doi:10.1246/cl.2011.81

New Molecular Metals Based on a Tetrathiapentalene Donor with Peripheral Methoxy Groups

Tetsuya Ito,[1] Ken-ichi Nakamura,[1] Takashi Shirahata,*[1] Tadashi Kawamoto,[2] Takehiko Mori,[2] and Yohji Misaki*[1]
[1]*Department of Applied Chemistry, Graduate School of Science and Engineering, Ehime University,*
3 Bunkyo-cho, Matsuyama, Ehime 790-8577
[2]*Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,*
Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552

(Received October 5, 2010; CL-100851; E-mail: shirahata.takashi.mj@ehime-u.ac.jp)

A new tetrathiapentalene (TTP) donor 2-(4,5-dimethoxy-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (DMO-TTP) has been synthesized, and the PF_6 and AsF_6 salts have also been prepared by electrochemical crystallization. X-ray structure analyses have revealed that intermolecular and intramolecular CH···O hydrogen bondings are constructed in the neutral crystal and the cation radical salts, respectively. The PF_6 and AsF_6 salts have a so-called β-type arrangement of the donors and show metallic behavior down to around 10 K.

Tetrathiafulvalene (TTF) derivatives containing oxygen atoms have attracted attention because of their unique features of high solubility toward common organic solvents and the ability to form hydrogen bonding in their charge-transfer complexes.[1] TTF and tetraselenafulvalene (TSF) derivatives with an ethylenedioxy group, which contains two oxygen atoms, yielded peculiar materials such as $(EDO\text{-}TTF)_2PF_6$ (EDO-TTF: ethylenedioxy-TTF)[2] and κ-$(DMEDO\text{-}TSeF)_2[Au(CN)_4]$(solv.) [DMEDO-TSeF: dimethyl(ethylenedioxy)tetraselenafulvalene].[3] The former shows an ultra-fast photoinduced phase transition, and the latter exhibits a superconducting transition and the critical temperature (T_c) of the system is tunable by using the effect of the solvent of crystallization. On the other hand, molecular complexes based on TTFs containing methoxy groups show low electric conductivity except for the 1:1 TCNQ complex of tetramethoxy-TTF (TMO-TTF), and there are no reports on the crystal structure of molecular complexes based on these donors.[4] To obtain single crystalline metallic molecular conductors based on donors with the methoxy group, we have focused on a bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP) (Chart 1), because TTP and its derivatives have afforded many metallic molecular conductors down to liquid helium temperature.[5] Since substituents on the TTP skeleton often dominate their molecular packing motifs, investigation of the substitution effect of the methoxy group on the molecular packing motif is of great interest. In this letter, we report the synthesis and structure of DMO-TTP, where DMO-TTP is 2-(4,5-dimethoxy-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, together with the structures and conducting properties of the PF_6 and AsF_6 salts.

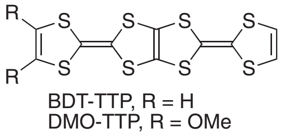
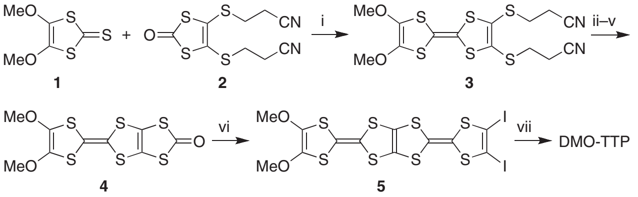


Chart 1.



Scheme 1. *Reagents and conditions*: i) $P(OEt)_3$, toluene, 100 °C, ii) $CsOH \cdot H_2O$, iii) $ZnCl_2$, iv) TBABr, v) triphosgene, vi) 4,5-diiodo-1,3-dithiole-2-thione, $P(OMe)_3$, toluene, 100 °C, vii) $TBABH_4$, DMF, room temperature.

