1,3-BIS(1,3-DITHIOL-2-YLIDENE)-1,3-DIHYDROBENZO[*c*]HETEROPHENES. NEW FUSED HETEROCYCLE-EXTENDED DONORS AND THEIR CONDUCTING TCNQ-COMPLEXES

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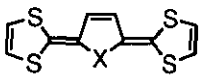
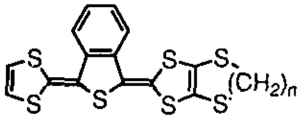
Abstract – A series of new fused-heterocycle-extended donors have been synthesized by convenient and short-step reactions. Of these benzo[c]furoquinonoid-extended one has the lowest oxidation potential. TCNQ complexes of these donors exhibit fairly high conductivities even when measured on compressed pellets.

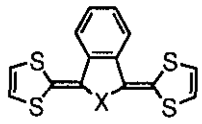
Electron-donating molecules with conjugation-extended π-systems have recently received much attention in the search for organic conductors with high superconducting transition temperatures (T_C), since T_C's are roughly proportional to the thickness of the donor layers of the conductors.[1] The extension of donor π-systems also contributes to stabilize the dication state, because the extension decreases the intramolecular Coulombic repulsive energy and suppresses Mott-type metal-insulator transitions. Given this information, we have recently synthesized thieno- and selenoquinonoid-extended TTF type of donors (BDTT: **1** and BDTS: **2**) as well as their di- and tetra-chalcogen derivatives[2] and have proved that the central sulfur or selenium atom plays very important role to stabilize the radical cations and dications of these donors. Although the di- and tetra-chalcogen derivatives of **1** and **2** gave fairly high conducting charge-transfer (CT) complexes, mother compounds (**1**) and (**2**) are so powerful as donors that they are unstable and gave fully ionic TCNQ complexes with a low conductivity. To overcome this disadvantage, we have designed and synthesized benzo-fused alkylenedithio derivatives (MDT-, EDT-, PDT-BDTBT: **3a—c**).[3] However, nonchalcogenated benzo-fuzed derivatives with C_{2v} symmetrical structures, which will obviously stack in a different crystal packing modes from the unsymmetrical **3a—c** in their conducting complexes, have never been reported so far. We have now synthesized new donors (BDTBF: **4**, BDTBT: **5**, BDTBS: **6**) as well as naphtho-fused donor (BDTNT: **7**), and clarified conducting properties of their TCNQ complexes. Of these, BDTBF: **4** is the first example of the heteroquinonoid-extended donors with a central oxygen atom.



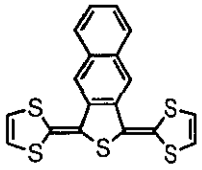
BDTT: **1**: X = S
BDTS: **2**: X = Se



MDT-BDTBT: **3a**: n = 1
EDT-BDTBT: **3b**: n = 2
PDT-BDTBT: **3c**: n = 3

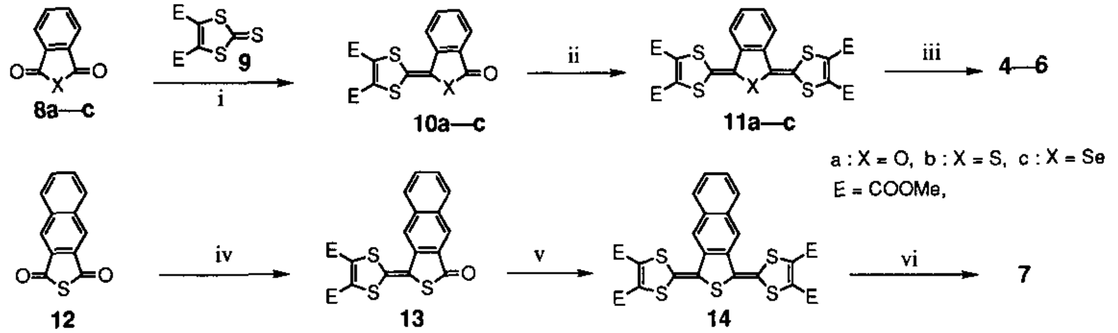


BDTBF: **4**: X = O
BDTBT: **5**: X = S
BDTBS: **6** : X = Se



BDTNT: **7**

The synthetic method for the new donors (**4**—**7**) includes very convenient and short-step reactions starting from commercially available or easily accessible acid anhydrides[4] as shown in Scheme 1.



