Synthesis and X-ray crystal structure of a vinylogue of tetramethyltetraselenafulvalene

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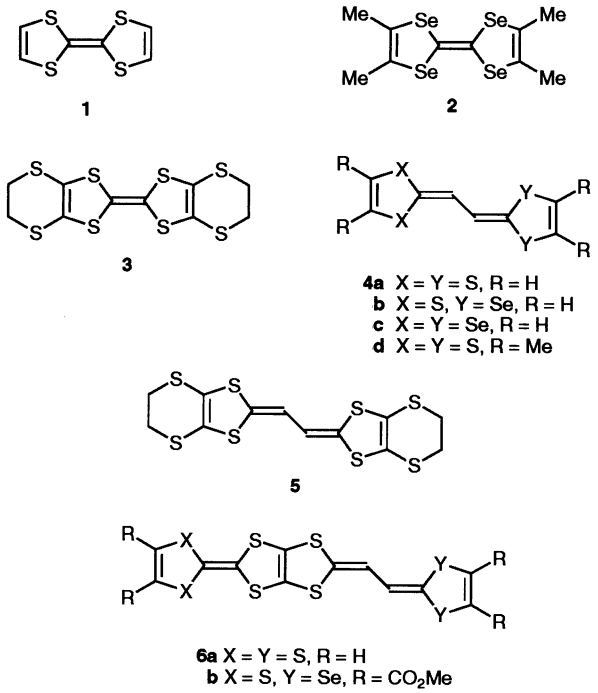
Efficient syntheses of 2,2′-ethanediylidenebis(4,5-dimethyl-2*H*-1,3-diselenole) **14** and the 1,3-dithiole analogue **16** are described. Cyclic voltammetry establishes that they are efficient π-electron donors. The molecular structures of **14** and **16** have been determined by single crystal X-ray analysis: the crystals are isomorphous and the molecules form planar layers parallel to the crystallographic (1 0 2) plane.

The study of molecular conductors[1] has progressed rapidly since the discovery that the charge-transfer complex of the π-electron donor tetrathiafulvalene (TTF) **1** and the π-electron acceptor tetracyano-*p*-quinodimethane (TCNQ) exhibited metallic conductivity.[2] Salts of the related π-donor molecule tetramethyltetraselenafulvalene (TMTSF) **2** provided the first family of organic superconductors[3] and the synthesis of new multi-chalcogen π-electron donors has remained at the forefront of research, with a few systems, notably bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) **3**, providing radical cation salts which are organic superconductors with T_c values as high as *ca.* 12 K.[4] The complex TTF–TCNQ, is considered to be a one-dimensional metal, whereas salts of TMTSF **2** and BEDT-TTF **3** are characterised by an increase in dimensionality of their transport properties, arising from close interstack chalcogen···chalcogen interactions. This effect is known to stabilise the metallic state by suppressing the Peierls distortion, which is a charge-density wave localisation inherent to one dimensional conducting systems.[5]

