Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Tetracyanoquinodimethanes Fused With A [1,2,5]Chalcogenadiazole Ring

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Version of record first published: 24 Sep 2006

To cite this article: Takanori Suzuki, Yoshiro Yamashita, Takanori Fukushima & Tustomu Miyashi (1997): Tetracyanoquinodimethanes Fused With A [1,2,5]Chalcogenadiazole Ring, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 296:1, 165-180

To link to this article: http://dx.doi.org/10.1080/10587259708032319

Mol. Cryst. Liq. Cryst., 1997, Vol. 296, pp. 165–180
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TETRACYANOQUINODIMETHANES FUSED WITH A [1,2,5]CHALCOGENADIAZOLE RING*

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(Received 3 July 1996; In final form 4 September 1996)

Abstract The title compounds were designed as novel electron acceptors and prepared from 4,7-dihalobenzo[1,2,5]chalcogenadiazoles in two steps. Comparisons of X-ray structures indicate that the packing arrangements of the different chalcogenadiazole derivatives are quite different from each other in spite of their similar molecular geometries. In the crystal of the selenadiazole derivative (**3**) are observed very short intermolecular contacts between Se and N to form infinite "sheet"-like network, whereas coplanar dyads are formed by C-H•••N≡C hydrogen bonds in the oxadiazole (**1**) and thiadiazole derivatives (**2**). These acceptors afforded stable anion-radical salts upon one-electron reduction and gave highly conductive charge-transfer complexes with tetrathiafulvalene derivatives.

Keywords: *Organic conductor, electron acceptor, multi-redox system, intermolecular interaction, TCNQ*

INTRODUCTION

Since the discovery of metallic behavior in charge-transfer (CT) crystals of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ),[1] the chemistry of molecular conducting materials has been widely developed,[2] and chemists have been making much effort to produce novel multi-stage redox systems which afford organic solids with high electrical conductivities. In 1980 the cation radical salts of tetramethyltetraselenafulvalene (TMTSF)[3] and in 1983 bis(ethylenedithio)-TTF (ET)[4] were reported to exhibit superconducting behavior at low temperature. To date more than sixty entries of ion radical salts and CT crystals are known as organic superconductors,[5] and all of them excluding fullerenes are based on molecules possessing chalcogen atoms on the periphery like TTF-type donors. So that, it seems natural that much attention has been focused on developing novel chalcogen-containing donor molecules related to TMTSF or ET.[6] In these systems the metal-insulator transition is suppressed by the multi-dimensionality in electronic and crystal structures by the interaction between chalcogen atoms.[7]

On the other hand, the chemistry of electron acceptors is left undeveloped in this field when compared with that of electron donors. Although there has been reported the superconducting behavior in some metal complexes of 1,3-dithiole-2-thione-4,5-dithiolate [M(dmit)$_2$],[8] organic acceptors containing no metal atoms never afford superconductors so far. The reason is that most acceptors are unable to interact in the lateral direction.

In this connection TCNQ derivatives fused with chalcogen-heterocycles[9] are of interest because the intermolecular interactions in these molecules are expected to suppress the metal-insulator transition. In fact bis([1,2,5]thiadiazolo)-TCNQ (**4**) afforded an organic metal whose metallic state is stable down to 4 K.[10] Its selenium congeners (**5** and **6**) exhibit further stronger interactions than **4**,[11] so that they might be better candidates to form organic metals. However, CT crystals of **6** were hard to form because of its lower electron affinity (E_1^{red} = -0.23 V vs. SCE) than **4** (E_1^{red} = -0.02 V) or TCNQ (E_1^{red} = +0.18 V). Although **4** forms highly conductive complexes with several donors,[12] another disadvantage of this skeleton is the inclusion behavior in its CT crystals[11,13] facilitating the formation of unfavorable mixed-stack complexes.

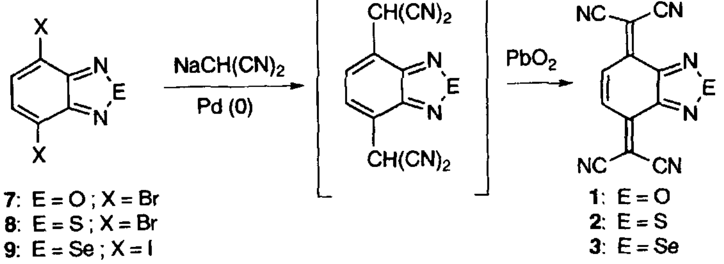
On the basis of these results we have now designed the TCNQ derivatives fused with only one heterocycle, **1** - **3**, in the anticipation that the clathration ability would be diminished by intercepting the infinite network formation of **4** - **6**. Stronger electron affinity than **4** - **6** are also expected by removing one aromatic ring fused to the TCNQ skeleton.[14] The effects of the chalcogen atoms on their molecular and solid-state properties are another subject to be explored, which would be helpful in developing a new concept of molecular design for superior electron acceptors.

RESULTS AND DISCUSSION

Preparation and Molecular Structure

4,7-Dihalobenzo[1,2,5]chalcogenadiazoles, **7** - **9**, were prepared according to the literature.[15-18] By using Takahashi's method[19] they were converted into the corresponding 4,7-bis(dicyanomethyl) derivatives which were directly oxidized with PbO$_2$ to give new acceptor molecules, **1** - **3** (Scheme 1). A TCNQ derivative fused with a thiadiazolo[3,4-b]pyrazine ring was also another target molecule in this work, which would exhibit further stronger electron affinity than **1** - **3**. Its precursor **10** was prepared according to Scheme 2. However, attempts to convert **10** into the TCNQ derivative in the similar manner to **1** - **3** were unsuccessful.

