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NOVEL MOLECULAR METALS COMPOSED OF A [3]RADIALENE TYPE ACCEPTOR : 1,2-BIS(*p*-BENZOQUINO)-3-[2-(DICYANOMETHYLENE)-2,5-SELENOQUINO]CYCLOPROPANE DERIVATIVE

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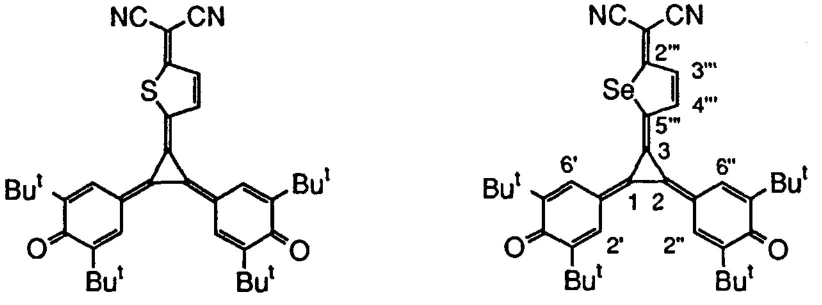
Abstract A new acceptor, 1,2-bis(*p*-benzoquino)-3-[2-(dicyanomethylene)-2,5-selenoquino]cyclopropane derivative (DCNS-CP) has been efficiently synthesized by the reaction of a cyclopropenone derivative with selenienylmalononitrile and subsequent oxidation. DCNS-CP proved to be a powerful acceptor and its anion radical and dianion are very thermodynamically stable. Single crystals of [TTF][DCNS-CP] and [TTT][DCNS-CP] complexes showed metallic temperature dependencies of the conductivities down to 182 and 80 K, recording σ_{max} values of 500 and 760 Scm^{-1}, respectively. These are a new class of metals based on a functionally different type of organic acceptor consisting of three electron-accepting groups in full conjugation.

keywords: Molecular metals, electron-acceptor, [3]radialene derivative, (dicyanomethylene)selenoquinonoid moiety, cyclopropane derivative

INTRODUCTION

Active investigations have been continued toward the synthesis of a variety of organic π-acceptors to decrease on-site Coulombic repulsion and to increase intermolecular interactions to suppress the metal-insulator transitions. 5,5'-Bis(dicyanomethylene)-5,5'-dihydro-2,2'-bithiophene (BT-TCNQ),[1] a higher thiophene homologue of thiophene-tetracyanoquinodimethane (T-TCNQ)[2], and isothianaphthene-TCNQ[3] have been synthesized so far according to this concept, but the electron-accepting ability is rather weakened by such elongation of the acceptor π-system. This disadvantage could be overcome by our recent synthesis of [3]radialene type acceptors, where we can introduce three electron-accepting groups in one molecule, all of which are in full conjugation through the cyclopropane framework. Indeed a thienoquinonoid-extended [3]radialene-type acceptor, 1,2-bis(*p*-benzoquino)-3-[2-(dicyanomethylene)-2,5-thienoquino]cyclopropane (DCNT-CP), **1**,[4] exhibits a strong electron-accepting ability although it has only one dicyanomethylene group, and gave a TTF complex with a fairly high room temperature conductivity of 3.1 Scm^{-1} on a compressed pellet. However, no single crystals of the complex have been prepared and characterized so far. The crystal growth as well as the intermolecular interaction in the single crystal would be much improved by replacing the sulfur atom of DCNT-CP with a selenium atom, since the diffused *p*-orbitals of the selenium atom may enhance the mutual intermolecular contacts.[5] To this end, we have now synthesized another new [3]radialene type acceptor, DCNS-CP, **2**,[6] incorporating a selenoquinonoid moiety and succeeded in obtaining single-crystalline charge-transfer (CT) complexes exhibiting metallic properties, which are reported herein.



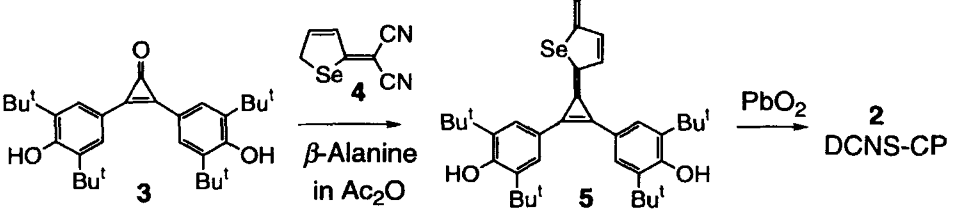
1: DCNT-CP **2**: DCNS-CP

FIGURE 1 Structures of DCNT-CP and DCNS-CP.

