

## Alternative Synthesis of TTF Donors with a Dioxolane Ring, and Synthesis of Their Dithiolane and Oxathiolane Analogues

Jun-ichi Yamada,<sup>a\*</sup> Rika Oka,<sup>a</sup> Hiroyuki Anzai,<sup>a</sup>  
Hiroyuki Nishikawa,<sup>b</sup> Isao Ikemoto,<sup>b</sup> and Koichi Kikuchi<sup>b</sup>

<sup>a</sup>Department of Material Science, Faculty of Science, Himeji Institute of Technology,  
1475-2 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan

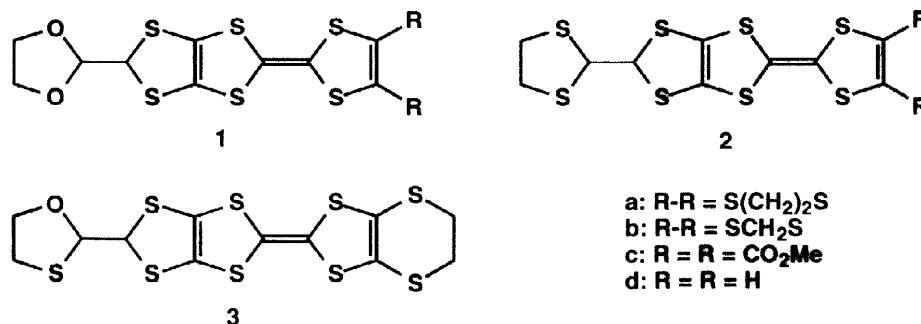
<sup>b</sup>Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,  
Hachioji, Tokyo 192-0397, Japan

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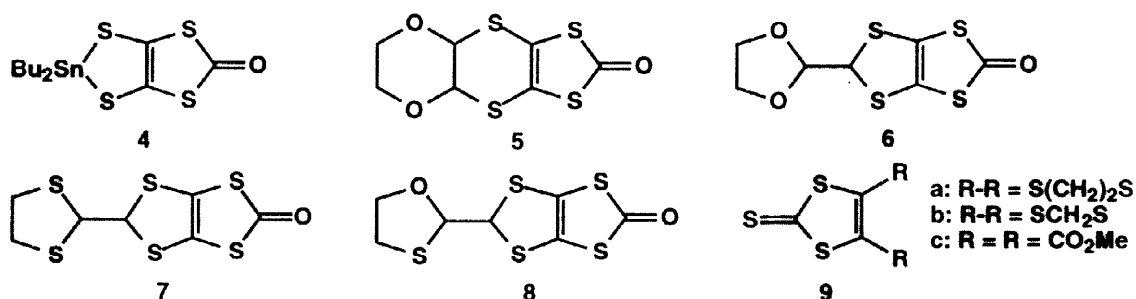
**Abstract:** Synthesis of the TTF (tetrathiafulvalene) donors with a 1,3-dioxolane, 1,3-dithiolane, or 1,3-oxathiolane ring (1–3) has been accomplished via the (MeO)<sub>3</sub>P-promoted cross-coupling reaction of the corresponding new ketones (6–8) and thiones (9a–c). The radical-cation salts derived from **2a** with AuI<sub>2</sub><sup>+</sup>, BF<sub>4</sub><sup>−</sup>, and AsF<sub>6</sub><sup>−</sup> exhibited metallic conducting behavior for single crystals.