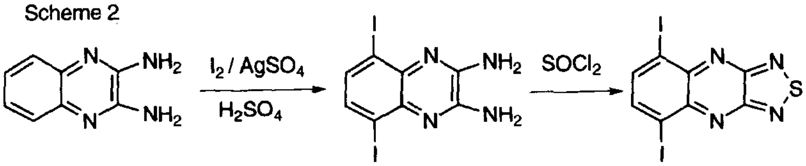
Scheme 1



7: E = O ; X = Br
8: E = S ; X = Br
9: E = Se ; X = I

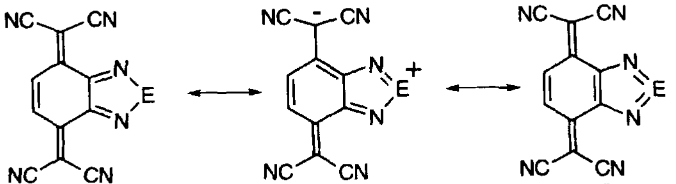
1: E = O
2: E = S
3: E = Se

Scheme 2



10

Scheme 3

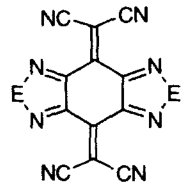


Form A Form B Form C

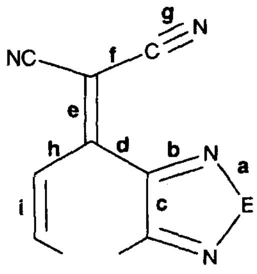
TABLE I Comparisons of bond distances.[a]

	1 (E = O)	**2** (E = S)	**3** (E = Se)
a (E = O)	1.391(3)	-	-
a (E = S)	-	1.622(3)	-
a (E = Se)	-	-	1.791(4)
b	1.306(3)	1.328(4)	1.319(6)
c	1.418(3)	1.418(4)	1.434(6)
d	1.457(4)	1.453(4)	1.461(6)
e	1.355(3)	1.356(4)	1.360(6)
f	1.443(4)	1.435(4)	1.434(8)
g	1.133(4)	1.132(4)	1.135(9)
h	1.446(4)	1.442(4)	1.448(6)
i	1.342(4)	1.336(4)	1.341(7)

a) Averaged over assumed mm symmetry.



4: E = S,S
5: E = S,Se
6: E = Se,Se



X-ray structural analyses of **1** - **3** indicate that they are almost planar molecules (Figure 1).[20] The largest deviations from the molecular plane are only 0.11 Å (N4) in **1** and 0.06 Å (N2) in **2**, whereas that in **3** is a little larger (0.5 Å at N4) due to the intermolecular interaction (*vide infra*). Slight deformation of the TCNQ skeleton was observed in all cases as the widening (av. 124°) of the bond angles of C1-C3-C7 and C2-C4-C8. The bowing of two cyano groups are also evident in the case of **2** and **3** (C7-C9≡N3 and C8-C10≡N4; av. 175° in **2** and 174° in **3**). These distortions may be due to the steric interaction between the cyano groups and lone pairs of nitrogens in heterocycles.[21]

Close inspections of the bond distances in Table I indicate that there are no significant differences in the TCNQ skeleton (bonds d - i) in **1** - **3**. The bond d is longer than bond h in all cases, showing a negligible contribution of Form B in Scheme 3. Thus, the differences in bonds a - c reflect the nature of chalcogenadiazole rings. Aromaticity of chalcogenadiazole had been well discussed previously,[22] yet there still is a discrepancy in the conclusion. From our results it is evident that the bond alternation in thiadiazole is much smaller than in selenadiazole, thus the thiadiazole is proven more aromatic with a larger contribution of Form C. The C=N bond length in parent oxadiazole was reported 1.300 Å,[23] suggesting a high degree of diene character in this heterocycle. A similar value for bond b in **1** indicates that the aromatic character in oxadiazole is smaller than thiadiazole and selenadiazole because of lack of contribution of Form C.

Molecular Packing and Intermolecular Interaction

In contrast to the tendency to form isomorphous crystals in **4** - **6**, none of the new acceptors crystallizes isomorphously to each other. The short contacts of E•••N≡C were

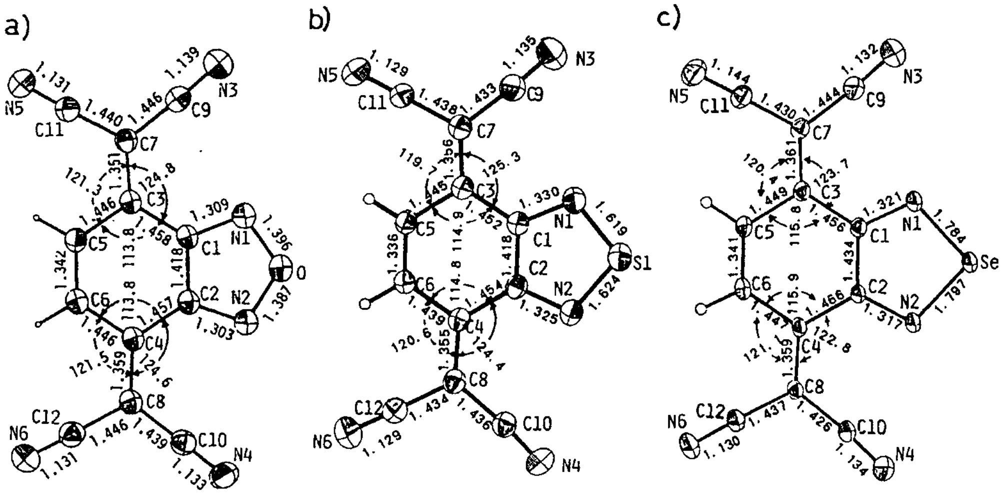


FIGURE 1 Thermal ellipsoids of (a) **1**, (b) **2**, and (c) **3** with the bond distances and selected bond angles.

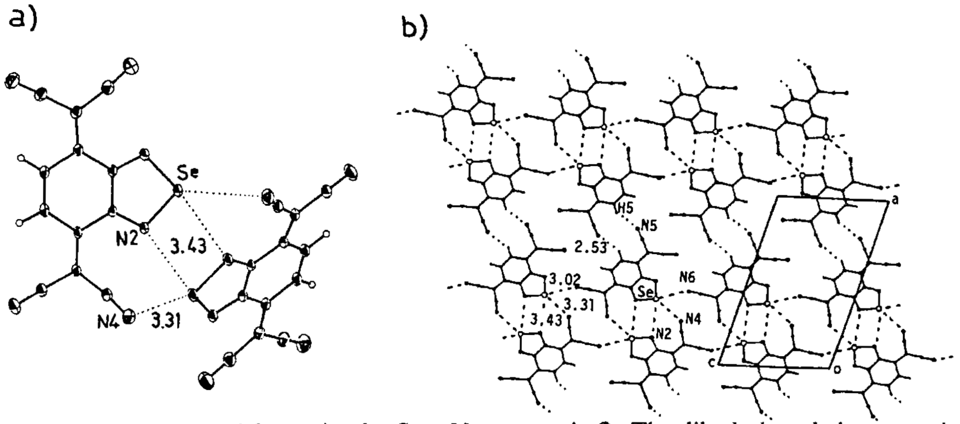


FIGURE 2 (a) Dyad formation by Se•••N contacts in **3**. The dihedral angle between the two molecular planes is 57.4°. (b) Infinite "sheet"-like network by Se•••N interactions and C-H•••N≡C hydrogen bonds in **3**.