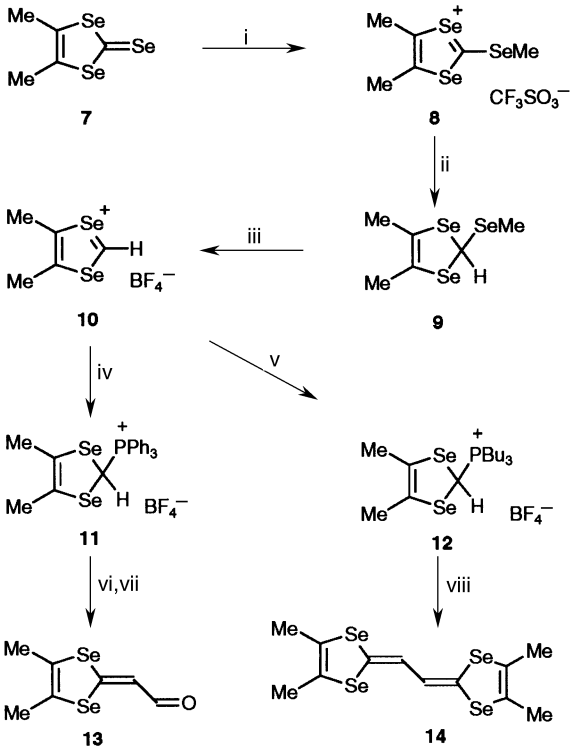


The incorporation of conjugated alkene linking groups between the two 1,3-dithiole rings of TTF has been widely explored as a structural modification to the π-donor unit.[6,7] The rationale behind the design of TTF derivatives with extended conjugation is twofold: (i) the oxidised states responsible for conduction in charge-transfer complexes and radical cation salts should be stabilised by decreased intramolecular Coulombic repulsion, and (ii) increased spacial extension of the π-framework should lead to increased dimensionality. There is now clear evidence from detailed solution electrochemical studies on several 2,2′-ethanediylidenebis(1,3-dithiole) derivatives, *e.g.* the parent system **4a**,[6a,b] that the second oxidation potential is significantly lower than that of TTF **1**. The vinylogue **5** of BEDT-TTF **3** was recently synthesised independently and concurrently by three research groups.[6c–e] Although, to date, donor **5** has not yielded any superconducting salts, a recent report that donor **6a**, which comprises a closely-related vinylogous TTF framework, affords a superconducting $Au(CN)_2$ salt[6h] has added a new impetus to studies on these systems, and a 1,3-diselenole analogue **6b** has been synthesised.[8] Here we describe the synthesis of compound **14**, which is the first reported vinylogue of TMTSF **2**, along with the X-ray crystal structure and solution electrochemical properties of this new π-electron donor. The synthesis, X-ray crystal structure and electrochemistry of the tetramethyldiselenadithiafulvalene analogue **16** are also reported for the first time.

Results and Discussion

Synthesis

The synthesis of **14** is presented in Scheme 1. The key step in assembling the vinylogous TMTSF skeleton is the Wittig reaction of aldehyde **13** with the phosphorus ylide derived from reagent **12**, for which the starting material was the known selone **7**.[9] Methylation of **7** using methyl trifluoromethanesulfonate yielded the 1,3-diselenolium cation salt **8** which, upon reduction with sodium cyanoborohydride, yielded the unstable selenoether **9**. Conversion of compound **9** into the 1,3-diselenolium cation **10** was achieved by treatment with tetrafluoroboric acid in diethyl ether. Salt **10** was isolated as a very hygroscopic,

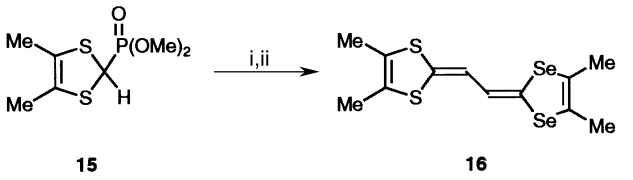


Scheme 1 *Reagents and conditions*: i, CF_3SO_3Me, CH_2Cl_2, 20 °C, 2 h; ii, $NaCNBH_3$, THF, 20 °C, 0.25 h; iii, HBF_4, Et_2O, 0 °C, 0.5 h; iv, PPh_3, MeCN, 20 °C, 12 h; v, PBu_3, MeCN, 20 °C, 0.5 h; vi, Et_3N, MeCN, 20 °C, 0.25 h; vii, glyoxal (aq), 20 °C, 3 h; viii, $KOBu^t$, MeCN, 20 °C, then immediately compound **13**, 20 °C, 0.66 h

