Stable Molecular Metals Based on a Novel Unsymmetrical Diselenadithiafulvalene

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Novel unsymmetrical π-electron donors have been synthesized and electrical conductivities of their radical cation salts have been studied: among them 4,5-ethylenedithio-4′,5′-(isopropylidenemethylenedithio)diselenadithiafulvalene salts are all metallic down to 4.2 K, and exhibit two-dimensional nature in the anisotropy of the conductivity.

For preparation of organic metals stable down to low temperature, multi-dimensional intermolecular interactions play a key role. We have mentioned molecular design strategies for two-dimensional systems by means of enhancing intermolecular chalcogen–chalcogen contacts, and proposed two very promising candidates: BEDT-TSeF and BIDT-TTF.[1†] The former donor indeed gave various types of two-dimensional organic metals stable down to 4.2 K.[2] They are, however, sparingly soluble in conventional organic solvents, and this prevents the preparation of radical cation salts. Therefore, improved solubility is intended by unsymmetrical combination of these donors. We also expect that the hybridization will bring about novel electrical and struct-

Table 1 Cyclic voltammetric data[a]

Donor	$E_1^{1/2}$/V	$E_2^{1/2}$/V	$\Delta E^{1/2}$	$E_3^{\mathrm{pa}\,b}$
ETIT	0.17	0.41	0.24	0.95
ETMT	0.18	0.41	0.23	
DMeIT	0.07	0.36	0.29	1.00
BEDT-TSeF	0.27	0.49	0.22	
BIDT-TTF	0.11	0.32	0.21	0.8_2
BMDT-TTF	0.10	0.33	0.23	
BEDT-TTF	0.10	0.41	0.31	
TMTSF	0.04	0.38	0.34	

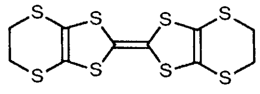
[a] *Experimental conditions*: donor (*ca.* 5×10^{-4} mol dm^{-3}), electrolyte $\mathrm{Bu^n_4N^+ClO_4^-}$ (0.1 mol dm^{-3}) in dry benzonitrile under argon, at room temp., *vs.* $\mathrm{Ag/AgNO_3}$ (0.01 mol dm^{-3}), Pt electrode, scan rate 0.1 V s^{-1}. [b] Irreversible anodic peak potential.

[†] *Abbreviations used*: BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene; BEDT-TSeF, bis(ethylenedithio)tetraselenafulvalene; BIDT-TTF, bis(isopropylidenemethylenedithio)tetrathiafulvalene; ETIT, 4,5-ethylenedithio-4′,5′-(isopropylidenemethylenedithio)diselenadithiafulvalene; ETMT, 4,5-ethylenedithio-4′,5′-(methylenedithio)diselenadithiafulvalene; DMeIT, 4,5-dimethyl-4′,5′-(isopropylidenemethylenedithio)diselenadithiafulvalene; BMDT-TTF, bis(methylenedithio)tetrathiafulvalene; TMTSF, tetramethyltetraselenafulvalene.

Table 2 Electrical conductivities of the radical cation salts

Radical cation salt[a]	Solvent[b]	Shape[c]	ρ_{RT}/Ω cm[d]	Conductivity[e]
$(ETIT)_2ClO_4(TCE)$	TCE	P	4×10^{-3}	M down to 4.2 K
$(ETIT)_3ReO_4(TCE)$	TCE	P	5×10^{-3}	M down to 4.2 K
$(ETIT)_2PF_6(TCE)_{0.5}$	TCE	P	2×10^{-2}	M down to 4.2 K
$(ETIT)_3AsF_6(TCE)$	TCE	P	3×10^{-2}	M down to 4.2 K
$(ETIT)_2TaF_6$	TCE	P	5×10^{-3}	M down to 4.2 K
$(ETIT)_2Ag(CN)_2(TCE)_{0.33}$	TCE	P	2×10^{-2}	M down to 4.2 K
$(ETIT)_5[Au(CN)_2]_2(TCE)_{0.33}$	TCE	P	3×10^{-3}	M down to 4.2 K
$(DMeIT)_2I_3$	THF	N	2×10^{-2}	Semiconductive
$(DMeIT)_3(PF_6)_2$	TCE–PhCl[f]	N	3×10^{-4}	$T_{M\text{-}I}$ 13 K
$(DMeIT)_2PF_6$	TCE–PhCl[f]	P	3×10^{1}	Semiconductive
$(ETMT)_2ClO_4$	THF	N	3×10^{1}	Semiconductive