The synthesis of DMO-TTP is outlined in Scheme 1. Triethyl phosphite-mediated cross-coupling reaction of thione **1**[4a] and ketone **2** in toluene at 100 °C afforded unsymmetrical TTF **3** in 60% yield. Compound **3** was allowed to react with excess cesium hydroxide monohydrate in THF, followed by treatment with anhydrous zinc chloride, tetrabutylammonium (TBA) bromide, and then with an excess of triphosgene in THF at −78 °C to provide TTF-fused 1,3-dithiol-2-one **4** (66%). The diiodo-substituted compound **5** was obtained by a cross-coupling reaction of **4** and 4,5-diiodo-1,3-dithiole-2-thione[6] with a large excess of trimethyl phosphite in toluene at 100 °C (62%). Reduction of **5** by using $TBABH_4$ in DMF afforded the target compound DMO-TTP in 76% yield (total 19%). The unsubstituted derivatives were often synthesized by the demethoxycarbonylation with an excess of $LiBr \cdot H_2O$ in HMPA, however, the usual procedure cannot be applied to the present system due to the possibility of the elimination of methoxy groups. DMO-TTP showed a higher solubility in common solvents than other TTP derivatives. The cross-coupling reaction between the known 1,3-dithiol-2-one fused with pristine TTF[7] and **1** afforded DMO-TTP in low yield (1.9%). The molecular structure of the DMO-TTP was characterized by NMR, MS, IR, elemental analysis, and X-ray structure analysis,[8,9] and electrochemical properties were investigated by cyclic voltammetry in benzonitrile. The cyclic voltammogram of DMO-TTP (0.1 M $TBAPF_6$, Pt working and counter electrodes, scan rate 50 mV s^{-1} at 25 °C) showed four pairs of reversible redox waves at 0.02, 0.21, 0.51, and 0.68 V vs. Fc/Fc^+ couple. The first oxidation potential of DMO-TTP is higher by 0.03 V than that of BDT-TTP, indicating that the electron-donating ability of DMO-TTP is slightly weaker than that of BDT-TTP.

Figure 1 shows the molecular structure and packing motif of neutral DMO-TTP. Both TTF moieties adopt a boat conformation, which orient in opposite directions. As a result, the central

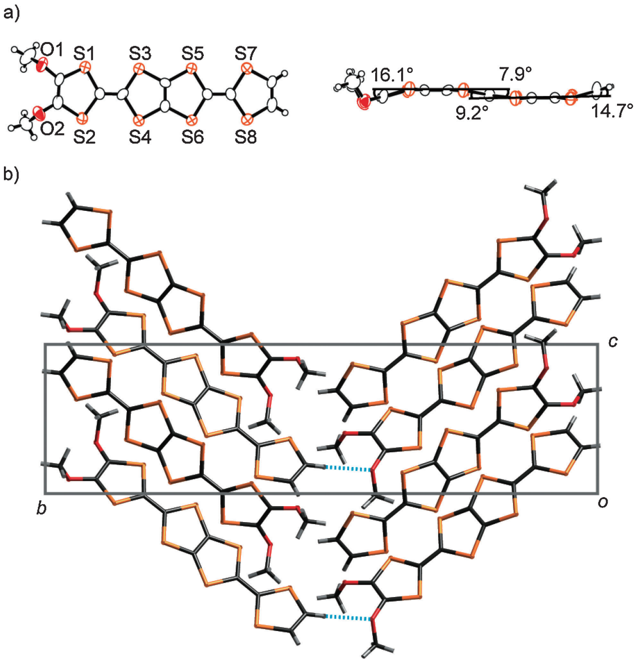


Figure 1. a) Molecular structure of DMO-TTP at 273 K. b) Molecular packing motif viewed along the crystallographic *a* axis. The dotted lines indicate CH···O hydrogen bondings shorter than 2.72 Å.[10]

TTP moiety adopts a chair conformation. The folding angles between two planes are 16.1, 7.9, 9.2, and 14.7°, as depicted in Figure 1a. The two methoxy groups are bent in the same direction in contrast to the previous result. In the case of TMO-TTF, the two methyl groups of methoxy-substituents in the 1,3-dithiole ring are bent in opposite directions.[4a] The DMO-TTP molecule forms two crystallographically equivalent donor layers in the unit cell and they are connected by intermolecular CH···O hydrogen bondings (2.57 Å) shorter than the sum of the van der Waals radii[10] (Figure 1b).

