

Design and synthesis of novel chalcogen-containing organic metals

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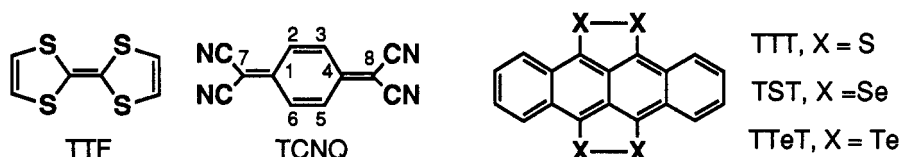
Abstract

Importance of the introduction of heteroatoms, especially heavy chalcogens, into the component molecules of organic metals is recognized as one of the requisites to attain superior electric conductivity. As one of such examples, the results of our recent research on the design and synthesis of organic metals containing chalcogen atoms are now presented. A variety of novel electron donors such as peri-dichalcogen bridged polyacenes, heteroarenes isoelectronic with perylene and pyrene, and 2-(chalcogenopyran-4'-ylidene)-1,3-dichalcogenoles as well as hetero-TCNQs have been synthesized to form conductive charge-transfer complexes and radical ionic salts which are qualified as candidates of organic metals. High conductivities of the radical cation salts of peri-dichalcogen bridged anthracenes are especially remarkable. In addition, importance of reduced on-site Coulomb repulsion is emphasized by ready formation of highly conductive charge-transfer complexes with extensively conjugated hetero-TCNQs.

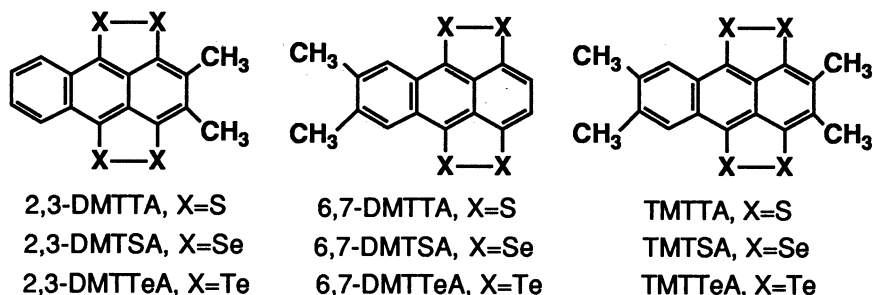
Since the striking discovery of the charge-transfer (CT) complex of tetrathiafulvalene, TTF, and 7,7,8,8-tetracyanoquinodimethane, TCNQ, as the first synthetic metal (ref. 1-7), the development of novel electron donors (D) and acceptors (A) to afford organic metals has attracted great current interest (ref. 8). Highly conductive complexes generally consist of segregated columns of the donors and acceptors with incomplete charge transfer. Such components have been proposed to satisfy a number of requirements: ready oxidation or reduction, a high degree of planarity, high symmetry, high polarizability, strong heteroatomic intra- as well as intercolumnar interaction, and reduced on-site Coulomb repulsion etc. (ref. 9-12). Here syntheses and properties of new organic electron donors as well as acceptors and their CT complexes, developed recently by our group, are described with special attention to heteroatomic effects.

NOVEL CHALCOGEN-CONTAINING ORGANIC DONORS AND THEIR CHARGE-TRANSFER COMPLEXES

Polyacenes carrying peri-dichalcogen bridges are known as the prototypes of superior electron donors. Naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole, abbreviated as tetrathiotetracene or TTT, is a representative and has a stronger donating property than does TTF (ref. 13). However, it has a very low solubility in common solvents, limiting any wide study concerning its molecular complexes. Although the selenium and tellurium isologues (TST and TTeT) as well as analogues have aroused interest because of introduction of interactive heavy chalcogens, they are intractable because of their poor solubilities (ref. 13-15). We have designed the lower benzologues, anthra[1,9-cd:4,10-c'd'] bis[1,2]dichalcogenoles with methyl substituents at 2,3-, 6,7-, and 2,3,6,7-positions, as new and tractable electron donors (see formulae below). We have already reported their syntheses, including tellurium isologues, and their molecular complexes with various acceptor molecules (ref. 16). Introduction of methyl groups served not only to compensate the reduction of donor ability due to the decrease of aromatic rings but also to enhance the solubility, enabling a detailed study of their CT complexes. Donating ability increases in the order of