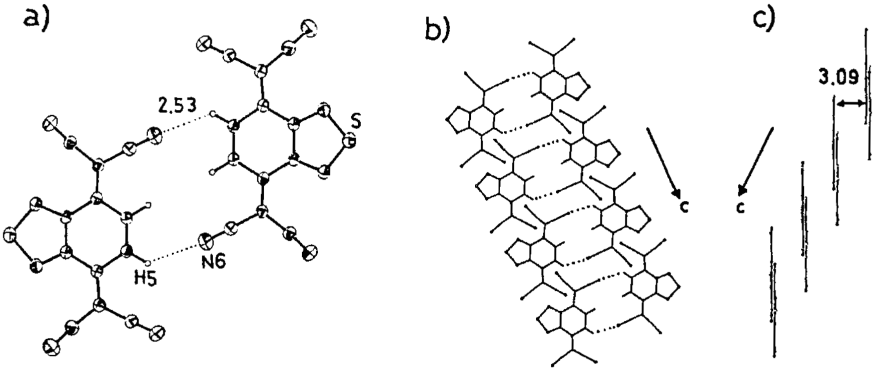


FIGURE 3 (a) Coplanar dyad formation in **2**. The dihedral angle and interplanar distance are 0° and 0.34 Å, respectively. The dyads are stacked along the c axis with the interplanar distance of 3.09 Å; (b) top view, and (c) side view.

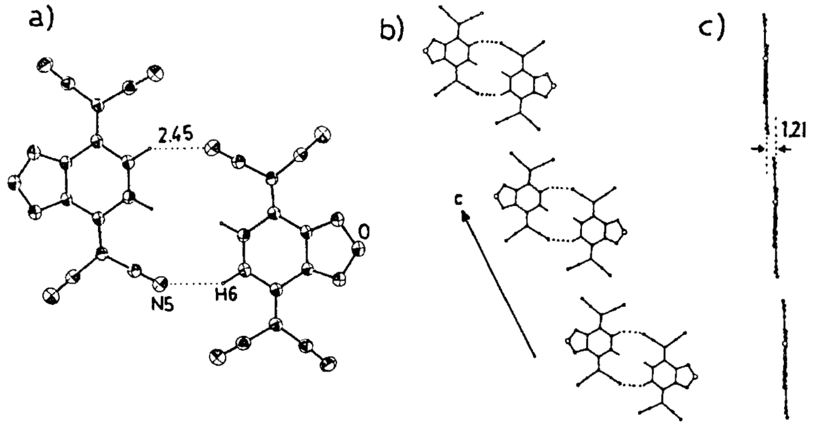


FIGURE 4 (a) Coplanar dyad formation in **1**. The dihedral angle and interplanar distance are 0° and 0.21 Å, respectively. Coplanar arrangement of dyads along the c axis; (b) top view, and (c) side view.

observed without exception in **4** - **6**, their CT crystals, and their anion radical salts, so that the electrostatic interaction through these contacts seems to be the determining factor of their packing arrangements.

Similar short contacts[24] of Se•••N≡C (3.31 Å) as well as the Se•••N contacts between heterocycles (3.43 Å) are present in the crystal of **3**, by which two molecules related by a 2-fold axis are connected (Figure 2a). The dyads thus formed are further connected by C-H•••N≡C hydrogen bonds (2.58 Å) and by another Se•••N≡C interaction (3.02 Å), resulting in the formation of two-dimensional corrugated "sheet"-like network on the ac plane (Figure 2b).

On the other hand, no short S•••N contacts exist in the crystal of **2**, yet molecules are connected to form coplanar dyads by C-H•••N≡C hydrogen bonds (2.53 Å) as shown in Figure 3a. The coplanarity of the molecules in the dyad suggests that the hydrogen bonds in **2** is stronger than in **3**. The dyads are stacked along the c axis to form one-dimensional columnar stacks but the molecular planes are slipped to each other with a marginal overlap as shown in Figures 3b and 3c. This packing arrangement indicates that the electrostatic interaction through S•••N≡C contacts is less effective than the hydrogen bond of C-H•••N≡C type in determining the crystal packing, and again confirms that the interaction between S and N≡C is weaker than the Se•••N≡C interaction.

Since it is probable that the stabilization by the O•••N≡C interaction is further smaller than the S•••N≡C type, the short contacts between O•••N≡C are absent in the crystal of **1**. Similar to the case of **2** the molecules related by an inversion center are connected by C-H•••N≡C hydrogen bonds (2.45 Å) to form coplanar dyads (Figure 4a). These dyads are also arranged to form a coplanar array along the c axis (Figure 4b and 4c), which is different from the stacking arrangement in **2**.

Multi-Redox Behavior

Redox potentials of these new acceptors were measured by cyclic voltammetry and summarized in Table II along with those of TCNQ. All the waves in voltammograms are reversible, indicating that their anions are quite stable. As expected, the values of E_1^{red} of **2** and **3** are much higher than those of **4** - **6**, showing their high electron affinities. Because of the strongly electron-withdrawing property of C=N-O moieties, **1** is even a stronger acceptor than TCNQ itself.

In these planar systems, the values of K_{sem} correspond to the degree of delocalization of negative charge into the annelated ring. In all cases the K_{sem} values are smaller than that of TCNQ, thus the intramolecular Coulombic repulsion is reduced in **1** - **3**. The values are also different from each other in **1** - **3**, and that in **3** is smallest and comparable with that of **4** fused with two thiadiazole rings (log K_{sem} = 8.10). This is in accord

TABLE II Redox potentials$^{a)}$ and semiquinone formation constants (K_{sem})$^{b)}$ of acceptors.