The black plate crystals of $(DMO\text{-}TTP)_2X$ ($X = PF_6$ and AsF_6) were prepared by the galvanostatic oxidation (0.2 µA) of DMO-TTP (3.0 mg) in the presence of corresponding tetrabutylammonium salts (PF_6: 27.9 mg; AsF_6: 31.1 mg) as a supporting electrolyte in 1,2-dichloroethane (6% EtOH, v/v, 18 mL) for the PF_6 salt and in chlorobenzene (6% EtOH, v/v, 18 mL) for the AsF_6 salt. The PF_6 and AsF_6 salts are isomorphic and crystallize in triclinic space group $P\bar{1}$.[9] The crystal structure of $(DMO\text{-}TTP)_2PF_6$ is shown in Figure 2 as a representative. The unit cell contains two donor molecules and one PF_6 anion, giving a donor to anion ratio of 2:1. The DMO-TTP molecules are stacked along the *a* axis with interplanar distances of 3.50 (*a*1) and 3.51 (*a*2) Å for the PF_6 salt, and 3.48 (*a*1) and 3.50 (*a*2) Å for the AsF_6 salt. The donor columns are linked by S···S contacts (3.566(1) Å for the PF_6 salt; 3.565(1) Å for the AsF_6 salt) and S···O contacts (3.209(3) Å for the PF_6 salts; 3.219(4) Å for the AsF_6 salt) shorter than the sum of the van der Waals radii. As shown in Figure 2b, the packing motif of the donors is a β-type arrangement and resembles those of $(BDT\text{-}TTP)_2SbF_6$, $(EO\text{-}TTP)_2AsF_6$, and β-$(BTM\text{-}TTP)_2PF_6$.[11] The donors form face-to-face stacks in a head-to-tail manner. The slipping distances D[12] along the molecular long axis for overlap modes *a*1 and *a*2 are 1.65 and 1.67 Å for the PF_6 salt, and 1.67 and 1.71 Å for the AsF_6 salt, respectively. When steric hindrance between the bulky substituents exists, the slipping distances along the long and/or short molecular axis tend to have large values. In the θ-BTM-TTP salt, the BTM-TTP molecules, in which both bulky methyl groups of methylsulfanyl(SCH_3)-substituents are bent orthogonally (Table S2[8]), slip along both the short and long molecular axes. Owing to the formation of intramolecular CH···O hydrogen bonding (2.59 Å for the PF_6 salt; 2.63 Å for the AsF_6 salt) as shown in Figure 2d, one bulky methoxy group is located in the molecular plane and is directed toward the inside of the molecular framework. As a result, the steric hindrance is reduced in the present system.

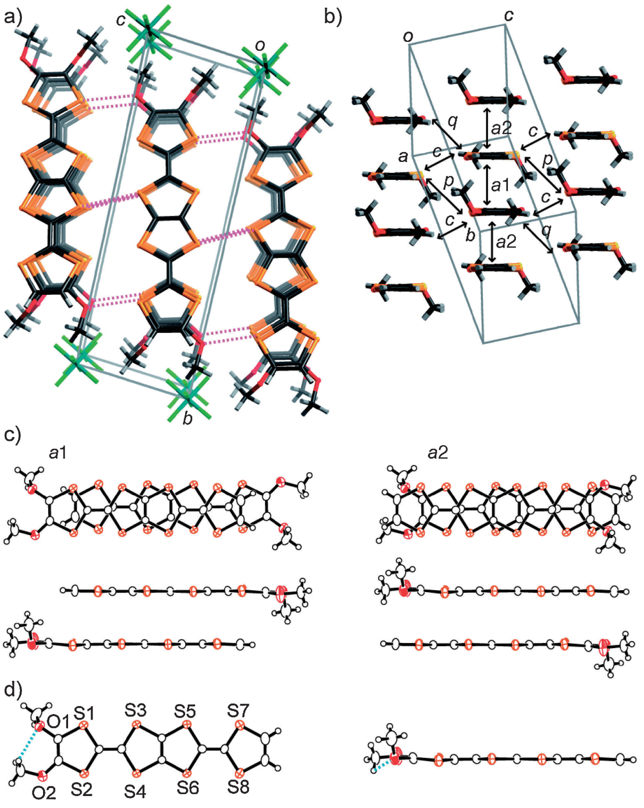


Figure 2. Crystal structure for $(DMO\text{-}TTP)_2PF_6$ at 273 K. a) Molecular packing motif viewed along the crystallographic *a* axis. The dotted lines indicate short S···S and S···O contacts shorter than the sum of the van der Waals radii.[10] b) Donor sheet structure viewed along the donor long axis. c) Overlap modes of donor molecules *a*1 (left) and *a*2 (right). d) Molecular structure of DMO-TTP. The dotted line indicates CH···O hydrogen bonding shorter than 2.72 Å.[10]