S~Se<<Te and non-substituted<2,3~6,7-dimethyl<tetramethyl isologues. Solubility increases generally in the order of Te<<Se<S and non-substituted<tetramethyl <6,7-dimethyl<2,3-dimethylanthracenes; for example TSA<2,3,6,7-TMTSA<6,7-DMTSA<2,3-DMTSA. Among them, 2,3-DMTTeA and TMTTeA have very strong donor abilities which are either comparable to or better than that of TTT. Some of the molecular complexes also show fairly high electric conductivities. 2,5-Dimethyl substituted TCNQ (DMTCNQ) complexes of 2,3-DMTSA, 6,7-DMTSA, TMTSA, and TMTTA were scrutinized on their molecular as well as crystal structures and physical properties. Of them, only 2,3-DMTSA complexes has a high electric conductivity, a complete CT state, and an electronic absorption band in infrared region. However, all of them have the same 2/1 ratio of donor and acceptor (D/A) and belong to the same monoclinic space group. They are isostructural with mixed stack columns of D-D-A sequence holding quite similar overlapping modes. The high conductivity and large CT of 2,3-DMTSA•DMTCNQ complex are explained by strong Se-Se and Se-N heteroatomic interactions. The radical cation salts prepared from these anthracenes by electrocrystallization are shown together with related physical data in Table 1. Almost all the salts exhibit high electric conductivities. Especially NO₃ and BF₄ salts of 2,3-DMTSA showed very high room temperature conductivities and behaved metallically down to 150K in spite of the 1:1 stoichiometry (Fig. 1). X-Ray crystal structure analyses of these salts clarify the presence of segregated stacks of donor cations with good overlap. Thus, the interfacial distances of the overlapped neighboring donors are uniform



and the distances between Se atoms in the column as well as between Se and F or O atoms are less than the sum of van der Waals radii as indicated in Fig. 2. We consider the very high room temperature conductivities and metallic behavior of these salts are due to the presence of the one-dimensional columns and the strong heteroatomic interactions. Recently we have reported synthesis and properties of peridichalogen bridged phenanthrenes (TTPh and TSPh) as a new type of polyacene donors, whose dications are isoelectronic with perylene. Although they are weaker donors than the corresponding anthracene analogues, some of their CT complexes showed high conductivities at room temperature (ref. 17).

TABLE 1. Electric conductive properties of the radical salts, prepared by electrocrystallization^{a)} of anthracene donors.

Radical salt	D : A ^{b)}	σ ^{c)} /Scm ⁻¹	E_{act} / eV
2,3-DMTTA•NO ₃	1 : 1	4.4	0.065
2,3-DMTTA•BF ₄	1 : 1	7.0	0.063
2,3-DMTTA•ClO ₄	1 : 1	0.50	0.072
2,3-DMTTA•PF ₆	2 : 1	0.12	0.073
2,3-DMTTA•AsF ₆	2 : 1	0.19	0.079
2,3-DMTSA•NO ₃	1 : 1	4.4×10^2	metallic
2,3-DMTSA•BF ₄	1 : 1	4.5×10^2	metallic
2,3-DMTSA•ClO ₄	1 : 1	40	0.020
2,3-DMTSA•PF ₆	1 : 1	0.65	0.092
2,3-DMTSA•AsF ₆	2 : 1	0.10 ^{d)}	0.117 ^{d)}

- a) Experimental conditions: solvent, 1,1,2-trichloroethane; electrode, Pt; supporting electrolyte, n-Bu₄N⁺ salts; current, 1-3 μ A. b) Determined by elemental analysis. c) Measured on single crystal with a four-probe method at RT. d) Measured on compressed sample with a four-probe method at RT.