unstable solid, which was used immediately in the next step. The overall yield for the three-step sequence **7**→**10** was typically 70–75%. Cation salt **10**, upon reaction with triphenylphosphine or tributylphosphine, yielded the unstable salts **11** and **12**, respectively: the former could be isolated as a pink solid, but the latter decomposed rapidly and could not be isolated. Therefore, compound **12** was used immediately after preparation. Deprotonation of **11** with triethylamine at 0 °C gave a transient ylide which was intercepted *in situ* with aqueous glyoxal to furnish the desired vinylogous aldehyde **13** (70% yield) as a pale yellow solid which could be conveniently stored under an inert atmosphere at 0 °C for up to four weeks. The ylide from triphenylphosphine reagent **11** was not sufficiently activated to react with the conjugated aldehyde group of **13**, so we used the more reactive tributylphosphine analogue **12**, drawing on our experience of 1,3-dithiole Wittig chemistry.[10] Thus, sequential addition of potassium *tert*-butoxide and aldehyde **13** to salt **12** yielded the target compound **14** as an air-stable, bright yellow crystalline solid in 70% yield. Similarly, the tetramethyldiselenadithiafulvalene analogue **16** was obtained (78% yield) by deprotonation of 1,3-dithiole reagent **15** using butyllithium, following the known procedure,[11] followed by addition of aldehyde **13** (Scheme 2).

X-Ray molecular structures of 14 and 16

The molecular structures of compounds **14** and **16** have been determined by single crystal X-ray analysis. Crystals of **14** and **16** are isomorphous. Both molecules (Fig. 1, Tables 1 and 2)



Scheme 2 *Reagents and conditions*: i, BuLi, THF, −78 °C, 0.25 h; ii, **13**, THF, −78→20 °C, 12 h

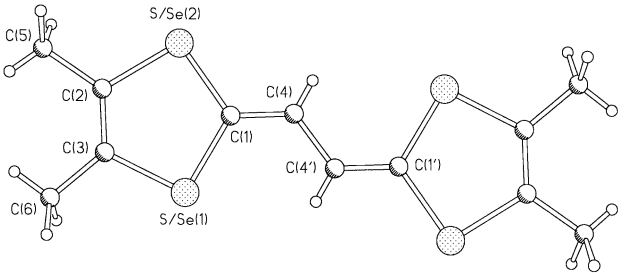


Fig. 1 Molecular structure of **16**; symmetrically related atoms are primed

Table 1 Bond lengths from the crystal structures of **14** and **16**

	bond lengths/Å	
	14(X = Se)	**16**(X = Se/S)
C(1)–X(1)	1.897(3)	1.847(3)
C(1)–X(2)	1.895(3)	1.848(3)
C(1)–C(4)	1.353(4)	1.348(5)
X(1)–C(3)	1.906(3)	1.865(3)
X(2)–C(2)	1.908(3)	1.870(3)
C(2)–C(3)	1.342(4)	1.344(5)
C(4)–C(4′)	1.437(5)	1.440(7)

Table 2 Crystal data for **14** and **16**

	16	**14**
formula	$C_{12}H_{14}S_2Se_2$	$C_{12}H_{14}Se_4$
M	380.3	474.1
a/Å	6.411(1)	6.483(1)
b/Å	6.837(1)	6.873(1)
c/Å	8.337(1)	8.378(1)
α(°)	70.35(1)	70.48(1)
β(°)	81.76(1)	81.67(1)
γ(°)	82.47(1)	82.44(1)
setting reflns	478	512
θ range(°)	10–30	10–30
V/Å^3	339.25(8)	346.75(8)
D_x/g cm^{-3}	1.86	2.27
μ(Mo-$K\alpha$)/cm^{-1}	57.3	105.5
crystal size/mm	0.4 × 0.1 × 0.06	0.4 × 0.22 × 0.14
min./max. transmission	0.338/0.736	0.077/0.325
data total	2833	3106
data unique	1808	1841
R_{int}[a]	0.080, 0.040	0.122, 0.033
data observed, $\|F\| > 4\sigma(F)$	1615	1694
$R(F$, obs. data)	0.039	0.028
$wR(F^2$, all data)	0.100	0.073
goodness-of-fit	1.23	1.15
$\Delta\rho$ max, min/e Å^{-3}	0.73, −0.67	0.45, −1.16

[a]Before and after the absorption correction.

