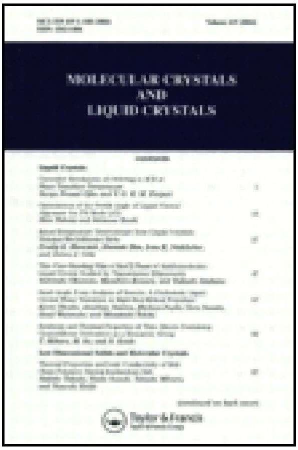

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Development of Organic Metals Based on the Extended TTF Donors by the [sgrave]-Bond Framework

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Development of Organic Metals Based on the Extended TTF Donors by the σ-Bond Framework

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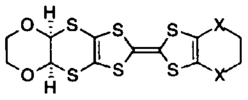
Investigations of the tetrathiafulvalene (TTF) derivatives extended by the σ-bond frameworks, such as saturated heterocycles (**3**–**8**) and alkyl groups (**9**), have been undertaken to explore new molecular-based organic metals. TTF donors with the periphery extended by the cis-fused dioxane ring (**3**) and by linkage of a dichalocogenolane or dioxane ring (**4**–**6** or **7**) produce metallic radical-cation salts. While radical-cation salts of the methylated TTF donor (**9a**) are semiconductive, the ClO_4 and PF_6 salts of the ethylated one (**9b**) exhibit metallic conducting behavior for compressed pellets. The crystal structure of the metallic $(\mathbf{4})_2AsF_6$ salt is also presented.

Keywords: organic metals; TTF derivatives; σ-bond framework; X-ray analyses; electrical conducting behavior

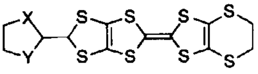
INTRODUCTION

Tetrathiafulvalene (TTF) derivatives serve as important π-electron donors for developing molecular-based organic metals and superconductors,[1,2] and a variety of studies on the modification of the TTF skeleton have been made.[3] One major trend in these studies has been directed toward the construction of the extended TTF-type donors by π-conjugation, whereas our own interest in this field has involved the use of TTF derivatives with the periphery extended by the σ-bond framework containing heteroatoms as donor components to develop new organic metals.[4] For example, we found that DOET[5] (**1**) and its selenium analogue DOES (**2**), in each of which a cis-fused heterobicyclic system is condensed on one side of the TTF core, produce metallic radical-cation salts, including β-$(DOET)_2BF_4$ and β-$(DOES)_2(AuI_2)_{0.75}$.[6] In the course of our study on these bulky TTF donors, we also discovered a metallic

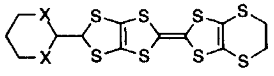
TCNQ (tetracyanoquinodimethane) complex of DO-MET (**4**), which seems still bulkier than DOET and DOES since the dioxolane ring is attached perpendicularly to the MET molecule.[7] These results prompted us to be engaged in further development of organic metals derived from TTF donors extended by the σ-bond frameworks such as saturated heterocycles and alkyl groups, because, if such donors could yield metallic charge-transfer (CT) materials, further extension of the molecular design for donor components providing organic metals, as well as the novel suggestions for the donor packing mode in the metallic CT materials, would be possible. In this paper, we summarize recent studies concerning 1) the oxygen analogue of DOET, DOEO (**3**), 2) DO-MET and related donors, DT-MET (**5**) and OT-MET (**6**), 3) the dichalcogenane-appended MET derivatives, DOA-MET (**7**) and DTA-MET (**8**), and 4) the alkylated MET derivatives (**9**).



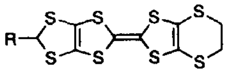
DOET (**1**: X = S)
DOES (**2**: X = Se)
DOEO (**3**: X = O)



DO-MET (**4**: X = Y = O)
DT-MET (**5**: X = Y = S)
OT-MET (**6**: X = O, Y = S)



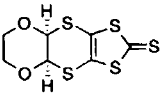
DOA-MET (**7**: X = Y = O)
DTA-MET (**8**: X = Y = S)



Me-MET (9a: R = CH_3)
Et-MET (9b: R = C_2H_5)
nBu-MEt (9c: R = n-C_4H_9)
nOct-MET (9d: R = n-C_8H_{17})

STUDIES ON DOEO

Synthesis of DOEO (**3**) was carried out by the cross-coupling reaction between two thiones **10**[8] and **11**[9] (2 equiv.) in neat $(MeO)_3P$ at 90 °C for 2 h (16% yield).