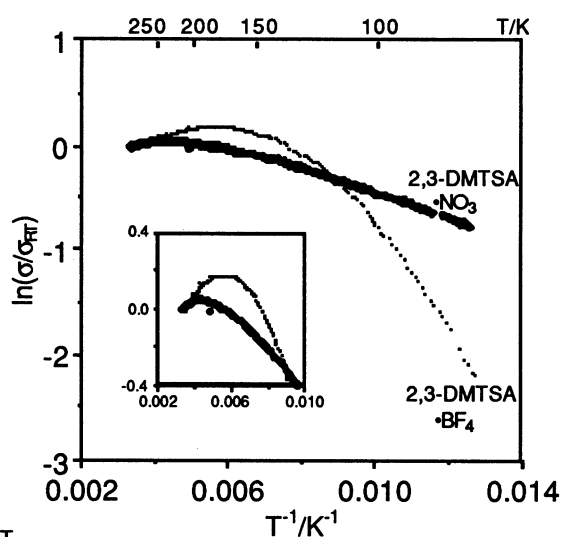
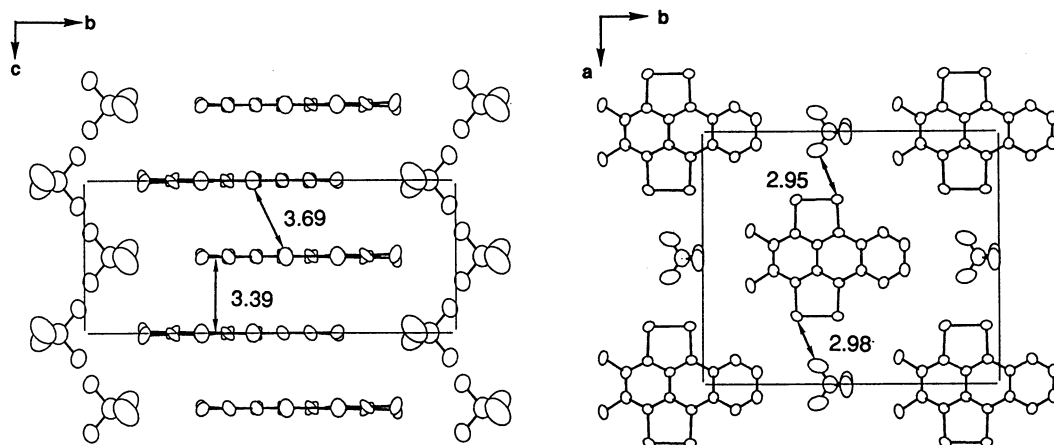
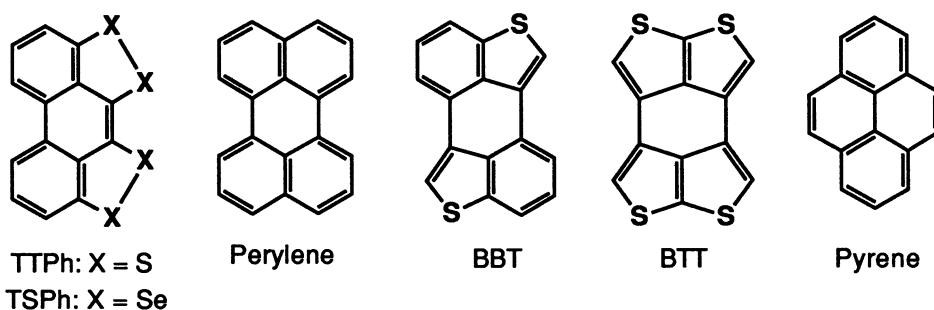
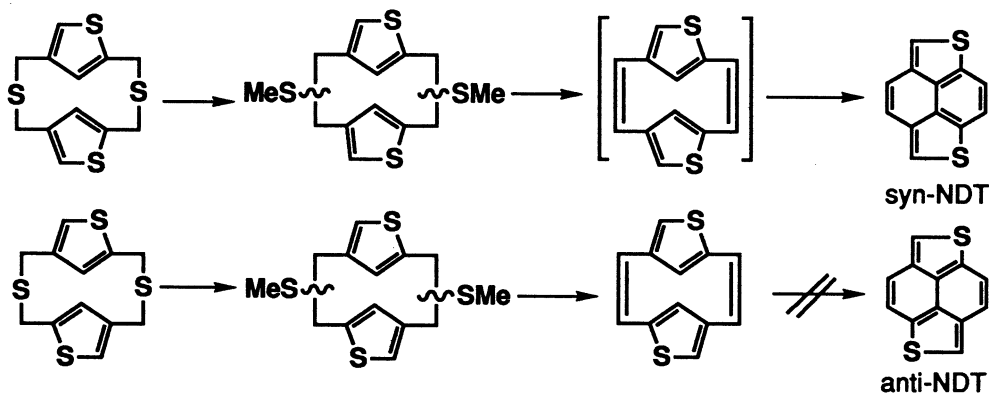