possess a crystallographic inversion centre and adopt small chair-like distortions, the dithiole/diselenole rings folding by 7.8 (**14**) and 7.0° (**16**) along the S(Se)···S(Se) vectors. In **16** the C_i molecular symmetry is spurious, due to disorder, which makes the S and Se atoms indistinguishable. This observation has precedent in other mixed sulfur/selenium tetrachalcogenofulvalene derivatives.[12] The C(1)=C(4) and C(4)–C(4′) bond distances are similar to those in other planar systems of this kind[6d,f] and indicate a small degree of π-delocalisation (*ca.* 10%).[13]

Molecules in the crystals are arranged in planar layers parallel to the crystallographic (1 0 2) plane (Fig. 2). Molecules within a layer, related *via* the *b* translation, form intermolecular chalcogen···chalcogen contacts of 3.87 (in **14**) and 3.90 Å (in **16**). The latter (effectively, Se···S) distance is slightly longer than the sum of the van der Waals radii of selenium (2.0 Å)[13] and sulfur (1.8 Å),[14] while the former (Se···Se) contact is shorter than the double radius of selenium. It is noteworthy that the substitution of Se for S causes no appreciable expansion of the structure along the *y* axis [$b = 6.837(1)$ Å in **16** *vs.* 6.873(1) Å in **14**, while the difference between the S and Se radii should have contributed 0.2 Å per unit cell translation]. The effect can be attributed to the higher atomic polarisability of Se compared to S (3.77×10^{-24} and 2.90×10^{-24} cm^3, respectively[15]), which makes the electron shell of the former easier to deform to maximise the packing density elsewhere, but is also favourable for stronger intermolecular interactions. The interplanar separations between the layers are *ca.* 3.68 (**14**) and 3.64 Å (**16**), with only partial overlap between the molecules.

Solution electrochemistry

The solution redox properties of donors **14** and **16** have been studied by cyclic voltammetry and the results are collated in Table 3, along with selected model compounds for comparison. The new extended compounds are very efficient π-electron donors; they display the expected two reversible, one-electron redox couples. These data are entirely consistent with previous work with vinylogous TTF systems,[6] which has established

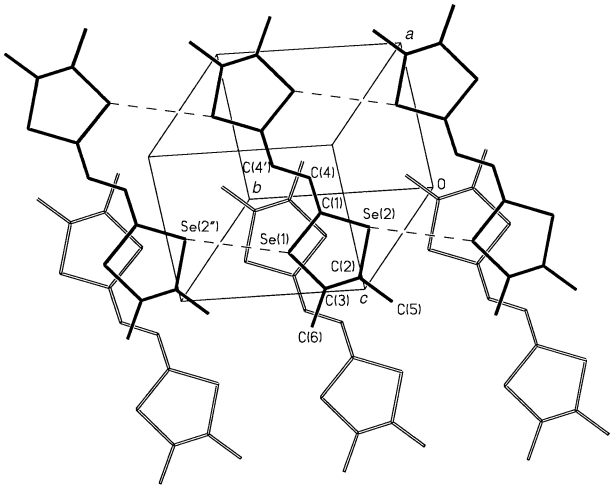


Fig. 2 Crystal packing of **14**, showing short intermolecular Se···Se contacts (<4 Å). Symmetrically related atoms are primed; H atoms are omitted.

Table 3 Cyclic voltammetric data for new vinylogous systems **14** and **16**, with selected compounds for comparison. Data are *versus* Ag/AgCl, unless otherwise stated

Compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V	ΔE/V
1 TTF	0.34	0.71	0.37
TSF[a,b]	0.48	0.76	0.28
4a[c]	0.20	0.36	0.16
4b[c]	0.26	0.40	0.14
4c[c]	0.32	0.47	0.14
TMTTF[a,c]	0.25	0.61	0.36
2 TMTSF[d]	0.44	0.72	0.28
4d[c]	0.19	0.34	0.15
16	0.29	0.44	0.15
14	0.36	0.50	0.14

[a]TSF = tetraselenafulvalene; TMTTF = tetramethyltetrathiafulvalene. [b]Ref. 16. [c]Ref. 6(*b*). [d]Ref. 17. Data taken from ref. 16, reported using Et_4NClO_4 in MeCN *versus* SCE.