Scheme 1. i : 2 mol equiv. **9**, 20 mol equiv. $P(OMe)_3$, in Benzene, reflux, 6 h; ii : 4 mol equiv. **9**, in $P(OMe)_3$, 90 °C, 3 h; iii : 10 mol equiv. $LiBr\cdot H_2O$, in HMPA, 95 °C, 1 h and 155 °C, 1 h; iv : 2 mol equiv. **9**, 20 mol equiv. $P(OMe)_3$, in Toluene, reflux, 6 h; v : 4 mol equiv. **9**, in $P(OMe)_3$, 100 °C, 3 h; vi : 10 mol equiv. $LiBr\cdot H_2O$, in HMPA, 95 °C, 1 h and 155 °C, 1 h.

Mono-capped compounds (**10a**—**c**) and (**13**) were synthesized in 60—75% yields by the cross-coupling reaction of anhydrides (**8a**—**c**) and (**12**) with 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-thione (**9**) in the presence of excess of trimethyl phosphite in refluxing benzene or toluene. The bis-capped tetra-esters (**11a**—**c**) and (**14**) were synthesized in 41—52% yields by the reactions of **10a**—**c** and **13** with **9** in trimethyl phosphite at 90—100 °C. The second-step capping reactions did not occur in refluxing benzene or toluene. The new donors (**4**—**7**)[5] were obtained in 78—87% yields by heating **11a**—**c** and **14** with an excess of lithium bromide monohydrate in HMPA.

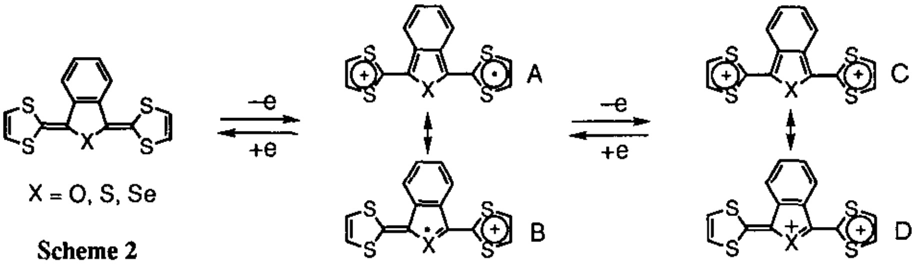
The donors (**4**—**7**) are stable both in the solid state and in solution, and have rigid conformations in solution, because the two protons (H-4,5) and two carbons (C-4,5) in the dithiol rings are nonequivalent in the ^1H and ^{13}C NMR spectra. Coplanar conformations of these donors are demonstrated by an intense absorption maximum in the electronic spectra at around 456—431 nm (log ε=4.48—4.38).

The cyclic voltammograms of **4**—**7** showed two well-defined reversible one-electron oxidation waves. The first half-wave oxidation potentials (E_1^{ox}) of **5** and **6** are higher by 0.2 and 0.19 V than those of **1** and **2**, respectively (Table 1). This can be mainly ascribed to the contribution of the nonaromatic ortho-quinodimethane structure (A) in the radical cations of **5** and **6** (Scheme 2). The higher E_1^{ox} value of BDTBS (**6**) by 0.06 V than that of BDTBT (**5**) can be ascribed to the less aromaticity of the selenophene

Table 1. Electrochemical data and electrical conductivities of the 1:1 TCNQ complexes

Donor	Electrochemical property[a]				Conductivity[b] and IR band[c] of the 1:1 TCNQ complex			
	E_1^{ox}	E_2^{ox}	ΔE^{ox}	log K_{sem}	σ_{RT} /Scm^{-1}	Ea/eV	ν_{CN} /cm^{-1}	ν_{CT} /cm^{-1}
BDTBF: **4**	+0.24	+0.55	0.31	5.25	1.9	0.130	2179, 2156	3000 (br)
BDTBT: **5**	+0.31	+0.55	0.24	4.07	5.8	0.050	2177	3000 (br)
BDTBS: **6**	+0.37	+0.59	0.22	3.73	4.4	0.047	2175	2000 (br)
BDTNT: **7**	+0.36	+0.65	0.29	4.92	9.7	0.039	——	2500 (br)
BDTT: **1**	+0.11	+0.34	0.23	3.90	6.9×10^{-3}	——	2152, 2125	5500 (br)
BDTS: **2**	+0.18	+0.36	0.18	3.05	1.6×10^{-2}	——	2177, 2152	5500 (br)

a Potentials are given in V *vs*. SCE and were determined by cyclic voltammetry / 1.0 mM solutions in PhCN with 0.1 M TBAP : 50 mV / sec. b Four-probe method on a compaction pellet. c ν_{CN} of TCNQ: 2220 cm^{-1}.