Fig. 1. Temperature dependence of conductivities of 2,3-DMTSA salts.

Fig. 2. Crystal structure of 2,3-DMTSA·BF₄ salt.

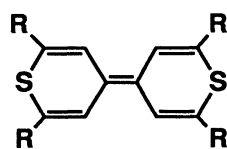
Next we report the synthesis and properties of naphtho[1,8-bc:4,5-b'c']dithiophene (syn-NDT) as a novel electron donor which is an isoelectronic heteroarene with pyrene. Wudl's group and our group already reported syntheses and properties of two heteroarenes isoelectronic with perylene, BBT and BTT, respectively (ref. 18). These heteroarenes like perylene formed conductive iodine complexes. On the other hand, nothing has been reported concerning conductive heteroarenes which are isoelectronic with pyrene. Considering that [2.2]metacyclophane-1,9-diene readily gives pyrene, we took a route (Scheme 1) via [2.2](2,4)thiophenophane-1,8-diene to approach NDT (ref.19). As expected, syn-NDT was synthesized from the C₂ symmetric 2,10-dithia[3.3](2,4)thiophenophane by either successive Stevens rearrangement and Hofmann elimination or Stevens rearrangement and sulfoxide elimination, with spontaneous valence tautomerization followed by dehydrogenation. The starting dithiathienophane is prepared by high-dilution coupling of 2,4-bis(bromomethyl)thiophene and 2,4-bis(mercaptomethyl)thiophene under basic conditions and separated from the 1:1 mixture by fractional crystallization. On the other hand, the isomeric C_i dithiathienophane afforded the corresponding C_i symmetric diene by a similar combination of Stevens rearrangement and the subsequent Hofmann elimination, and valence tautomerization and dehydrogenation

Scheme 1



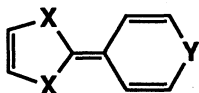
did not occur even if it was treated with oxygen or iodine under UV light. syn-NDT (mp 187-188°C) shows electronic absorption spectrum ($\lambda_{\text{max}}/\text{nm}$ (ϵ) in cyclohexane: 239(17900), 287(7140), 299(9490), 321(17300), 336(30900), 353(29000)) similar to that of pyrene. The cyclic voltammetry shows one irreversible oxidation wave at +1.01V vs. a Ag/AgCl standard electrode. This value indicates that syn-NDT belongs to a rather weak electron donor, but is considerably lower than that (+1.35V) of pyrene. It formed black highly conducting CT complexes with DDQ and I_2 , $\sigma = 2.11$ and 0.92Scm^{-1} , respectively. Particularly, the conductivity of the iodine complex is approximately two orders of magnitude higher than that of (0.0135cm^{-1}) of pyrene-iodine complex (ref. 19).

