Synthetic and structural study of trioxytriphenylamine radical cation salts

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Abstract. Radical cation salts, (TOT)PF6, (TOT)ClO4, and (TOT)ReO4, were prepared by means of galvanostatic electrocrystallization, where TOT is 2,2':6',2":6",6-trioxytriphenylamine, and the crystal structures were solved. Calculated overlap integrals between highest occupied molecular orbitals of TOT molecules indicated very weak intermolecular interactions in these salts. Virtually isolated electronic structure of TOT molecule in the salts was also confirmed by UV-vis-IR spectral study.

1. Introduction
The development of the research field of molecular conductor has created a huge variety from semiconducting to metallic and even superconducting materials. Among them, phase transition systems attract much interest from both scientific and practical points of view. Recently, the origins of carrier-localization observed in charge ordering and Mott insulating systems have been actively investigated and clarified [1]. In order to design a novel phase transition system, the control of localization and delocalization of carrier in molecular conductor is an important issue.

For example, (EDO-TTF)2PF6 exhibits a peculiar metal-insulator transition accompanied with a distinct molecular deformation, in which three phase transition mechanisms of Peierls, charge ordering, and anion ordering cooperatively work [2]. In the insulating phase at low temperature, the shapes of the charge poor and rich molecules are boat and planar, respectively. Furthermore, the ultra-fast and highly efficient photo-induced phase transition is demonstrated, and the lattice deformation (and/or the molecular vibrations) of EDO-TTF molecule is claimed to play an important role [3]. In this system, the deformation of donor molecule between boat and planar shapes depending on the molecular charge plays an important role in the transition. Therefore, when a molecular deformation is intentionally
incorporated into a mixed-valence compound, a novel transition system based on molecular degree of freedom might be realized. When the site charge on each molecule is changed from homogeneous (delocalized) to inhomogeneous (localized) in a mixed-valence system, the transport property is switched from high to low conducting.

2,2'·6',2'·6',6'-Trioxotriphenylamine (TOT) is known to show a molecular deformation depending on the molecular charge: bowl and planar shapes for neutral TOT and TOT⁺ radical cation, respectively [4]. Therefore, TOT is a candidate for producing a new transition system related to molecular degree of freedom. Although several radical cation salts of (TOT)PF₆ [4], (TOT)FeCl₄, and (TOT)GaCl₄ [5] have been prepared by chemical oxidation so far, these salts are not mixed-valent. However, a mixed-valence compound of TOT molecule should be obtained when the counter component is appropriately selected. In this paper, we report electrochemical preparations, crystal structures, UV-vis-IR spectra, and transport properties of TOT radical cation salts.

Scheme 1. Molecular structures of EDO-TTF and TOT

2. Experimental

2.1. General
TOT was prepared according to the literature [4]. Tetrabutylammonium (TBA) salts, (TBA)PF₆, (TBA)ClO₄, and (TBA)ReO₄, were recrystallized from the appropriate solvent. 1,2-Dichloroethane (DCE) was washed with conc. H₂SO₄, deionized water, and aqueous K₂CO₃, dried over CaCl₂, and fractionally distilled under nitrogen atmosphere after passing through an alumina column. Tetrahydrofuran (THF) was distilled from benzophenone/Na under argon atmosphere.

The radical cation salts were prepared by the electrochemical oxidation method of TOT in an H-shaped electrochemical cell with a glass frit separating anode and cathode arms. Typically, TOT was placed in the anode arm of the cell and the corresponding TBA salt in each arm, evacuated, back flushed with nitrogen or argon gas, and then filled with a solvent. The mixture was stirred to give the homogeneous solution. Using Pt electrodes (2 mm in diameter for anode; 1 mm for cathode), the galvanostatic electrolysis (0.5~1.0 µA) at room temperature afforded green solid on the anode side.

UV-vis-NIR spectra were measured on KBr pellets (240–2600 nm) with a Shimadzu UV-3100 spectrophotometer. FT-IR spectra were taken on KBr pellets with a Perkin-Elmer Paragon 1000 Series spectrophotometer (400–7800 cm⁻¹; resolution 2 cm⁻¹). Electrical conductivities were measured by the conventional two-probe method. Gold wires (15 µm in diameter) were attached to the samples using carbon paste.

