (50), 488 (100), 450 (44), 409 (36), 375 (48), 283 (54). Ir (KBr): 1605, 1566, 1485, 1395, 1343, 1065 cm^{-1}. ^1H-Nmr ($CDCl_3$) δ : 2.37

(t, H_a and H_b, 4H), 5.01-5.46 (m, H_c and H_d, 4H), 5.85 (d, H_e, 2H), 6.20 (d, H_f, 2H), 7.10-7.60 (m, aromatic protons, 8H). Coupling constants in Hz; $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.5$, $J_{ce}=9.9$, $J_{df}=9.3$.

General Procedure of the Preparation of Bistropylium ions (7). To a suspension of **6** (1.0 mmol) in acetonitrile (3.0 ml) was slowly added a solution of nitrosonium tetrafluoroborate (0.35 g, 3.0 mmol) in acetonitrile (5.0 ml) at 0 °C for 15 min. The solution was poured into ether with strring at room temperature. The precipitated crystals of bistropylium ions (**7**) were filtered, washed with ether, and used for the next step without further purification.

7a: Purplish black powder. 85% yield. mp 215-220° C (decomp.). FABms: 623 $(M - BF_4)^+$. Uv-vis (MeOH): 552 nm (log ε , 4.26), 314 (4.71), 281 (4.77), 254 (4.87), 231 (4.99). Ir (KBr): 2926, 2854, 1612, 1510, 1454, 1253, 1230, 1084 cm^{-1}. ^1H Nmr (MeCN-d_3) δ: 3.97 (s, OMe, 6H), 7.33 (d, aromatic protons, 4H, J=8.4 Hz), 7.52 (d, aromatic protons, 4H, J=8.4 Hz), 7.79 (d, 2H, J=10.5 Hz), 8.26 (m, 6H), 8.64 (d, 2H, J=9.7 Hz). Anal. Calcd for $C_{30}H_{24}N_4O_2B_2F_8S_2 \cdot H_2O$: C, 49.48; H, 3.60; N, 7.69. Found : C, 49.05; H, 3.53; N, 7.79.

7b: Purplish black powder. 78% yield. mp 165-169° C (decomp.). FABms: 591 $(M - BF_4)^+$. Uv-vis (MeOH): 560 nm (log ε , 4.50), 333 (sh. 4.87), 284 (4.63), 252 (4.96). Ir (KBr): 2924, 2853, 1616, 1510, 1454, 1229, 1084 cm^{-1}. ^1H Nmr (DMSO-d_6) δ : 2.08 (s, Me, 6H), 7.56 (d, aromatic protons, 4H, J=8.4 Hz), 7.62 (d, aromatic protons, 4H, J=8.4 Hz), 7.66 (d, 2H, J=11.3 Hz), 8.23 (t, 2H, J=9.5 Hz), 8.37 (m, 4H), 8.99 (d, 2H, J=9.7 Hz). Anal. Calcd for $C_{30}H_{24}N_4B_2F_8S_2 \cdot 3/2H_2O$: C, 51.09; H, 3.87; N, 7.94. Found : C, 50.77; H, 3.87; N, 7.95.

7c: Purplish black powder. 96% yield. mp 215-218° C (decomp.). FABms: 631 $(M - BF_4)^+$. Uv-vis (MeOH): 555 nm (log ε , 4.43), 310 (4.79), 282 (4.84), 254 (4.94). Ir (KBr): 2926, 2854, 1615, 1491, 1452, 1261, 1091 cm^{-1}. ^1H Nmr (DMSO-d_6) δ :7.75 (d, aromatic protons, 4H, J=8.4 Hz), 7.79 (d, 2H, J=10.3 Hz), 7.93 (d, aromatic protons, 4H, J=8.3 Hz), 8.26 (t, 2H, J=9.5 Hz), 8.39 (m, 4H), 9.02 (d, 2H, J=9.7 Hz). Anal. Calcd for $C_{28}H_{18}N_4B_2Cl_2F_8S_2 \cdot 3H_2O$: C, 43.50; H, 3.13; N, 7.24. Found : C, 43.12; H, 2.78; N, 7.79.

7d: Purplish black powder. 96% yield. mp 215-218° C (decomp.). FABms: 721 $(M - BF_4)^+$. Uv-vis (MeOH): 525 nm (log ε , 4.38), 286 (4.74), 254 (4.98). Ir (KBr): 2926, 2854, 1612, 1485, 1454, 1261, 1084 cm^{-1}. ^1H Nmr (DMSO-d_6) δ :7.67 (d, aromatic protons, 4H, J=8.6 Hz), 7.79 (d, 2H, J=10.5 Hz), 8.06 (d, aromatic protons, 4H, J=8.6 Hz), 8.26 (t, 2H, J=9.5 Hz), 8.39 (m, 4H), 9.02 (d, 2H, J=9.7 Hz). Anal. Calcd for $C_{28}H_{18}N_4B_2Br_2F_8S_2 \cdot 2H_2O$: C, 39.85; H, 2.62; N, 6.63. Found : C, 39.61; H, 2.54; N, 7.17.

