

Synthesis and properties of methyl-EDO-TTF and the radical cation salts

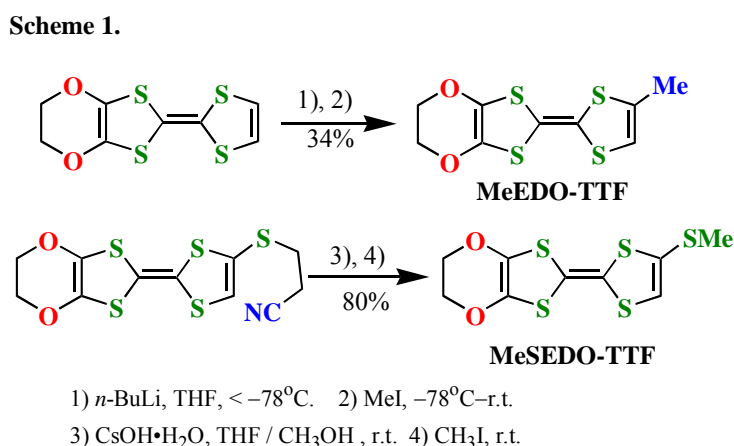
X.F. Shao ^{a,c}, H. Yamochi ^a, G. Saito ^b, Y. Nakano ^a, S. Koshihara ^{c,d}

a) Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan. b) Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan. c) Non-equilibrium Dynamics Project, ERATO, Japan Science and Technology Agency, c/o KEK, 1-1 Oho, Tsukuba, Ibaraki, 305-0801, Japan. d) Department of Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan.

Recently, we reported that (EDO-TTF)₂PF₆ shows peculiar metal-insulator transition due to the multi-instability of the metallic state. ^[1] This material also shows an ultra-fast highly efficient photo induced phase transition, of which response time is around 1.5 ps. ^[2] Since the strong electron-molecular vibration coupling is regarded to be an origin of the peculiar features of (EDO-TTF)₂PF₆, a minor chemical modification of EDO-TTF is expected to provide a donor molecule, of which the cation radical salts show the similar peculiarities. Here, we report the synthesis and the properties of the title compound along with those of the recently obtained new donor molecule of methylthio-EDO-TTF (MeSEDO-TTF).

Although methyl-EDO-TTF (MeEDO-TTF) is a known molecule, the detailed features have not been reported. ^[3] The synthetic approach of the two donor molecules is shown in Scheme 1.

MeEDO-TTF was prepared directly from EDO-TTF, that was different from the reported method ^[3] and the yield was higher in our case. MeEDO-TTF was purified by means of a gel permeation chromatography. MeSEDO-TTF was prepared from the cyanoethylthio-EDO-TTF by general procedures with the yield of 80%.



Both of MeEDO-TTF and MeSEDO-TTF showed two reversible redox potentials in CH₃CN as shown in Table 1. Although the difference is not distinct, the first redox potentials were in the order of MeEDO-TTF < EDO-TTF < MeSEDO-TTF. Also, the difference between the first and the second redox potentials was almost the same value for these three donor molecules.

The UV-Vis spectra of MeEDO-TTF and MeSEDO-TTF exhibited slight difference to that of EDO-TTF. The transition energy ($\times 10^{-3}\text{cm}^{-1}$) at the low energy region of EDO-TTF, MeEDO-TTF and MeSEDO-TTF were 20.6, 20.4 and 20.3, respectively.

Table 1. Redox Potentials (V vs. SCE, in 0.1 M Bu₄N⁺BF₄⁻ / CH₃CN at 50 mV/s)

	$E_{1/2}^1$ (V)	E_{ox}^2 (V)	ΔE (V)
MeEDO-TTF	0.36	0.71	0.32
EDO-TTF	0.39	0.74	0.32
MeSEDO-TTF	0.43	0.76	0.29

The single crystals of neutral MeSEDO-TTF were obtained by recrystallization from hexane, and the molecular structure was shown in Figure 1. In the neutral molecule, the substitution by methylthio group seems to give minor effects on the bond lengths as listed in Table 2.

