New Semiconducting Benzo-TTF Salts: Synthesis and Physical Properties

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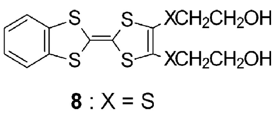
Abstract: The synthesis of new π-electron donors of benzotetrathiafulvalene derivatives **4–11** with one or two hydroxyl functions and additional sulfur or selenium atoms is described. Their redox potentials were measured by cyclic voltammetry. Radical cation salts (RCS) and charge-transfer complexes (CTC) were prepared and their conductivities were measured. Some of the RCS are semiconductors.

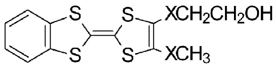
Key words: 1,3-dithiol-2-thio(oxo) benzotetrathiafulvalene, deprotection, oxidation potential, conductivity

The field of organic molecular conductors and superconductors is in constant evolution. It has been established that the physical properties of the radical cation salts (RCS) and charge-transfer complexes (CTC) depend on the electronic and structural features of TTF derivatives.[1,2] From this view point, and within the wider context of exploiting TTF as a building block in supramolecular chemistry,[3] much attention has been focused on the generation of new functionalized tetrathiafulvalene derivatives. To improve the conducting properties of the synthetic metals, efforts have been concentrated to enhance the planarity of the donors, on the one hand by introducing aromatic groups[4] or conjugated systems,[5] and on the other hand by introducing hydrogen bonds.[2,6,7] These result in the increase of the dimensionality of the salts formed. On the basis of these considerations and pursuing our studies on extended hetero-TTFs, we have focused on the benzo system and alcohol group as such potential substituents and designed 4,5-(buta-1,3-diene-1,4-diyl)-4′,5′-bis(2-hydroxyethylthio)tetrathiafulvalene (**8**), 4,5-(buta-1,3-diene-1,4-diyl)-4′,5′-bis(2-hydroxyethylseleno)tetrathiafulvalene (**9**) (Figure 1), 4,5-(buta-1,3-diene-1,4-diyl)-4′-methylthio-5′-(2-hydroxyethylthio)tetrathiafulvalene**10**), and 4,5-(buta-1,3-diene-1,4-diyl)-4′-methylseleno-5′-(2-hydroxyethylseleno)tetrathiafulvalene (**11**) (Figure 2). 4,5-(Buta-1,3-diene-1,4-diyl)-4′-methylthio-5′-(2-hydroxyethylthio)tetrathiafulvalene (**10**), and 4,5-(buta-1,3-diene-1,4-diyl)-4′-methylseleno-5′-(2-hydroxyethylseleno)tetrathiafulvalene (**11**) (Figure 2).



8 : X = S
9 : X = Se

Figure 1 Substituted TTFs **8** and **9**



10 : X = S
11 : X = Se

Figure 2 Substituted TTFs **10** and **11**

Several strategies towards the selective synthesis of unsymmetrical benzo-TTFs have been investigated by a number of groups.[8,9] However, the most general route appears to be that reported in the literature,[10,11] which involves the coupling reaction utilizing trialkyl phosphite as the key step. The synthetic route to benzo-TTFs **4** and **5** is outlined in Scheme **5**. This methodology is based upon the previous work for the synthesis of 1,3-dithiol analogues **1–3** according to the literature.[12–14]

The key starting material **1** was prepared first in three steps as shown in Scheme 1. Thus, a solution of anthranilic acid in dioxane was added to a mixture of carbon disulfide, 3-methylnitrobutane and 3-methylbutanol at reflux to provide 2-(3-methylbutoxy)-1,3-benzodithiol as an oil. Treatment of this intermediate with tetrafluoroboric acid at 0 °C in diethyl ether led immediately to the formation of the tetrafluoroborate of 1,3-benzodithiolium as a pink powder in 75% yield. The deprotonation of the resulting salt in refluxing pyridine gave the carbene intermediate, which was reacted with elemental sulfur in benzene in a small scale. The reaction mixture was analyzed by mass spectrometry. The formation of the needed starting reagent 4,5-benzo-1,3-dithiol-2-thione (**1**) (70% yield) was observed as a yellow solid, but a second compound, identified as the symmetrical dibenzotetrathiafulvalene (DBzTTF) was also formed (26% yield) (Scheme 1). The reaction is not completely specific, because a second side-reaction takes place by dimerization of the intermediate carbene.[13]