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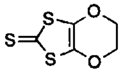

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The cyclic voltammogram (CV) of DOEO showed two reversible redox waves. For comparison with DOET (**1**) and DOES (**2**), the oxidation potentials for these donors were measured under identical conditions and in the same equipment (Table 1). The E_1 value of DOEO is lower than those of DOET and DOES, indicating an enhancement of the electron-donating ability, whereas its ΔE (E_2-E_1) value is almost equal to that of DOET, suggesting an on-site Coulombic repulsion of the same magnitude in the two donors.

TABLE 1 Oxidation potentials of DOEO (**3**), DOET (**1**), and DOES (**2**).[a]

Compound	E_1	E_2	ΔE (E_2-E_1)
DOEO (**3**)	0.50	0.81	0.31
DOET (**1**)	0.58	0.88	0.30
DOES (**2**)	0.54	0.90	0.36

[a] V vs. saturated calomel electrode (SCE); 0.1 M *n*-Bu_4NClO_4 in PhCN; Pt electrode; at room temperature; under nitrogen; scan rate 50 mV s^{-1}.

Preparation of the DOEO salts with various counter anions was examined by electrochemical oxidation with a controlled current[10] or a constant current (1 μA) in 1,1,2-trichloroethane (TCE) or PhCl containing the corresponding tetra-*n*-butylammoniun salts. The resulting DOEO salts had electrical conductivities of the order of 10^{-7}–10^2 S cm^{-1} (Table 2). Among them, the salts with $Au(CN)_2^-$, BF_4^-, and PF_6^- anions showed high conductivities (10^1–10^2 S cm^{-1}), and essentially remained metallic down to low temperatures. Particularly, the $Au(CN)_2$ and PF_6 salts exhibited no MI (metal-to-insulator) transition down to 2 K, in contrast to our reported metallic DOET and DOES salts which undergo MI transitions.

TABLE 2 Conducting behavior of the DOEO (**3**) salts.

Anion	**3**:A[a]	Solvent	σ_{rt} / S cm^{-1} [b]
I_3^- [c]	1:1	TCE	4.5×10^{-7} (E_a = 230 meV)
AuI_2^- [c]	1:1	TCE	8.6×10^{-5} (E_a = 130 meV)
$Au(CN)_2^-$ [d]	–[e]	PhCl	227 (metallic ≥ 2 K)
BF_4^- [c]	2:1[f]	TCE	27 (metallic ≥ 13 K)
ClO_4^- [c]	1:1	TCE	4.5×10^{-5} (E_a = 300 meV)
PF_6^- [d]	2:1	PhCl	173 (metallic ≥ 2 K)

[a] Determined by elemental analysis unless otherwise noted. [b] Room temperature conductivity measured on a single crystal by a four-probe technique. [c] Prepared by electrocrystallization with a controlled current. [d] Prepared by electrocrystallization with a constant current [e] Not determined due to insufficient amount of sample for elemental analysis. [f] Determined by X-ray analysis.

STUDIES ON DO-MET, DT-MET, AND OT-MET

We have established a practically valuable route to DO-MET (**4**), DT-MET (**5**) and OT-MET (**6**),[11] and also, revealed the molecular structures of DO-MET[7,8b] and DT-MET,[11] and their redox behavior together with that of OT-MET; the values of its oxidation potentials are very similar to those of DT-MET rather than those of DO-

MET.[11] In this section, we describe the molecular structure of OT-MET, the electrical conducting behavior of the CT materials based on DO-MET, DT-MET, and OT-MET, and the crystal structure of the metallic $(DO\text{-}MET)_2AsF_6$ salt.

The molecular structure of OT-MET was determined by X-ray diffraction analysis to compare with the conformations of DO-MET and DT-MET. The OT-MET molecule crystallized as a just 1:1 racemic mixture in the monoclinic space group $P2_1/a$,[12] and is isostructural with the DT-MET molecule (Figure 1).

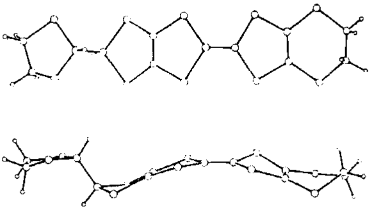


FIGURE 1 Top and side views of the molecular structure of OT-MET (**6**).