the following general trends in the redox properties. With increasing conjugative length there is (i) a lowering of both redox potentials (especially $E_2^{1/2}$) due to the increased electron delocalisation and (ii) a smaller difference (ΔE) between $E_1^{1/2}$ and $E_2^{1/2}$ (tending to zero as the conjugation length increases), indicative of increased stabilisation of the dicationic state as a result of increased charge separation (and thus reduced on-site Coulombic repulsion). For the series **4d**,[6b] **16** and **14** it is noteworthy that the oxidation becomes harder by sequentially substituting selenium atoms for sulfur whilst ΔE is essentially unaffected by selenium replacement. These observations are attributable to a decrease in π-orbital interaction between the carbon framework and the heteroatom as a result of increasing heteroatom size.[16]

Conclusions

In summary, we have achieved the first synthesis of a vinylogue of TMTSF **2**, namely 2,2′-ethanediylidenebis(4,5-dimethyl-2*H*-1,3-diselenole) **14**. The 1,3-dithiole analogue **16** is also reported. These new compounds are very efficient π-electron donors, and X-ray structural analysis of **14** and **16** reveals that the molecules are arranged in planar layers. This combination of structural and electrochemical properties makes compounds **14** and **16** promising candidates for the formation of conducting or superconducting radical ion salts.

Experimental

General details

Details of equipment and procedures are the same as those reported recently.[18] Solvents and reagents employed were standard reagent grade and were used as received unless otherwise stated. All anhydrous solvents were obtained by standard techniques and acid-free CH_2Cl_2 was prepared by either washing with dilute sodium hydrogen carbonate or filtration through basic alumina, followed by distillation prior to use. Cyclic voltammetric experiments were performed using 10^{-5} M donor and 0.1 M Bu_4NClO_4 in dry MeCN under argon *versus* Ag/AgCl, Pt working and counter electrodes, 20 °C, recorded on a BAS 50 W electrochemical analyser.

4,5-Dimethyl-2-methylseleno-1,3-diselenolium trifluoromethanesulfonate 8

To a stirred solution of 4,5-dimethyl-2*H*-1,3-diselenole-2-selone **7**[9] (300 mg, 0.98 mmol) in dry CH_2Cl_2 (25 cm^3) was added methyl trifluoromethanesulfonate (0.14 cm^3, 1.22 mmol). The resultant mixture was stirred under an argon atmosphere for 2 h at 20 °C whereupon the volume of the mixture was reduced to *ca.* 5 cm^3 *in vacuo*. Addition of anhydrous diethyl ether precipited a solid, which was filtered, washed with diethyl ether and dried to give **8** (400 mg, 87%) as an unstable pale yellow solid, mp 120–121 °C (Calc. for $C_7H_9F_3O_3SSe_3$: C, 17.87; H, 1.91. Found: C, 19.19; H, 2.37%); δ_H ($CDCl_3$) 3.17 (3H, s), 2.67 (6H, s).

4,5-Dimethyl-2-methylseleno-2*H*-1,3-diselenole 9

To a solution of salt **8** (400 mg, 0.86 mmol) in anhydrous THF (30 cm^3) under argon at 20 °C was added sodium cyanoborohydride (1 M in THF, 1.07 mol, 1.07 cm^3) dropwise over 2 min. The yellow solution rapidly turned light orange and was maintained at 20 °C for 15 min. At this point, the THF was removed *in vacuo* and the residue taken up in a mixture of diethyl ether (50 cm^3) and water (50 cm^3). The aqueous phase was separated and washed with diethyl ether (2 × 50 cm^3), the organic layers were combined and dried ($MgSO_4$). Removal of the solvent *in vacuo* afforded compound **9** (257 mg, 93%) as a bright yellow solid (mp 61–63 °C) which was essentially pure by ^1H NMR spectroscopy. Correct elemental analysis could not be obtained due to the rapid decomposition of **9** during handling (with the liberation of methyl selenol) (Calc. for $C_6H_{10}Se_3$: C, 22.59; H, 3.16. Found: C, 24.15; H, 3.00%); *m/z* (DCI, ^{80}Se) 322 (M^+, 5%), 226 ($M^+ - MeSeH$, 100); δ_H($CDCl_3$) 5.9 (1H, s), 2.2 (3H, s), 1.95 (6H, s).

