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New unsymmetrical donor dimethyl(ethylenedioxy)tetraselenafulvalene (DMEDO-TSeF): structures and properties of its cation radical salts

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Synthesis

Dimethyl(ethylenedioxy)tetraselenafulvalene (DMEDO-TSeF)

To a mixture of selone **1** (226 mg, 0.68 mmol) and selone **2** (215 mg, 0.71 mmol) in benzene (90 ml) was added hexamethylphosphorous triamide (HMPT 0.74 ml, 4.08 mmol), and the solution was stirred for 2 hours under argon atmosphere. After the removal of the solvent under reduced pressure, the crude products were separated by column chromatography (SiO_2/CS_2–CH_2Cl_2) and then purified by preparative gel permeation chromatography (GPC/CS_2). The target DMEDO-TSeF was isolated as purple red needles (31 mg, 0.065 mmol, 10%) together with the self-coupling products TMTSF (12.5 mg, 0.028 mmol, 8%) and BEDO-TSeF (18.7 mg, 0.0368 mmol, 11%).

DMEDO-TSeF: mp 199 °C (decomp.); *m/z* (EI, 70 eV): 480 (M^+ for $C_{10}H_{10}O_2{}^{78}Se^{80}Se_3$); δ_H (270 MHz, CD_2Cl_2) 4.27 (4H, s, OCH_2CH_2O), 2.00 (6H, s, CH_3); IR (neat, ν/cm^{-1}) 1624 (s), 1443 (m), 1368 (m), 1268 (m), 1240 (w), 1134 (s); Elemental analysis: Calc. for $C_{10}H_{10}O_2Se_4$: C, 25.13; H, 2.11. Found: C, 25.14; H, 2.11%.

X-ray crystal structure analysis for neutral DMEDO-TSeF

CCDC reference number is 281659

Table 1. Crystal data and structure refinement for DMEDO-TSeF.

Empirical formula	$C_{10}H_{10}O_2Se_4$	
Formula weight	478.02	
Temperature	293 K	
Wavelength	0.71073 Å	
Crystal system	*Monoclinic*	
Space group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 13.958(4) Å	α = 90°.
	b = 8.285(2) Å	β = 109.478(6)°.
	c = 11.867(3) Å	γ = 90°.
Volume	1293.8(6) Å^3	
Z	4	
Density (calculated)	2.454 Mg/m^3	
Absorption coefficient	11.323 mm^{-1}	
F(000)	888	
Crystal size	0.50 × 0.06 × 0.05 mm^3	
Theta range for data collection	1.55 to 28.48°.	
Index ranges	−16<=h<=18, −9<=k<=11, −15<=l<=15	
Reflections collected	9395	
Independent reflections	3223 (R_{int} = 0.0571)	
Completeness to theta = 28.48°	98.9 %	
Absorption correction	Empirical (SADABS; Sheldrick 1996)	
Max. and min. transmission	0.6013 and 0.0703	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3223 / 0 / 147	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2σ(I)]	R_1 = 0.0501, wR_2 = 0.1262	
R indices (all data)	R_1 = 0.0790, wR_2 = 0.1405	
Largest diff. peak and hole	0.718 and −0.792 e Å^{-3}	

