Unsymmetrically Substituted Dithiadiselenafulvalene Donors for Organic Metals. Synthesis and Conductivity of the Charge-transfer Salts

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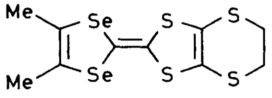
New unsymmetrical dithiadiselenafulvalene donors and their radical cation salts with inorganic anions have been prepared; among the salts dimethyl(ethylenedithio)dithiadiselenafulvalene salts exhibit the highest electrical conductivity.

The design and synthesis of new donor species for conducting charge-transfer salts are of current interest. Unsymmetrical substitution on the tetrathiafulvalene (TTF) framework provides interesting structural modifications and a variety of such donors have been extensively investigated.[1,2] Little work has been directed towards the corresponding selenium compounds, *i.e.*, unsymmetrically substituted tetraselenafulvalene (TSF). Previously we and French workers have independently synthesized dimethyltrimethyleneTSF (DMtTSF) and reported the physical properties and crystal structure of its radical cation salts.[3,4] We now report the synthesis of a new series of unsymmetrically substituted dithiadiselenafulvalenes, a hybrid of TTF and TSF, and their charge-transfer salts.

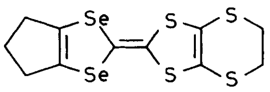
New donors (**1**), (**2**), (**3**), and (**4**) were prepared by cross-coupling of the appropriate 1,3-dithiole-2-one and 1,3-diselenole-2-selenone [*e.g.* (**5**) and (**6**) for (**1**)] using excess of trimethyl phosphite in refluxing toluene. The desired cross-coupling product was formed along with the symmetrical self-coupling products as revealed by h.p.l.c. It is surprising that the product distribution favours the unsymmetrical donor [*e.g.* 10:2:1 for (**1**) : tetramethyltetraselenafulvalene (TMTSF) : bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)] rather than being that expected for complete random coupling (2:1:1). For the preparation of (**1**), 1,3-dithiole-2-thione (**7**) was also employed as the sulphur containing moiety. In this case, however, the yield of the desired compound was not improved owing to the formation of scrambled by-products and self-coupling products. This was also the case when 1,3-dithiole-2-selenone (**8**) was used in place of (**5**).

Separation of the cross-coupling products from symmetrical co-products was accomplished by chromatography on a SiO$_2$ column followed by preparative gel permeation chromatography (g.p.c.). A recycle operation of the g.p.c., which exerts an effect equivalent to an increase in the number of columns, was necessary for complete separation. Thus, by the end of eight cyclic elutions, three distinct peaks were obtained and the desired fraction was collected. The purity of the collected sample was verified by h.p.l.c.

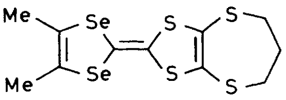
Some properties of the new donors are summarized in Table 1. Close similarities in the electronic spectra were observed between (**1**) and (**2**) and between (**3**) and (**4**). Cyclic voltammetry exhibited two reversible one-electron oxidation waves in all cases. The first and the second oxidation



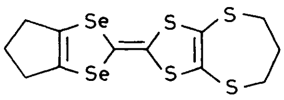
(**1**)



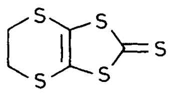
(**2**)



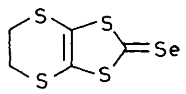
(**3**)



(**4**)



(**7**)



(**8**)

Table 1. Properties of unsymmetrical dithiadiselenafulvalene donors.

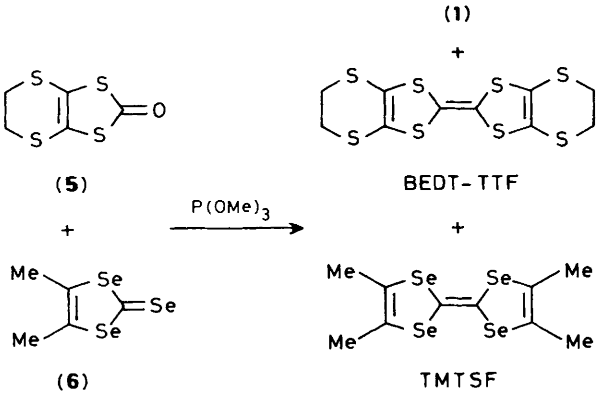
Compound	M.p./°C	U.v.-visible (log ε)[a] λ/nm	Redox potentials[b] $E^1_{1/2}$/V	$E^2_{1/2}$/V
(**1**)	198	490 (2.81), 340 (sh 3.78) 313 (4.18), 208 (4.29)	0.52	0.78
(**2**)	214	480 (2.48), 335 (sh 3.80) 315 (4.15), 209 (4.29)	0.48	0.73
(**3**)	232	380 (3.17), 336 (3.88) 300 (4.17), 212 (4.30)	0.48	0.75
(**4**)	234	378 (3.17), 332 (3.89) 303 (4.20), 208 (4.33)	0.44	0.74

[a] In acetonitrile. [b] V *vs.* standard calomel electrode at a glassy carbon electrode, 0.1 M Bu$_4$NClO$_4$–MeCN, scan rate 100 mV s^{-1}.

Table 2. Room temperature conductivities of the radical cation salts.

Donor	Conductivity^a/S cm^{-1} PF_6^- salt	 ClO_4^- salt	 I_3^- salt
(1)	300	260	$<10^{-4}$
(2)	0.087	9.9	2.5×10^{-3}
(3)	41	1.5×10^{-3}	$<10^{-4}$
(4)	—^{b}	10^{-4}	$<10^{-4}$

^{a} Measured on single crystals. ^{b} No single crystals were obtained.



potentials are almost comparable to those of BEDT-TTF. The difference of the two potentials is apparently smaller than those of the corresponding unsymmetrical TTF donors,[2] indicating that on-site Coulomb repulsion is significantly decreased.

Electrochemical growth of charge-transfer salts with the inorganic acceptors PF_6, ClO_4, and I_3 has been accomplished using a constant current (1—2 μA) at room temperature with tetrahydrofuran–PhCl as the electrolytic solvent. Elemental analysis for the PF_6^- salts gave a 2:1 stoicheiometry, *i.e.* $(donor)_2PF_6$. Electrical conductivities were measured for single crystals by a standard four-probe, low-frequency A.C. technique at room temperature; the results are listed in Table 2. The salt $(\mathbf{1})_2PF_6$ exhibited the highest conductivity; conductivity for other salts ranged from semi-conductors to metals. Dimethyl(ethylenedithio)dithiadiselenafulvalene (**1**) is, in particular, of interest, as this is a hybrid of TMTSF and BEDT-TTF, both of which form super-conducting radical salts. Preliminary data obtained from a single crystal of $(\mathbf{1})_2PF_6$, however, showed semiconductor-type temperature dependence. However the ClO_4^- salt of (**1**) showed metallic behaviour near room temperature.

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