[a] TCE = 1,1,2-Trichloroethane. Stoichiometries were determined by electron probe microanalysis (EPMA). [b] Solvent used in the electrochemical oxidation. TCE contains 10 vol% ethanol. [c] P = plate; N = needle. [d] Room-temperature resistivity on a single crystal. [e] M = metallic. [f] 1 : 1 by volume.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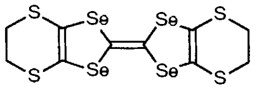
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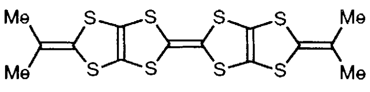
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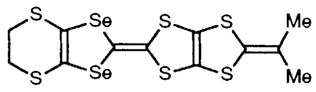
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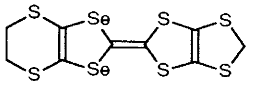
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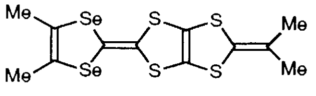
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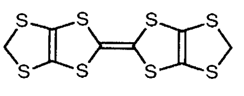
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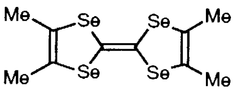
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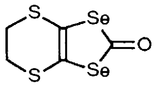
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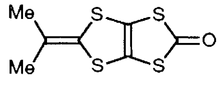
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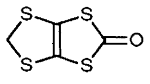
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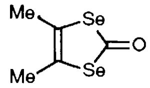
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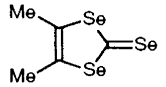
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ural properties. We herein report the syntheses of unsymmetrical donors based on the units of BEDT-TSeF or BIDT-TTF, *i.e.* ETIT, ETMT and DMeIT.† Electrical properties of their radical cation salts are also described.

The desired compounds were obtained by cross-coupling reactions between the precursor ketones **1**,[2] **2**,[3] **3**[4] and **4**[5] (*e.g.* **1** + **2** → ETIT).‡ As expected, the solubilities of these unsymmetrical donors are improved especially in case of ETIT, where both BEDT-TSeF and BIDT-TTF are extremely insoluble. This improvement would be ascribed to the intramolecular polarization caused by the unsymmetrical coupling.

Table 1 compares cyclic voltammetric data for these donors with other analogues. As can be seen, oxidation potentials of each unsymmetrical donor fall between those of the corresponding symmetrical donors. The difference between the first and second oxidation potentials for the unsymmetrical ones are considerably less than those for TMTSF and BEDT-TTF, indicative of decreased Coulombic repulsions in the dicationic state. The subsequent irreversible third oxidation process is observed for the donors with an isopropylidene moiety, *i.e.* ETIT, DMeIT and BIDT-TTF.

Each radical cation salt listed in Table 2 was obtained as a single crystal by electrochemical oxidation (at a constant current of 1.0 μA) of a solution containing the donor and the tetra(n-butyl)ammonium salt of the corresponding anion. Electrical conductivities of these crystals were measured by the standard four-probe method down to 4.2 K.

Seven salts of ETIT were obtained with octahedral, tetrahedral and linear anions as very thin plates. They exhibit low resistivities (*ca.* 10^{-2} Ω cm) at room temperature, and are metallic down to 4.2 K in every case. It is notable that ETIT affords stable metals without exception so far. The anisotropy of the resistivity in the crystal plane for these salts ranges from 2 to 4, suggesting two-dimensional electronic structures. Thus, ETIT is a good donor, in respect of the strong ability to afford two-dimensional stable metals.

In some ETIT salts, the donor : anion ratios are larger than the frequently encountered 2 : 1. This suggests new types of

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‡ Treatment of the two ketones in refluxing toluene with $P(OEt)_3$ at 120 °C for 2 h under argon provided the mixture containing the desired unsymmetrical donor, self-coupling products, and other complex by-products. The crude mixture was chromatographed (MPLC) over SiO_2 applying CS_2 as an eluent: ETIT, red–brown microcrystals; 4.4% yield; ^1H NMR δ (CS_2) 1.72 (s, 6 H) and 3.27 (s, 4 H); *m/z* (EI) 505.7460 (calc. 505.7437; $C_{12}H_{12}S_6{}^{80}Se_2$); IR ν(KBr)/cm^{-1} 2950m, 2921s, 2853m, 1617m, 1510s, 1433s, 1404s, 1366s, 1287s, 1256w, 1125w, 1082m, 1059w, 963vs, 941w, 868w, 841m, 824w and 712s. ETMT, red–orange microcrystals; 6.8% yield; ^1H NMR δ (CS_2) 3.27 (s, 4 H) and 4.89 (s, 2 H); *m/z* (EI) 465.7173 (calc. 465.7124; $C_9H_6S_6{}^{80}Se_2$): IR ν(KBr)/cm^{-1} 2989w, 2955w, 2923m, 2853w, 1736br.m, 1509s, 1462m, 1408s, 1283s, 1260m, 1171w, 1125w, 1092m, 953s, 920w, 880w, 849m, 810m, 710vs and 681s. DMeIT, dark red–brown microcrystals; 0.4% yield; ^1H NMR δ(CS_2) 1.69 (s, 6 H) and 1.97 (s, 6 H); *m/z* (EI) 443.8111 (calc. 443.8152; $C_{12}H_{12}S_4{}^{80}Se_2$); IR ν(KBr)/cm^{-1} 2903m, 2845w, 1674m, 1618m, 1509w, 1433vs, 1370s, 1144w, 1114w, 1082m, 1067m, 963s, 870w and 714s. For preparation of DMeIT, the selenone **5** was also used in place of **4**, however, no DMeIT was isolated.

two-dimensional molecular packing. It is rare for a radical cation salt of such stoichiometry to be metallic.

The cation radical salts of ETMT and DMeIT prepared to date are semiconductive, except for $DMeIT_3(PF_6)_2$ which exhibits metallic behaviour down to 13 K.

In conclusion, hybidization between BEDT-TSeF and BIDT-TTF affords various two-dimensional metals all of which are stable down to 4.2 K. This indicates that our molecular design strategies[1] are applicable to unsymmetrical donors as well as symmetrical ones.[2]

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