TABLE 3 Conducting behavior of CT materials based on DO-MET (**4**), DT-MET (**5**), and OT-MET (**6**).

Donor	Acceptor	D:A[a]	Solvent	σ_{rt} / S cm^{-1b}
DO-MET (**4**)	I_3	1:1	TCE	1.9×10^{-1c} (E_a = 170 meV)
	AuI_2	1:1	TCE	5.0×10^{-2d} (E_a = 77 meV)
	BF_4	5:2	TCE	22^d (metallic ≥ 3 K)
	ClO_4	–[e]	TCE	20^d (E_a = 16 meV)
	PF_6	5:2	5% EtOH-TCE	7.3^d (E_a = 6 meV)
	AsF_6	2:1[f]	PhCl	9.4^d (metallic ≥ 2 K)
DT-MET (**5**)	PF_6	3:2	TCE	1.5^d (metallic ≥ 55 K)
OT-MET (**6**)	TCNQ	–[g]	TCE	1.2×10^{-1d} (E_a = 50 meV)
	I_3	7:3	TCE	8.2^c (E_a = 8 meV)
	AuI_2	1:1	TCE	3.1^c (E_a = 25 meV)
	BF_4	2:1	TCE	7.5^c (metallic ≥ 100 K)
	ClO_4	–[e]	TCE	1.6^c (E_a = 37 meV)
	PF_6	5:2	TCE	1.8×10^{-1c} (E_a = 32 meV)
	AsF_6	3:1	TCE	9.1×10^{-2c} (E_a = 66 meV)

[a] Determined by elemental analysis unless otherwise noted. [b] Room temperature conductivity measured by a four-probe technique. [c] Measured on a compressed pellet. [d] Measured on a single crystal. [e] Not determined because this complex may explode during analysis. [f] Determined by X-ray diffraction analysis. [g] Not determined due to insufficient amount of sample for elemental analysis.

Small amounts of the TCNQ complex with OT-MET were obtained by heating with TCNQ (1 equiv.) in TCE at 80 °C, and no crystalline complex was formed by stirring at room temperature overnight; the same can be found in the preparation of the

TCNQ complex with DT-MET.[11] Preparation of the DO-MET, DT-MET, and OT-MET salts was carried out by the controlled-current electrocrystallization method[10] in TCE, 5% EtOH-TCE, or PhCl. The conducting behavior of the resultant TCNQ complex and radical-cation salts are summarized in Table 3. OT-MET produced a semiconductive TCNQ complex, whose room temperature conductivity is much higher than that of the TCNQ complex composed of the isostructural DT-MET ($\sigma_{rt} < 10^{-7}$ S cm^{-1} for a single crystal).[11] Among the DO-MET salts, while the salts with I_3^-, AuI_2^-, ClO_4^-, and PF_6^- were semiconductors, the BF_4 and AsF_6 salts retained the metallic state down to very low temperatures. In addition to the metallic DT-MET salts with AuI_2^-, BF_4^-, and AsF_6^- anions so far obtained,[11] the salt with PF_6^- also exhibited metallic conducting behavior with an MI transition. Although compressed pellets of the I_3, AuI_2, ClO_4, PF_6 and AsF_6 salts of OT-MET were semiconductive, the activation energy of the I_3 salt was very small (8 meV), suggesting that it can be expected to disclose metallic conducting behavior in the single crystalline state. Further, the resistivity of the OT-MET salt with BF_4^- showed metallic temperature dependence down to near 100 K despite the fact that the measurement was taken on a compressed pellet.

From among the single crystals of metallic radical-cation salts listed in Table 3, the crystal structure of $(DO\text{-}MET)_2AsF_6$ was determined by X-ray diffraction.[13] Surprisingly, in spite of the existence of the perpendicularly attached dioxolane ring, the DO-MET molecules are stacked head-to-head to form columns (Figure 2), in sharp contrast with the radical-cations of unsymmetrical TTF donors which ordinarily stack head-to-tail.[14] In $(DO\text{-}MET)_2AsF_6$, there are many intermolecular S···S contacts shorter than the van der Waals distance (3.70 Å) between stacks, and further, one shorter S···S contact can be observed within a stack (Figure 3), which is responsible for metallic behavior of this salt down to low temperatures.