	E_1^{red}	E_2^{red}	E_3^{red}	log K_{sem}
1 (E = O)	+0.22	-0.29	-1.98	8.79
2 (E = S)	+0.12	-0.38	-$^{c)}$	8.62
3 (E = Se)	+0.04	-0.43	-1.79	8.10
TCNQ	+0.18	-0.36	-$^{c)}$	9.31

a) E/V vs.SCE, 0.1 mol dm^{-3} Et$_4$NClO$_4$ in MeCN, Pt electrode, scan rate 100 mV s^{-1}. b) $K_{sem} = [A^{-\bullet}]^2/[A^o][A^{2-}]$, log $K_{sem} = (E_1^{red} - E_2^{red})/0.058$. c) The third cathodic peak could not be observed down to -2.0 V.

TABLE III Electrical resistivities$^{a)}$ and molar ratios$^{b)}$ of the CT complexes.

donor$^{c)}$	(E^{ox} / V)$^{d)}$	**1** (E = O)	**2** (E = S)	**3** (E = Se)
TTF	(+0.31)	1.1 x 10^3 [~1:1]	0.78 [~1:1]	1.5 [~4:3]
TMTSF	(+0.41)	1.3 [4:3]	1.4 [1:1]	0.72 [1:1]
BMDT	(+0.45)	3.0 [3:2]	6.3 [3:2]	3.6 [3:2]
BEDT	(+0.45)	9.1 [3:2]	1.6 x 10^6 [1:1]	> 10^8 [1:1]
TMTTTF	(+0.47)	7.3 [1:1]	> 10^8 [1:1]	2.5 x 10^3 [1:2]
DBTTF	(+0.57)	7.5 x 10^3 [~3:2]	> 10^8 [~1:1]	> 10^8 [~1:1]

a) ρ / ohm cm, measured at room temperature on compressed pellets by the two-probe technique. b) Donor:acceptor ratio, based on the elemental analyses. c) TTF, tetrathiafulvalene; TMTSF, tetramethyltetraselenafulvalene; BMDT, bis(methylenedithio)-TTF; BEDT, bis(ethylenedithio)-TTF; TMTTTF, tetrakis(methylthio)-TTF; DBTTF, dibenzo-TTF. d) E/V vs. SCE, 0.1 mol dm^{-3} Et$_4$NClO$_4$ in MeCN, Pt electrode, scan rate 100 mV s^{-1}.

TABLE IV Electrical resistivities$^{a)}$ and molar ratios$^{b)}$ of the anion radical salts.

cation	**2** (E = S)		**3** (E = Se)	
H_4N^+	9.6 x 10^2	[~1:1]	1.6 x 10^4	[~1:1]
Me_4N^+	12	[~1:1]	-$^{c)}$	
Et_4N^+	5.7 x 10^2	[1:2]	3.0 x 10^3	[1:2]
nPr$_4$N$^+$	28	[1:2]	2.0 x 10^2	[1:2]
nBu$_4$N$^+$	5.6 x 10^4	[1:2]	1.3 x 10^2	[2:5]

a) ρ / ohm cm, measured at room temperature on compressed pellets by the two-probe technique. b) Cation:anion ratio, based on the elemental analyses. c) This salt could not be obtained in pure form because of the concomitant precipitation of Me$_4$NI.

with the fact that log K_{sem} of **6** (5.52) is much smaller than that in **4**, and incorporation of a selenium atom with large polarizability is very effective in reducing the Coulombic repulsion.

It is noteworthy that acceptors **1** and **3** also showed the third redox couples in their voltammograms, and the value is higher in selenadiazole **3** than in oxadiazole **1**. The order of E_3^{red} of **1** - **3** in magnitude is the same as E_1^{red} of the unsubstituted benzo[1,2,5]chalcogenadiazoles (-1.30 V for Se, -1.48 V for O, and -1.53 V for S), suggesting that the NLUMOs in **1** - **3** are mainly participated by the same character in LUMOs of benzochalcogenadiazoles.

CT Complexes and Anion Radical Salts.

In contrast to the fact that **4** formed insulating CT complexes with TTF derivatives,[12] new acceptors afforded highly conducting complexes as shown in Table III. These results indicate that the inclusion behavior of **4** is diminished by eliminating one fused heterocycle, preventing formation of inclusion cavities. A noteworthy example is TMTSF•**3** (1:1) complex where incomplete charge transfer is realized between the donor and acceptor molecules. The C≡N stretching frequency of this complex (2194 cm^{-1}) is just between those of neutral **3** (2218 cm^{-1}) and Li^+ $\mathbf{3}^{-\bullet}$ (2175 cm^{-1}), supporting this idea.

Different from **4** - **6** that form isomorphous CT crystals,[11] the donor-to-acceptor ratios are different in the series of the complexes of **1** - **3** with the same donor, thus their packing arrangements in CT crystals are diverted by changing the chalcogen atom in the heterocycle. From these results it is suggested that the crystal structures in neutral **4** - **6** and their CT complexes are determined by the shape of their skeleton, while the nature of the chalcogen atom affects the packing arrangement more apparently in the case of the molecular framework of **1** - **3**.

In accord with the reversible redox properties, new acceptors afforded stable anion radical salts upon one-electron reduction. Because **1** was obtained only in low yield, the properties of anion radicals were investigated on **2** and **3** in detail (Table IV). When Et_4NI and $n$$Pr_4NI$ were used as reducing agents, only 1:2 salts were obtained even in the presence of an excess amount of iodide ion. The molar ratios of the salts are unique for the kind of ammonium ions, and the ratios change from 1:1 to 1:2 or 2:5 with elongation of the alkyl chain of ammonium ions. These features are quite similar to the case of $\mathbf{4}^{-\bullet}$ salts, in which two-dimensional structures formed by S•••N≡C interaction result in such unique behavior.[25] It is likely that the E•••N≡C and/or C-H•••N≡C interactions are at work in these salts to form two-dimensional structures.[26]

Among these salts the properties of Me_4N^+ $\mathbf{2}^{-\bullet}$ is outstanding because this salt exhibits relatively high conductivity in spite of the fact that the partial CT state is unable to be achieved. This behavior would be related to the small intramolecular Coulombic repulsion of this molecule and one of the characteristic features induced by annelating the chalcogen hetetocycle.