General Procedure of the Preparation of TCNQ Radical Anion Complexes (8). To a boiling solution of TCNQ radical anion litium salt (5.0 mmol) in ethanol (5.0 ml) was added a boiling solution of bistropylium ion derivative (**6**) (1.0 mmol) in a 1:1 mixture of acetonitrile and ethanol (10 ml). The mixture was allowed to stand at room temperature over night. The black precipitate were filtered and washed with ethanol.

8a: Black powder. mp 176-188°C (decomp.). Uv-vis (MeOH): 836 nm (log ε , 4.08), 818 (sh. 3.98), 758 (3.78), 740 (3.86), 678 (3.59), 662 (3.60), 470 (3.97), 434 (4.04), 418 (4.08), 406 (4.05), 317 (4.12), 278 (4.14), 221 (sh. 4.46). Ir (KBr): 3058, 2956, 2923, 2852, 2180, 1600, 1571, 1560, 1508, 1452, 1438, 1253, 1174 cm^{-1}. Anal. Calcd for $C_{96}H_{60}N_{20}O_4BF_4S_4$: C, 65.04; H, 3.41; N, 15.79. Found : C, 65.47; H, 3.69; N, 15.44.

8b: Black powder. mp 186-195°C (decomp.). Uv-vis (MeOH): 836 nm (log ε , 4.01), 818 (3.90), 758 (3.67), 740 (3.77), 678 (3.35), 664 (3.30), 476 (3.32), 394 (4.30), 336 (4.10), 280 (4.00), 222 (sh. 4.43). Ir (KBr): 3058, 2923, 2852, 2180, 1600, 1587, 1569, 1560, 1450, 1436, 1324, 1276, 1230, 1174, 1126 cm^{-1}. Anal. Calcd for $C_{42}H_{28}N_8BF_4S_2$: C, 63.40; H, 3.52; N, 14.09. Found : C, 62.75; H, 3.68; N, 14.54.

8c: Black powder. mp 188-200°C (decomp.). Uv-vis (MeOH): 838 nm (log ε , 3.90), 820 (3.80), 757 (3.58), 740 (3.66), 678 (3.22), 663 (3.22), 472 (3.72), 434 (3.86), 420 (3.93), 406 (3.93), 393 (3.93), 324 (4.07), 280 (4.02), 225 (sh. 4.46). Ir (KBr): 3058, 2923, 2854, 2180, 1602, 1569, 1560, 1490, 1436, 1357, 1322, 1280, 1232, 1174, 1091 cm^{-1}. Anal. Calcd for $C_{41.2}H_{22.4}N_{8.4}BCl_2F_4S_2$: C, 57.75; H, 2.63; N, 13.75. Found : C, 58.28; H, 2.79; N, 13.24.

8d: Black powder. mp 201-212°C (decomp.). Uv-vis (MeOH): 836 nm (log ε , 3.91), 820 (3.82), 758 (3.56), 740 (3.62), 678 (3.10), 662 (3.06), 470 (3.76), 434 (3.86), 420 (3.90), 404 (3.87), 324 (4.00), 276 (3.98) 224 (sh. 4.45). Ir (KBr): 3058, 2925, 2854, 2178, 1604, 1577, 1560, 1488, 1436, 1324, 1280, 1232, 1174, 1068, 1012 cm^{-1}. Anal. Calcd for $C_{42.4}H_{22.8}N_{8.8}BBr_2F_4S_2$: C, 52.71; H, 2.38; N, 12.75. Found : C, 52.99; H, 2.63; N, 12.39.

REFERENCES AND NOTES

1. a) G. Saito and J. P. Ferraries, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2141; b) G. Saito and K. Yamachi, "Chemistry of the Low-Dimensional Conductive Materials", Gakujutsu Center, 1983.
2. a) D. J. Sandman, *J. Am. Chem. Soc.*, 1978, **100**, 5230. b) J. B. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79; J. H. Perlston, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 519.
3. L. R. Melgy, R. J. Harden, W. R. Herlter, W. Malher, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.
4. Y. Yamashita, K. Hagiya, G. Saito, and T. Mukai, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 271.
5. K. Ito and K. Saito, *Heterocycles*, 1994, **38**, 2691.
6. K. Ito, K. Saito, and K. Takahashi, *ibid.*, 1991, **32**, 1117.
7. S. Hunig, G. Kiesslish, F. Linhart, and H. Schalaf, *Liebigs Ann. Chem.*, 1971, **752**, 182.
8. Bistropylium ions (**7**) can be considered to be composed of two components; an electron acceptor (tropylium ion) part and an electron donor (azine) part. There is a possibility to generate unimolecular charge transfer complexes forming organic conductors. However, the conductivities of them were *ca.* 2.0X10^{-9} Scm^{-1}.
9. M. Meneghetti, A. Girlando, and C. Pecile, *J. Chem. Phys.*, 1985, **83**, 3134.

Received, 5th June, 1995