

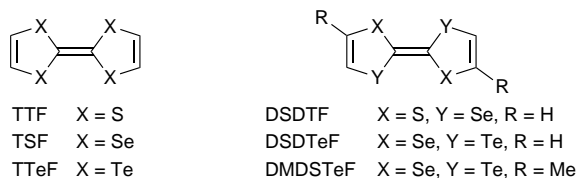
New hybrid tetrachalcogenofulvalenes: diselenaditellurafulvalene and its dimethyl derivative

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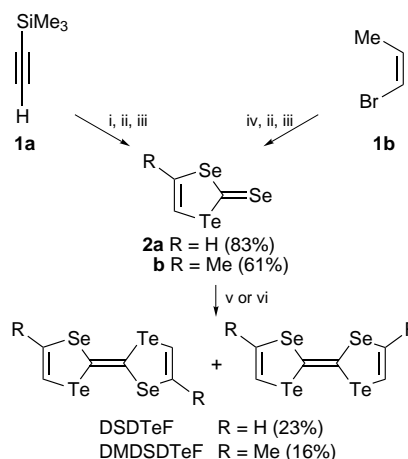
A simple two-stage synthesis of hybrid tetrachalcogenofulvalenes containing two tellurium and two selenium atoms and the properties of their highly conductive TCNQ complexes are described.

Since the discovery of the metallic conductivity of the TTF–TCNQ complex,¹ much effort has been devoted to the development of novel TTF-type electron donor molecules.² One of the successful structural modifications of TTF is to replace the skeletal sulfur atoms by selenium or tellurium atoms with large polarizabilities.³ Thus the TCNQ complexes of tetra-



selenafulvalene (TSF)⁴ and tetratellurafulvalene (TTeF)⁵ showed much higher conductivities (800 and 2200 S cm⁻¹, respectively) than TTF–TCNQ (500 S cm⁻¹). Of them, TTeF has attracted more attention, not only in that the complex has an extraordinarily high conductivity, but also in that it remains metallic down to a measurable low temperature (2 K). In contrast, the TTF–TCNQ and TSF–TCNQ complexes demonstrate a metal–insulator transition (Peierls transition) at 59 and 40 K, respectively, characteristic of a one-dimensional organic metal. In the TTeF–TCNQ complex, strong nonbonded tellurium–tellurium interactions are responsible for the suppression of the Peierls transition. Compared to TTF and TSF, a disadvantage of TTeF is its poor accessibility,⁶ and the fact that only a limited number of its derivatives have been prepared.⁷ Although a hybrid of TTF and TSF, diselenadithiafulvalene (DSDTF), has long been known,^{8,9} no analogous tellurium-hybrid tetrachalcogenofulvalenes have been studied. Such hybrid compounds are expected not only to offer additional examples of tellurium-containing conductive complexes, but also to provide useful information on the contribution of the tellurium atoms to the design of organic metals. Here we describe the simple two-stage synthesis and properties of diselenaditellurafulvalene (DSDTeF) and its dimethyl derivative (DMDSDTeF) as the first tellurium-hybrid tetrachalcogenofulvalenes.

All the preceding TTeF donors were synthesized by a three-component reaction of 1,2-ditelluroate anion and tetrachloroethene. On the other hand, DSDTeF was obtained by the simple two-stage route as shown in Scheme 1, previously used for the syntheses of TSF⁴ and DSDTF.⁹ The precursor, 1,3-selenatellurole-2-selone **2a** was readily obtained in 83% yield by metallation of commercially available trimethylsilylacetylene **1a** with 1 equiv. of BuLi in THF at –78 °C followed by successive *in situ* treatment with 1 equiv. tellurium powder at –78 °C and then with 1 equiv. carbon diselenide at –90 °C, and finally quenching with water.¹⁰ Subsequent triethyl phosphite-promoted homocoupling reaction of **2a** in refluxing toluene



Scheme 1 Reagent and conditions: i, BuLi (1 equiv.), Me₂NC₂H₄NMe₂, THF, –78 °C, 0.5 h; ii, Te powder (1 equiv.), –78 °C then room temp., 3 h; iii, CSe₂ (1 equiv.), –90 °C, 3 min., then H₂O–THF (1 : 1, v/v); iv, BuLi (2 equiv.), THF, –78 °C, 2 h; v, excess P(OEt)₃, toluene, reflux, 2 h (for DSDTeF); vi, excess P(OEt)₃, benzene, reflux, 10 h (for DMDSDTeF)

afforded DSDTeF in 23% yield.[†] Similarly, 5-methyl-1,3-selenatellurole-2-selone **2b** was prepared in 61% yield from lithium 1-propynide, *in situ* generated by dehydrobromination of 1-bromopropene **1b** with BuLi, and subjected to a similar homocoupling reaction, producing DMDSDTeF in 16% yield.