4,5-Dimethyl-1,3-diselenolium tetrafluoroborate 10

To an ice-cooled solution of **9** (240 mg, 0.75 mmol) in anhydrous diethyl ether (20 cm^3) was added dropwise over 5 min tetrafluoroboric acid (0.82 mmol, 0.14 cm^3 of a 54% complex in diethyl ether). After 0.5 h, the pink solid which had precipitated was rapidly filtered and washed with dry diethyl ether (50 cm^3) to afford **10** (217 mg, 89%) as an extremely hygroscopic, salmon-pink solid which was used directly in subsequent reactions.

(4,5-Dimethyl-2*H*-1,3-diselenol-2-yl)triphenylphosphonium tetrafluoroborate 11

Tetrafluoroborate salt **10** (250 mg, 0.77 mmol) was dissolved in dry MeCN (30 cm^3) under argon at 20 °C and treated with triphenylphosphine (220 mg, 0.85 mmol). The resultant solution was stirred under argon for 12 h, by which time the solution had turned deep red. The volume of the mixture was reduced *in vacuo* to *ca.* 2 cm^3 before ice-cold anhydrous diethyl ether (50 cm^3) was added. The resultant solution was stirred at room temperature for 15 min, whereupon an off-white solid precipitated. The diethyl ether was decanted off and the solid washed rapidly with ice-cold anhydrous diethyl ether (2 × 20 cm^3). The solid was dried under high vacuum to afford **11** (260 mg, 70%) as a hygroscopic pink solid, mp 46–50 °C; δ_H($CDCl_3$) 7.8–7.6 (15H, m), 6.85 (1H, d, *J* 4.7†), 2.0 (6H, s).

† *J* values given in Hz.

(4,5-Dimethyl-2*H*-1,3-diselenol-2-yl)tributylphosphonium

Tetrafluoroborate salt **10** (65 mg, 0.198 mmol) was dissolved in dry MeCN (20 cm^3) under argon at 20 °C and treated with freshly distilled tributylphosphine (0.07 cm^3, 0.26 mmol). The orange solution immediately decolorised and was left to stir for 0.5 h whereupon it was used directly in the preparation of **14**.

2-(4,5-Dimethyl-2*H*-1,3-diselenol-2-ylidene)ethanal 13

To a solution of reagent **11** (260 mg, 0.53 mmol) in MeCN (20 cm^3) was added triethylamine (0.11 cm^3, 0.8 mmol) and the mixture was stirred for 15 min at 20 °C, whereupon glyoxal (1.0 cm^3 of a 40% aqueous solution, excess) was added and the solution stirred at room temperature for 3 h. The mixture was diluted with water (50 cm^3), extracted with CH_2Cl_2 (2 × 50 cm^3), the organic portions were combined and dried ($MgSO_4$), and the solvent removed *in vacuo*. The residue was purified by column chromatography on neutral alumina, initially with CH_2Cl_2–hexane as eluent (1:2 v/v) followed by CH_2Cl_2, to afford **13** (100 mg, 70%) as a pale yellow solid, mp 65–67 °C; *m/z* (^{80}Se, DCI) 269 (MH^+, 100%) (HRMS: Calc. for $C_7H_8OSe_2$, 267.8906. Found, 267.9071); δ_H($CDCl_3$) 9.46 (1H, d, *J* 1.8), 7.20 (1H, d, *J* 1.8), 2.17 (3H, s), 2.13 (3H, s); δ_C ($CDCl_3$) 182.7, 161.5, 133.0, 126.5, 114.0, 15.7, 15.6; ν_{max}(KBr)/cm^{-1} 1605 (C=O).

