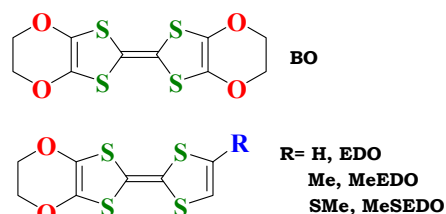


## Physical properties of the radical cation salts of mono-substituted EDO-TTFs

X.F. Shao<sup>a,c</sup>, Y. Nakano<sup>a</sup>, H. Yamochi<sup>a,c</sup>, G. Saito<sup>a,b</sup>, S. Koshihara<sup>c,d</sup>

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) Frontier Collaborative Research Center & Department of Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan.

BO is known to provide metallic radical cation salts almost exclusively due to the self-assembling nature.<sup>[1]</sup> The molecular shape and the existence of ethylenedioxy groups are assigned to the origin of this novel property. While the partial suppression of the self-assembling nature has been attempted by removing one of the terminal groups, the complete vanishing of the nature has been observed for EDO.



In fact, most of the radical cation salts so far obtained show highly conducting but weakly metallic or semiconducting transport properties. Among them, (EDO)<sub>2</sub>X (X = PF<sub>6</sub>, AsF<sub>6</sub>) shows peculiar metal-insulator (MI) transitions associated with the distinct molecular deformations, which should cause the observed mixing of the MI transition mechanisms.<sup>[2]</sup> Furthermore, ultra-fast and highly efficient photo-induced insulator-to-metal transition is observed for the radical cation salt with PF<sub>6</sub>.<sup>[3]</sup> Aiming to investigate the self-assembling nature and find out new systems which exhibit the similar peculiarities to that of (EDO)<sub>2</sub>PF<sub>6</sub>, the EDO derivatives having a small substituent are studied.

MeEDO and MeSEDO were synthesized to show the similar electronic states of the neutral species to that of EDO.<sup>[4]</sup> This report presents the overview of the radical cation salts obtained and characterized up to now.

The electrocrystallization in EtOH provided the radical cation salts only in the powder forms. The stoichiometries listed in Table 1 were estimated by the elemental analyses. Despite the difference in the compositions, whole the radical cation salts showed similar optical spectra (See Figure 1 for MeEDO salts). The low energy charge-transfer band was observed for each salt at around 3300 cm<sup>-1</sup>. The temperature dependences of conductivities, however, were classified into three classes. The conductivity ( $\sigma$ ) was measured on the compressed pellet by usual four-probe and two-probe methods at high and low temperature regions, respectively.

(MeEDO)<sub>2</sub>BF<sub>4</sub> showed metallic behavior down to the lowest temperature measured (10 K) to give the 10 times enhancement of the  $\sigma$  as shown in the upper panel of Figure 2. The transport property was consistent with the temperature dependence of magnetic susceptibility ( $\chi$ ). Although a small reduction of the  $\chi$  was observed on cooling, which was similar to that of the metallic BO radical cation salts (e.g. (BO)<sub>5</sub>(HCTMM)(PhCN)<sub>2</sub>), the magnetic behavior is understood as Pauli paramagnetism.

(MeEDO)<sub>2</sub>AsF<sub>6</sub>, (MeEDO)<sub>2</sub>SbF<sub>6</sub>, and (MeSEDO)<sub>2</sub>SbF<sub>6</sub> formed the second class of the radical cation salts, which exhibited weak metallic or almost temperature independent conducting behaviors from room temperature (rt) down to around 250 K associated with the weakly temperature dependent  $\chi$  like that of (MeEDO)<sub>2</sub>BF<sub>4</sub> (See the bottom panel of Figure 2). Although the activation energy ( $E_a$ ) showed variety of modulation below the temperature of the maximum conductivity ( $T\sigma_{\max}$ ), no anomaly was observed for the temperature dependence of  $\chi$  at around  $T\sigma_{\max}$ . The significant deviation

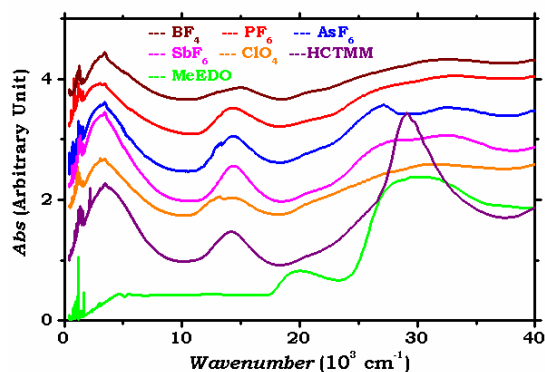


Figure 1 Optical spectra of MeEDO radical cation salts dispersed in KBr. For reference, that of neutral MeEDO is indicated with the green solid line.

from the Pauli paramagnetism (inflection point in  $\chi-T$  plot) was observed at lower temperature region for each species.