EXPERIMENTAL

DCNS-CP, **2** was synthesized according to Scheme 1. We have first synthesized novel 2-(dicyanomethylene)-2,5-dihydroselenophene **4** in 61% yield by the reaction of 2-iodoselenophene with sodium dicyanomethanide in the presence of $PdCl_2(PPh_3)_2$ in THF.[7] Compound **4** is a very useful synthon for the preparation of selenoquinonoid-extended dicyanomethylene chromophores. Thus we prepared DCNS-CP, **2** in 70% overall yield starting from 2,3-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone **3**.[8]

Scheme 1



Single crystals of **2** with tetrathiotetracene (TTT), [TTT][DCNS-CP], were grown in carbon disulfide by diffusion of the reactants. Single crystals of **2** with tetrathiafulvalene

(TTF), [TTF][DCNS-CP], were obtained by slow diffusion of hexane vapor into a chlorobenzene solution of DCNS-CP and TTF. We have prepared some poly-crystalline CT complexes and radical anion salts of DCNS-CP. We have also prepared CT-complexes of 1,2-bis(*p*-benzoquino)-3-dicyanomethylenecyclopropane (DCN-CP), **7**[9] as for the reference complexes to know the effect of the selenoquinonoid-extension. Experimental details are as follows.

2-[2,3-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenylidene]-5-dicyanomethylene-2,5-dihydroselenophene (5). A suspension of the cyclopropenone **3**[8] (590 mg, 1.28 mmol), 2-(dicyanomethylene)-2,5-dihydroselenophene **4**[7] (500 mg, 2.56 mmol), and β-alanine (11.4 mg, 0.128 mmol) in acetic anhydride (5 ml) was heated to reflux for 15 min under argon atmosphere. The reaction mixture was cooled to room temperature, and an orange crystalline product which separated out was collected by filtration and washed with dichloromethane to remove easily soluble impurities, giving **5** as orange fine needles (625 mg, 0.973 mmol, 76%). The product was too difficultly soluble in usual organic solvents to be purified further, but was sufficiently pure for submitting to the next reaction: mp > 300 °C; FTIR (KBr, cm^{-1}) 3480, 2956, 2918, 2873, 2195, 1836, 1593, 1572, 1527, 1475, 1435, 1360, 1313, 1259, 1236, 1201, 1163, 1119, 1095, 1024, 953, 926, 883, 779, 758, 729; UV-Vis (THF) λ_{max} nm (log ε) 524 (4.98), 494 sh (4.72), 340 (4.50), 325 (4.46), 278 (4.14), 266 sh (4.13); LRMS (DEI, 70 eV) *m/z* (rel. int. %) 644 (M^++4, 1.32), 643 (M^++3, 8.19), 642 (M^++2, 24.29), 641 (M^++1, 39.89), 640 (M^+, 100), 639 (M^+–1, 23.16), 638 (M^+–2, 53.29), 637 (M^+–3, 23.67), 636 (M^+–4, 18.30), 635 (M^+–5, 1.32); HRMS (DEI, 70 eV) Found: *m/z*, 640.2557. Calcd for $C_{38}H_{44}O_2N_2Se$: M, 640.2568; Anal. Found: C, 71.21; H, 6.98; N, 4.27%. Calcd for $C_{38}H_{44}O_2N_2Se$: C, 71.35; H, 6.93; N, 4.38%.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(2-dicyanomethylene-2,5-dihydroselenophen-5-ylidene)cyclopropane (DCNS-CP, 2). To a suspension of **5** (500 mg, 0.782 mmol) in benzene (200 ml) was added lead dioxide (3.51 g, 7.82 mmol). The mixture was stirred for 5 h at room temperature under argon atmosphere. Lead dioxides were removed by filtration, and the filtrate was then concentrated *in vacuo*. The crude residue (543 mg) was chromatographed through silica gel (benzene) to give DCNS-CP as green crystals (457 mg, 0.719 mmol, 92%). Further recrystallization from benzene gave pure DCNS-CP as green lustrous needles: mp 229—230 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, 1H, *J* =5.85 Hz, H-4'''), 7.53 (d, 1H, *J* =5.85 Hz, H-3'''), 7.48 (d, 1H, *J* =2.31 Hz, H-2''), 7.47 (d, 1H, *J* =2.32 Hz, H-2'), 7.38 (d, 1H, *J* = 2.31 Hz, H-6''), 7.33 (d, 1H, *J* = 2.32 Hz, H-6'), 1.42 (s, 9H, *t*-Bu at C-5'), 1.40 (s, 9H, *t*-Bu at C-5''), 1.39 (s, 9H, *t*-Bu at C-3'), 1.39

(s, 9H, *t*-Bu at C-3''); ^{13}C NMR (150 MHz, CDCl$_3$): δ 185.8 (C-4'), 185.6 (C-4''), 175.8 (C-2'''), 152.1 (C-3''), 151.9 (C-3'), 151.8 (C-5'), 151.2 (C-5''), 145.9 (C-4'''), 133.8 (C-3'''), 130.7 (C-6''), 130.6 (C-6'), 130.3 (C-2''), 130.2 (C-2'), 127.1 (C-5'''), 126.8 (C-1), 125.8 (C-2), 125.5 (C-3), 121.9 (C-1''), 120.2 (C-1'), 114.4, 112.7 (CN), 74.8 ($\underline{C}$(CN)$_2$); FTIR (KBr, cm^{-1}) 2954, 2210 (CN), 1599 (C=O), 1516, 1481, 1456, 1363, 1250, 1174, 1090, 894; UV/vis/NIR (CH$_2$Cl$_2$): λ_{max} nm (log ε) 830 (4.57), 731 (4.68), 672sh (4.54), 425 (4.64), 408sh (4.60), 323 (3.96), 300 (3.96), 238 (4.09); LRMS (DEI, 70 eV) *m/z* (rel. int. %) 641 (M$^+$+3, 3.45), 640 (M$^+$+2, 8.10), 639 (M$^+$+1 10.55), 638 (M$^+$, 25.30), 149 (100); HRMS (DEI, 70 eV) Found: *m/z*, 638.2474. Calcd for $C_{38}H_{42}O_2N_2Se$: M, 638.2411; Anal. Found: C, 71.65; H, 6.63; N, 4.35 %. Calcd for $C_{38}H_{42}O_2N_2Se$: C, 71.57; H, 6.63; N, 4.39 %.