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In the course of our search for the development of new molecular-based organic metals composed of the bulky TTF donors,<sup>1</sup> we have found that the 1,3-dioxolane derivative of MET<sup>2</sup> (**1a**) produces a metallic TCNQ<sup>2</sup> complex even though the dioxolane ring is attached perpendicularly to the MET framework.<sup>1c</sup> This donor was synthesized via the Me<sub>3</sub>Al-mediated rearrangement reaction, but its yield was relatively low.<sup>1c,d</sup> The replacement of the outer ring oxygen atom(s) in **1a** with the larger and more polarizable sulfur atom(s) can be expected to result in an enhancement of intermolecular S⋯S interactions in their CT<sup>2</sup> complexes. However, the dithiolane analogue of **1a** (**2a**) could not be obtained by the Me<sub>3</sub>Al-promoted reaction of the corresponding tin-masked dithiolate with an ester, since the analogous rearrangement as can be found in the synthesis of **1a** did not take place.<sup>1a,d</sup> This paper describes the synthesis of the dioxolane derivatives **1a–d** via a different synthetic route and a synthetic approach to the construction of their dithiolane analogues **2a–d** and the oxathiolane derivative of MET (**3**). We also disclose the electrochemical properties of new compounds (**1b**, **2a,b,d**, and **3**), the molecular structure of **2a**, and the electrical conducting behavior of the **2a**-based CT complex and radical-cation salts.



Our strategy for synthesizing **1-3** was based on the  $(\text{MeO})_3\text{P}$ -promoted cross-coupling reaction, and to this end, the preparation of new ketones **6-8** utilized for this reaction was developed. An excess of  $\text{BF}_3 \cdot \text{OEt}_2$  (10 equiv.) was added to the dioxane-fused ketone **5**, prepared from tin dithiolate **4** and 2,3-dichloro-1,4-dioxane in the presence of 2 equiv. of  $\text{BF}_3 \cdot \text{OEt}_2$ ,<sup>1a,d</sup> in  $\text{CHCl}_3$ , and the mixture was reacted at room temperature for one day. Isomerization of the bis-fused six-membered heterocycle to the five-membered biheterocycle progressed to afford the dioxolane-appended ketone **6** in 80% yield together with a trace amount of **5**. The ratio of **6:5** determined by  $^1\text{H-NMR}$  was 46:1.<sup>3,4</sup> Further, the addition of 1,2-ethanedithiol in this reaction followed by stirring for two days gave the dithiolane-added ketone **7** in 95% yield. While conversion of **5** into the oxathiolane-appended ketone **8** could not be effected by the  $\text{BF}_3$ -promoted reaction of **5** with 2-mercaptoethanol even under prolonged reaction time, the analogous reaction of **6** in  $\text{CH}_2\text{Cl}_2$  for two days gave **8** in 40% yield. The synthesis of **1a-c**, **2a-c**, and **3** was carried out by cross-coupling of the resulting ketones **6-8** with 2 equiv. of thiones **9a-c** using  $(\text{MeO})_3\text{P}$  as a phosphite reagent in toluene at 110 °C for 2 h (**1a**, 80%; **1b**,<sup>5</sup> 52%; **1c**, 96%; **2a**,<sup>5</sup> 94%; **2b**,<sup>5</sup> 66%; **2c**, 72%; **3**,<sup>5</sup> 83%).<sup>6</sup> Demethoxycarbonylation of **1c** and **2c** was performed by heating with  $\text{LiBr} \cdot \text{H}_2\text{O}$  (10 equiv.) in HMPA at 90 °C for 1 h, and then at 130 °C for 1 h, furnishing the dioxolane derivative of MDT-TTF<sup>2</sup> (**1d**) and its dithiolane analogue (**2d**)<sup>5</sup> in 46% and 63% yields, respectively.



