

Crystal structures and properties of radical salts of a new series of tetrathiafulvalene derivatives incorporating fused ethyleneoxymethylene and ethylenethiomethylene units

Tomoko Inayoshi

Department of Chemistry and Biological Science, College of Science & Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagami-hara, Kanagawa, 252-5258, Japan



ARTICLE INFO

Keywords:

Tetrathiafulvalene (TTF) derivatives
Ethyleneoxymethylene (EOM)
Ethylenethiomethylene (ETM)
Radical cation salts
Crystal structure
Conductivity

ABSTRACT

Tetrathiafulvalene (TTF) derivatives have been widely investigated as functional molecular materials with conducting properties. Radical salts of tetrathiafulvalene (TTF) derivatives incorporating fused ethyleneoxymethylene (EOM) and ethylenethiomethylene (ETM) units were prepared by electrochemical oxidation. Crystal structures of some salts were determined by X-ray structure analyses. The AuI₂ salt of bis(ethyleneoxymethylene)-TTF (BEOM-TTF) (1) exhibits a metal-to-semiconductor (MS) transition at 295 K with a high room-temperature conductivity (σ_{RT}) of 25 S cm⁻¹ as determined by a two-probe method. Bis(ethylenethiomethylene)-TTF (BETM-TTF) (2) salts with 1:1 stoichiometry are insulators. The Br salt of 4,5-ethyleneoxymethylene-4',5'-ethylenedithio-TTF (EOMEDT-TTF) (3) exhibits a MS transition at 297 K with a high σ_{RT} of 11 S cm⁻¹. 3_2X salts (X = ClO₄⁻, PF₆⁻) have columnar structures and form head-to-tail dimers with O...H short contacts of the EOM groups. The ReO₄ salt of 4,5-ethyleneoxymethylene-4',5'-methylenedithio-TTF (EOMMDT-TTF) (4) exhibits a MS transition at 297 K with σ_{RT} of 4.2 S cm⁻¹ and a small activation energy of 0.023 eV below 297 K, and adopts κ -type packing. The salts of ethyleneoxymethylene-TTF (EOM-TTF) (5) and ethylenethiomethylene-TTF (ETM-TTF) (6) donors exhibit semiconductive behaviors. The salt of $5_3(\text{ClO}_4)_2$ has three crystallographically independent molecules and adopts head-to-head stacking with S...S and O...H short contacts in the triad. By comparing the intramolecular bond lengths of the molecules and splitting of the Raman bands, it was found that the $5_3(\text{ClO}_4)_2$ salt is in a charge order state. Incorporation of the EOM and ETM functional substituents on the TTF skeleton gives rise to many intermolecular interactions between donors in their salts.

1. Introduction

Tetrathiafulvalene (TTF) derivatives have been widely investigated as functional molecular materials with conducting properties. The fused outer heterocycles on the TTF skeleton play a very important role in intermolecular interactions through S...S and O...H short contacts. Syntheses and properties of nine new TTF derivatives containing one oxygen or one sulfur atom in the six-membered ring and their charge-transfer complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) derivatives have been described [1]. The four-probe dc electrical measurement of crystalline EOMMDT-TTF (4) complex with TCNQ gave

a room-temperature conductivity (σ_{RT}) value of 169 S cm⁻¹ with a metallic temperature dependence down to 102 K. The incorporation of ethyleneoxymethylene (EOM) and ethylenethiomethylene (ETM) functional groups on the TTF skeleton gave rise to specific intermolecular interactions between donors; many S...S, O...H, and S...H short contacts were produced in the crystal structures. In the present work, the preparation of TTF radical salts composed of donors (1–6 in Fig. 1), their electrical conductivities, and the crystal structures of 3_2ClO_4 , 3_2PF_6 , 4_2ReO_4 , and $5_3(\text{ClO}_4)_2$ salts are reported.