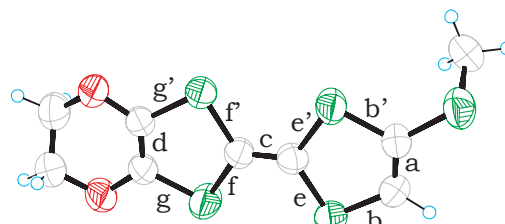


Figure 1. Molecular structure of MeSEDO-TTF

Table 2. Selected Bond Lengths (Å) of MeSEDO-TTF compared with EDO-TTF

	a	b	b'	c	d	e	e'	f	f'	g	g'
MeSEDO-TTF	1.320 (6)	1.734 (5)	1.756 (4)	1.339 (6)	1.312 (6)	1.755 (4)	1.756 (4)	1.746 (4)	1.766 (4)	1.748 (4)	1.744 (4)
EDO-TTF ^[4]	1.324 (7)	1.738 (8)	1.738 (8)	1.318 (3)	1.317 (7)	1.765 (4)	1.765 (4)	1.761 (6)	1.761 (6)	1.743 (4)	1.743 (4)

The preparation of the cation radical salts of MeEDO-TTF with PF₆, BF₄, Br, and SCN has been examined in different solvents, but no single crystalline products have been obtained at the present stage. Among these experiments, the stoichiometry of the powder sample of PF₆ salt was determined by the elemental analysis as (MeEDO-TTF)₂PF₆, and the conductivity of this salt on the compressed pellet was 8.5×10^{-3} Scm⁻¹ at room temperature.

The optical spectra of MeEDO-TTF and (MeEDO-TTF)₂PF₆ in KBr disc are shown in Figure 2. Summarizing the results, the transition energy ($\times 10^{-3}$ cm⁻¹) and the assignment at present are as follow: A: (3.3): D⁺ + D⁰ → D⁰ + D⁺; C: (14.3): intramolecular transition of D⁺ (plausibly, second HOMO to HOMO); D: (27-32): intramolecular transition.

The physical properties of other cation radical salts of MeEDO-TTF are under investigation. The electrocrystallization of MeSEDO-TTF complexes with PF₆, ClO₄, and ReO₄ anions has provided solid products so far, but no single crystals were obtained.

As expected, the slight chemical modification of EDO-TTF brought about minor effects on the electronic states of the donor molecules. But the preparation of single crystals of cation radical salts for the mono-substituted EDO-TTF are quite difficult compared with EDO-TTF, maybe due to the steric hindrance which has effects on the packing pattern of the donor molecules.

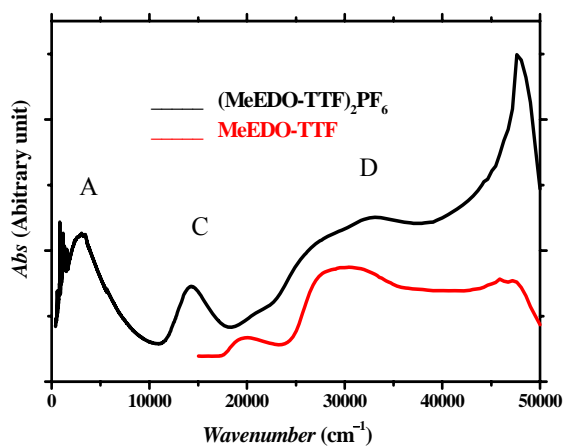


Figure 2. Optical spectra of (MeEDO-TTF)₂PF₆ and MeEDO-TTF in KBr disc.

References:

1. A. Ota *et al.*, *J. Mater. Chem.* 2002, **12**, 2600-2602; O. Drozdova *et al.*, *Phys. Rev. B*, 2004, **70**, 075107.
2. M. Chollet *et al.*, *Science* 2005, **307**, 86-89; N.Ushida *et al.*, *J. Phys. IV France*, 2004, **114**, 143-145.
3. A. Miyazaki *et al.*, *Synth. Met.* 2001, **120**, 939-940.
4. C. Meziere *et al.*, *C. R. Acad. Sci. Paris, Serie IIC, Chimie / Chemistry*. 2000, **3**, 387-395.