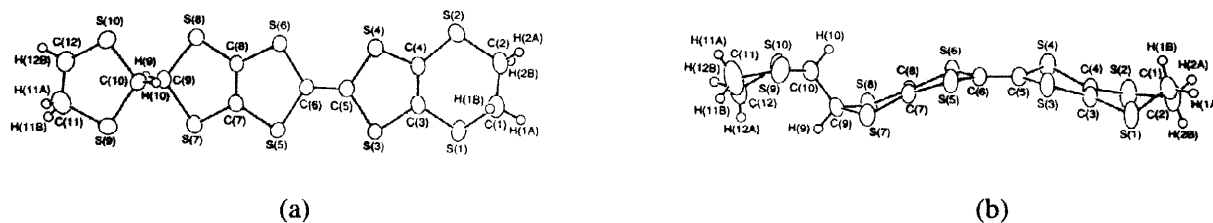
Oxidation potentials of **1b**, **2a,b,d**, and **3** were measured by using cyclic voltammetry, and the results are summarized in Table 1. For **2a,b,d** and **3**, three pairs of reversible redox waves were observed, whereas **1b** showed three pairs of reversible redox waves and one irreversible oxidation wave.<sup>7</sup> The  $E_1$  value of the dithiolane derivative of MET (**2a**) is equal to that of the derivative of BMDT-TTF<sup>2</sup> (**2b**), and the derivative of MDT-TTF (**2d**) shows a lower  $E_1$  value than those of **2a,b** probably owing to the absence of the electron-withdrawing group, that is, the alkylenedithio group. The values of oxidation potentials ( $E_1$ ,  $E_2$ , and  $E_3$ ) for **3** are closer to those of **2a** than those of **1a** ( $E_1 = +0.57$  V,  $E_2 = +0.84$  V, and  $E_3 = +1.58$  V).<sup>1c,d</sup>

**Table 1.** Oxidation potentials of **1b**, **2a,b,d**, and **3**<sup>a</sup>

Compound	$E_1$	$E_2$	$E_3$	$E_4$	$\Delta E (E_2 - E_1)$
<b>1b</b>	0.53	0.76	1.38	1.56 <sup>b</sup>	0.23
<b>2a</b>	0.55	0.83	1.63		0.28
<b>2b</b>	0.55	0.77	1.57		0.22
<b>2d</b>	0.48	0.80	1.67		0.32
<b>3</b>	0.55	0.83	1.64		0.28

<sup>a</sup>V vs. saturated calomel electrode (SCE); 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> in PhCN; Pt electrode; at room temperature; under nitrogen; scan rate 50 mV s<sup>-1</sup>. <sup>b</sup>Irreversible wave.

An X-ray diffraction analysis of the neutral **2a** was undertaken to compare with the molecular structure of **1a**.<sup>8</sup> As shown in Figure 1, **2a** has a distorted structure, wherein the plane formed by two sulfur atoms and one carbon atom linking them in the 1,3-dithiolane ring is roughly parallel to the central tetrathioethylene medium plane of the MET molecule. The conformation of the dithiolane ring appended to MET evidently makes it nonplanar, but the whole molecular structure of **2a** is less bulky than that of **1a**.<sup>1c,d</sup>



**Figure 1.** Molecular structures of **2a**: (a) top view and (b) side view

The TCNQ complex with **2a** was obtained in a small amount by reaction between **2a** and TCNQ (1 equiv) in TCE<sup>2</sup> at 80 °C for 2 h, although no complex was formed when the same reaction was carried out at room temperature overnight. In contrast to a metallic TCNQ complex of **1a**, the room temperature conductivity for a single crystal of this complex, prepared by recrystallization from TCE with slow cooling, was very low ( $\sigma_{\text{RT}} < 10^{-7} \text{ S cm}^{-1}$ ).<sup>9</sup> On the other hand, the **2a**-based radical-cation salts listed in Table 2 were accessible by controlled-current electrocrystallization<sup>10</sup> in TCE containing the corresponding tetrabutylammonium salts, and their room temperature conductivities were  $10^{-2} - 10^1 \text{ S cm}^{-1}$ . While compressed pellets of the  $\text{I}_3$  and  $\text{ClO}_4$  salts showed semiconducting behavior with small or relatively small activation energy, single crystals of the  $\text{AuI}_2$ ,  $\text{BF}_4$ , and  $\text{AsF}_6$  salts were all metallic, which underwent metal-to-semiconductor (or insulator) transitions. The temperature dependence of their resistances is shown in Figure 2.

Further investigation on the preparation of good single crystals suitable for X-ray crystallography and the development of other organic metals derived from the dichalcogenolane-added TTF donors is currently in progress.