2.2. X-ray structure determination
X-ray diffraction data of (TOT)ClO₄ were collected on an imaging plate type diffractometer (Mac Science DIP-2020K). Raw data reduction to $F^2$ was carried out using the DENZO program [6]. The data of (TOT)ReO₄ were collected on an automatic four-circle diffractometer (Mac Science MXC⁵). The structure was solved by a direct method of SIR2004 [7], and refined by a full matrix least-squares method on $F^2$ by means of Shelxl-97 [8]. Positional parameters of hydrogen atoms were calculated assuming the sp² configuration of carbon atoms. In (TOT)ClO₄, ClO₄ anions were severely disordered, and three orientations with the 0.34/0.33/0.33 occupancies were assumed. The parameters were refined
adopting anisotropic for non-hydrogen atoms and isotropic temperature factors for hydrogen and disordered oxygen atoms. The crystal structures were depicted by using Ortep-3 for Windows [9]. All computations were performed on the WinGX program package [10]. The crystallographic data of (TOT)ClO$_4$ and (TOT)ReO$_4$ are shown in table 1.

CCDC 696351 and 696352 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table 1.** Crystallographic data, data collection parameters, and structure refinement for (TOT)ClO$_4$ and (TOT)ReO$_4$

|                  | (TOT)ClO$_4$ | (TOT)ReO$_4$ |
|------------------|--------------|--------------|
| **Empirical formula** | C$_{18}$H$_9$ClNO$_7$ | C$_{18}$H$_9$NO$_7$Re |
| **Formula weight** | 386.71       | 537.47       |
| **Crystal appearance** | green platelet | green platelet |
| **Crystal dimensions (mm)** | 0.56 × 0.10 × 0.03 | 0.56 × 0.13 × 0.08 |
| **Temperature** | room temperature | room temperature |
| **Crystal system** | orthorhombic | monoclinic |
| **Space group** | Pbca (#61) | P2$_1$/n (#14) |
| **a (Å)** | 15.737(3) | 11.735(2) |
| **b (Å)** | 12.9690(9) | 12.306(2) |
| **c (Å)** | 15.446(3) | 11.061(2) |
| **β (º)** | 91.45(2) | 91.45(2) |
| **V (Å$^3$)** | 3152.4(9) | 1596.8(5) |
| **Z** | 8 | 4 |
| **$\rho_{obs}$ (g cm$^{-1}$)** | 1.63 | 2.236 |
| **$\mu$ (Mo K$_\alpha$) (mm$^{-1}$)** | 0.289 | 7.655 |
| **Absorption correction** | none | Ψ scan |
| **Max. and minimum transmission** | 1.000, 0.680 | 1.000, 0.680 |
| **No. measured reflections** | 23117 | 7490 |
| **No. unique reflections** | 2993 | 3665 |
| **$R_{int}$** | 0.065 | 0.052 |
| **No. reflections ($I > 2\sigma (I)$)** | 1317 | 2519 |
| **No. parameters** | 257 | 244 |
| **$R^2$ ($I > 2\sigma (I)$)** | 0.080 | 0.033 |
| **$wR^2$ (all data)** | 0.280 | 0.072 |
| **Goodness-of-fit, $S^c$** | 0.966 | 1.014 |
| **Max. shift/error in final cycle** | 0.00 | 0.00 |
| **Max. and minimum peaks** | 0.54, −0.47 | 0.86, −0.77 |

*a R = $\sum |F_{o}|-|F_{c}|/\sum |F_{o}|$.
*b wR = $\sum |F_{o}|^2 - |F_{c}|^2/\sum w|F_{o}|^2)^{1/2}$.
*c S = $\sum (|F_{o}|-|F_{c}|)^2/(N_{o} - N_{p})^{1/2}$, $N_{o}$: number of reflections observed, $N_{p}$: number of parameters.

2.3. Computational

The highest occupied molecular orbital (HOMO) of TOT molecule and the intermolecular overlap integrals between HOMO’s were calculated based on the crystal structure by means of extended Hückel method. The ζ-parameters of atomic orbitals were taken from ref. 11 for carbon and hydrogen atoms and from ref. 12 for nitrogen and oxygen atoms. All computation were carried out on the program developed by Mori et al. [11]
3. Results and discussion

3.1. Syntheses of (TOT)PF$_6$, (TOT)ClO$_4$, and (TOT)ReO$_4$

Radical cation salts of (TOT)PF$_6$, (TOT)ClO$_4$, and (TOT)ReO$_4$ were prepared by galvanostatic electrochemical oxidation in the presence of corresponding TBA salt. The experimental conditions are listed in Table 2. During the electrocrystallization, the colours of all electrolysis solutions changed from pale yellow to green, which are the colours of neutral TOT molecule and TOT$^+$ radical cation, respectively. The anode electrode was always partially-covered with green solid, and green platelets suitable for X-ray analysis were simultaneously obtained. The compositions of the salts were determined as 1:1 from X-ray structural analyses as described below. The electrochemical method in this work afforded the same PF$_6$ salt as that prepared by chemical oxidation [4]. Therefore, this report concentrates on (TOT)ClO$_4$ and (TOT)ReO$_4$.