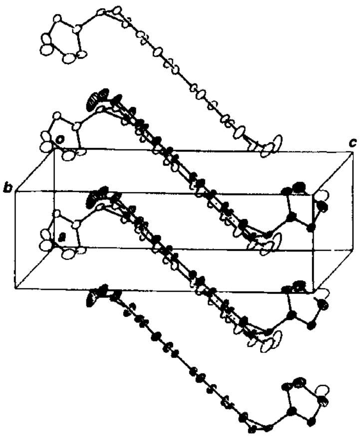


FIGURE 2. Donor arrangement of $(DO\text{-}MET)_2AsF_6$.

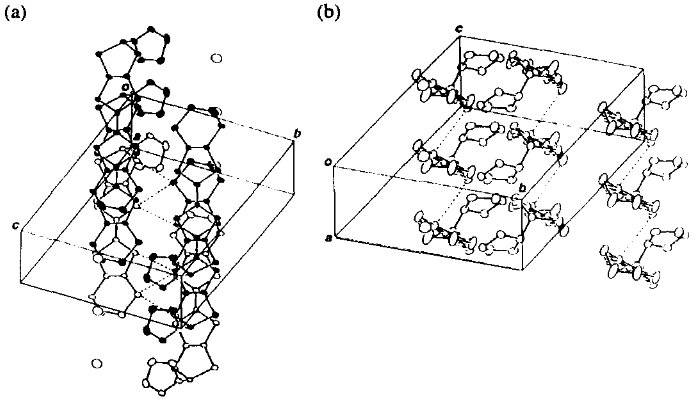
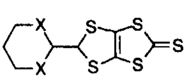


FIGURE 3 Crystal structure of $(DO\text{-}MET)_2AsF_6$: (a) interstack shorter S···S contacts (< 3.70 Å) and (b) an intrastack shorter S···S (< 3.70 Å) contact shown by the dotted lines.

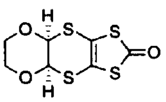
STUDIES ON DOA-MET AND DTA-MET

The results from the above studies indicate that the extension of TTF donors by linkage of saturated heterocycles through the σ-bond is recognized as a novel molecular design for π-electron donors leading to organic metals. Thus, our next attention has been focused on the development of organic metals derived from TTF donors with a bulkier appendant than a dichalcogenolane ring, and to this end, we first chose to begin studies on the dichalcogenane-added MET derivatives, DOA-MET (**7**) and DTA-MET (**8**).

Ketone **12a**, prepared from ketone **13** and 1,3-propanediol (2.4 equiv.) with the aid of $BF_3 \cdot OEt_2$ (10 equiv.) in 59% yield, reacted with thione **14** (2 equiv.) in $(MeO)_3P$/toluene at 110 °C for 2 h to give DOA-MET in 89% yield. Similarly, the $(MeO)_3P$-promoted cross-coupling of ketone **12b**[15] with **14** (2 equiv.) furnished DTA-MET in 81% yield.



12a: X = O
12b: x = S



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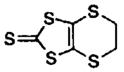

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The CV of DOA-MET, measured under the same conditions as noted in the footnote given to Table 1, showed two reversible oxidation waves, whose values are 0.58 (E_1) and 0.85 (E_2) V, respectively. On the other hand, the CV of DTA-MET consisted of three reversible oxidation waves, in which the E_1 and E_2 values are exactly equal to those of DOA-MET and the E_3 value is 1.65 V.

An X-ray analysis of DOA-MET was undertaken to reveal the effect of the dioxane ring appended to MET on the conformation.[16] The dioxane ring of DOA-MET has the zigzag conformation, and the whole molecular structure of DOA-MET is considerably planar in comparison with that of its dioxolane analogue, DO-MET (**4**).

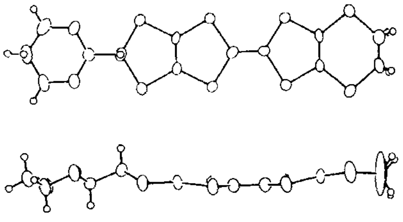


FIGURE 4. Top and side views of the molecular structure of DOA-MET (**6**).

TABLE 4 Conducting behavior of the DOA-MET (**7**) and DTA-MET (**8**) salts.