The ¹H NMR spectrum of DSDTeF contains two sets of AB multiplets in a ratio of 4 : 6, indicating that it consists of a mixture of the *cis*- and *trans*- (*E* and *Z*) isomers, as seen in the case of DSDTF.^{8,9} These geometrical isomers could not be separated by conventional purification methods. DMDSDTeF was also obtained as an isomeric mixture (3 : 7 ratio), but its recrystallization from benzene precipitated the pure main isomer. The cyclic voltammetry of DSDTeF showed two reversible one-electron oxidation waves at +0.43 and +0.73 V vs. Ag/AgCl; thus DSDTeF is a somewhat stronger electron donor than TSF (*E*_{1/2} +0.49 and +0.78 V). Furthermore, DMDSDTeF has slightly lower oxidation potentials, as expected from the substituent effect of the methyl groups (*E*_{1/2} +0.41 and +0.71 V).

Upon equimolar reaction of DSDTeF with TCNQ and TCNQF₂ in MeCN, crystalline 1 : 1 charge-transfer complexes were formed.[‡] The room temperature conductivity of the DSDTeF–TCNQ complex measured on a single needle crystal was very high (1400 ± 300 S cm⁻¹, 10 samples), as was that of the DSDTeF–TCNQF₂ complex (900 ± 200 S cm⁻¹, 5 samples). DMDSDTeF also formed a conductive 1 : 1 complex with TCNQ ($\sigma_{\text{rt}} = 37 \text{ S cm}^{-1}$ measured on a compressed pellet). The conductivity of DSDTeF–TCNQ is just in between those of TSF–TCNQ and TTeF–TCNQ. In addition, variable temperature measurements demonstrate that, as shown in Fig. 1, the conductivity steadily increases to 2.5 times this value as the temperature drops to 4 K, and there is no metal–insulator transition as seen for TTeF–TCNQ.⁵ These results clearly indicate that the two tellurium atoms of DSDTeF serve to

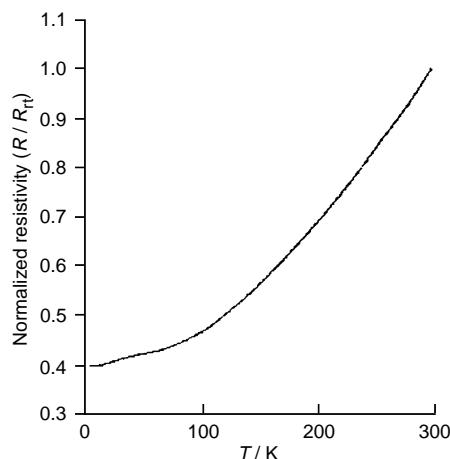


Fig. 1 Electrical resistance of 1-TCNQ

enhance intermolecular interactions enough not only to induce the high conduction of its charge-transfer complexes but also to suppress the Peierls transition. On considering their ready accessibility as compared to TTeF, the present tellurium-hybrid tetrachalcogenofulvalenes are electron donors of choice to study tellurium-containing organic metals.

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Footnotes and References

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† New compounds were characterized by elemental analysis and NMR and mass spectroscopy. *Selected data* for DSDTeF: black prisms from benzene, mp 139.0–140.0 °C; δ_{H} (CDCl₃, 400 MHz) (major isomer) 7.60 (d, *J* 8.23) and 8.15 (d, *J* 8.23); (minor isomer) 7.76 (d, *J* 8.23) and 8.08 (d, *J* 8.23); *m/z* 492 (M⁺) with an isotopic pattern containing two selenium and two tellurium atoms. Calc. for C₆H₄Se₂Te₂: C, 14.73; H, 0.82. Found: C, 14.96; H, 0.87%. For DMDSDeF: black crystals from benzene (major isomer); mp 189.0–190.0 °C (decomp.); δ_{H} (CDCl₃, 400 MHz) 2.23 (d, *J* 1.46, 6 H) and 7.50 (q, *J* 1.46, 2 H); *m/z* 520 (M⁺) with an isotopic pattern containing two selenium and two tellurium atoms. Calc. for C₈H₈Se₂Te₂: C, 18.58; H, 1.56. Found: C, 18.60; H, 1.47%. Minor isomer: δ_{H} (CDCl₃, 400 MHz) 2.22 (d, *J* 1.46, 6 H) and 7.44 (q, *J* 1.46, 2 H). For **2a**: black plate from chlorobenzene; mp 128 °C (decomp. without melting); δ_{H} (CDCl₃, 400 MHz) 8.27 (d, *J* 8.46) and 8.80 (d, *J* 8.46); ν_{max} (KBr)/cm⁻¹ 845 (C=Se); *m/z* 326 (M⁺) with an isotopic pattern containing two selenium and one

tellurium atoms. Calc. for C₃H₂Se₂Te: C, 11.14; H, 0.62. Found: C, 11.27; H, 0.60%. For **2b**: black prisms from chlorobenzene; mp 115.5–116.0 °C; δ_{H} (CDCl₃, 400 MHz) 2.53 (d, *J* 1.32, 3 H) and 8.23 (q, *J* 1.32, 1 H). ν_{max} (KBr)/cm⁻¹ 851 (C=Se); *m/z* 340 (M⁺) with an isotopic pattern containing two selenium and one tellurium atoms. Calc. for C₄H₄Se₂Te: C, 14.23; H, 1.19. Found: C, 14.22; H, 1.15%.

‡ The ratio of donor to acceptor was determined as 1 : 1 based on elemental analyses.

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