Preparation of single-crystalline complexes

[TTT][DCNS-CP]. DCNS-CP (20 mg) was placed in one chamber and TTT (12 mg) was placed in the other chamber of an H-shaped glass cell with a glass frit separating the two chambers. To this was added carbon disulfide (20 ml). The period of the crystal growth was about one month at room temperature. Deep violet needles with a metallic luster were collected on a filter paper and washed with methanol. A typical dimension of the crystal was 1.0 mm × 0.2 mm × 0.02 mm. The stoichiometry of the complex was evaluated by elemental analysis: mp > 300 °C; FTIR (KBr, cm^{-1}) 2997, 2951, 2914, 2885, 2864, 2212, 1703, 1633, 1541, 1479, 1454, 1373, 1304, 1255, 1167, 1155, 1097, 1041, 1020, 972, 849, 791, 742, 715, 661; Anal. Found: C, 67.66; H, 5.02; N, 2.61 %. Calcd for $C_{56}H_{50}O_2N_2S_4Se$: C, 67.93; H, 5.09; N, 2.83 %.

[TTF][DCNS-CP]. A 10-ml beaker with three spouts (apertures) was charged with a solution of DCNS-CP (2 mg) and TTF (1 mg) in chlorobenzene (1 ml) and covered with a glass plate. This was allowed to stand in a desiccator charged with hexane (300 ml) at the bottom. The period of the crystal growth was about one week at room temperature. Deep red plates with a metallic luster were collected on a filter paper and washed with methanol. A typical dimension of the crystal was 2.0 mm × 0.5 mm × 0.01 mm. The stoichiometry of DCNS-CP and TTF was evaluated by elemental analysis: mp 187 – 188 °C, decomp; FTIR (KBr, cm^{-1}) 2951, 2924, 2877, 1718, 1631, 1593, 1537, 1489, 1446, 1381, 1352, 1311, 1252, 1228, 1205, 1169, 1103, 1084, 1065, 1016, 883, 870, 806, 783, 754, 744, 721, 665; Anal. Found: C, 62.96; H, 5.50; N, 3.21 %. Calcd for $C_{44}H_{46}O_2N_2S_4Se$: C, 62.76; H, 5.51; N, 3.33 %.

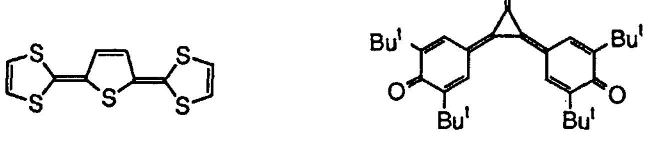
Preparation of poly-crystalline complexes

[TTT][DCNS-CP]. To a hot saturated solution of TTT in carbon disulfide was added a hot saturated solution of DCNS-CP in carbon disulfide, and the combined solution was heated to reflux for 1 h. The solution was then concentrated by heating to three fourths of its original volume, and gradually cooled to room temperature to deposit a precipitate, which was collected by filtration and washed with carbon disulfide to give [TTT][DCNS-CP], having the same stoichiometry to the single-crystalline complex, as deep violet fine needles in 57% yield.

[TTF][DCNS-CP]. A hot saturated solution of DCNS-CP in benzene was combined with a hot saturated solution of TTF in benzene. The resulting solution was concentrated by heating to about one fourth of its original volume, allowed to cool gradually to room temperature, and fine crystals which separated out were collected by filtration and washed with a small amount of benzene to give [TTF][DCNS-CP], having the same stoichiometry to the single-crystalline complex, as dark red fine needles in 62% yield.

[BDTT][DCNS-CP]. In a manner similar to that for [TTF][DCNS-CP] complex, [BDTT][DCNS-CP] was prepared as green needles in 83% yield starting with hot benzene solutions of DCNS-CP and 2,5-bis(1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (BDTT), **6**[10]: mp > 300 °C; FTIR (KBr, cm^{-1}) 2954, 2914, 2871, 2189, 1716, 1668, 1633, 1591, 1541, 1473, 1444, 1415, 1354, 1317, 1257, 1200, 1163, 1097, 1018, 891, 870, 779, 742, 667; Anal. Found: C, 61.41; H, 5.04; N, 2.88 %. Calcd for $C_{48}H_{48}O_2N_2S_5Se$: C, 61.19; H, 5.13; N, 2.97 %.