The reduction of carbon disulfide by sodium in DMF at room temperature, followed by reaction of the generated 1,3-dithiol-2-thione-4,5-dithiolate with 0.5 equimolar amounts of zinc chloride and tetrabutylammonium bromide gave the zinc bis(tetrabutylammonium)-bis(4,5-dithiolate-1,3-dithiol-2-thione)[14] $[Zn(dmit)_2](Bu_4N)_2$ (Scheme 2).

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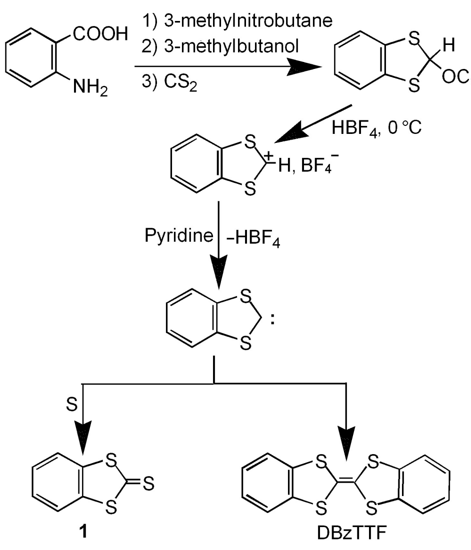
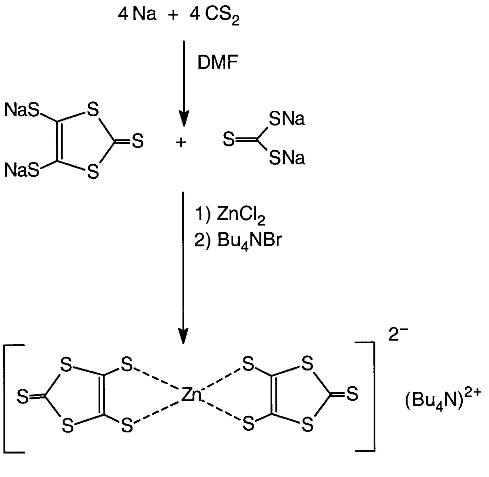
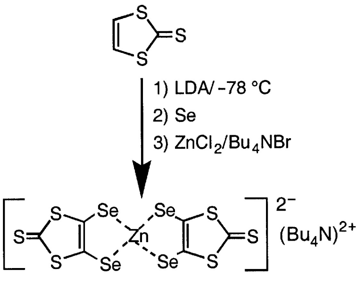


Scheme 1

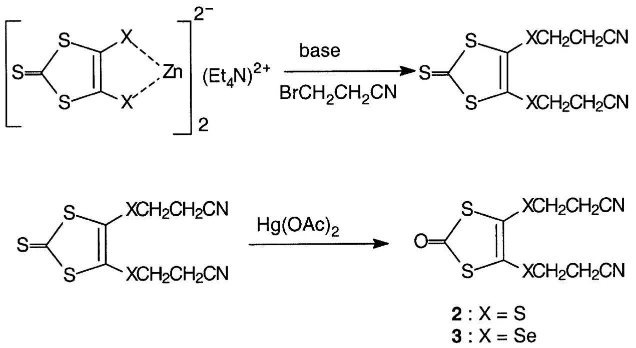


Scheme 2

An efficient method to prepare stable dianionic alkali metal salts of bis(tetrabutylammonium)-bis(4,5-diselenolate-1,3-dithiol-2-thione) $[Zn(dsit)_2](Bu_4N)_2$ analogue of dmit have been reported.[15] The 1,3-dithiol-2-thione in THF reacts with strong base such as lithium diisopropylamide at −78 °C, and therefore nucleophilic carbons would be expected to be capable of reacting with elemental selenium followed by reaction of the diselenolate with zinc chloride and tetrabutylammonium bromide (Scheme 3).