Abbreviations: TTF, tetrathiafulvalene; EDO, ethylenedioxy; EDT, ethylenedithio; EOM, ethyleneoxymethylene; ETH, ethylenethio; ETM, ethylenethiomethylene; MDT, methylenedithio; PT, propylenethio; BEDT-TTF or ET, bis(ethylenedithio)tetrathiafulvalene; BEDO-TTF, bis(ethylenedioxy)tetrathiafulvalene; BET-TTF, bis(ethylenethio)tetrathiafulvalene; BPT-TTF, bis(propylenethio)tetrathiafulvalene; BEOM-TTF, bis(ethyleneoxymethylene)tetrathiafulvalene; BETM-TTF, bis(ethylenethiomethylene)tetrathiafulvalene; EOMEDT-TTF, 4,5-ethyleneoxymethylene-4',5'-ethylenedithiotetrathiafulvalene; ETEDT-TTF, 4,5-ethylenethio-4',5'-ethylenedithiotetrathiafulvalene; EOMMDT-TTF, 4,5-ethyleneoxymethylene-4',5'-methylenedithiotetrathiafulvalene; SIET, symmetric isomer of ET; TCNQ, 7,7,8,8-tetracyano-*p*-quinodimethane

E-mail address: inayoshi@chem.aoyama.ac.jp.

<https://doi.org/10.1016/j.synthmet.2018.07.014>

Received 18 April 2018; Received in revised form 16 July 2018; Accepted 23 July 2018

0379-6779/ © 2018 Elsevier B.V. All rights reserved.

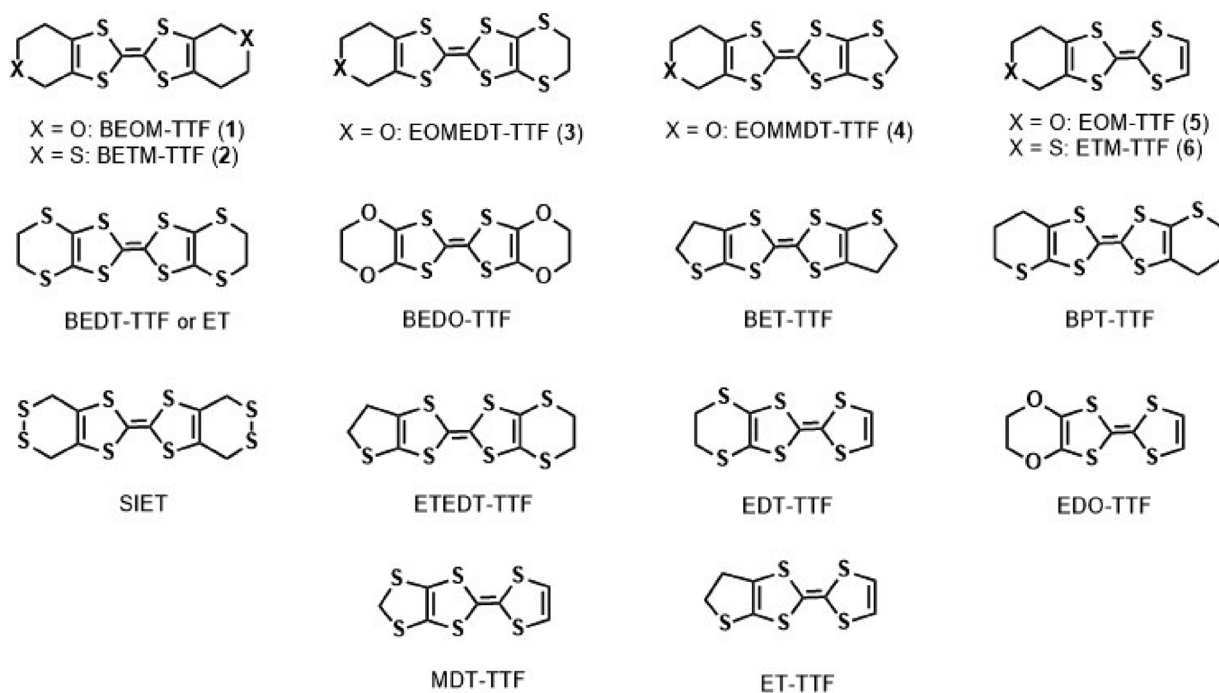


Fig. 1. Donors.