[TMTSF][DCNS-CP]$_2$. In a manner similar to that for [TTF][DCNS-CP] complex, [TMTSF][DCNS-CP]$_2$ was prepared as black fine needles in 59% yield starting with hot benzene solutions of DCNS-CP and tetramethyltetraselenafulvalene (TMTSF): mp > 300 °C; FTIR (KBr, cm^{-1}) 2954, 2916, 2883, 2862, 2206, 1736, 1633, 1597, 1512, 1477, 1456, 1387, 1360, 1335, 1246, 1171, 1113, 1088, 1011, 926, 892, 849, 814, 783, 679; Anal. Found: C, 59.66; H, 5.63; N, 3.21 %. Calcd for $C_{86}H_{96}O_4N_4Se_6$: C, 59.94; H, 5.61; N, 3.25 %.



6: BDTT

7: DCN-CP

FIGURE 2 Structures of BDTT and DCN-CP.

[TTF][DCN-CP]. A hot saturated solution of TTF (8.0 mg, 0.039 mmol) in acetonitrile (5 ml) and a hot saturated solution of DCN-CP (20 mg, 0.039 mmol) in acetonitrile (10 ml) was combined. The resulting solution was concentrated by heating to 2 ml, allowed to cool gradually to room temperature, and fine crystals which separated out were collected by filtration and washed with a small amount of acetonitrile to give [TTF][DCN-CP] as black plates (18.3 mg) in 65% yield: mp 184 – 185 °C; FTIR (KBr, cm^{-1}) 2956, 2920, 2879, 2204, 1774, 1741, 1631, 1589, 1533, 1479, 1448, 1383, 1356, 1321, 1252, 1205, 1099, 1011, 930, 903, 887, 810, 729, 663; Anal. Found: C, 67.10; H, 6.23; N, 3.92 %. Calcd for $C_{40}H_{44}O_2N_2S_4$: C, 67.38; H, 6.22; N, 3.93 %.

[BDTT]$_5$[DCN-CP]$_3$. A hot saturated solution of BDTT (11.3 mg, 0.039 mmol) in benzene (3 ml) and a hot saturated solution of DCN-CP (20 mg, 0.039 mmol) in benzene (3 ml) was combined. After the resulting solution was concentrated by heating to 2 ml, acetonitrile (3 ml) was added, and then the solution was concentrated to 1 ml and allowed to cool gradually to room temperature. The fine crystals which separated out were collected by filtration and washed with a small amount of acetonitrile to give [BDTT]$_5$[DCN-CP]$_3$ as a brown powder (19.3 mg) in 83% yield: mp > 300 °C; FTIR (KBr, cm^{-1}) 2956, 2920, 2870, 2208, 1849, 1782, 1728, 1666, 1618, 1508, 1489, 1460, 1429, 1363, 1333, 1255, 1217, 1180, 1092, 1053, 926, 879, 827, 658; Anal. Found: C, 61.82; H, 5.35; N, 3.04 %. Calcd for $C_{152}H_{150}O_6N_6S_{25}$: C, 61.71; H, 5.11; N, 2.84 %.

Preparation of anion radical salts

[NMQ][DCNS-CP]$_3$. A hot saturated benzene solution of DCNS-CP and a hot saturated acetonitrile solution of *N*-methyquinolinium iodide (NMQI) were combined. The resulting solution was concentrated to two thirds of its original volume and then allowed to cool to room temperature. Crystals which separated out were collected and washed with a small amount of acetonitrile to afford [NMQ][DCNS-CP]$_3$ as black needles in 75% yield. The stoichiometry of the salt was determined by elemental analysis: mp 246 – 248 °C, decomp; FTIR (KBr, cm^{-1}) 2956, 2916, 2881, 2187, 1716, 1631, 1593, 1547, 1483, 1454, 1415, 1377, 1352, 1323, 1255, 1228, 1207, 1165, 1093, 1047, 1020, 987, 895, 885, 862, 822, 798, 779, 742, 719, 633; Anal. Found: C, 72.13; H, 6.44; N, 4.70 %. Calcd for $C_{124}H_{136}O_6N_7Se_3$: C, 72.39; H, 6.65; N, 4.76 %.

[DEBPy][DCNS-CP]$_4$•8H$_2$O. In a manner similar to that for [NMQ][DCNS-CP]$_3$, [DEBPy][DCNS-CP]$_4$•8H$_2$O was prepared as black needles in 39% yield starting with a hot benzene solution of DCNS-CP and a hot acetonitrile solution of *N*,*N'*-diethylbipyridinium diiodide (DEBPyI$_2$): mp >300 °C; FTIR (KBr, cm^{-1}) 3400 br, 2956, 2918, 2877, 2183, 1711, 1633, 1597, 1543, 1485, 1450, 1415, 1377, 1354, 1317, 1255, 1227, 1207, 1161, 1095, 1045, 1020, 995, 860, 796, 783, 746, 721, 663; Anal. Found: C, 68.32; H, 7.05; N, 4.81 %. Calcd for $C_{166}H_{202}O_{16}N_{10}Se_4$: C,68.53; H, 7.00; N, 4.81 %.