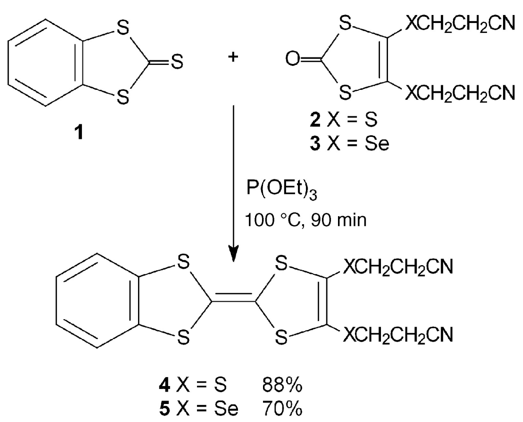
Scheme 3



Scheme 4

Reaction of the zincate salts with 3-bromopropionitrile in refluxing acetonitrile led to the protected thione derivatives. The transchalcogenation was accomplished with mercuric acetate in chloroform and glacial acetic acid to yield the starting reagents **2** and **3** in 98% and 96%, respectively (Scheme 4).

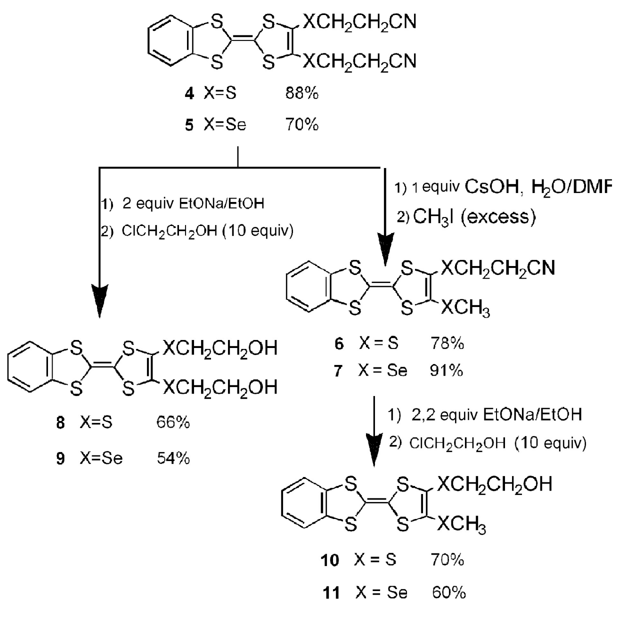
Thus, coupling of the two different half units 4,5-benzo-1,3-dithiol-2-thione (**1**) with either 4,5-bis(2′-cyanoethylthio)-1,3-dithiol-2-one (**2**)[16] or with 4,5-bis(2′-cyanoethylseleno)-1,3-dithiol-2-one (**3**)[17] using triethyl phosphite as a base at 100 °C gave the unsymmetrical benzoTTFs **4** and **5** (in 88% and 70% yields, respectively) (Scheme 5) and three symmetrically self-coupled products.



Scheme 5

Compounds **4–7** are particularly versatile TTF derivatives, as further functionalization of the thiolate and selenolate anions can be readily achieved by the mono or double deprotection, followed by addition of electrophile. Accordingly, TTFs **4** and **5** were reacted with two equivalents of sodium ethoxide in ethanol to remove two cyanoethyl groups. The resulting dithiolate and selenolate species was then reacted in situ with 2-chloroethanol to afford compounds **8** and **9** in 66% and 54% yields, respectively.