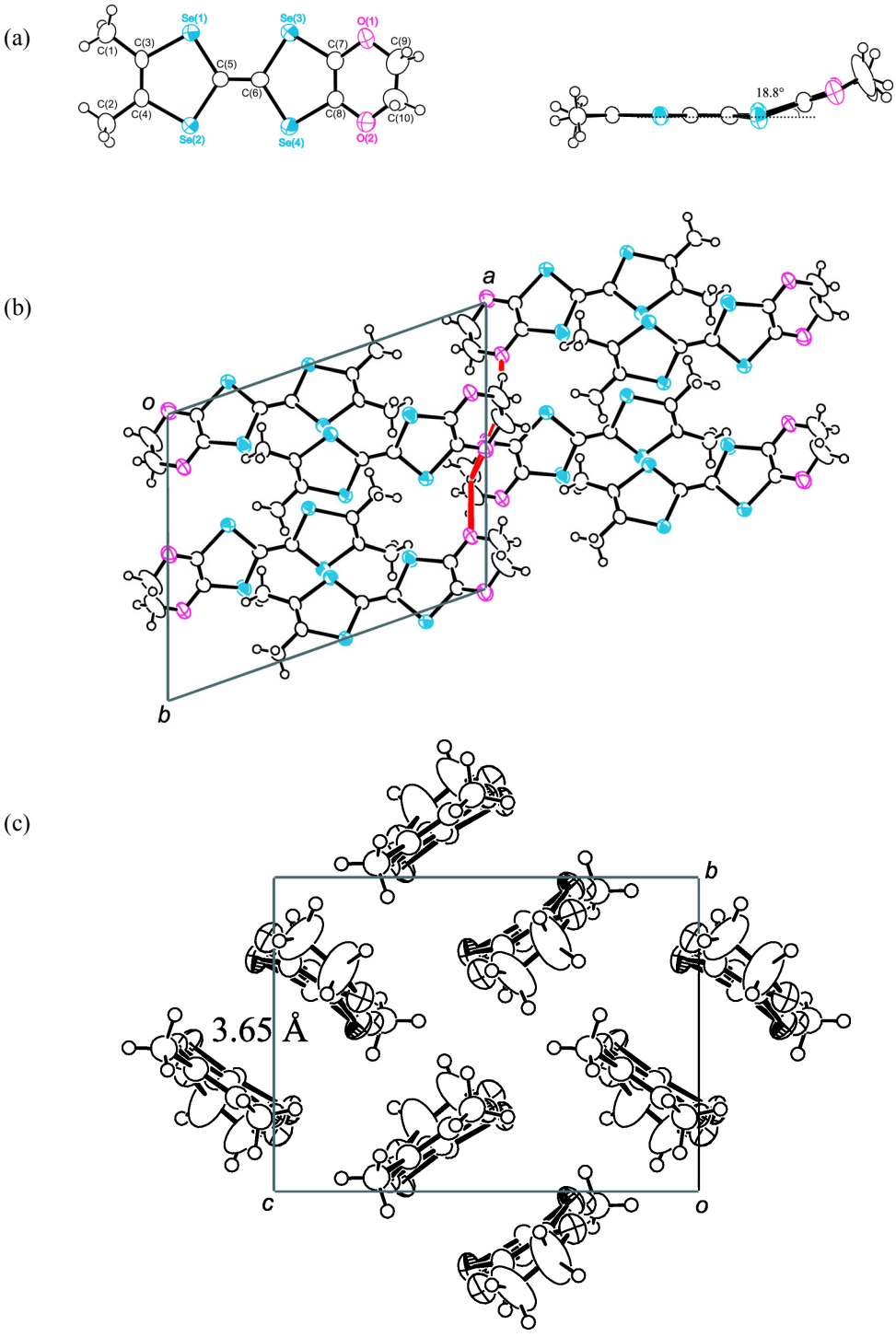

Fig. 1 Crystal structure of DMEDO-TSeF: (a) molecular structures; (b) crystal packing diagram viewed along the crystallographic *c*-axis, the orange line indicate short CH···O contacts shorter than 3.0 Å; (c) κ-type layer structure viewed along the crystallographic *a*-axis.

Band calculation

Intermolecular overlap integrals were calculated using HOMOs of the donor molecules obtained by the extended Hückel MO calculations using semiempirical parameters for the *s* and *p* Slater-type atomic orbitals listed in Table 3. The transfer integral (t) is approximately in proportion to the overlap integral (S), $t = \varepsilon S$ (ε = –10 eV; ε is a constant with order of the orbital energies of HOMOs). The electronic band dispersions and Fermi surfaces were calculated using the intermolecular overlap integrals under the tight-binding approximation.[1]

[1] T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 627; M.-H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, H. H. Wang, K. D. Carlson and G. W. Crabtree, *J. Am. Chem. Soc.*, 1985, **107**, 5815.

Table 2 Calculated overlap integrals S ($\times 10^{-3}$) for $(DMEDO\text{-}TSeF)_2X$ (X = PF_6, AsF_6 and SbF_6)

	PF_6	AsF_6	SbF_6
p	–26.49	–21.28	–20.82
q	–27.06	–22.50	–22.03
r	–0.28	–1.71	–0.84
s	–2.22	0.51	3.81
t	–0.68	0.26	1.69

Table 3 Semi-empirical parameters for Slater-type orbitals

orbitals	ζ	I_P / Ry
Se 4s	2.44	–1.40
Se 4p	2.07	–0.74
O 2s	2.275	–2.375
O 2p	2.275	–1.088
C 2s	1.625	–1.573
C 2p	1.625	–0.838
H 1s	1.30	–1.0

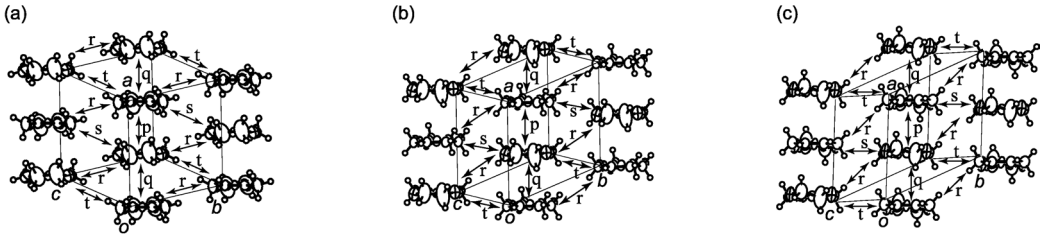

Fig. 2 Donor arrangement of $(DMEDO\text{-}TSeF)_2X$; (a) X = PF_6, (b) X = AsF_6 and (c) X = SbF_6.

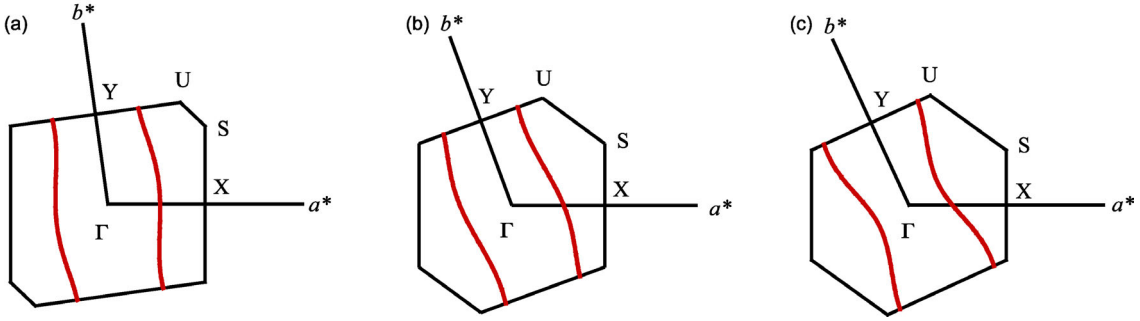

Fig. 3 Calculated Fermi surfaces of $(DMEDO\text{-}TSeF)_2X$; (a) X = PF_6, (b) X = AsF_6 and (c) X = SbF_6.