[DMBPy][DCNS-CP]$_4$•4H$_2$O. In a manner similar to that for [NMQ][DCNS-CP]$_3$, [DMBPy][DCNS-CP]$_4$•4H$_2$O was prepared as black needles in 52% yield starting with a hot benzene solution of DCNS-CP and a hot acetonitrile solution of *N*,*N'*-dimethylbipyridinium diiodide (DMBPyI_2): mp > 300 °C; FTIR (KBr, cm^{-1}) 3400 br, 2958, 2916, 2877, 2187, 1712, 1635, 1597, 1543, 1485, 1450, 1412, 1377, 1356, 1323, 1257, 1228, 1203, 1163, 1095, 1055, 1018, 893, 866, 783, 665; Anal. Found: C, 69.77; H, 6.77; N, 4.84 %. Calcd for $C_{164}H_{190}O_{12}N_{10}Se_4$: C, 70.12; H, 6.82; N, 4.99 %.

[NMPy][DCNS-CP]•0.5C_6H_6. A hot saturated benzene solution of DCNS-CP and a hot saturated acetonitrile solution of *N*-methylpyridinium iodide (NMPyI) were combined and the resulting solution was concentrated to one twenty-fifth of its original volume. The volume of the solution was then increased to seven times by adding benzene and the resulting solution was cooled to room temperature. Crystals which separated out were collected and washed with a small amount of benzene to afford [NMPy][DCNS-CP]•0.5C_6H_6 as a brown powder in 57% yield. The 1 : 1 stoichiometric ratio containing 0.5 mol of benzene was determined by elemental analysis: mp > 300 °C; FTIR (KBr, cm^{-1}) 3047, 3001, 2949, 2912, 2875, 2187, 1766, 1720, 1637, 1593, 1535, 1487, 1441, 1415, 1379, 1352, 1315, 1196, 1113, 1090, 1020, 903, 777; Anal. Found: C, 73.26; H, 6.88; N, 5.21 %. Calcd for $C_{47}H_{53}O_2N_3Se$: C, 73.23; H, 6.92; N, 5.45 %.

RESULTS AND DISCUSSION

The new acceptor, DCNS-CP, **2**, is air-stable and exhibited two pairs of reversible one-electron redox waves in its cyclic voltammogram. The electrochemical data obtained by the CV method are summarized in TABLE I. The first half-wave reduction potential ($E_1^{1/2}$) of DCNS-CP is higher by 0.23 V than that of BT-TCNQ[1] and is almost comparable to that of TCNQ, indicating that DCNS-CP possesses a strong electron-accepting ability. Fortunately, the on-site Coulombic repulsion in the dianion state of DCNS-CP is markedly decreased compared with that of TCNQ since the ΔE ($= |E_2^{1/2} - E_1^{1/2}|$) value for DCNS-CP is significantly smaller than that of TCNQ. The anion radical of DCNS-CP is significantly thermodynamically stabilized due to the delocalization of the negative charge over the two oxygen atoms and the (dicyanomethylene)selenoquinonoid moiety, which is revealed by its log K_{sem} value of 5.42.

DCNS-CP formed CT complexes with TTF, TTT, BDTT (**6**),[10] and TMTSF whose conductivities and related physical properties are listed in TABLE II. [TTF][DCNS-CP], [TTT][DCNS-CP], and [BDTT][DCNS-CP] showed an extremely broad and characteristic intrastack CT absorption band (ν_{CT})[11] at a very low energy region of 2700 – 3300 cm^{-1} (TABLE II), revealing a segregated stacking mode in a

TABLE I Electrochemical data[a] of DCNS-CP and reference compounds in CH_2Cl_2

Compound	$E_1{}^{1/2}$	$E_2{}^{1/2}$	ΔE	log K_{sem}
DCNS-CP	+0.19	−0.13	0.32	5.42
DCNT-CP	+0.20	−0.12	0.32	5.42
TCNQ	+0.22	−0.36	0.58	9.83
DCN-CP	+0.29	−0.22	0.51	8.64

[a] Potentials are given in V *vs.* saturated calomel electrode (SCE), determined with 1.0 mmol dm^{-3} in CH_2Cl_2 with 0.1 mol dm^{-3} Bu_4NClO_4 at room temperature (scan rate: 50 mV s^{-1}). $E_1{}^{1/2}$ and $E_2{}^{1/2}$ values were obtained by averaging the cathodic and anodic peak potentials.

mixed valence state. The partial CT conditions of these salts are also revealed by the ν_{CO} bands in their IR spectra, which appeared at a lower wave-number region than that of DCNS-CP itself and at a higher region than that of fully ionic [DCNS-CP][Li] (1533 cm^{-1}). In consequence, the conductivities on compaction pellets of these salts are fairly high. In contrast, [TMTSF][DCNS-CP]$_2$ does not show such a shift of the ν_{CO} band to the low wave-number region, so that the low conductivity of the TMTSF complex can be attributed to its insufficient CT state. The ν_{CN} band appears to be significantly influenced by the stacking mode of the conduction column,[12] although the ν_{CO} band is roughly pro-

TABLE II Conductivities[a] and related physical data of the poly-crystalline complexes

