Selenienoquinonoid-Extended Analogues of TTF, EDT-TTF, and BEDT-TTF. New Donors and Their Conductive Complexes

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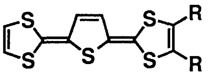
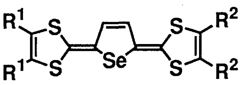
2,5-Bis(1,3-dithiol-2-ylidene)-2,5-dihydroselenophene (BDTS) and its ethylenedithio (EDT-BDTS) and bis(ethylenedithio) (BEDT-BDTS) derivatives, novel extended donors with a central selenium atom, have been synthesized by convenient methods. Of these, EDT-BDTS and BEDT-BDTS having outer chalcogen atoms afforded highly conducting molecular complexes with TCNQ (σ=13 Scm^{-1} on a compressed pellet).

The largest numbers of organic superconductors, including those with the highest *T*c value, are radical cation salts derived from BEDT-TTF.[1,2] However, donor molecules with a more elongated π-system than that of BEDT-TTF are currently receiving attention in seeking new conducting compounds for high *T*c organic superconductors, because it has recently been pointed out that *T*c's are roughly proportional to the volume of the space in which the carrier can delocalize effectively.[3] Elongation of donor π-systems is also very important molecular design strategy to decrease on-site Coulomb repulsion and then increase the transfer integral, which is essential to suppress metal-insulator transitions. Elongated donors **1** and **2** have been synthesized by us recently,[4] but **1** is a little air-sensitive.



1 (BDTT): R = H

2 (EDT-BDTT): 2R = SCH$_2$CH$_2$S



3 (BDTS): R^1= R^2= H

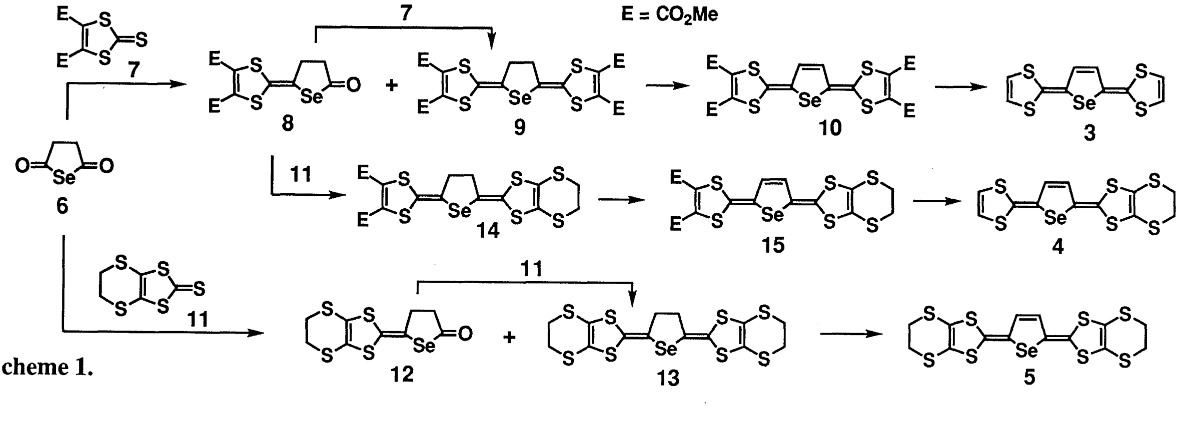
4 (EDT-BDTS): R^1= H, 2R^2= SCH$_2$CH$_2$S

5 (BEDT-BDTS): 2R^1= 2R^2= SCH$_2$CH$_2$S

We have now designed and successfully synthesized bis(ethylenedithio)-2,5-bis(1,3-dithiol-2-ylidene)-2,5-dihydroselenophene (BEDT-BDTS) **5** and ethylenedithio derivative **4** (EDT-BDTS), as well as the parent donor **3** (BDTS), novel donors with a selenium atom as an integral π-extending group, and investigated electrical properties of their charge-transfer (CT) complexes. The outer chalcogen atoms of **4** and **5** would play an important role in increasing the dimensionality[5] of the conductive complexes and the central selenium atom embedded in **3**–**5** would stabilize effectively their radical cations and enhance the intermolecular orbital overlap owing to its diffused π-orbitals.