Scheme 2

ring than the thiophenering in **A**, namely the energetic benefit of gaining aromaticity on affording the radical cation is less in **6** than in **5**, since the same trend was observed in the E_1^{OX} values of **1** and **2**. The low E_1^{OX} value and the large log K_{sem} value of **4** mean that the radical cation of **4** should be more stable than those of **5** and **6**. This fact can not be explained by using the structure **A**, because the furan ring has much less aromaticity than the thiophene ring. Thus we must consider the resonance structure **B** which contributes significantly in the radical cation of **4** than those of **5** and **6**, since **B** can acquire an extra stabilization energy by aromatization of the fused benzene ring instead of missing the small aromatic stabilization energy of the furan ring. In the same reason, the dication of **4** may be contributed more significantly by the resonance structure **D** than **C**. Indeed, the dicationic salts ($BDTBF^{2+}$), ($BDTBT^{2+}$), ($BDTBS^{2+}$), and ($BDTNT^{2+}$), isolated as dark blue to violet powders by two-electron oxidation of the corresponding donors with $NOBF_4$ in dichloromethane, showed a strong absorption maximum and a strong fluorescence emission maximum in acetonitrile, in which the stokes shift is smallest (40 nm) and the quantum yield is largest in $BDTBF^{2+}$. These experimental results show that the radical cation and dication of BDTBF: **4** exist in the most rigid and planar conformation among the donors (**4**—**7**).

New donors (**4**—**7**) formed 1:1 CT complexes with tetracyanoquinodimethane (TCNQ) on mixing a hot benzene solution of the donor with a hot acetonitrile solution of TCNQ. The room temperature conductivities measured on a compressed pellet and characteristic IR bands of the complexes are summarized in Table 1 along with the corresponding values for the TCNQ complexes of BDTT and BDTS measured under the same conditions. The conductivities of [BDTBT][TCNQ] and [BDTBS][TCNQ] are 10^3 and 10^2 times higher than those of [BDTT][TCNQ] and [BDTS][TCNQ], respectively. All the complexes of the fused donors showed an extremely broad and characteristic intrastack CT absorption band (ν_{CT}) at a very low energy region of 2000—3000 cm^{-1} (Table 1), revealing a segregated stacking mode in a mixed valence state.[6] Taking the high energy ν_{CT} bands of 5500 cm^{-1} and the low energy ν_{CN} bands of 2152—2155 cm^{-1} of [BDTT][TCNQ] and [BDTS][TCNQ] into account, the low conductivities of these two complexes can be ascribed to the complete CT state.

Interestingly, the conductivity of [BDTBF][TCNQ] is almost identical with those of [BDTBT][TCNQ] and [BDTBS][TCNQ], although BDTBF does not contain the central heavy chalcogen atom. Probably, a tight intermolecular contact may be possible in the donor columns of [BDTBF][TCNQ] owing to the rigid and coplanar conformations of the BDTBF molecules in the radical cation state. The naphthalene ring of BDTNT does not prevent the conduction since the conductivity of [BDTNT][TCNQ] is very close to that of [BDTBT][TCNQ]. The single crystal growth of cation radical salts by electrochemical oxidation may easily take place in BDTNT owing to its moderately low solubility. The electrochemical crystal growth of cation radical salts and preparation of single-crystalline TCNQ complexes are in progress.