Table 2. Experimental condition for electrocrystallization

| Salt          | TOT (mg) | Supporting electrolyte (mg) | Solvent (mL) | Current (µA) |
|---------------|----------|-----------------------------|--------------|--------------|
| (TOT)PF$_6$   | 5.3      | (TBA)PF$_6$, 62.3           | DCE, 18      | 0.5          |
| (TOT)ClO$_4$  | 11.6     | (TBA)ClO$_4$, 67.4          | THF, 18      | 1.0          |
| (TOT)ReO$_4$  | 7.9      | (TBA)ReO$_4$, 91.2          | THF, 18      | 1.0          |

*Total amount placed in anode and cathode arms.

Figure 1. (a) Crystal structure of (TOT)ClO$_4$. Donor arrangements projected along (b) the c-axis, (c) the a-axis, and (d) the b-axis. In (a) and (b), TOT molecules and ClO$_4$ anions in colour and gray are located at z = 3/4 and 1/4, respectively. (c) TOT molecules are located at x = 3/4. (d) TOT molecules are located at y = 3/4. The overlap integrals ($10^{-3}$) between HOMO’s are s = −0.10, t = −1.34, p = −1.21, q = −0.05, and r = 0.11.
3.2. Crystal structure of (TOT)ClO₄

Crystal structure of (TOT)ClO₄ and overlap integrals between HOMO’s are shown in figure 1. (TOT)ClO₄ crystallized in an orthorhombic system with space group Pbca. This salt shows very similar structure to that of (TOT)PF₆ which belongs to the same space group [4]. One TOT molecule and one ClO₄ anion were crystallographically unique. ClO₄ anions were located on the general position, and severely disordered. TOT⁺ radical cation showed a planar shape. TOT⁺ radical cation and ClO₄ anions were alternately-packed along the b and c-axes, which should interrupt the interaction between TOT⁺ radical cations. Although the structure is reminiscent of NaCl, anisotropic intermolecular interactions seem to arise from the size and shape mismatches between a planar TOT⁺ radical cation and a tetrahedral ClO₄ anion.

Overlap integrals between HOMO’s of TOT molecules were estimated based on extended Hückel method. As anticipated, calculated overlap integrals were anisotropic and considerably small. Even the maximum value was \( t = -1.34 \times 10^{-3} \), indicating a monomeric TOT⁺ radical cation.

![Figure 2](image)

Figure 2. (a) Crystal structure of (TOT)ReO₄. TOT molecules and ReO₄ anions in colour and gray are located at \( x = 3/4 \) and \( 1/4 \), respectively. Donor arrangements projected along (b), (c) the \( a \)-axis and (d) the \( c \)-axis. (e) Overlap mode in p1 and p2 projected perpendicular to molecular plane. (b) TOT molecules in colour and gray are located at \( x = 3/4 \) and \( 1/4 \), respectively. (c) TOT molecules in colour and gray are located at \( x = 5/4 \) and \( 3/4 \), respectively. (d) TOT molecules in colour and gray are located at \( z = 3/4 \) and \( 1/4 \), respectively. The overlap integrals \( (10^{-3}) \) between HOMO’s are \( a = 0.01, \ b = -0.01, \ p1 = 2.28, \ p2 = -0.02, \ q1 = 0.07, \ q2 = -0.19, \ r1 = 0.20, \) and \( r2 = 0.13 \).
3.3. Crystal structure of (TOT)ReO$_4$

Crystal structure of (TOT)ReO$_4$ and overlap integrals between HOMO’s are shown in figure 2. (TOT)ReO$_4$ crystallized in a monoclinic system with space group $P2_1/n$. One TOT molecule and one ReO$_4$ anion were crystallographically unique. Unlike ClO$_4$ anion in (TOT)ClO$_4$, ReO$_4$ anion were ordered even at room temperature. TOT$^+$ radical cation showed a planar shape similar to that in the ClO$_4$ salt. Although the crystal system is different from that of (TOT)ClO$_4$, an alternating arrangement of TOT molecule and ReO$_4$ anion was also observed in (TOT)ReO$_4$. All calculated overlap integrals were as small as those in (TOT)ClO$_4$. Paying attention to the overlap mode in the maximum overlap integral of p1 = $2.28 \times 10^{-3}$, only a peripheral part of TOT$^+$ radical cation was overlapped as shown in figure 2 (e), and the interplanar distance was 3.36 Å, indicating a very weak face-to-face interaction. Therefore, a monomeric electronic structure of TOT$^+$ radical cation is also expected in (TOT)ReO$_4$.