CONCLUSION

The results described above clearly show the validity of molecular designing in this work. The systematic study using **1-3** indicates that the different nature of chalcogen atoms affects the redox and solid-state properties in these molecules. It is noteworthy that the on-site Coulombic repulsion is much decreased by annelation of selenadiazole, whereas the outstanding effect of oxadiazole is the enhancement of the electron affinity when attached to the TCNQ acceptor skeleton. This work has also revealed the relative importance of the intermolecular forces that determine the molecular packing, and the following order was deduced: Se•••N≡C > C-H•••N≡C > S•••N≡C > O•••N≡C. Such a finding is also useful in designing the new acceptor molecules although the effects of the C-H•••N≡C hydrogen bonds on the solid-state properties are not clear at this moment.

This work was in part supported by Grant-in-Aid for Scientific Research on Priority Areas (2), No. 7232205.

EXPERIMENTAL

Preparation of 5,8-diiodo[1,2,5]thiadiazolo[3,4-b]quinoxaline (**10**)

To a solution of 2,3-diaminoquinoxaline[27] (1.08 g, 6.75 mmol) in conc. H_2SO_4 (10 ml) was added $AgSO_4$ (4.21 g, 13.5 mmol) and iodine (8.57 g, 33.8 mol), and the whole mixture was heated at 110 °C for 12 h. The resulting precipitates were filtrated and washed with conc. H_2SO_4. The filtrate was poured into 120 g of ice water, and yellow powder was collected by suction. The crude product was washed with water and 2 M NH_3 aq, and purified by sublimation (4 x 10^{-2} Torr, 240 °C), giving yellow crystals of 2,3-diamino-5,8-diiodoquinoxaline (1.29g) in 46% yield. mp 310 - 313 °C [decomp] ; IR 3520-2920 (NH_2), 1656, 1496, 1456 cm^{-1}; MS m/z (relative intensity) 412 (M^+, 100), 158 (20). Anal. Found: C, 23.15; H, 1.60; N, 13.35. Calcd for $C_8H_6N_4I_2$: C, 23.32; H, 1.47; N, 13.60.

To a suspension of 2,3-diamino-5,8-diiodoquinoxaline (2.33 g, 5.66 mmol) in dry CH_2Cl_2 (60 mL) and dry pyridine (11.5 mL) was added $SOCl_2$ (6.47 g, 56.6 mmol) over 20 min at 0 °C under nitrogen. After stirring at room temperature for 45 h, the volatile material was completely removed under a reduced pressure and the residue was dried *in vacuo* for 24 h. The remaining solid was triturated with MeOH (60 mL), and the reddish precipitates (2.13 g) were filtrated and washed with MeOH (300 mL). Purification of the crude product by sublimation (4 x 10^{-2} Torr, 200 °C) afforded deep red crystals of **10** (1.86 g) in 75% yield. mp 253 - 255 °C [decomp] ; IR 1397, 1339, 1305, 922, 893, 869, 548 cm^{-1}; MS m/z (relative intensity) 440 (M^+, 100), 313 (32), 186 (11). Anal. Found: C, 21.69; H, 0.78; N, 12.43. Calcd for $C_8H_2N_4SI_2$: C, 21.84; H, 0.46; N, 12.73.

Preparation of [1,2,5]Oxadiazolotetracyanoquinodimethane (**1**)

Under a nitrogen atmosphere, malononitrile (475 mg, 7.21 mmol) was added to a suspension of sodium hydride (60%, oil suspension) (500 mg, 12.5 mmol) in dry THF (10 mL) and the mixture was stirred for 20 min at room temperature. After addition of 4,7-dibromobenzo[1,2,5]oxadiazole[15] (500 mg, 1.80 mmol) and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), the whole mixture was heated under reflux for 14 h. The resulting blue-black suspension was poured into water (500 mL) and washed with CH_2Cl_2 (300 mL x 2). The aqueous layer containing blue-violet dianion of **1** was acidified with conc. HCl and extracted with CH_2Cl_2 (300 mL x 2, 100 mL). The extract was washed with brine. Removal of the solvent gave the dihydro derivative of **1** as a pale violet solid, which was suspended in benzene (30 mL), EtOH (4 mL), and 5% aqueous HCl (10 mL). The mixture was shaken vigorously with PbO_2 (2.0 g, 8.3 mmol) for 20 min. The resulting insoluble material was removed through a celite pad and washed with CH_2Cl_2 (300 mL). The filtrate was washed with water (300 mL) and brine, dried over anhydrous sodium sulfate, and concentrated to 10 mL. After addition of MeOH (10 mL), the crude product was filtrated and purified by sublimation (4 x 10^{-2} Torr, 230 °C), giving yellow crystals of **1** (70 mg) in 16% yield. mp 299 - 300 °C ; IR (C≡N) 2223 cm^{-1}; MS m/z 246 (M^+). Anal. Found: C, 58.62; H, 0.98; N, 34.10. Calcd for $C_{12}H_2N_6O$: C, 58.55; H, 0.82; N, 34.14. NMR spectrum of **1** could not be measured for its low solubility in $CDCl_3$ as well as rapid decomposition in acetone-d_6 or DMSO-d_6.

Preparation of [1,2,5]Thiadiazolotetracyanoquinodimethane (**2**)

Under a nitrogen atmosphere, a suspension of 4,7-dibromobenzo[1,2,5]thiadiazole[16] (10.0 g, 34.0 mmol), sodium hydride (60%, oil suspension) (8.0 g, 200 mmol), $Pd(PPh_3)_4$ (1.44 g, 1.25 mmol), and malononitrile (8.80 g, 133 mmol) in dry THF (200 mL) was heated under reflux for 22 h. The mixture was poured into water (1 L) and washed with CH_2Cl_2 (500 mL x 2). The aqueous layer containing violet dianion was acidified with conc. HCl and extracted with CH_2Cl_2 (500 mL x 2, 100 mL x 2). The extract was washed with brine. Removal of the solvent gave the dihydro derivative as a pale green solid, which was suspended in benzene (400 mL), EtOH (60 mL), and 5% aqueous HCl (160 mL). The whole mixture was shaken vigorously with PbO_2 (34.0 g, 142 mmol) for 15 min. The resulting insoluble material was removed through a celite pad and washed with benzene. The organic layer was separated from the filtrate, washed with brine, and dried over anhydrous sodium sulfate. Removal of the solvent gave a yellow-brown solid (8.0 g), which was purified by sublimation (4 x 10^{-2} Torr, 230 °C), giving yellow crystals of **2** (3.97 g) in 45% yield. mp 298 - 300 °C ; IR 2218 (C≡N) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) d 7.72 (s, 2H); UV (MeCN) λmax 391 nm (log ε 4.68), 372 (4.60), 322 (4.03), 309 (3.94), 300 (sh, 3.76), 261 (3.90), 245 (sh, 3.85); MS m/z 262 (M^+). Anal. Found: C, 55.12; H, 1.06; N, 32.04; S, 12.44. Calcd for $C_{12}H_2N_6S$: C, 54.96; H, 0.77; N, 32.05; S, 12.23.