2. Experimental

2.1. Preparation of cation radical salts

The donor molecules 1–6 in Fig. 1 were prepared according to methods reported in the literature [1]. Tetrahydrofuran (THF), 1,1,2-trichloroethane (TCE), chlorobenzene (PhCl), and 1,2-dichloroethane (DCE) were freshly distilled according to standard procedures. $(n\text{-Bu})_4\text{NX}$ ($X = \text{Br}^-$, AuBr_2^- , ReO_4^- , CF_3SO_3^- , PF_6^- , HSO_4^- , BF_4^- , and ClO_4^-) salts, $\text{Et}_4\text{NFeCl}_4$ salt, and KX ($X = \text{ReO}_4^-$, AsF_6^- , and SbF_6^-) salts were obtained commercially from Aldrich Chemicals and purified by several recrystallizations. 18-Crown-6, KSCN, CuSCN, and $(n\text{-Bu})_4\text{NX}$ ($X = \Gamma^-$, IBr_2^- , I_3^- , and AuBr_2^-) were purchased from Tokyo Kasei Kogyo and purified by recrystallization. $(n\text{-Bu})_4\text{NAuI}_2$ was prepared from $(n\text{-Bu})_4\text{NAuBr}_2$ and $(n\text{-Bu})_4\text{NI}$ according to the literature [2]. $\text{K}[\text{Ag}(\text{CN})_2]$ was purchased from Kanto Chemical and used without further purification. The charge-transfer salts were prepared by electrochemical oxidation under constant or variable current conditions, or a constant voltage condition using an H-shaped cell with Pt electrodes, typical conditions of which are given in Table 1. The composition of the charge-transfer salts was determined by elemental analyses or X-ray structure analyses.

2.2. Single-crystal X-ray structure analysis

Diffraction data for all of the donors were collected with Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$) on a Bruker AXS APEX II CCD diffractometer equipped with a Japan Thermal Engineering Cryosystem DX-CS10KLD. All the structures were solved by a direct method using SHELXS-97 [3] and refined by the full-matrix least squares technique. Absorption corrections were applied using the multiscan procedure with SADABS. All non-hydrogen atoms were refined anisotropically for all the structures. The positions of hydrogen atoms were calculated with sp^2 or sp^3 configurations of the bonding carbon atoms and included in the analysis.

2.3. Raman spectroscopy

Raman spectra were recorded using a Renishaw inVia Reflex Raman microscope at room temperature. The sample was irradiated by a 532 nm laser. The intensity of the excitation light was reduced below 0.5 mW to avoid radiation damage. The spectral resolution was 2 cm^{-1} .

2.4. Electrical resistivity measurements

The temperature dependence of dc electrical resistivities were measured by four-probe or two-probe methods. The activation energy was calculated from the plot of $\ln(\rho_T)$ vs. $1/T$. Gold wires (25 μm o.d.) were glued to the samples with gold paint (Tokuriki Chemical, No. 8560). For powder samples, measurements were performed with pellets that were cut to form orthorhombic shapes.

3. Results and discussion

3.1. Crystal structures of salts

Single crystal X-ray structure analyses of radical salts were carried out as shown in Table 2.

Unfortunately, the crystal structure of the $1_2\text{AuI}_2(\text{THF})_{0.5}$ salt, which exhibited the highest electrical conductivity of the 34 radical salts, could not be solved due to the poor quality of the crystal.

3.1.1. Crystal structures of 3_2ClO_4 and 3_2PF_6 salts

Fig. 2 shows crystallographically independent two donor molecules of **3** and one ClO_4^- anion in the 3_2ClO_4 salt at 300 K. The 3_2PF_6 salt at 90 K is drawn as crystallographically independent one donor molecule and one-half of the PF_6^- anion in Fig. 3. The ratios of donor to anion for both salts were found to be 2:1. These crystal structures were solved with disorder for EOM and EDT groups and ClO_4^- anion, and without disorder for PF_6^- anion. The unit cells of both salts contain four donor molecules constructed by crystallographically equivalent two columns and two anions along the a -axis (Figs. 4 and 5). The donor radical cations in both salts are dimerized and form head-to-tail pairs (D1 in Fig. 4(a) and D1 in Fig. 5(b)) with O \cdots H short contacts of EOM groups

Download English Version:

<https://daneshyari.com/en/article/7873419>

Download Persian Version:

<https://daneshyari.com/article/7873419>

[Daneshyari.com](https://daneshyari.com)