The synthetic routes to **3**–**5** are outlined in Scheme 1. Selenasuccinic anhydride **6** was allowed to react with 2 equiv. of thione **7** in benzene containing excess of trimethylphosphite at refluxing temperature to give **8** (37%) and **9** (20%). By a similar cross-coupling reaction of **6** with 2 equiv. of thione **11**, **12** and **13** were prepared in 25 and 18% yields, respectively. The bis-capped compounds **9** (80%) and **13** (25%) were prepared in higher yields when ketones **8** and **12** were cross-coupled with 4 equiv. of **7** and 3 equiv. of **11**, respectively. When **8** was allowed to react with 3.5 equiv. of **11**, the unsymmetric intermediate **14** was obtained in 40% yield. Compounds **9** and **14** were readily dehydrogenated with DDQ in xylene at refluxing temperature to give **10** and **15** in 99% and 75% yields, respectively. DDQ formed a complex with **5**, hence **13** was dehydrogenated with chloranil in refluxing xylene to produce **5** in 51% yield. The parent **3** and **4** were obtained by heating **10** and **15** with excess of LiBr-H$_2$O in hexamethylphosphoric triamide (HMPA) at 95–155 °C in 98% yield and at 90–110 °C in 75% yield, respectively.[6] The yields of the cross-coupling reactions would be much improved by further efforts. However, it is quite noticeable that the electron-rich selenalactone-type carbonyl groups of **6**, **8**, and **12** are able to react not only with thione **7**, but also with less reactive thione **11**. The donors **3**–**5** have been proved to exist in rigid conformations even in solution, since the dithiol ring protons of **3** and **4** exhibited different chemical shifts in the ^{1}H NMR spectra.[6]

The donors **3**–**5** showed two pairs of reversible one-electron redox waves in their cyclic voltammograms. The oxidation potentials are summarized in Table 1 together with those of TTF and sulfur analogues **1** and **2**. The BDTS-system exhibits a little lower electron-donating ability than BDTT-system, because the first oxidation potentials (E_1^{ox}) of **3** and **4** are more positive by 0.07–0.06 V than those of **1** and **2**, respectively.[7] Therefore, BDTS-system appears to be more stable and favorable for submitting electrochemical oxidation or CT complex formations.



Scheme 1.

Table 1. Electrochemical data of **3**, **4**, **5**, **1**, **2**, and TTF, and electrical conductivities of their TCNQ complexes

Donor	Electrochemical property^a				Conductivity^b and IR band^c of the TCNQ complex			
	E_1^{ox}	E_2^{ox}	ΔE^{ox}	$\log K_{sem}$	D : A	σ_{RT} /Scm^{-1}	ν_{CN} /cm^{-1}	ν_{CT} /cm^{-1}
3	+0.18	+0.36	0.18	3.05	1 : 1	1.6×10^{-2}	2177	5500 (br)
4	+0.24	+0.40	0.16	2.71	1 : 1	13	2191	3000 (br)
5	+0.30	+0.45	0.15	2.55	1 : 1	13	2195	3000 (br)
TTF	+0.37	+0.75	0.38	6.44	—	—	—	—
1	+0.11	+0.34	0.23	3.90	1 : 1	6.9×10^{-3}	2152	5500 (br)
2	+0.18	+0.38	0.20	3.39	3 : 2	3.3	2177	3000 (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: 2224 cm^{-1}.