Preparation of [1,2,5]Selenadiazolotetracyanoquinodimethane (3)

Under a nitrogen atmosphere, a suspension of 4,7-diiodobenzo[1,2,5]selenadiazole[17,18] (1.50 g, 3.45 mmol), sodium hydride (60%, oil suspension) (870 g, 21.8 mmol), $Pd(PPh_3)_2Cl_2$ (200 mg, 0.28 mmol), and malononitrile (1.00 g, 15.2 mmol) in dry THF (50 mL) was heated under reflux for 38 h. The mixture was poured into water (1 L) and washed with CH_2Cl_2 (300 mL x 3). The aqueous layer was acidified with conc. HCl and extracted with CH_2Cl_2 (200 mL x 4). The extract was washed with brine. Removal of the solvent gave a green tar, which was suspended in benzene (60 mL), EtOH (9 mL), and 5% aqueous HCl (27 mL). The whole mixture was shaken vigorously with PbO_2 (6.0 g, 25 mmol) for 20 min. The resulting insoluble material was removed through a celite pad and washed with benzene. The organic layer was separated from the filtrate, washed with brine, and dried over anhydrous sodium sulfate. Removal of the solvent gave a yellow-brown semisolid (354 mg). Chromatographic separation on SiO_2 (100g, CH_2Cl_2) followed by sublimation (4 x 10^{-2} Torr, 250 °C) afforded 220 mg of yellow crystals of **3** in 21% yield. Starting from 4,7-dibromobenzo[1,2,5]selenadiazole[17] resulted in much lower yield of **3**. mp 295 - 297 °C [decomp] ; IR 2218 (C≡N) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) d 7.67 (s, 2H); UV (MeCN) λmax 398 nm (sh, log ε 4.33), 375 (4.57), 357 (4.50), 339 (4.40), 328 (sh, 4.26), 299 (sh, 3.82), 269 (sh, 3.63), 263 (sh, 3.63); MS m/z (relative intensity) 310 (M^+, 100), 308 (M^+, 45). Anal. Found: C,46.57; H, 0.79; N, 27.51. Calcd for $C_{12}H_2N_6Se$: C, 46.62; H, 0.65; N, 27.18.

Preparation of CT complexes

To a hot solution of **1** (25 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added a solution of TTF (20 mg, 0.10 mmol) in CH_2Cl_2 (2 mL), and the mixture was heated for a few minutes. After cooling, TTF•**1** complex (40 mg) was filtrated and obtained as black-green fibers, mp 204-205 °C [decomp]; IR 2181 (C≡N) cm^{-1}. Anal. Found: C, 47.94; H, 1.90; N, 19.13. Calcd for $C_{18}H_6N_6OS_4$: C, 47.99; H, 1.34; N, 18.65. Although the observed analytical values do not completely agree with the calculated ones, they strongly suggest the 1:1 molar ratio.

Other CT complexes were prepared by a similar direct method in CH_2Cl_2. Because of low solubilities of BEDT and BMDT in this solvent, a soxhlet apparatus was used to obtain their complexes in pure form. In the case of TTF and DBTTF complexes the observed analytical values do not completely agree with the calculated ones, yet they strongly suggest the molar ratios shown below.