2-(Thiopyran-4'-ylidene)-1,3-dithiole (TPDT) is a hybrid of two typical electron donors, TTF and BTP, and was first synthesized by Sandman's group (ref. 20). Although Sandman's group also reported its spectral as well as structural properties (ref.21), it attracted little attention because it formed a less conductive complex with TCNQ than either TTF or BTP. However, electron donating abilities of these donors are in the order of $\text{TTF} < \text{TPDT} < \text{BTP}$. Furthermore, the recent development of organic metals derived from unsymmetrical donors directed our interests to TPDT and its modifications. We recently reported selenium analogs, in which some or all of the sulfur atoms of TPDT are replaced by selenium (SPDT, TPDS and SPDS), and some other derivatives (ref. 22). These modifications demonstrated their potentials as good electron donors and prompted us further to explore other TPDT derivatives. Since 2,2',6,6'-tetraphenyl-4,4'-bithiopyranylidene (TPBTP) behaves as a better donor than BTP itself (ref. 23), phenylation of TPDT and its selenium analogues was undertaken (ref. 24). The redox properties and electronic absorption spectra are summarized in Table 2. A comparison of the half-wave oxidation potentials indicates that the phenyl substitution at the thiopyran ring does not affect oxidation potential, but that at the dithiole ring somewhat decreases donating ability. 2',6'-Diphenyl and 4,5,2',6'-tetraphenyl TPDT (2',6'-DPTPDT and 4,5,2',6'-TPTPDT) show a considerable bathochromic shift of the longest wavelength maximum around 350nm of their mother beyond 400nm. On the other hand, 4,5-DPTPDT shows little shift of the absorption (Table 2). These results clearly indicate that the phenylation of the thiopyran ring causes extensive conjugation of π -system and, in contrast, that of the dithiole moiety can not bring about such conjugation. The structure of TPTPDT was elucidated by an X-ray crystallographic analysis. As shown in Fig. 3, the phenyl groups attached to the thiopyran ring are nearly coplanar with the TPDT skeleton, but the phenyl substituents on the dithiole ring deviate clearly from this plane. Furthermore, a beautiful stacks of donors to induce mutual interactions are observed, though TPDT itself forms a dimer structure in the crystal (ref. 21). These findings perfectly consistent with the electronic spectra. The electronic absorption spectra of 4,5-dimethyl and 4,5-



BTP: R = H

TPBTP: R = Ph

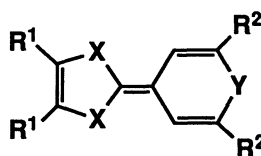


TPDT: X = Y = S

TPDS: X = Se, Y = S

SPDT: X = S, Y = Se

SPDS: X = Y = Se



4,5-DPTPDT: R¹ = Ph, R² = H, X = Y = S

2',6'-DPTPDT: R¹ = H, R² = Ph, X = Y = S

4,5,2',6'-TPTPDT: R¹ = R² = Ph, X = Y = S

4,5-DM-2',6'-DPTPDT: R¹ = CH₃, R² = Ph, X = Y = S

4,5-DM-2',6'-DPSPDT: R¹ = CH₃, R² = Ph, X = S, Y = Se

4,5-DMT-2',6'-DPTPDT: R¹ = CH₃S, R² = Ph, X = Y = S

4,5-DMT-2',6'-DPSPDT: R¹ = CH₃S, R² = Ph, X = S, Y = Se

TABLE 2. Half-wave redox potentials (V)^a) and electronic absorption maxima of TPDT donors.

Donor	E ¹ _{1/2}	E ² _{1/2}	ΔE	λ _{max} /nm (log ε) in CH ₃ CN
TPDT	0.23	0.61	0.38	251 (3.52), 348 (4.36), 359 (4.38), 398sh (3.35)
2',6'-DPTPDT	0.24	0.61	0.37	248 (4.36), 410 (4.43), 460sh (3.41)
4,5-DPTPDT	0.27	0.63	0.36	250sh (4.07), 355sh (4.45), 364 (4.50), 395sh (3.81)
4,5,2',6'-TPTPDT	0.28	0.62	0.34	222 (4.51), 251 (4.57), 415 (4.50), 460sh (3.88)

a) Cyclic voltammetry was measured at 100mV/s scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in $10^{-3} \text{mol dm}^{-3}$ PhCN solution containing 0.1mol dm^{-3} $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ as supporting electrolyte.