2,2′-Ethanediylidenebis(4,5-dimethyl-2*H*-1,3-diselenole) 14

To a stirred solution of phosphonium salt **12** in anhydrous MeCN, as prepared above, at 20 °C was added potassium *tert*-butoxide (22 mg, 0.198 mmol) followed by the immediate addition of an MeCN solution of aldehyde **13** (58 mg, 0.216 mmol). The mixture turned deep orange on addition of the butoxide and then bright yellow with the formation of a white precipitate on addition of the aldehyde. The mixture was stirred for 40 min and then the solvent was evaporated *in vacuo* to afford a brown residue which was flushed through a column containing a short plug of neutral alumina using acid-free CH_2Cl_2–hexane mixture (1:1 v/v) as the eluent, to yield yellow crystals contaminated with a small amount of an unidentified orange oil. After washing this product with diethyl ether, compound **14** (80 mg, 85%) was isolated as bright yellow crystals, mp 244–245 °C (from CS_2) (Calc. for $C_{12}H_{14}Se_4$: C, 30.37; H, 2.95. Found: C, 30.22; H, 2.91%); *m/z* (^{80}Se, DCI) 477(M^+, 100%); δ_H($CDCl_3$) 5.95 (2H, s), 1.95 (12H, s); ν_{max}(KBr)/cm^{-1} 1647, 1519, 792; λ_{max}(MeCN)/nm (ε) 371 (1.9×10^4). A crystal of **14** suitable for X-ray analysis was grown by slow evaporation of a CS_2 solution.

2-[2-(4,5-Dimethyl-2*H*-1,3-diselenol-2-ylidene)ethylidene]-4,5-dimethyl-2*H*-1,3-dithiole 16

To a stirred solution of compound **15**[11] (35 mg, 0.15 mmol) in dry THF (20 cm^3) under argon at −78 °C was added BuLi (0.1 cm^3 of a 1.6 M solution in hexane, 0.16 mmol) and the solution stirred for 15 min. Compound **13** (35 mg, 0.13 mmol) in dry THF (5 cm^3) was then added and stirring continued at −78 °C for 1 h and the reaction mixture was allowed to reach 20 °C (*ca.* 15 h). The solvent was evaporated, water (10 cm^3) was added and the residue was extracted with CH_2Cl_2 (acid-free, 3 × 25 cm^3). The combined extracts were washed with

water ($2 \times 10\ cm^3$) and dried ($MgSO_4$), and the solvent was evaporated. Column chromatography of the residue on neutral alumina eluting with hexane–toluene (2:1 v/v) afforded compound **16** (39 mg, 78%) as a yellow solid, mp 242–243 °C (from CS_2) (Calc. for $C_{12}H_{14}S_2Se_2$: C, 37.90; H, 3.71. Found: C, 38.13 H, 3.98%); *m/z* (^{80}Se, DCI) 382 (M^+, 100%); $\delta_H[CS_2–(CD_3)_2CO]$ 6.12 (1H, d, *J* 10.5), 5.55 (1H, d, *J* 10.5), 1.95 (3H, s), 1.94 (3H, s), 1.90 (3H, s), 1.89 (3H, s); ν_{max}(KBr)/cm^{-1} 1630, 1501; λ_{max}(MeCN)/nm (ε) 393 (1.8×10^4). A crystal suitable for X-ray analysis was grown by slow evaporation of a CS_2–hexane solution.

X-Ray crystallography

Single-crystal diffraction experiments were carried out at $T=$ 150 K on a Siemens 3-circle diffractometer with a CCD area detector, using graphite monochromated Mo-Kα radiation ($\lambda=0.71073$ Å). The yellow plate-like crystals of **14** and **16** were isomorphous, in triclinic space group $P\bar{1}$ (No. 2), $Z=1$. A hemisphere of data with $2\theta \leq 61°$ were collected in an ω scan mode (0.3° steps) and corrected for absorption using the Gaussian integration technique for the real crystal shape (8 and 6 faces indexed, respectively). The structures were solved by direct methods and refined by full-matrix least-squares (non-H atoms with anisotropic displacement parameters; the disordered Se/S atoms in **16** were refined at common sites with 0.5/0.5 occupancies; all H atoms refined in isotropic approximation; 101 variables) against F^2 of all data, using SHELXTL software.[19] Crystal data and experimental details are listed in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 11451/24.

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