TMTSF•**1** (4:3) complex: black solid, mp 238-240 °C [decomp]; IR 2192 (C≡N) cm^{-1}. Anal. Found: C, 35.87; H, 2.19; N, 9.94. Calcd for $C_{76}H_{54}N_{18}O_3Se_{16}$: C, 36.07; H, 2.15; N, 9.96. BMDT•**1** (3:2) complex: black solid, mp > 400 °C; IR 2182 (C≡N) cm^{-1}. Anal. Found: C, 37.00; H, 1.39; N, 10.69. Calcd for $C_{48}H_{16}N_{12}O_2S_{24}$: C, 36.91; H, 1.03; N, 10.76. BEDT•**1** (3:2) complex: black solid, mp 238-239 °C [decomp]; IR 2180 (C≡N) cm^{-1}. Anal. Found: C, 39.19; H, 1.80; N, 9.91. Calcd for $C_{54}H_{28}N_{12}O_2S_{24}$: C, 39.39; H, 1.71; N, 10.21. TMTTTF•**1** (1:1) complex: black needles, mp 112-116 °C [decomp]; IR 2188 (C≡N) cm^{-1}. Anal. Found: C, 39.95; H, 2.30; N, 12.56. Calcd for $C_{22}H_{14}N_6OS_8{\bullet}1.5H_2O$: C, 39.92; H, 2.59; N, 12.70. DBTTTF•**1** (~3:2) complex: black microcrystals, mp 238-242 °C [decomp]; IR 2202 (C≡N) cm^{-1}. Anal. Found: C, 56.08; H, 1.96; N, 11.93. Calcd for $C_{66}H_{28}N_{12}O_2S_{12}$: C, 56.39; H, 2.00; N, 11.96. TTF•**2** (~1:1) complex: black solid, mp 222-224 °C [decomp]; IR 2172 (C≡N) cm^{-1}. Anal. Found: C, 45.64; H, 1.51; N, 17.44. Calcd for $C_{18}H_6N_6S_5$: C, 46.34; H, 1.30; N, 18.01. TMTSF•**2** (1:1) complex: black solid, mp 262-264 °C [decomp]; IR 2165 (C≡N) cm^{-1}. Anal. Found: C, 37.30; H, 2.12; N, 11.80. Calcd for $C_{22}H_{14}N_6SSe_4$: C, 37.20; H, 1.99; N, 11.83. BMDT•**2** (3:2) complex: black solid, mp 205-210 °C [decomp]; IR 2171 (C≡N) cm^{-1}. Anal. Found: C, 36.15; H, 1.17; N, 10.28. Calcd for $C_{48}H_{16}N_{12}S_{26}$: C, 36.16; H, 1.01; N, 10.54. BEDT•**2** (1:1) complex: black-green microcrystals, mp 263-265 °C [decomp]; IR 2208 (C≡N) cm^{-1}. Anal. Found: C, 40.78; H, 1.66; N, 12.81. Calcd for $C_{22}H_{10}N_6S_9$: C, 40.85; H, 1.56; N, 12.99. TMTTTF•**2** (1:1) complex: black needles, mp 146-148 °C [decomp]; IR 2212 (C≡N) cm^{-1}. Anal. Found: C, 40.61; H, 2.14; N, 12.75. Calcd for $C_{22}H_{14}N_6S_9$: C, 40.59; H, 2.17; N, 12.91. DBTTTF•**2** (~1:1) complex: brown needles, mp 238-240 °C [decomp]; IR 2208 (C≡N) cm^{-1}. Anal. Found: C, 54.77; H,1.92; N, 14.73. Calcd for $C_{26}H_{10}N_6S_5$: C, 55.11; H, 1.78; N, 14.83. TTF•**3** (~4:3) complex: black solid, mp 238-240 °C [decomp]; IR 2167 (C≡N) cm^{-1}. Anal. Found: C, 41.37; H, 1.35; N, 14.96. Calcd for $C_{60}H_{22}N_{18}S_{16}Se_3$: C, 41.30; H, 1.27; N, 14.45. TMTSF•**3** (1:1) complex: black solid, mp 264-267 °C [decomp]; IR 2194 (C≡N) cm^{-1}. Anal. Found: C, 34.73; H, 1,82; N, 10.99. Calcd for $C_{22}H_{14}N_6Se_5$: C, 34.90; H, 1.86; N, 11.10. $\underline{\text{BMDT}\bullet\mathbf{3}}$ (3:2) complex: green-black solid, mp 185-190 °C [decomp]; IR 2179 (C≡N) cm^{-1}. Anal. Found: C, 33.99; H, 1.01; N, 9.96. Calcd for $C_{48}H_{16}N_{12}S_{24}Se_2$: C, 34.15; H, 0.96; N, 9.96. $\underline{\text{BEDT}\bullet\mathbf{3}}$ (1:1) complex: black-green fibers, mp 246-248 °C [decomp]; IR 2207 (C≡N) cm^{-1}. Anal. Found: C, 38.25; H, 1.62; N, 12.23. Calcd for $C_{22}H_{10}N_6S_8Se$: C, 38.09; H, 1.45; N, 12.11. $\underline{\text{TMTTTF}\bullet\mathbf{3}}$ (1:2) complex: black microcrystals, mp 191-196 °C [decomp]; IR 2212 (C≡N) cm^{-1}. Anal. Found: C, 40;.52 H, 1.57; N, 16.94. Calcd for $C_{34}H_{16}N_{12}S_8Se_2$: C, 40.55; H, 1.60; N, 16.69. $\underline{\text{DBTTTF}\bullet\mathbf{3}}$ (~1:1) complex: brown microcrystals, mp 220-225 °C [decomp]; IR 2212 (C≡N) cm^{-1}. Anal. Found: C, 50.11; H,1.79; N, 13.79. Calcd for $C_{26}H_{10}N_6S_4Se$: C, 50.89; H, 1.64; N, 13.70.

Preparation of Anion Radical Salts

To a hot solution of **2** (262 mg, 1.00 mmol) in MeCN (15 mL) was added a solution of LiI (450 mg, 3.36 mmol) in MeCN (5 mL), and the mixture was heated for a few minutes. After cooling, black needles of $Li^+\mathbf{2}^{-\bullet}$ (122 mg) was filtrated and washed with MeCN (1 mL x 2) and ether (1 mL), mp > 400 °C; IR 2176 (C≡N) cm^{-1}; UV (MeCN) λmax 810 nm (log ε 3.99), 658 (4.74), 366 (4.24), 352 (4.26), 290 (4.10), 282 (4.07), 280 (sh, 4.07), 234 (3.83); Anal. Found: C, 50.20; H, 1.75; N, 29.22. Calcd for $C_{12}H_2N_6SLi\bullet H_2O$: C, 50.18; H, 1.40; N, 29.26.

Other anion radical salts were prepared similarly by using a variety of iodide salts. In the case of H_4N^+ and Me_4N^+ salts the observed analytical values do not completely agree with the calculated ones, yet they strongly suggest the molar ratios shown below.

$\underline{H_4N^+\mathbf{2}^{-\bullet}}$ (~1:1) salt: green microcrystals, mp 280-300 °C [decomp]; IR 2176 (C≡N) cm^{-1}. Anal. Found: C, 51.13; H, 2.53; N,34.63. Calcd for $C_{12}H_6N_7S$: C, 51.42; H, 2.16; N, 34.98. $\underline{Me_4N^+\mathbf{2}^{-\bullet}}$ (~1:1) salt: black fibers, mp 282-283 °C [decomp]; IR 2172 (C≡N) cm^{-1}. Anal. Found: C, 55.33; H, 3.89; N, 28.75. Calcd for $C_{16}H_{14}N_7S\bullet 0.5H_2O$: C, 55.64; H, 4.38; N, 28.39. $\underline{Et_4N^+\mathbf{2}^{-\bullet}}$ (1:2) salt: black needles, mp 274-275 °C [decomp]; IR 2175 (C≡N) cm^{-1}. Anal. Found: C, 58.77; H, 3.93; N, 27.86. Calcd for $C_{32}H_{24}N_{13}S_2$: C, 58.70; H, 3.69; N, 27.81. $\underline{n\text{Pr}_4N^+\mathbf{2}^{-\bullet}}$ (1:2) salt: black fibers, mp 238-240 °C [decomp]; IR 2171 (C≡N) cm^{-1}. Anal. Found: C, 60.92; H, 4.71; N, 25.68. Calcd for $C_{36}H_{32}N_{13}S_2$: C, 60.83; H, 4.54; N, 25.62. $\underline{n\text{Bu}_4N^+\mathbf{2}^{-\bullet}}$ (1:2) salt: black microcrystals, mp 195-200 °C [decomp]; IR 2167 (C≡N) cm^{-1}. Anal. Found: C, 62.69; H, 5.39; N, 23.75. Calcd for $C_{40}H_{40}N_{13}S_2$: C, 62.64; H, 5.26; N, 23.74. $\underline{Li^+\mathbf{3}^{-\bullet}}$ (1:1) salt: black fibers, mp > 400 °C; IR 2175 (C≡N) cm^{-1}; UV (MeCN) λmax 788 nm (log ε 3.77), 684 (4.75), 628 (4.19), 376 (4.26), 365 (sh, 4.23), 309 (4.20), 233 (3.87); Anal. Found: C, 43.02; H, 1.41; N, 25.10. Calcd for $C_{12}H_2N_6SeLi\bullet H_2O$: C, 43.14; H, 1.21; N, 25.15. $\underline{H_4N^+\mathbf{3}^{-\bullet}}$ (~1:1) salt: black microcrystals, mp >400 °C; IR 2183 (C≡N) cm^{-1}. Anal. Found: C, 43.83; H, 3.41; N, 29.66. Calcd for $C_{12}H_6N_7Se$: C, 44.05; H, 1.85; N, 29.97. $\underline{Et_4N^+\mathbf{3}^{-\bullet}}$ (1:2) salt: black needles, mp 260-262 °C [decomp]; IR 2167 (C≡N) cm^{-1}. Anal. Found: C, 51.49;