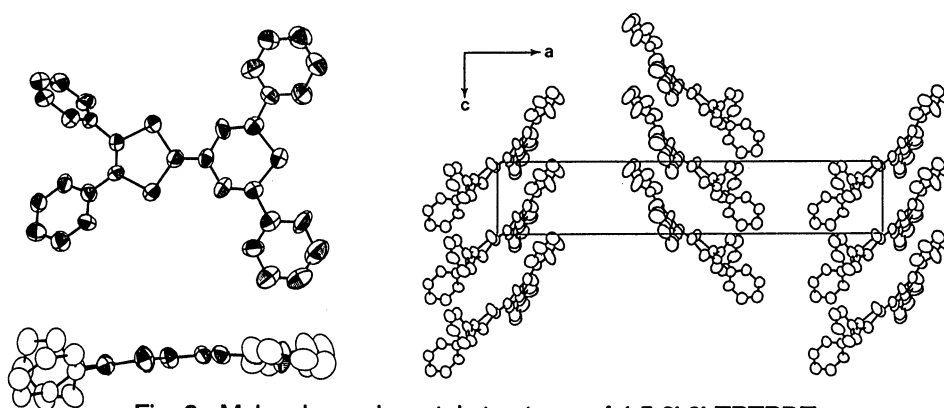


Fig. 3. Molecular and crystal structures of 4,5,2',6'-TTPDPT.

bis(methylthio) derivatives of 2',6'-DTPDPT as well as 2',6'-DPSPDT (4,5-DM-2',6'-DTPDPT, 4,5-DM-2',6'-DPSPDT, 4,5-DMT-2',6'-DTPDPT, and 4,5-DMT-2',6'-DPSPDT) are quite similar to that of TTPDPT. The X-ray crystal structure analyses of the latter two donors show the essentially same features of coplanarity and stacking as TTPDPT. Concerning the electric conductive properties of CT complexes from these donors, the following interesting features are observed: 1. Modifications of dithiole rings, including heteroatom replacement and substituent introduction, do not influence much their conductivities. On the other hand, modifying thio- or selenopyran ring affects significantly, sometimes much improves, their conductive properties. 2. CT complexes of 2',6'-diphenyl substituted donors show a CT band in the infrared region, suggesting a segregated stacked structure (Table 3, ref. 24).

TABLE 3. Electric conductivities^{a)} and CT bands in the infrared region^{b)} of CT complexes of TPDT donors.

Complex ^{c)}	D:A	Appearance	Dp/°C	σ/Scm^{-1}	CT Band/ $\times 10^3\text{cm}^{-1}$
TPDPT·TCNQ	1:1	Black Powder	216	7.4×10^{-3}	none
2',6'-DTPDPT·TCNQ ^{d)}	2:3	Black Powder	218	1.5	3.5
4,5,2',6'-TTPDPT·TCNQ	1:1	Black Powder	211	9.3×10^{-2}	none
4,5-DM-2',6'-DTPDPT·TCNQ	3:2	Black Powder	208	1.5×10^{-1}	3.4
4,5-DMT-2',6'-DTPDPT·TCNQ	1:1	Black Powder	195	2.4	3.5

a) Measured on compressed pellets at RT with a four-probe method. b) Measured with a KBr disk method. c) Obtained from CH₃CN unless otherwise stated. d) Obtained from chlorobenzene.