Intermolecular overlap integrals were calculated using the HOMO of the donor molecule obtained by extended Hückel MO calculation[12] and are summarized in Table 1 together with the geometric parameters. The overlap integrals *a*1 and *a*2 along the stacking direction for these salts are comparable values, because the geometric parameters ϕ, D, and z are similar to each other. This indicates that the donor column is intrinsically a uniform stacking column. The calculated energy band dispersion and Fermi surface of the PF_6 salt based on the above overlap integrals are shown in Figure 3.[12] There are two energy bands

Table 1. Calculated overlap integrals[a] S ($\times 10^{-3}$) and geometric parameters[b] for $(\text{DMO-TTP})_2X$ ($X = PF_6$ and AsF_6)

		$a1$	$a2$	c	p	q
$(\text{DMO-TTP})_2PF_6$	S	23.64	25.80	−0.86	5.82	8.39
	$\phi/°$	87.1	88.9	12.4	19.4	19.8
	D/Å	1.65	1.67	1.69	3.34	3.34
	z/Å	3.50	3.51			
$(\text{DMO-TTP})_2AsF_6$	S	23.90	25.35	−1.03	6.07	7.98
	$\phi/°$	87.1	88.9	12.5	19.2	19.7
	D/Å	1.67	1.71	1.66	3.34	3.37
	z/Å	3.48	3.50			

[a] See Figure 2b for the symbols of the overlap integrals. [b] See ref. 12.

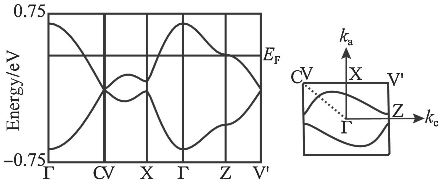


Figure 3. Calculated energy band dispersions and Fermi surfaces of $(\text{DMO-TTP})_2PF_6$.

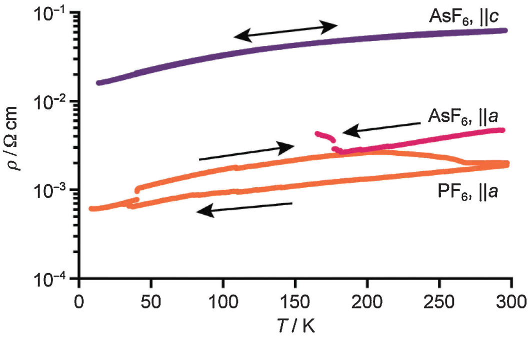


Figure 4. Temperature dependence of the resistivity of $(\text{DMO-TTP})_2X$ ($X = PF_6$ and AsF_6).

and a pair of quasi-one-dimensional Fermi surfaces is obtained. The electrical conductivities of these salts are measured along the a axis down to 10 K. The room-temperature conductivities are 530 S cm^{-1} for the PF_6 salt and 210 S cm^{-1} for the AsF_6 salt. As shown in Figure 4, the PF_6 salt shows metallic behavior down to 10 K, however, the resistivity for the AsF_6 salts cannot be measured below around 170 K due to crystal fragility along the a axis in spite of many efforts. On the other hand, the resistivity for the AsF_6 salt along the c axis can be measured down to 10 K. The room-temperature conductivity is 16 S cm^{-1}, and metallic behavior down to 10 K has been observed. The stable metallic nature of $(\text{DMO-TTP})_2X$ ($X = PF_6$ and AsF_6) are derived from the features of β-type TTP-based conductors.[5]

In summary, we successfully synthesized a new TTP donor DMO-TTP containing two methoxy groups. Novel molecular metals $(\text{DMO-TTP})_2X$ ($X = PF_6$ and AsF_6) have been prepared. Intramolecular CH···O hydrogen bondings have been observed in these salts, and this type of intramolecular interaction has not been found in cation radical salts containing other chalcogenomethyl groups. Further study of the relation between the crystal structure and intramolecular hydrogen bondings is now in progress together with the preparation of related salts.

This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 21750148 and 18GS0208) from JSPS, and a Grant-in-Aid for Scientific Research on Innovative Areas (No. 20110006) from MEXT. We are grateful to the Instrument Center of the Institute for Molecular Science for the X-ray structure analysis using the Rigaku AFC-8R Mercury CCD system.

References and Notes

1 a) S. Horiuchi, H. Yamochi, G. Saito, K. Sakaguchi, M. Kusunoki, *J. Am. Chem. Soc.* **1996**, *118*, 8604. b) M. Fourmigué, P. Batail, *Chem. Rev.* **2004**, *104*, 5379. c) H. Yamochi, *Oxygen Analogues of TTFs* in *TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene*, ed. by J. Yamada, T. Sugimoto, Kodansha and Springer, Tokyo, **2004**, Chap. 4, pp. 83–118.