CT-salt	FTIR data[b]			compaction pellet	
	ν_{CN}	ν_{CO}	ν_{CT}	$\sigma_{r.t.}$	E_a
		cm^{-1}		Scm^{-1}	eV
[TTF][DCNS-CP]	very weak	1537	2700	6.4	0.060 [c]
[TTT][DCNS-CP]	2212	1541	2800	1.2	0.039 [d]
[BDTT][DCNS-CP]	2189	1541	3300	0.16	—
[TMTSF][DCNS-CP]$_2$	2206	1597	>8000	6.0×10^{-6}	—
[TTF][DCNT-CP]	2211	1539	2700	3.1	0.073 [e]
[TTT][DCNT-CP]	2185	1543	2800	0.72	0.045 [d]
[TTF][DCN-CP]	2204	1533	>8000	3.7×10^{-5}	—
[BDTT][DCN-CP]	2208	1508	>8000	7.7×10^{-9}	—

[a] Four-probe method. [b] Measured with FTIR using KBr disk; ν_{CN} of DCNS-CP and DCN-CP are 2210 and 2216 cm^{-1}, respectively; ν_{CO} of DCNS-CP and DCN-CP are 1599 and 1597 cm^{-1}, respectively. [c] Temperature range of 142—56 K. [d] Near to room temperature. [e] From room temperature down to 80 K.

portional to the degree of CT. The compaction pellets prepared from the poly-crystalline [TTF][DCNS-CP] and [TTT][DCNS-CP] exhibited semiconductive temperature dependencies, but with fairly small activation energies (E_a's) as shown in TABLE II.

After many fruitless efforts of searching conditions to grow crystals, we have succeeded in preparing single crystals of [TTF][DCNS-CP] and [TTT][DCNS-CP]. The room temperature conductivities of these single crystals (TABLE III) are surprisingly high values of 420 and 450 Scm^{-1} at ambient pressure, which are almost the same magnitudes as that of the [TTF][TCNQ] complex (500 Scm^{-1}).

TABLE III Conductivities[a] of the single-crystalline complexes

CT-salt	$\sigma_{r.t.}$ Scm^{-1}	σ_{max} (T) Scm^{-1} (K)	T(MI) (K)
[TTF][DCNS-CP]	420	500 (220)	182
[TTT][DCNS-CP]	450	760 (155)	80

[a] Conductivities were taken only in the direction of the longest crystal face.

The temperature dependencies of the resistivities of these two single crystals are shown in FIGURES 3 and 4. As temperature decreases, the resistivity decreases monotonically down to 220 K for [TTF][DCNS-CP] and down to 155 K for [TTT][DCNS-CP], where the conductivity reaches maximum values of 500 Scm^{-1} and 760 Scm^{-1}, respectively. After passing through the maximum, the metallic state of the complexes becomes unstable and a metal-to-insulator (M-I) transition occurs at 182 K for [TTF][DCNS-CP]. The metallic state of [TTT][DCNS-CP] appears to be unstable in the temperature region from 155 to 80 K. The conductivity was unmeasurable below about 80 K, since the crystal was broken at this temperature. The conductivity enhancement in the metallic region is larger in [TTT][DCNS-CP] than in [TTF][DCNS-CP], and the M-I transition temperature is lower in the former than in the latter. In this respect the metallic state is more stable in [TTT][DCNS-CP] than in [TTF][DCNS-CP] in the temperature range investigated here. Although single crystals of DCNT-CP complexes have not yet been available, activation energies for the conductivities measured on compaction pellets of [TTF][DCNT-CP] and [TTT][DCNT-CP] were also as small as those for [TTF][DCNS-CP] and [TTT][DCNS-CP] (TABLE II). Therefore, these DCNT-CP complexes are expected to show a metallic temperature dependence on a single crystal.

The crystal structures of the metallic complexes have not been determined since the poor quality of the crystals precluded the crystal analysis. However, the following evidence shows that the metallic conduction column is constructed from the partially filled LUMO state of DCNS-CP molecules, not from the donor molecules. DCNS-CP yielded

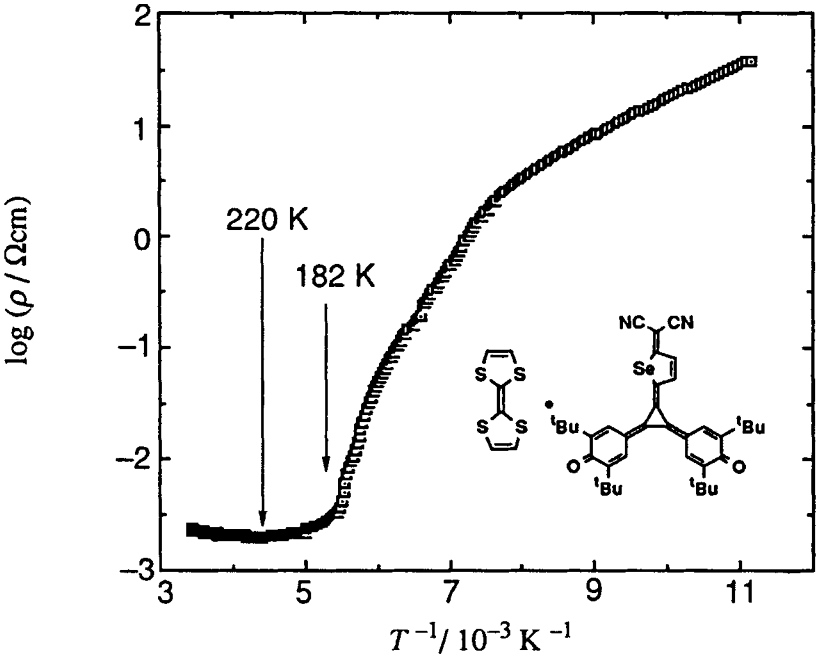


FIGURE 3 Temperature dependence of resistivity for a single crystal of [TTF][DCNS-CP].