NOVEL CHALCOGEN-CONTAINING ORGANIC ACCEPTORS AND THEIR CHARGE-TRANSFER COMPLEXES

Since the success of TCNQ as a superior electron acceptor, considerable efforts have been devoted to develop new electron acceptors with extended π -system for better overlap to widen band widths and for small on-site Coulomb repulsion due to charge dispersal, though the varieties and numbers are rather limited in comparison with donors (ref. 8, 25). We also have reported the syntheses and properties of linearly as well as annularly conjugated TCNQ analogs containing heteroquinoid structures as hetero-TCNQs (ref. 26). Furan, thiophene, selenophene, their linear as well as condensed homologs, and pyridine are related heteroaromatics. Hetero-TCNQs are synthesized by either Gronowitz-Uppström reaction of tetracyanoethylene oxide with the corresponding halides of heteroaromatics or Pd(0) catalyzed substitution of the halides with sodium dicyanomethanide and successive oxidation. The hetero-TCNQs are very stable (except not isolable pyridine-TCNQ) and take planar conjugated transoid structures because of reduced steric requirements of heteroatoms. They show regular bathochromic shifts in electronic absorption spectra with expansion of conjugation. They are generally weaker acceptors than TCNQ (Table 4 and 5), reflecting less aromaticity of the central heterocyclic moieties formed upon reduction. However, the differences between the first and second reduction potentials (ΔE in Tables 4 and 5) become smaller, when the conjugations are expanded. Especially, ΔE s of F3, T3, and S3 are almost nil, demonstrating effective reduction of on-site Coulomb repulsion in the dianion states. This is one of the important requisites to obtain organic metals and reflected in the conductivities of the following series of molecular complexes: T1·TTF, 6.8×10^{-9} ; T2·TTF, 2.2×10^{-4} ; T3·TTF, 3.3×10^{-3} ; T1·HMTTeF, 5.5×10^{-9} ; T3·HMTTeF, 1.1 Scm^{-1} . The lower accepting abilities of hetero-TCNQs are improved by introduction of electron attracting groups to afford highly conducting CT complexes. Further, to improve the accepting ability of FT3, we designed to incorporate benzene ring in its

TABLE 4. Half-Wave redox potentials (V) of linearly conjugated hetero-TCNQs, TCNQ, and CNBDT.

Redox Potential	F1	T1	S1	F2	T2	S2	F3	T3	S3
$E^1_{1/2}$	0.03	0.07	0.03	-0.09	-0.03	-0.05			
$E^2_{1/2}$							-0.09	-0.03	-0.07
ΔE	0.58	0.61	0.57	0.22	0.23	0.20	0.00	0.00	0.00
Redox Potential	F2-Br	T2-Br	S2-Br	T2-Br2	T2-Cl	F3-Br	F3-Br2		
$E^1_{1/2}$	0.08	0.20	0.15	0.28	0.18			-0.01	+0.14
$E^2_{1/2}$	-0.12	0.03	-0.08	0.13	-0.06				
ΔE	0.20	0.17	0.23	0.15	0.24	0.00	0.00	0.00	0.00
Redox Potential	TS	TS-Br	TS-Cl	TCNQ	CNBDT				
$E^1_{1/2}$	-0.07	+0.11	+0.13	+0.25	+0.26*	+0.20*			
$E^2_{1/2}$	-0.30	-0.10	-0.12	-0.47	-0.32*	-0.05*			
ΔE	0.23	0.21	0.25	0.72	0.58*	0.25*			

Measuring conditions: Pt working and counter electrodes, Ag/AgCl reference electrode, scan rate 100mV/sec in dichloromethane solution containing 0.1M tetrabutylammonium perchlorate as supporting electrolyte at room temperature. * Values in DMF solution.