H, 3.21; N, 24.53. Calcd for $C_{32}H_{24}N_{13}Se_2$: C, 51.35; H, 3.23; N, 24.33. $\underline{n\mathrm{Pr}_4\mathrm{N}^{+}\mathbf{3}^{-\bullet}}$ (1:2) salt: black fibers, mp 250-252 °C [decomp]; IR 2168 (C≡N) cm^{-1}. Anal. Found: C, 53.76; H, 3.90; N, 22.60. Calcd for $C_{36}H_{32}N_{13}Se_2$: C, 53.74; H, 4.01; N, 22.63. $\underline{n\mathrm{Bu}_4\mathrm{N}^{+}\mathbf{3}^{-\bullet}}$ (2:5) salt: black fibers, mp 229-230 °C [decomp]; IR 2170 (C≡N) cm^{-1}. Anal. Found: C, 54.53; H, 4.07; N, 22.03. Calcd for $C_{92}H_{82}N_{32}Se_5$: C, 54.42; H, 4.07; N, 22.07.

X-ray Structural Analysis of [1,2,5]Oxadiazolotetracyanoquinodimethane (1)

A yellow plate-like crystal with an approximate dimension of 0.3 x 0.2 x 0.2 mm^3 was grown by sublimation onto Teflon. Crystal data are as follows: $C_{12}H_2N_6O$, MW 246.19, orthorhombic Pbca, a = 12.715(1), b = 10.596(1), c = 16.519(1) Å, V = 2225.5(2) $Å^3$, Z = 8, Dc = 1.470 g cm^{-3}, $\mu_{CuK\alpha}$ = 8.270 cm^{-1}. Reflection data were collected on an AFC-5R (45 kV, 180 mA) diffractometer at 13 °C by using graphite monochromated CuKα radiation (λ = 1.5418 Å). A total of 1786 independent reflections was collected within $2\theta < 126°$. The structure was solved by the direct method (RANTAN 81 program)[28] and refined by the block-diagonal least-squares method using anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were found in the D-map and refined isotropically. The final R value was 0.0455 for 1704 non-zero reflections. The estimated standard deviations for the bond distances and angles were 0.003 - 0.0045 Å and 0.1 - 0.3°, respectively.

X-ray Structural Analysis of [1,2,5]Thiadiazolotetracyanoquinodimethane (2)

A yellow plate-like crystal with an approximate dimension of 0.2 x 0.1 x 0.1 mm^3 was grown by sublimation onto Teflon. Crystal data are as follows: $C_{12}H_2N_6S$, MW 262.25, monoclinic $P2_1/n$, a = 14.325(2), b = 10.515(1), c = 7.765(1) Å, β = 95.28(1)°, V = 1164.6(3) $Å^3$, Z = 4, Dc = 1.496 g cm^{-3}, $\mu_{MoK\alpha}$ = 2.583 cm^{-1}. Reflection data were collected on an AFC-5R (45 kV, 200 mA) diffractometer at 13 °C by using graphite monochromated MoKα radiation (λ = 0.71049 Å). A total of 2659 independent reflections was collected within $2\theta < 55°$. The structure was solved by the direct method (RANTAN 81 program)[28] and refined by the block-diagonal least-squares method using anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were found in the D-map and refined isotropically. The final R value was 0.0470 for 1881 reflections with $|Fo| > 3\sigma |Fo|$. The estimated standard deviations for the bond distances and angles were 0.003 - 0.005 Å and 0.1 - 0.3°, respectively.

X-ray Structural Analysis of [1,2,5]Selenadiazolotetracyanoquinodimethane (3)

A yellow rod-like crystal with an approximate dimension of 0.5 x 0.3 x 0.2 mm^3 was grown by sublimation onto Teflon. Crystal data are as follows: $C_{12}H_2N_6Se$, MW

309.15, monoclinic P2/a, a = 15.948(2), b = 7.498(1), c = 10.060(1) Å, β = 107.16(1)°, V = 1149.4(3) Å^3, Z = 4, Dc = 1.787 g cm^{-3}, $\mu_{MoK\alpha}$ = 32.234 cm^{-1}. Reflection data were collected on an AFC-5R (45 kV, 200 mA) diffractometer at 13 °C by using graphite monochromated MoKα radiation (λ = 0.71049 Å). A total of 4180 independent reflections was collected within 2θ < 65°. An absorption correction was applied. The structure was solved by the Patterson method followed by the Fourier Synthesis and refined by the block-diagonal least-squares method using anisotropic temperature factors for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and refined isotropically. The final R value was 0.0533 for 2939 reflections with $|Fo| > 3\sigma|Fo|$. The estimated standard deviations for the bond distances and angles were 0.004 - 0.009 Å and 0.2 - 0.6°, respectively.

All the calculations for **1** - **3** were carried out on an ACOS 2020 computer at Tohoku University by using applied library programs of UNICSIII system.[29]

Measurement of Redox Potentials

Redox potentials were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte and using Pt wire as a working electrode. All the values shown in the text and Tables are in *E*/V vs. SCE and were measured under the same conditions. E_1^{red}, E_2^{red}, E_3^{red}, and E_1^{ox} are the average value of the cathodic and anodic peak potentials for $A^o + e = A^{-\bullet}$, $A^{-\bullet} + e = A^{2-}$, $A^{2-} + e = A^{3-\bullet}$, and $D^o - e = D^{+\bullet}$, respectively.

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