TTF-monothiolate and TTF-monoselenolate can be efficiently regenerated (as 1 equiv of cesium salt) by treatment with cesium hydroxide monohydrate in ethanol at room temperature. This was established by trapping the thiolate and selenate anions with iodomethane, which gave 4,5-benzo-6-methylthio-7-(2′-cyanoethylthio)TTF (**6**) and 4,5-benzo-6-methylseleno-7-(2′-cyanoethylseleno)TTF (**7**) in 78 and 91% yields, respectively. The same reaction of thiolate and selenolate anions **6** and **7** with one equivalent of 2-chloroethanol at room temperature proceeded less efficiently to provide the monohydroxyl function benzoheteroTTFs **10** and **11** (70% and 60% yields) (Scheme 6).



Scheme 6

The electrochemical behavior of the new donors has been studied by cyclic voltammetry (CV) to measure their oxidation potentials. In each case, the two standard one-electron reversible oxidation waves were observed and collected in Table 1. The potentials Eox_1, Eox_2, $E^1_{1/2}$ and $E^2_{1/2}$ of all donors are higher than those of the parent unsubstituted tetrathiafulvalene (TTF) taken as reference. This implies that the introduction of benzo and chalcogenoalkyl substituents reduces the electron-donating ability of the substituted TTFs, because of their high electron-attracting effect. Nevertheless, by decreasing the number of cyano substituents or replacing it by a hydroxy group, which is less electron-attracting than cyano group, the first oxidation potentials Eox_1 decreases for all new compounds (**6**–**11**). In the same context, all the new mono and dihydroxy functionalized TTF compounds (**10**, **11** and **8**, **9**, respectively) show a cathodic shift relative to their parent 4,5-benzo-4′,5′-dicyanoethylheteroTTF. A comparison between the $E^1_{1/2}$ data between **4** and **8** and between **5** and **9** reveals that there is a large cathodic shift of the oxidation potentials by 61–82 mV with decreasing strength of electron-attracting substituents.

The presence of the methyl substituents in compounds **6** and **7** shifts the oxidation potential Eox_1 by ca. 49 mV compared to dicyanoethyl analogues **4** and **5**. It is also clear that increasing the number of hydroxy functions as hydroxyethyl groups as electron-donating substituent on the 4,5-dichalcogeno-1,3-dithiol-2-ylidene ring results in a large anodic shift in the oxidation wave. Incorporation of a benzene ring instead of cyanoethyl groups may be responsible for a large higher cathodic shift value of E_{ox1}, E_{ox2}, $E^1_{1/2}$, $E^2_{1/2}$.

A comparison of the data for compounds **6**–**11** and TCEX-TTF (tetracyanoethylchalcogeno)TTF shows that upon incorporation of a benzene ring instead of cyanoethyl groups may be responsible for a large higher cathodic shift value of $E^1_{1/2}$, $E^2_{1/2}$. Moreover, it is observed that compounds **4**–**7** exhibit a more important splitting ($\Delta E_{1/2} = 410–421$) than compounds **8**–**11** ($\Delta E_{1/2} = 359–414$); this could be due to the presence of the cyano groups inducing a more efficient stabilizing interaction on the radical cation. The ($E^2_{1/2}$–$E^1_{1/2}$) can be related to the semiquinone formation constant K_{SEM}, which represents the thermodynamic stability of cation radicals in the SEM stage by the equation:

$$E^1_{1/2} - E^2_{1/2} = 0.059 \log K_{SEM} \ (\mathrm{V}, 25°\mathrm{C})^{18,19}$$

$$\begin{array}{ccccc} \mathrm{TTF} & \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} & \mathrm{TTF}^{+\cdot} & \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} & \mathrm{TTF}^{2+} \\ \mathrm{Red} & E^1_{1/2} & \mathrm{SEM} & E^2_{1/2} & \mathrm{Ox} \end{array}$$

Equation 1

$K_{SEM} = [SEM]^2/[Red][Ox]$, where K_{SEM} is the equilibrium constant in equation:

$$D + D^{2+} \overset{K_{SEM}}{\rightleftharpoons} 2D^{+\cdot}$$

Equation 2

In Table 1, the K_{SEM} values of **4**–**11** are also included. The values for TTFs are in the order of 10^6–10^7, while **8**, **9** and **10** have smaller values. Therefore, the thermodynamic stabilities of cation radicals diminishes in the order **5** = **7** > **11** > **4** = **6** > **9** = **10** > **8**, due to a decrease in intramolecular coulombic repulsions. The TCNQ complex formation was obtained by mixing hot acetonitrile solutions of the donor and TCNQ in equimolar amounts.[20,21] The donor **4** gave orange platelets, compounds **6**, **8**–**11** gave black powders, while compounds **5** and **7** gave fine black crystals.