Donor	Anion	D:A[a]	σ_{rt} / S cm^{-1}[b]
DOA-MET (**7**)	I_3^-	3:1	1.3×10^{-1}[c] (E_a = 16 meV)
	AuI_2^-	–[d]	6.5[c] (metallic ≥ 180 K)
	BF_4^-	2:1	2.2[e] (E_a = 160 meV)
	ClO_4^-	–[f]	4.9×10^{-1}[e] (E_a = 310 meV)
	AsF_6^-	2:1	2.6[c] (E_a = 100 meV)
DTA-MET (**8**)	I_3^-	2:1	2.5[c] (E_a = 34 meV)
	AuI_2^-	2:1	2.5×10^{-3}[c] (E_a = 66 meV)
	BF_4^-	3:2	8.2×10^{-2}[c] (E_a = 54 meV)
	ClO_4^-	–[f]	6.5×10^{-3}[c] (E_a = 72 meV)
	PF_6^-	2:1	8.3×10^{-1}[c] (E_a = 54 meV)
	AsF_6^-	2:1	2.3×10^{-2}[c] (E_a = 42 meV)

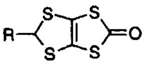
[a] Determined by elemental analysis. [b] Room temperature conductivity measured by a four-probe technique. [c] Measured on a single crystal. [d] Not determined due to insufficient amount of sample for elemental analysis. [e] Measured on a compressed pellet. [f] Not determined because this complex may explode during analysis.

The DOA-MET and DTA-MET salts were obtainable by the controlled-current electrocrystallization method[10] in TCE, and their conducting behavior are summarized in Table 4. In a series of the DOA-MET salts, only the resistivity of the AuI_2 salt exhibited weak metallic behavior with decreasing temperatures to near 180 K, after which a gradual change to semiconductive behavior was observed. On the other hand, all the obtained DTA-MET salts showed semiconductive behavior with activation energies ranging from 34 meV to 72 meV for single crystals.

STUDIES ON THE ALKYLATED MET DERIVATIVES

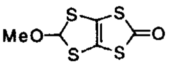
Thus far we have investigated only the utilization of saturated heterocycles as the σ-bond framework for extending the outer hemisphere of the TTF core, and have not yet made a study of the TTF derivatives attaching a simple alkyl group, such as a methyl, ethyl, *n*-butyl, or *n*-octyl group. Finally, we describe the synthesis and redox properties of the alkylated MET derivatives (**9a–d**), and the conducting behavior of the Me-MET (**9a**) and Et-MET (**9b**) salts.[17]

Considering the molecular symmetry to avoid chirality problems, the achiral 4,5-(alkylmethylenedithio)-1,3-dithiole-2-ones (**15**) are a good source of the mono-alkylated TTF donors, but a practically systematic preparation of **15** has not been realized.[18] Therefore, our first study was to develop an expedient method for preparation of **15a–d**. Reaction of ketone **16**, obtained by basic cleavage of thiapentalenedione **17** with NaOMe (2 equiv.) followed by treatment with dichloromethyl methyl ether (2 equiv.) in 53% yield, with Me_3Al (1.2 equiv.) and Et_3Al (2 equiv.) gave the methylated and ethylated products **15a,b** in 63% and 56% yields, respectively. For introduction of the *n*-butyl and *n*-octyl groups into **16**, we used the reaction of **16** with the readily preparable *n*-$BuMgCl/TiCl_4$ (2 equiv.) and *n*-$C_8H_{17}MgBr/TiCl_4$ (2 equiv.) complex reagents, and **15c,d** were obtained in 34% and 38% yields, respectively.



15 (R = alkyl)

a: R = Me
b: R = Et
c: R = *n*-C_4H_9
d: R = *n*-C_8H_{17}



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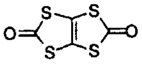

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TABLE 5 Oxidation potentials of MET and the alkylated MET derivatives **9a–d**.[a]

Compound	E_1	E_2	E_3	$\Delta E\,(E_2\text{-}E_1)$
MET	0.58	0.85	1.54	0.27
9a	0.59	0.85	1.61	0.26
9b	0.59	0.85	1.70	0.26
9c	0.58	0.84	1.72	0.26
9d	0.59	0.85	1.71	0.26

[a] For the measurement conditions, see the footnote in Table 1.

The $(MeO)_3P$-promoted coupling of the resulting ketones **15a–d** with thione **14** (2 equiv.) in toluene at 110 °C for 2 h furnished the alkylated MET derivatives **9a–d** in the following yields: **9a**, 66%; **9b**, 59%; **9c**, 40%; **9d**, 43%. Table 5 shows their oxidation potentials measured by cyclic voltammetry together with those of MET. Compounds **9a–d** showed three pairs of reversible redox wave, and their values of E_1 and E_2 are all comparable to those of MET independent of the type of alkyl group.