2 a) A. Ota, H. Yamochi, G. Saito, *J. Mater. Chem.* **2002**, *12*, 2600. b) M. Chollet, L. Guerin, N. Uchida, S. Fukaya, H. Shimoda, T. Ishikawa, K. Matsuda, T. Hasegawa, A. Ota, H. Yamochi, G. Saito, R. Tazaki, S. Adachi, S. Koshihara, *Science* **2005**, *307*, 86.

3 a) T. Shirahata, M. Kibune, T. Imakubo, *Chem. Commun.* **2006**, 1592. b) T. Shirahata, M. Kibune, H. Yoshino, T. Imakubo, *Chem.—Eur. J.* **2007**, *13*, 7619.

4 a) Y. Misaki, H. Nishikawa, K. Nomura, T. Yamabe, H. Yamochi, G. Saito, T. Sato, M. Shiro, *J. Chem. Soc., Chem. Commun.* **1992**, 1410. b) H. Nishikawa, Y. Misaki, T. Yamabe, M. Shiro, *Synth. Met.* **1999**, *102*, 1693.

5 For recent review of TTP-based organic conductors, see: Y. Misaki, *Sci. Technol. Adv. Mater.* **2009**, *10*, 024301.

6 T. Imakubo, H. Sawa, R. Kato, *Synth. Met.* **1997**, *86*, 1883.

7 Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe, M. Shiro, *Chem. Lett.* **1993**, 1337.

8 **DMO-TTP**: mp 175–177 °C (decomp.); MS (EI, 70 eV) m/z: 440 (M^+ for $C_{12}H_8O_2S_8$); ^{1}H NMR (270 MHz, CS_2–C_6D_6): δ 3.59 (6H, s), 6.09 (2H, s); IR (KBr): ν 2927, 1631, 1446, 1220, 1191, 1103, 941, 768 cm^{-1}; Anal. Calcd for $C_{12}H_8O_2S_8$: C, 32.70; H, 1.83%. Found: C, 32.68; H, 1.91%. Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 Crystal data for **DMO-TTP**: $C_{12}H_8O_2S_8$, fw 440.66, orange plate, orthorhombic, $P2_12_12_1$, $a = 7.956(2)$, $b = 27.745(8)$, $c = 7.490(2)$ Å, $V = 1653.3(8)$ Å^3, $Z = 4$, $R1 = 0.0781$, $wR2 = 0.1861$ for 2375 [$I > 2\sigma(I)$] observed reflections from 3784 unique data; **$(\text{DMO-TTP})_2PF_6$**: $C_{24}H_{16}F_6O_4PS_{16}$, fw 1026.30, black plate, triclinic, $P\bar{1}$, $a = 7.7655(15)$, $b = 18.790(3)$, $c = 6.3770(14)$ Å, $\alpha = 95.671(14)$, $\beta = 92.548(16)$, $\gamma = 74.993(12)°$, $V = 894.2(3)$ Å^3, $Z = 1$, $R1 = 0.0565$, $wR2 = 0.1496$ for 2382 [$I > 2\sigma(I)$] observed reflections from 4011 unique data; **$(\text{DMO-TTP})_2AsF_6$**: $C_{24}H_{16}F_6O_4AsS_{16}$, fw 1070.25, black plate, triclinic, $P\bar{1}$, $a = 7.773(2)$, $b = 19.015(5)$, $c = 6.3777(19)$ Å, $\alpha = 95.92(2)$, $\beta = 92.53(2)$, $\gamma = 74.738(18)°$, $V = 904.4(4)$ Å^3, $Z = 1$, $R1 = 0.0629$, $wR2 = 0.1604$ for 2523 [$I > 2\sigma(I)$] observed reflections from 4045 unique data. CCDC-800847–800849. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

10 A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

11 a) Y. Misaki, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Chem. Lett.* **1994**, 1653. b) Y. Misaki, K. Tanaka, M. Taniguchi, T. Yamabe, T. Kawamoto, T. Mori, *Chem. Lett.* **1999**, 1249. c) M. Noda, M. Yasuda, Y. Nakano, A. Ito, H. Fueno, K. Tanaka, H. Fujiwara, T. Sugimoto, Y. Misaki, *Chem. Lett.* **2008**, *37*, 396.

12 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627.