The electrical conductivities of **5**-TCNQ, (**7**–**11**)-TCNQ, DBzTTF-TCNQ, were measured by the two-probe method on single crystals or powder compressed pellets.[22] Table 2 shows the room temperature electrical conductivities (σ_{RT}, S/cm), activation energies (Ea, eV) and the nitrile stretching absorption bands ($\nu_{C\equiv N}$, cm^{-1}) in the IR spectra of the TCNQ complexes.

Table 1 Oxidation Potentials (mV) of Ponors **4–11**[a]

Donor	Eox_1	Eox_2	ΔEox	$E^1_{1/2}$	$E^2_{1/2}$	$\Delta E_{1/2}$	$K = 10^{(-\Delta E1/2)/0.059}$
4	778	1192	414	742	1152	410	08.9×10^6
6	730	1140	410	692	1102	410	08.9×10^6
10	708	1096	388	666	1052	386	3.4×10^6
8	718	1078	360	681	1040	359	1.2×10^6
5	760	1184	424	722	1143	421	1.3×10^7
7	710	1138	428	673	1094	421	1.3×10^7
11	688	1100	412	648	1062	414	1.0×10^7
9	676	1062	386	640	1026	386	3.5×10^6
TTF	414	840	426	375	807	432	–
DBz-TTF	724	1160	436	679	1114	435	–
TCET-TTF	838	1172	334	799	1134	335	–
TCES-TTF	750	1118	368	700	1070	370	–
TMT-TTF	638	984	346	601	942	341	–
TMS-TTF	610	990	380	572	957	385	–

[a] All oxidation potentials are determined in CH_2Cl_2 containing Bu_4NPF_6 (0.1 M) with SCE as the reference electrode and platinum as working and counter electrodes.

DBz: dibenzo, TCET: tetracyanoethylthio, TCES: tetracyanoethylseleno, TMT: tetramethylthio, TMS: tetramethylseleno.

Table 2 Electrical Conductivity (σ), Activation Energies (Ea), Nitrile Stretching Absorption Bands ($\nu_{C\equiv N}$)[a] and Degree of Charge Transfer (ρ) of CTC

Complexes	**4**-TCNQ	**5**-TCNQ	**10**-TCNQ	**11**-TCNQ	**6**-TCNQ	**7**-TCNQ	**8**-TCNQ	**9**-TCNQ	DBzTTF-TCNQ
σ (S/cm)	6.2×10^{-6}	3.2×10^{-6}	1.5×10^{-5}	1.0×10^{-5}	2.1×10^{-6}	3.9×10^{-6}	1.5×10^{-5}	1.2×10^{-5}	2.0×10^{-4}
Ea (eV)	0.41	0.42	0.40	0.42	0.42	0.42	0.41	0.39	–
$E^1_{1/2}$ (mV)	742	722	666	648	692	673	681	640	610
$\nu_{C\equiv N}$ (cm^{-1})	2216.2	2213.1	2203.8	2200.0	2211.0	2209.4	2204.8	2200.2	–
ρ (e^-/mol)	0.25	0.32	0.53	0.62	0.37	0.41	0.50	0.61	–

[a] Values of the $\nu_{C\equiv N}$ (cm^{-1}) for neutral TCNQ (2227) and for the donors **4** (2249.8), **5** (2245.9), **6** (2245.9), **7** (2244).

The complexes with alcohol donors **8–11** show a semiconducting behavior and the values of electrical conductivities were 1/13 of the DBzTTF-TCNQ complex measured under the same conditions. The other TCNQ complexes exhibited comparatively low electric conductivities (= 10^{-6} S/cm).