3.4. UV-vis-IR spectra and transport properties of (TOT)ClO$_4$ and (TOT)ReO$_4$

UV-vis-IR spectra of (TOT)ClO$_4$ and (TOT)ReO$_4$ along with TOT$^+$ radical cation and neutral TOT in CH$_2$Cl$_2$ [4] are shown in figure 3. The spectral feature of these two salts was remarkably similar to each other except for vibrational region of anion. Comparing with a solution spectrum of TOT$^+$ radical cation, the UV-vis-NIR region strikingly resembles the solution spectrum, and absorption bands more than 10000 cm$^{-1}$ are interpreted as intramolecular transitions. Judging from the absence of electronic absorption band less than 10000 cm$^{-1}$, the conjugated system of TOT$^+$ radical cation is virtually isolated in these salts. Single crystals of (TOT)ClO$_4$ and (TOT)ReO$_4$ exhibited low electrical conductivities of $\sigma_{RT} < 2 \times 10^{-6}$ and $2 \times 10^{-7}$ S cm$^{-1}$ at room temperature, respectively. These results are consistent with the extremely small overlap integrals estimated from the crystal structures of (TOT)ClO$_4$ and (TOT)ReO$_4$.

![Figure 3. UV-vis-IR spectra of (a) (TOT)ClO$_4$ in KBr, (b) (TOT)ReO$_4$ in KBr, (c) TOT$^+$ radical cation in CH$_2$Cl$_2$, and (d) neutral TOT in CH$_2$Cl$_2$.](image-url)
4. Conclusion
Radical cation salts, (TOT)PF$_6$, (TOT)ClO$_4$, and (TOT)ReO$_4$, were prepared by means of galvanostatic electocrystallization, two of which are new TOT radical cation salts. The crystal structures were solved. As well as the previous report of (TOT)PF$_6$, TOT$^+$ radical cation adopted a planar geometry also in (TOT)ClO$_4$ and (TOT)ReO$_4$. As was expected, TOT$^+$ radical cation seems to prefer a planar shape rather than a bowl one. Calculated overlap integrals between highest occupied molecular orbitals of TOT molecules indicated very weak intermolecular interactions in these salts. Although maximum overlap integrals of $t = -1.34 \times 10^{-3}$ in (TOT)ClO$_4$ and $p_1 = 2.28 \times 10^{-3}$ in (TOT)ReO$_4$ were numerically obtained, these values indicate no significant intermolecular interaction in these salts. In fact, virtually isolated electronic structure of TOT$^+$ radical cation in the salts was also confirmed by UV-vis-IR spectral study. Therefore, we can conclude that the overlap integrals of $1$~$2 \times 10^{-3}$ approximately means no intermolecular interaction by direct comparison with experimentally obtained UV-vis-IR spectra. At the present stage, a new phase transition system based on degree of freedom of TOT molecule is not obtained. However, the preparation toward such materials is now in progress.

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References
[1] Organic Conductors ed Kagoshima S, Kanoda K and Mori T 2006 J. Phys. Soc. Jpn. 75 051001-051016
[2] Ota A, Yamochi H and Saito G 2002 J. Mater. Chem. 12 2600
[3] Chollet M et al 2005 Science 307 86; Koshihara S and Adachi S 2006 J. Phys. Soc. Jpn. 75 011005
[4] Kuratsu M, Kozaki M and Okada K 2005 Angew. Chem. Int. Ed. 44 4056
[5] Kuratsu M, Suzuki S, Kozaki M, Shiomi D, Sato K, Takui T and Okada K 2007 Inorg. Chem. 46 10153
[6] Otwinowski Z and Minor W 1997 Processing of X-ray diffraction data collected in oscillation mode Methods in Enzymology 276 307
[7] Burla M C, Caliandro R, Camalli M, Carrozzini B, Cascarano G L, De Caro L, Giacovazzo C, Polidori G and Spagna R 2005 SIR2004: an improved tool for crystal structure determination and refinement J. Appl. Cryst. 38 381
[8] Sheldrick G M 1997 SHELX-97 A Program for Crystal Structure Refinement Univ. of Göttingen Germany Release 97-2
[9] Ortep-3 for Window Version 1.08 Farrugia L J, 1997 J. Appl. Cryst. 30 565
[10] WinGX Version 1.70.01 Farrugia L J 1999 J. Appl. Cryst. 32 837
[11] Mori T, Kobayashi A, Sasaki Y, Kobayashi H, Saito G and Inokuchi H 1984 Bull. Chem. Soc. Jpn. 57 627
[12] Summerville R H and Hoffmann R 1976 J. Am. Chem. Soc. 98 7240