The E_1^{ox} values become much more positive in the order of **3** < **4** < **5** as the increase in the number of the outer chalcogen atoms: in consequence, the donor ability of **5** has of coming close to that of TTF. The ΔE^{ox} ($=E_2^{ox} - E_1^{ox}$) values decrease with the substitution of the ethylenedithio group, indicating the diminution of on-site Coulomb repulsion in the dications of **4** and **5** whose positive charges are thus delocalizing on the outer chalcogen atoms. In comparing the ΔE^{ox} values of **3** and **4** with **1** and **2**, we note that the Coulomb repulsion in the dication state is relatively smaller in **3** and **4** than in **1** and **2**, respectively. The same trend is also seen in the log K_{sem} values, by which the radical cations of **3** and **4** are shown to be a little less stable thermodynamically than those of **1** and **2**, respectively. These phenomena can be attributed to the fact that the conjugative interaction between the terminal dithiol rings through the C–Se–C bond of the central ring is relatively weak as compared with the conjugation through the corresponding C–S–C bond.

New donors **3–5** formed 1:1 molecular CT complexes with TCNQ whose electric conductivities, as well as characteristic IR bands, are summarized in Table 1. The conductivities of TCNQ complexes of **4** and **5** are very high even the measurement was carried out on a compressed powder sample. In contrast, the conductivity of the TCNQ complex of **3** is 10^3 times lower than those of the complexes of **4** and **5**. The complexes of **4** and **5** exhibited a very broad absorption band centered at 3000 cm^{-1} corresponding to the intrastack CT transition in a segregated stack with a mixed valence state.[8] The complex of **3** showed the broad ν_{CT} band at around 5500 cm^{-1} and showed a ν_{CN} band at a lower wave-number region than those of the complexes of **4** and **5**. Therefore, the low conductivity of the TCNQ salt of **3** can be attributed to its fully ionic structure and high conductivities of the salts of **4** and **5** can be ascribed to their partial CT conditions of the segregated columns. On the other hand, the intermolecular intrastack bonding interaction seems to be strengthened by replacing the sulfur atom with selenium atom, since conductivities of the TCNQ salts of **3** and **4** are both 10 times higher than those observed in the TCNQ salts of **1** and **2**, respectively. Thus new donors **4** and **5** appear to have high potentials as component molecules of organic metals or organic superconductors. Preparations of single crystals of the CT complexes and radical salts with inorganic anions are in progress.

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6 Selected physical data of **3**: dark red microcrystals, mp 143—144 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 5.22 (2H, d, *J*=6.5 Hz, dithiH-4 or 5), 5.34 (2H, d, *J*=6.5 Hz, dithiH-5 or 4), 6.07 (2H, s, selenophH-3,4); UV-VIS (THF) λ_{max}/nm (log ε) 462 (4.54), 433sh (4.33), 292 (3.77), 252 (4.00); HRMS Found: *m/z* 333.8520. Calcd for $C_{10}H_6S_4Se$: M, 333.8517. **4**: dark brown microcrystals, mp 115—116 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 2.13 (4H, s, SCH_2CH_2S), 5.21 (1H, d, *J*=6.5 Hz, dithiH-4 or 5), 5.34 (1H, d, *J*=6.5 Hz, dithiH-5 or 4), 6.01 (1H, d, *J*=6.1 Hz selenophH-4), 6.06 (1H, d, *J*=6.1 Hz selenophH-3); UV-VIS (THF) λ_{max}/nm (log ε) 471 (4.51), 444sh (4.35), 269 (4.06); HRMS Found: *m/z* 423.8108. Calcd for $C_{12}H_8S_6Se$: M, 423.8115. **5**: brown microcrystals, mp 206—207 °C; ^{1}H NMR (200 MHz, $CS_2/CDCl_3$) δ 3.32 (8H, s, SCH_2CH_2S), 6.28 (2H, br. s, selenophH-3,4); UV-VIS (THF) λ_{max}/nm (log ε) 479 (4.35), 447 (4.28), 278 (4.15); HRMS Found: *m/z* 513.7697. Calcd for $C_{14}H_{10}S_8Se$: M, 513.7713.

7 This is due to the diference in driving force for the formation of a hetero-aromatic π-system upon one electron oxidation: selenophene has a weaker aromaticity than thiophene.

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