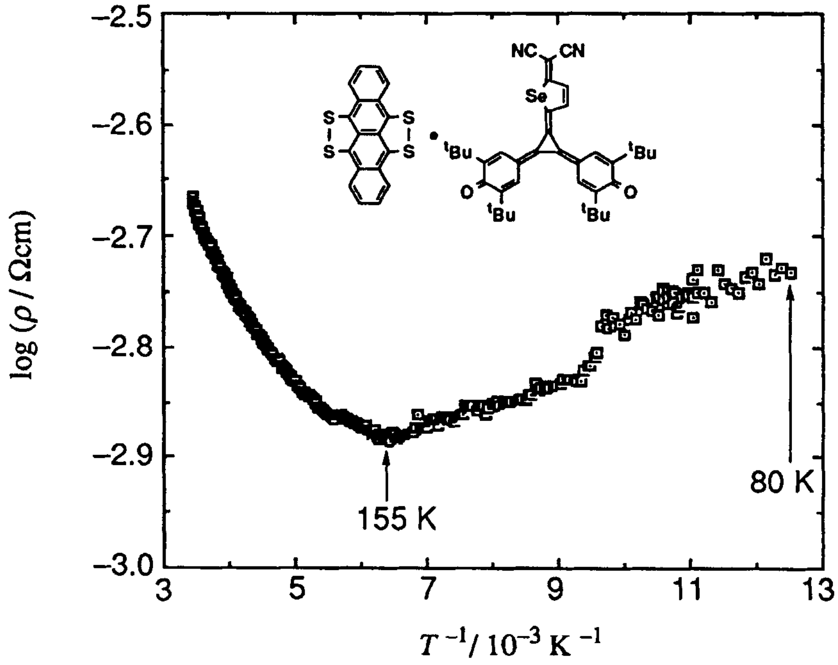


FIGURE 4 Temperature dependence of resistivity for a single crystal of [TTT][DCNS-CP].

TABLE IV Conductivities[a] and related physical data of anion radical salts of DCNS-CP

Anion radical salt	$\sigma_{r.t.}$ Scm^{-1}	ν_{CN}[b] cm^{-1}	ν_{CO}[b] cm^{-1}
[NMPy][DCNS-CP]	1.1×10^{-3}	2187m	1535vs
[NMQ][DCNS-CP]$_3$	0.42	2187w	1547vs
[DMBPy][DCNS-CP]$_4$	1.9×10^{-2}	2187w	1543vs
[DEBPy][DCNS-CP]$_4$	3.1×10^{-2}	2183w	1543vs

[a] Four-probe method on a compaction pellet measured at room temperature. [b] Measured with FTIR using KBr disk; ν_{CN} and ν_{CO} of DCNS-CP: 2210 and 1599 cm^{-1}, respectively.

anion radical salts with NMPyI, NMQI, DMBPyI$_2$, and DEBPyI$_2$. Of these, [NMQ][DCNS-CP]$_3$ showed a fairly high room temperature conductivity of 0.42 S cm^{-1}, even when the measurement was carried out on a compressed poly-crystalline sample (TABLE IV). In addition, the thermoelectic power of the metallic [TTF][DCNS-CP] is around -25 μVK^{-1} at room temperature.[13] The negative sign at the metallic temperature region tells us the electron conduction is surely concerned in the metallic conduction. Moreover the importance of the selenophene moiety of DCNS-CP for the conduction is proved by the fact that the conductivity of [BDTT][DCNS-CP] is 60 times higher than that of [BDTT][DCNT-CP]. The conductivity on the compaction pellet of [TTF][DCNS-CP] is 10^5 times higher than that of the reference complex, [TTF][DCN-CP], and the conductivity of [BDTT] [DCNS-CP] is 10^8 times higher than that of [BDTT][DCN-CP]. The low conductivities for the DCN-CP complexes can be ascribed to their fully ionic CT conditons, because these complexes showed ν_{CN} and ν_{CO} bands at very low wavenumber regions as seen in TABLE II. Interestingly, DCN-CP does not form CT-complexes with TMTSF, bisethylenedithiotetrathiafulvalene (BEDT-TTF), and hexamethylenetetratellurafulvalene (HMTTeF) having more weak electron-donating ability, although the complexes with these weak donors are expected to exist in a partial CT-condition. From this evidence it is suggested that the five-membered heterocyclic ring of DCNS-CP, as well as that of DCNT-CP, is absolutely essential to form a segregated stacked conduction column of the acceptor molecules.