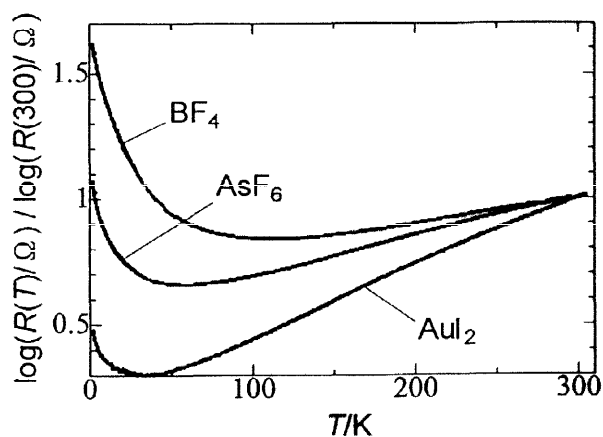
**Table 2.** Conducting behavior of the radical-cation salts based on **2a**

Anion	<b>2a</b> :Anion <sup>a</sup>	$\sigma_{\text{RT}} / \text{S cm}^{-1\text{b}}$
$\text{I}_3^-$	3:1	$3.2 \times 10^{-1\text{c}}$ ( $E_a = 15 \text{ meV}$ )
$\text{AuI}_2^-$	5:3	$13^{\text{d}}$ ( $T_{\text{MI}}^{\text{e}} = 35 \text{ K}$ )
$\text{BF}_4^-$	2:1	$7.0^{\text{d}}$ ( $T_{\text{MI}} = 110 \text{ K}$ )
$\text{ClO}_4^-$	- <sup>f</sup>	$9.5 \times 10^{-2\text{c}}$ ( $E_a = 58 \text{ meV}$ )
$\text{AsF}_6^-$	3:1	$19^{\text{d}}$ ( $T_{\text{MI}} = 60 \text{ K}$ )

<sup>a</sup>Determined by elemental analysis. <sup>b</sup>Room temperature conductivity measured by a four-probe technique.

<sup>c</sup>Measured on a compressed pellet. <sup>d</sup>Measured on a single crystal.

<sup>e</sup>Temperature of metal-to-semiconductor (insulator) transition. <sup>f</sup>Not determined because this complex may explode during analysis.