When a comparison was made between the $E^1_{1/2}$ values of the donors and $\nu_{C\equiv N}$ values of the TCNQ complexes, it was found that the $\nu_{C\equiv N}$ shifts to lower wave number with a decrease in the $E^1_{1/2}$ values. This means that the degree of electron transfer from the donor to TCNQ increases in the TCNQ complex, as the $E^1_{1/2}$ value of the donor becomes smaller.

The formation of radical cation salts (RCS) of the new 4′,5′-dichalcogeno donor systems with various anions was studied first. The formation of these salts were carried out by galvanostatic electrocrystallization with the appropriate anion under constant current (5 μA) in anhydrous THF.[23] The donors **8–11** provided black needles and black powders. On the other hand, no formation of radical cation salts was observed in the reaction of **10** and **11** with nitrate, chlorine and perchlorate anions. Also, no reaction of **9–11** with bromine and iodine anions was observed.

Now, various counter-anions were next used for salt formation with the new donors. The electrical conductivities of the RCS are shown in Table 3. The $(\mathbf{10})_2$-Br, $(\mathbf{11})_2$-Br, $(\mathbf{8})_2$-Cl and $(\mathbf{9})_2$-Cl showed increased electrical conductivities around 10^3–10^4 S/cm as compared to the corresponding TCNQ complexes.

Table 3 Electrical Conductivities (S/cm) and [Activation Energies (eV)] of the RCS

TTF	Br^-	NO_3^-	Cl^-	ClO_4^-	Br_3^-	I_3^-
8	8.9×10^{-6} [0.39]	10^{-5} [0.38]	9.2×10^{-3} [0.25]	1.9×10^{-5} [0.36]	4.7×10^{-6} [0.42]	1.2×10^{-5} [0.38]
9	2.7×10^{-6} [0.41]	1.5×10^{-5} [0.39]	9.3×10^{-3} [0.28]	6.5×10^{-5} [0.33]	–	–
10	2.4×10^{-2} [0.18]	–	–	–	–	–
11	5.0×10^{-2} [0.16]	–	–	–	–	–

For the RCS mentioned above, with comparatively higher electric conductivities, the Ea values were small (0.16–0.28 eV). On the other hand, the semiconducting and insulating salts such as (**8**)$_2$-NO$_3$, (**9**)$_2$-NO$_3$, (**8**)$_2$-ClO$_4$, (**9**)$_2$-ClO$_4$, (**8**)$_2$-I$_3$, (**8**)$_2$-Br, (**9**)$_2$-Br and (**8**)$_2$-Br$_3$ have considerably higher activation energies (0.33–0.42 eV). These results are consistent with those of the IR spectra of the salts in KBr pellets. Thus, the highly conducting salts (**10**)$_2$-Br and (**11**)$_2$-Br (0.025 and 0.05 S/cm respectively), revealed a broad absorption at the wavenumber of 2850 cm^{-1}, which can be assigned as a mixed-valence transition.

In summary, new TTF **4**–**11** containing benzo, heteroethylcyano, heteromethyl and heterohydroxyethyl substituents have been synthesized. Cyclic voltammetry showed two reversible single-electron oxidation waves. The new donors readily formed charge-transfer complexes with electron acceptor TCNQ and several radical cation salts with various anions. Electrical conductivity of thirteen complexes showed semi-conducting behavior and appear sufficiently promising to continue work in this area. Further studies on the electronic properties and structure determination of these salts are currently under investigation and wile be published separately.

NMR spectra were recorded on a Bruker AC 200 instrument. FAB mass spectra were recorded on a JEOL JMS-DX 300 spectrometer. IR spectra were recorded on a Equinox 55 (resolution 0.5 cm^{-1}). Melting points were measured on a Büchi apparatus. Cyclic voltammetry measurements were carried out on a PAR-273 potentiostat/galvanostat.