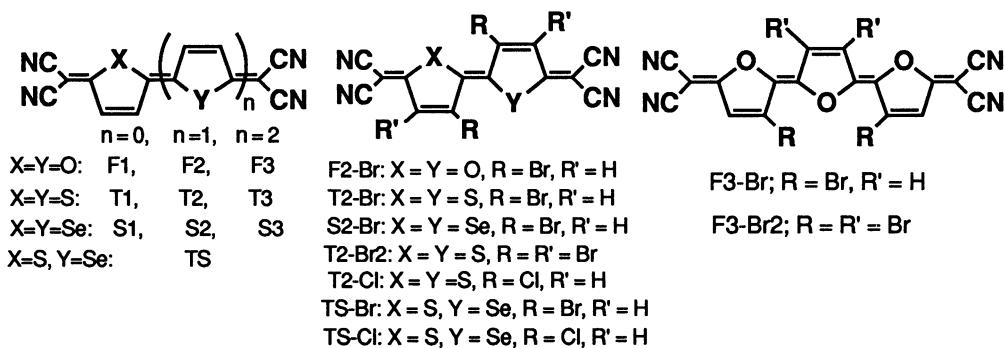
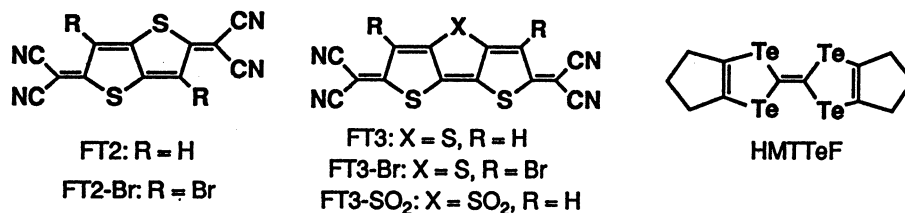


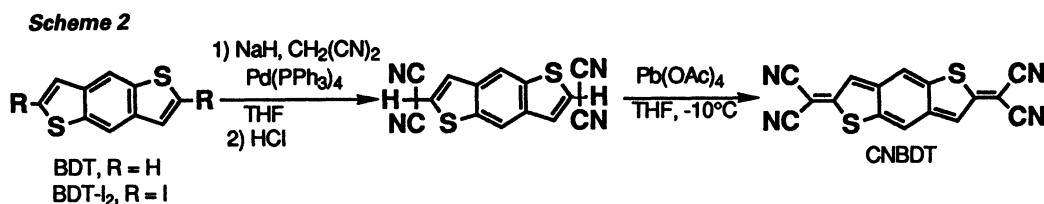
TABLE 5. Half-wave redox potentials (V) of fused thiophene-TCNQs

Redox Potential	FT2	FT2-Br	FT3	FT3-Br	FT3-SO ₂
$E^1_{1/2}$	0.06	0.25	0.05	0.16	0.28
$E^2_{1/2}$	-0.36	-0.13	-0.23	-0.11	-0.05
ΔE	0.42	0.38	0.28	0.27	0.33

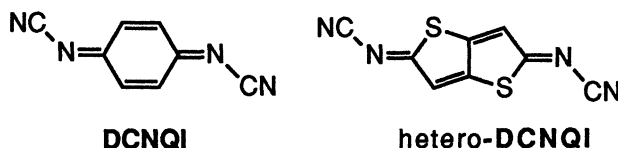
Measuring conditions: The same as shown in TABLE 4.



molecular skeleton and synthesize 2,6-bis(dicyanomethylene)-2,6-dihydrobenzo[1,2-b:4,5-b']dithiophene (CNBDT) (ref. 27). The synthetic route starting from benzo[1,2-b:4,5-b']dithiophene (BDT) is outlined in Scheme 2. The accepting property of CNBDT is much enhanced as shown in Table 4. It afforded CT complexes with TTT, HMTTeF, and 2,3-DMTTeA from o-dichlorobenzene solution. Their compositions (A:D) were determined by elemental analysis to be 1:1 for TTT and HMTTeF and 2:1 for 2,3-DMTTeA.



Their conductivities are measured on compressed pellets with a four-probe method at room temperature to be 4.5 (TTT), 25 (HMTTeF), and $7.0 \times 10^{-2} \text{Scm}^{-1}$ (2,3-DMTTeA), respectively. Furthermore, all the complexes have CT absorptions in infrared region to suggest segregated stacked solid state structures. Recently Hüning *et al.* reported novel hetero-DCNQI type acceptors, 2,5-bis(cyanoimino)-2,5-dihydrothieno[3,2-b]thiophene and its derivatives, which also behave as good electron acceptors with small on-site Coulomb repulsion and afford CT-complexes with high metallic conductivities (ref. 28).



Acknowledgement

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