**Figure 2.** Temperature dependence of relative electrical resistance of the metallic **2a**-based salts

## References and Notes

1. (a) Yamada, J.; Nishimoto, Y.; Tanaka, S.; Nakanishi, R.; Hagiya, K.; Anzai, H. *Tetrahedron Lett.*, **1995**, *36*, 9509-9512. (b) Yamada, J.; Tanaka, S.; Anzai, H.; Sato, T.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Mater. Chem.*, **1997**, *7*, 1311-1312. (c) Yamada, J.; Hamasaki, M.; Jinihi, O.; Tanaka, S.; Hagiya, K.; Anzai, H. *Tetrahedron Lett.*, **1997**, *38*, 3439-3442. (d) Yamada, J.; Tanaka, S.; Segawa, J.; Hamasaki, M.; Hagiya, K.; Anzai, H.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Org. Chem.*, **1998**, *63*, 3952-3960. (e) Nishikawa, H.; Ishikawa, H.; Sato, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Tanaka, S.; Anzai, H.; Yamada, J. *J. Mater. Chem.*, **1998**, *8*, 1321-1322.
2. Abbreviations used herein: MET = methylenedithio(ethylenedithio)tetrathiafulvalene; TCNQ = tetracyanoquinodimethane; CT = charge-transfer; MDT-TTF = methylenedithiotetrathiafulvalene; BMDT-TTF = bis(methylenedithio)tetrathiafulvalene; TCE = 1,1,2-trichloroethane.
3. The pure ketone **6** was obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-EtOH.
4. The use of 10 equiv. of BF<sub>3</sub>•OEt<sub>2</sub> in the reaction of **4** with dichlorodioxane under the same conditions furnished an 8:1 mixture of **6** and **5** in 89% yield.
5. Selected physical and spectroscopic data. **1b**: mp 180 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-CS<sub>2</sub>) δ 5.19 (d, J = 5.4 Hz, 1 H), 5.07 (d, J = 5.4 Hz, 1 H), 4.99 (d, J = 9.8 Hz, 1 H), 4.88 (d, J = 9.8 Hz, 1 H), 4.05-3.94 (m, 4 H); MS m/z (% relative intensity) 428 (100, M<sup>+</sup>); calcd for C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>S<sub>8</sub> m/z 427.8290, measured m/z 427.8309. **2a**: mp 168 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-CS<sub>2</sub>) δ 4.88 (d, J = 9.8 Hz, 1 H), 4.85 (d, J = 9.8 Hz, 1 H), 3.34-3.15 (m, 8 H); Anal. Found: C, 30.16; H, 2.16%. Calcd for C<sub>12</sub>H<sub>10</sub>S<sub>10</sub>: C, 30.35; H, 2.12%. **2b**: mp 184 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-CS<sub>2</sub>) δ 5.01 (d, J = 9.8 Hz, 1 H), 4.88 (d, J = 9.8 Hz, 1 H), 4.87 (d, J = 9.8 Hz, 1 H), 4.84 (d, J = 9.8 Hz, 1 H), 3.26-3.16 (m, 4 H); Anal. Found: C, 28.74; H, 1.66%. Calcd for C<sub>11</sub>H<sub>8</sub>S<sub>10</sub>: C, 28.67; H, 1.75%. **2d**: mp 137 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-CS<sub>2</sub>) δ 6.32 (s, 2 H), 4.87 (dd, J = 10.3, 10.3 Hz, 2 H), 3.25-3.15 (m, 4 H); MS m/z (% relative intensity) 384 (100, M<sup>+</sup>); calcd for C<sub>10</sub>H<sub>8</sub>S<sub>8</sub> m/z 383.8392, measured m/z 383.8393. **3**: mp 153 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-CS<sub>2</sub>) δ 5.48 (d, J = 8.8 Hz, 1 H), 5.07 (d, J = 8.8 Hz, 1 H), 4.23-4.18 (m, 1 H), 4.08-4.02 (m, 1 H), 3.34-3.21 (m, 4 H), 3.03-2.98 (m, 2 H); MS m/z (% relative intensity) 458 (100, M<sup>+</sup>); calcd for C<sub>12</sub>H<sub>10</sub>OS<sub>9</sub> m/z 457.8218, measured m/z 457.8246.
6. It is noted that, in the (MeO)<sub>3</sub>P-promoted reaction of **7** with **9a**, the use of benzene in place of toluene as a solvent gave BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] as a self-coupling product in 92% yield along with the recovered **7** (80%), and resulted in essentially no yield of **2a**.
7. Three oxidation waves in **1b**, **2a**, **b**, **d**, and **3** are presumably arisen from two 1,3-dithiole rings of the TTF core and the dichalcogenolane-added 1,3-dithiolane ring fusing onto the TTF molecule, but the reasons for the appearance of the fourth oxidation wave in **1b** are far from being fully interpreted.
8. Crystal data for **2a**: C<sub>12</sub>H<sub>10</sub>S<sub>10</sub>, *M* = 474.00, monoclinic, space group *P2<sub>1</sub>/a*, *a* = 18.75(1) Å, *b* = 9.791(5) Å, *c* = 10.165(7) Å, β = 103.73(5)°, *V* = 1812.43 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.737 g cm<sup>-3</sup>, *R* = 0.0575 (*R<sub>w</sub>* = 0.0924) for 3997 observed reflections.
9. The stoichiometry of this complex was not determined due to insufficient amount of sample for elemental analysis.
10. Anzai, H.; Delrieu, J. M.; Takasaki, S.; Nakatsuji, S.; Yamada, J. *J. Cryst. Growth*, **1995**, *154*, 145-150.