4,5-Bis(2′-cyanoethylthio)-6,7-benzoTTF (DCET-BzTTF) (4) and 4,5-Bis(2′-cyanoethylseleno)-6,7-benzoTTF (DCES-BzTTF) (5)

Each 4,5-bis(2′-cyanoethylthio)-1,3-dithiol-2-one (**2**; 0.31 g, 1.08 mmol) or 4,5-bis(2′-cyanoethylseleno)-1,3-dithiol-2-one (**3**; 0.41 g, 1.08 mmol) or 4,5-benzo-1,3-dithiol-2-thione (**1**; 0.2 g, 1.08 mmol) was suspended in freshly distilled triethyl phosphite (10 mL) under N$_2$ and heated with stirring at 100 °C for 90 min. Then, the mixture was cooled to 0 °C and the precipitate was collected by filtration. The product was washed with cold MeOH (3 × 10 mL), dried in vacuo and chromatographed (silica gel, CH$_2$Cl$_2$).

4

Orange-yellow powder; yield: 88%; mp 145 °C.

^{1}H NMR (CDCl$_3$): δ = 2.74 (t, 4 H, CH$_2$CN, *J* = 7.0 Hz), 3.09 (t, 4 H, CH$_2$S, *J* = 7.0 Hz), 7.20 (m, 4 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$): δ = 18.91 (CH$_2$CN), 31.30 (CH$_2$S), 118.2 (CN).

MS (FAB$^+$): *m*/*z* = 424 [M]$^+$.

Anal. Calcd for C$_{16}$H$_{12}$N$_2$S$_6$: C, 45.28; H, 2.83. Found: C, 45.35; H, 3.03.

5

Yellow needles; yield: 70%; mp 125 °C.

^{1}H NMR (CDCl$_3$): δ = 2.86 (t, 4 H, CH$_2$CN, *J* = 7.0 Hz), 3.08 (t, 4 H, CH$_2$Se, *J* = 7.0 Hz), 7.23 (m, 4 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$): δ = 19.26 (CH$_2$CN), 23.43 (CH$_2$Se), 118.2 (CN).

MS (FAB$^+$): *m*/*z* = 518 [M]$^+$.

Anal. Calcd for C$_{16}$H$_{12}$N$_2$S$_4$Se$_2$: C, 37.06; H, 2.31. Found: C, 37.37; H, 2.48.

4,5-Bis(2′-hydroxyethylthio)-6,7-benzoTTF (DHET-BzTTF) (8) and 4,5-Bis(2′-hydroxyethylseleno)-6,7-benzoTTF (DHES-BzTTF) (9)

These compounds were prepared by adaptation of a procedure described in the literature.[10,12]

8

Orange-yellow powder; yield: 66%; mp 128 °C.

^{1}H NMR (CDCl$_3$): δ = 2.92 (s, 2 H, OH), 3.01 (m, 4 H, CH$_2$S, *J* = 5.6 Hz), 3.75 (t, 4 H, CH$_2$O, *J* = 5.6 Hz), 7.20 (m, 4 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$): δ = 39.38 (CH$_2$S), 59.86 (CH$_2$O).

MS (FAB$^+$): *m*/*z* = 406 [M]$^+$.

Anal. Calcd for C$_{14}$H$_{14}$O$_2$S$_6$: C, 41.37; H, 3.44. Found: C, 41.38; H, 3.50.

9

Yellow needles; yield: 54%; mp 134 °C.

^{1}H NMR (CDCl$_3$): δ = 2.74 (s, 2 H, OH), 3.07 (m, 4 H, CH$_2$Se, *J* = 5.6 Hz), 3.81 (t, 4 H, CH$_2$O, *J* = 5.6 Hz), 7.20 (m, 4 H$_{\text{arom}}$).

^{13}C NMR (CDCl$_3$): δ = 23.50 (CH$_2$Se), 59.98 (CH$_2$O).

MS (FAB$^+$): *m*/*z* = 500 [M]$^+$.