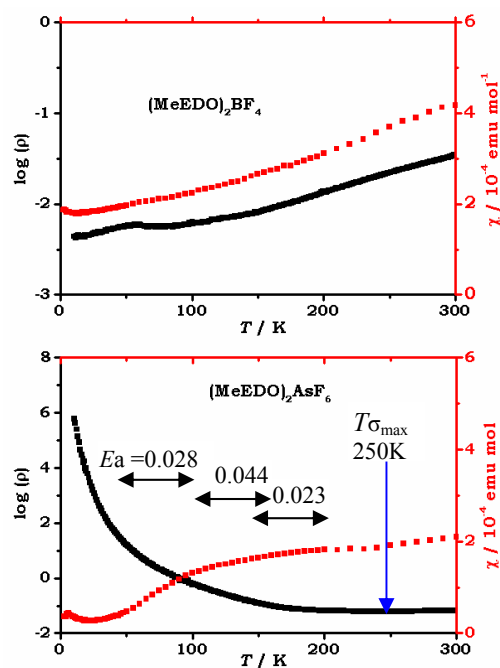
**Table 1** Composition, conductivity and magnetic properties of the radical cation salts of MeEDO and MeSEDO

Anion	MeEDO				MeSEDO			
	D : A	$\sigma_{\pi}^{*2}$ (S cm <sup>-1</sup> )	$E_a$ (eV)	$\chi_{\pi}^{*3}$	D : A	$\sigma_{\pi}^{*2}$ (S cm <sup>-1</sup> )	$E_a$ (eV)	$\chi_{\pi}^{*3}$
BF <sub>4</sub>	2 : 1	26 (M)		4.2	-			
PF <sub>6</sub>	2 : 1	3 (S)	0.100 (300-260K) 0.054 (250-100K) 0.022 (80-30K)	3.9	2 : 1	5 (S)	0.018 (300-200K) 0.032 (200-100K) 0.040 (100-40K)	5.2
AsF <sub>6</sub>	2 : 1	15 (M ≥ 240 K)	0.023 (200-165K) 0.044 (160-100K) 0.028 (100-50K)	2.1	2 : 1	7 (S)	0.011 (300-250K) 0.030 (200-100K) 0.035 (100-40K)	5.4
SbF <sub>6</sub>	2 : 1	6 (M ≥ 250 K)	0.014 (250-150K) 0.022 (150-20K)	2.3	2 : 1	4 (M ≥ 260 K)	0.014 (240-200K) 0.018 (200-100K) 0.022 (100-20K)	5.6
HCTMM <sup>*1</sup>	4 : 1	6 (S)	0.036 (300-50K) 0.024 (50-20K)	1.3	13 : 3			

\*1: Hexacyanotrimethylenemethanediide; \*2: (M ≥ 240 K), Metallic down to 240 K; (S), Semiconductor. \*3: Room temperature magnetic susceptibility in the unit of 10<sup>-4</sup> emu (mol of formula unit)<sup>-1</sup>.

The rest radical cation salts of (MeEDO)<sub>2</sub>PF<sub>6</sub>, (MeEDO)<sub>4</sub>(HCTMM), (MeSEDO)<sub>2</sub>PF<sub>6</sub> and (MeSEDO)<sub>2</sub>AsF<sub>6</sub> showed semiconducting behaviors in whole of the temperature region measured despite of the high conductivities at rt. The temperature dependences of  $\chi$ , however, resembled those of the second class of radical cation salts in the high temperature region and inflection points were observed in  $\chi-T$  plots in the case of latter two salts. These observations suggest that these two radical cation salts are metallic at around rt.

As concluding remarks, the physical properties of MeEDO and MeSEDO radical cation salts are sensitive to the counter anions like those of EDO salts, though the same type of phase transition observed in (EDO)<sub>2</sub>PF<sub>6</sub> could not be found. The variety of the conducting behavior of the salts examined here indicate that MeEDO and MeSEDO, as conducting component molecules, are similar to EDO rather than to the self-assembling BO molecule.



**Figure 2** Temperature dependent resistivity (black) and static susceptibility (red) of MeEDO salts. In the lower panel,  $T\sigma_{\max}$  and the variation of  $E_a$  (eV) for the transport property are also indicated.

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