The conducting behavior of the Me-MET and Et-MET salts, prepared by the controlled-current method[10] in TCE, are listed in Table 6. A compressed pellet of the Me-MET salt with I_3^- exhibited an almost constant resistivity near room temperature and semiconductive behavior with further decreases in temperature, whereas single crystals of the AuI_2, BF_4, ClO_4, PF_6, and AsF_6 salts are semiconductors. Although no single crystal of the Et-MET salts was obtained, the salts with ClO_4^- and PF_6^- anions exhibited metallic conducting behavior with MI transitions for compressed pellets.

TABLE 6 Conducting behavior of the Me-MET (**9a**) and Et-MET (**9b**) salts.

Donor	Anion	D:A^a	σ_{rt} / S cm^{-1b}
Me-MET (**9a**)	I_3^-	5:3	5.1^c [E_a = 5 meV (250–290 K)]^d
	AuI_2^-	5:2	8.4×10^{-3e} (E_a = 230 meV)
	BF_4^-	3:2	5.5×10^{-4e} (E_a = 190 meV)
	ClO_4	–^{f}	4.2×10^{-3e} (E_a = 180 meV)
	PF_6	5:2	1.4×10^{-1e} (E_a = 120 meV)
	AsF_6	5:2	3.6×10^{-1e} (E_a = 110 meV))
Et-MET (**9b**)	I_3	1:1	1.3×10^{-3c} (E_a = 300 meV)
	AuI_2	1:1	1.2×10^{-4c} (E_a = 110 meV)
	BF_4	5:2	2.5^c (E_a = 83 meV)
	ClO_4	–^{f}	26^c (metallic ≥ 240 K))
	PF_6	5:2	17^c (metallic ≥ 190 K)
	AsF_6	2:1	3.8^c (E_a = 37 meV)

[a] Determined by elemental analysis. [b] Room temperature conductivity measured by a four-probe technique. [c] Measured on a compressed pellet. [d] The activation energy from 90 to 270 K is 56 meV. [e] Measured on a single crystal. [f] Not determined because this complex may explode during analysis.

References

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[5] Abbreviations for TTF derivatives used herein: DOET, (1,4-dioxanediyl-2,3-dithio) ethylenedithiotetrathiafulvalene; DOES, (1,4-dioxanediyl-2,3-dithio)-ethylenediselenotetrathiafulvalene; DO-MET, [(1,3-dioxolan-2-yl)methylenedithio]ethylenedithiotetrathiafulvalene; MET, (methylenedithio)ethylenedithio-tetrathiafulvalene; DOEO, (1,4-dioxanediyl- 2,3-dithio)ethylenedioxytetrathiafulvalene; DT-MET, [(1,3-dithiolan-2-yl)methylenedithio] ethylenedithiotetrathiafulvalene; OT-MET, [(1,3-oxathiolan-2-yl)methylenedithio]ethylenedithiotetrathiafulvalene; DOA-MET, [(1,3-dioxan-2-yl) methylenedithio]ethylenedithiotetrathiafulvalene; DTA-MET, [(1,3-dithian-2-yl)methylenedithio]ethylenedithiotetrathiafulvalene; Me-MET, (methylmethylenedithio)ethylenedithiotetrathiafulvalene; Et-MET, (ethylmethylenedithio) ethylenedithiotetrathiafulvalene.

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[12] Crystal data for OT-MET (6): $a = 18.59(1)$ Å, $b = 9.663(3)$ Å, $c = 10.159(3)$ Å, $\beta = 104.79(4)°$, $V = 1765(1)$ Å^3, $Z = 4$, $R = 0.105$ ($R_w = 0.132$).

[13] Crystal data for $(DO\text{-}MET)_2AsF_6$: triclinic, space group $P1$, $a = 5.086(2)$ Å, $b = 11.500(3)$ Å, $c = 15.080(5)$ Å, $\alpha = 99.02(2)°$, $\beta = 90.16(3)°$, $\gamma = 91.09(2)°$, $V = 871.0(5)$ Å^3, $Z = 1$, $R = 0.073$ ($R_w = 0.097$).

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