Anal. Calcd for C$_{14}$H$_{14}$O$_2$S$_4$Se$_2$: C, 33.60; H, 2.80. Found: C, 33.72; H, 2.90.

4-(2′-Cyanoethylthio)-5-methylthio-6,7-benzoTTF (CETMT-BzTTF) (6) and 4-(2′-Cyanoethylseleno)-5-methylseleno-6,7-dimethylthioTTF (CESMS-BzTTF) (7)

These compounds were prepared by adaptation of a procedure described in the literature.[16,17]

6
Orange solid; yield: 78%; mp 126 °C.

^{1}H NMR ($CDCl_3$): δ = 2.48 (s, 3 H, SCH_3), 2.70 (t, 2 H, CH_2CN, J = 7.0 Hz), 3.03 (t, 2 H, CH_2S, J = 7.0 Hz), 7.20 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 18.74 (SCH_3), 19.20 (CH_2CN), 31.21 (CH_2S), 118.2 (CN).

MS (FAB^+): m/z = 385 $[M]^+$.

Anal. Calcd for $C_{14}H_{11}NS_6$: C, 43.63; H, 2.85. Found: C, 43.55; H, 2.78.

7
Orange powder; yield: 91%; mp 124 °C.

^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3 H, $SeCH_3$), 2.86 (t, 2 H, CH_2CN, J = 7.0 Hz), 3.03 (t, 2 H, CH_2Se, J = 7.0 Hz), 7.21 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 9.90 ($SeCH_3$), 19.45 (CH_2CN), 23.21 (CH_2Se), 118.2 (CN).

MS (FAB^+): m/z = 479 $[M]^+$.

Anal. Calcd for $C_{14}H_{11}NS_4Se_2$: C, 35.07; H, 2.29. Found: C, 35.12; H, 2.48.

4-(2′-Hydroxyethylthio)-5-methylthio-6,7-benzoTTF (HETMT-BzTTF) (10) and 4-(2′-Hydroxyethylseleno)-5-methylseleno-6,7-benzoTTF (HESMS-BzTTF) (11)

These compounds were prepared by adaptation of a procedure described in the literature.[17]

10
Orange-yellow powder; yield: 70%; mp 105 °C.

^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 1 H, OH), 2.47 (s, 3 H, SCH_3), 2.94 (t, 2 H, CH_2S, J = 5.6 Hz), 3.72 (t, 2 H, CH_2O, J = 5.6 Hz), 7.20 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 19.40 (SCH_3), 39.19 (CH_2S), 59.94 (CH_2O).

MS (FAB^+): m/z = 376 $[M]^+$.

Anal. Calcd for $C_{13}H_{12}OS_6$: C, 41.48; H, 3.19. Found: C, 41.60; H, 3.04.

11
Orange solid; yield: 60%; mp 93 °C.

^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 1 H, OH), 2.42 (s, 3 H, $SeCH_3$), 3.08 (m, 2 H, CH_2Se, J = 5.6 Hz), 3.89 (t, 2 H, CH_2O, J = 5.6 Hz), 7.24 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 9.90 ($SeCH_3$), 23.21 (CH_2Se), 60.00 (CH_2O).

MS (FAB^+): m/z = 470 $[M]^+$.

Anal. Calcd for $C_{13}H_{12}OS_4Se_2$: C, 33.19; H, 2.55. Found: C, 33.30; H, 2.46.

Electrocrystallization

The radical cation salts were prepared by galvanostatic electrochemical oxidation on a platinum electrode at a constant current (5 μA) in a 15 mL H-type cell from a solution of an appropriate tetrabutylammonium salt as an electrolyte (Bu_4NX, 0.5 M, typically in THF) containing the donor **8**, **9**, **10** or**11** (10^{-3} M).

Charge Transfer Complexes (CTC)

The charge transfer complexes were isolated by a chemical redox reaction between a donor (**4–11**) and TCNQ as the electron acceptor. In each experiment, equimolar amounts (0.1 mmol) of the donor and TCNQ were separately dissolved in boiling MeCN and then mixed.

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