ACKNOWLEDGMENTS

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3. K. Takahashi and T. Ise, *Chem. Lett.*, 1995, 77.
4. Synthetic details of acid anhydrides (**8b**) and (**12**) will be reported in more special journals.
5. Selected physical data for **4**: yellowish brown powder, mp 185—187 °C (decomp); EI-MS: *m/z* (%) 320 (M^+, 100); ^{1}H NMR (600 MHz, C_6D_6): δ 5.50 (4H, s, dithiH), 6.97 (2H, dd, $J_{5,4} = J_{6,7} = 5.8$ Hz, $J_{5,7} = J_{6,4} = 3.0$ Hz, ArH-5, 6), 7.34 (2H, dd, $J_{4,5} = J_{7,6} = 5.8$ Hz, $J_{4,6} = J_{7,5} = 3.0$ Hz, ArH-4, 7); ^{13}C NMR (150 MHz, C_6D_6): 117.2 (dithiC-4 or 5), 118.2 (dithiC-4 or 5), 120.9 (ArC-4, 7), 127.0 (ArC-5, 6), 128.5 (ArC-1, 3), 131.6 (dithiC-2), 139.0 (ArC-3a, 7a); FTIR (KBr): 3068, 1616, 1593, 1466, 1309, 1107, 1072, 1022, 800, 742, 640 cm^{-1}; UV/VIS (THF): λ_{max} nm (log ε) 456 (4.48), 431 (4.43), 400 (sh, 4.15), 345 (4.32), 329 (sh, 4.14); HRMS (70 eV, DEI): calcd for $C_{14}H_8OS_4$ $[M^+]$ 319.9458, found 319.9461; for **5** : brown powder mp 65 °C (decomp); EI-MS: *m/z* (%) 336 (M^+, 100); ^{1}H NMR (600 MHz, C_6D_6): δ 5.47 (2H, d, $J = 6.6$ Hz, dithiH-4 or 5), 5.53 (2H, d, $J = 6.6$ Hz, dithiH-4 or 5), 7.05 (2H, dd, $J_{5,4} = J_{6,7} = 5.9$ Hz, $J_{5,7} = J_{6,4} = 3.1$ Hz, ArH-5, 6), 7.64 (2H, dd, $J_{4,5} = J_{7,6} = 5.9$ Hz, $J_{4,6} = J_{7,5} = 3.1$ Hz, ArH-4, 7); ^{13}C NMR (150 MHz, C_6D_6): 117.3 (ArC-1, 3), 118.0 (dithiC-4 or 5), 119.0 (dithiC-4 or 5), 119.7 (dithiC-2), 123.4 (ArC-4, 7), 125.9 (ArC-5, 6), 137.8 (ArC-3a, 7a); FTIR (KBr): 3055, 1545, 1514, 1450, 1296, 1255, 970, 798, 737 cm^{-1}; UV/VIS (THF): λ_{max} nm (log ε) 548 (sh, 2.95), 452 (4.30), 429 (4.35), 344 (4.19), 327 (sh, 3.93); HRMS (70 eV, DEI): calcd for $C_{14}H_8S_5$ $[M^+]$ 335.9230, found 335.9217; for **6**: brown powder mp 105 °C (decomp); EI-MS: *m/z* (%) 384 (M^+, 100); ^{1}H NMR (600 MHz, C_6D_6): δ 5.43 (2H, d, $J = 6.6$ Hz, dithiH-4 or 5), 5.55 (2H, d, $J = 6.6$ Hz, dithiH-4 or 5), 7.04 (2H, dd, $J_{5,4} = J_{6,7} = 5.9$ Hz, $J_{5,7} = J_{6,4} = 3.2$ Hz, ArH-5, 6), 7.65 (2H, dd, $J_{4,5} = J_{7,6} = 5.9$ Hz, $J_{4,6} = J_{7,5} = 3.2$ Hz, ArH-4, 7); ^{13}C NMR (150 MHz, C_6D_6): 115.0 (ArC-1, 3), 117.5 (dithiC-4 or 5), 119.4 (dithiC-4 or 5), 122.9 (dithiC-2), 124.1 (ArC-4, 7), 125.7 (ArC-5, 6), 139.4 (ArC-3a, 7a); FTIR (KBr): 3062, 1541, 1510, 1448, 1292, 798, 775, 742 cm^{-1}; UV/VIS (THF): λ_{max} nm (log ε) 432 (4.40), 408 (sh, 4.30), 345 (4.18), 327 (sh, 3.94); HRMS (70 eV, DEI): calcd for $C_{14}H_8S_4Se$ $[M^+]$ 383.8674, found 383.8673; for **7**: brown powder mp 206—207 °C (decomp); EI-MS: *m/z* (%) 386 (M^+, 100); ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.59 (2H, d, $J = 6.2$ Hz, dithiH-4 or 5), 6.64 (2H, d, $J = 6.2$ Hz, dithiH-4 or 5), 7.45 (2H, mc, ArH-6, 7), 7.85 (2H, mc, ArH-4, 9), 7.86 (2H, mc, ArH-5, 8); FTIR (KBr): 3064, 1618, 1545, 1512, 1180, 1051, 798, 742 cm^{-1}; UV/VIS (THF): λ_{max} nm (log ε) 502 (sh, 3.73), 470 (sh, 3.98), 431 (4.38), 412 (4.41), 363 (4.58), 345 (4.31).
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