Thus, [TTF][DCNS-CP] and [TTT][DCNS-CP] are of special interest as the first examples of metallic CT complexes based on an organic π-acceptor not belonging to the TCNQ, DCNQI, and M(dmit)$_2$ families,[14] and containing three electron-accepting functional groups in full conjugation. Particularly DCNS-CP is the first [n]radialene derivative (n=3, 4, 5, and 6) affording molecular metals.[15]

A useful information on the mode of stacking has been provided by MNDO-PM3 MO calculations[16] on DCNS-CP. As shown in FIGURE 5, there are considerably large

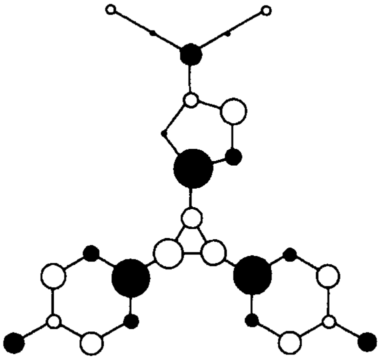


FIGURE 5 πAO coefficients in the LUMO of DCNS-CP obtained from MNDO-PM3 calculations.

πAO coefficients on the selenoquinonoid ring carbons and on the dicyanomethylene carbon, C(CN)2 in the π-LUMO, and there are antibonding orbitals at the C3'''—C4''' bond and at the exocyclic bonds of the selenoquinonoid ring. Thus the stacking mode shown in FIGURE 6 is most plausible for formation of the tight-binding one-dimensional conduction-band among the acceptor molecules in which effective in-phase bonding interactions can occur among the π-LUMO lobes of each atom of C(CN)2, C2''', C3''', C4''', C5''', C3 in one molecule and those of each atom of C3, C5''', C4''', C3''', C2''', C(CN)2 in the neighboring molecules stacked up and down, respectively.

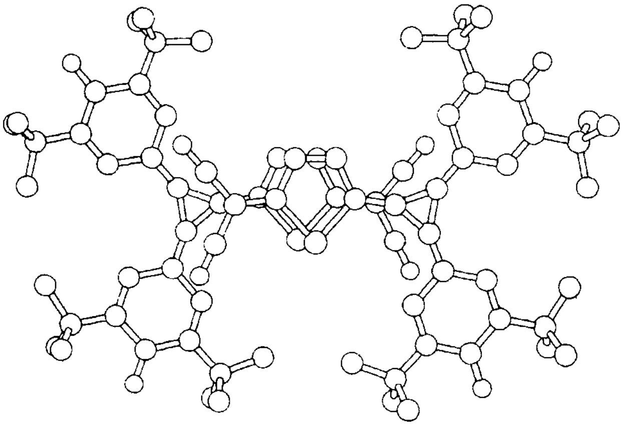


FIGURE 6 An expected stacking mode of the DCNS-CP molecules in the metallic complexes.

Intermolecular chalcogen – chalcogen atomic contacts can also be maintained in the stack. Moreover, the intermolecular overlapping mode illustrated in FIGURE 6 is quite suitable to avoid the steric hindrance of the four bulky *tert*-butyl groups and to stack the dicyanomethyleneselenoquinonoiod moieties in short face to face manner, since the *tert*-butyl groups of the neighboring molecules are stacked alternatively.

DEDICATION

This paper is dedicated to Professors Y. Maruyama and F. Ogura for their outstanding contribution to the fields of solid state science and material chemistry.

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REFERENCES AND NOTES

1. K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *J. Chem. Soc., Chem. Commun.*, 1816 (1987); K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *Bull. Chem. Soc. Jpn.*, **62**, 1539 (1989).
2. M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan, and S. Gronowitz, *J. Phys. Chem.*, **84**, 427 (1980).
3. D. Lorcy, K. D. Robinson, Y. Okuda, J. L. Atwood, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 345 (1993).
4. K. Takahashi and S. Tarutani, *J. Chem. Soc., Chem. Commun.*, 519 (1994).
5. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. -H. Whangbo in *Organic Superconductors (Including Fullerenes)* (Englewood Cliffs, NJ, 1992).
6. Preliminary communication: K. Takahashi and S. Tarutani, *Adv. Mater.*, **7**, 639 (1995).
7. K. Takahashi and S. Tarutani, *Heterocycles*, **43**, 1927 (1996).
8. R. West, D. C. Zeecher, and W. Goyert, *J. Am. Chem. Soc.*, **92**, 149 (1970).
9. K. Komatsu, R. West, and D. Beyer *J. Am. Chem. Soc.*, **99**, 6290 (1977).
10. K. Takahashi, T. Nihira, and K. Tomitani, *J. Chem. Soc., Chem. Commun.*, 1617 (1993); K. Takahashi, *Pure Appl. Chem.*, **65**, 127 (1993).
11. J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975); J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976).
12. From this evidence it is suggested that the conduction column may be constructed from the (dicyanomethylene)selenoquinonoid moiety as shown in FIGURE 6, not from the benzoquinonoid moieties.
13. The measurement of the thermoelectric power for the metallic single crystal is in progress. Details of the temperature dependence of the thermopower, as well as the spin susceptibility will be reported in a separate paper.
14. Metallic CT complexes derived from organic donor and various different type of organic acceptor molecules have been known, but the metallic conduction columns are not constructed from the acceptor molecules: S. Horiuchi, H. Yamochi, G. Saito, K. Sakaguchi, and M. Kusunoki, *J. Am. Chem. Soc.*, in press.
15. H. Hopf and G. Maas, *Angew. Chem. Int. Ed. Engl.*, **31**, 931 (1992).
16. J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 211 (1989).