Syntheses and structures of highly soluble bis(ethylenedithio)tetrathiafulvalene molecules with alkyl chains

I. Aoyagi, M. Katsuhara, T. Mori*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguroku, Tokyo 152-8552, Japan

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Abstract

Bis(ethylenedithio)tetrathiafulvalene (ET) molecules with one alkyl chain, CnET (n = 1–6) are synthesized. The solubility in usual organic solvents is remarkably improved without changing the electron donating ability, and good thin films are formed by the solution cast method. C1ET has the same dimer structure as ET, while the structures of the n = 2–4 molecules are composed of zig-zag columns.

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1. Introduction

Recently, organic devices, particularly organic thin-film transistors, have attracted a great deal of attention on account of the potential low-cost fabrication on large area and flexible substrates [1]. There are various fabrication methods of organic thin films such as thermal evaporation, spin-coat, dip-coat and solution cast methods. Among these methods, the solution cast method is easiest and most promising because of the relatively soft ambient-pressure and room-temperature conditions. On the other hand, bis(ethylenedithio)tetrathiafulvalene (ET) (Scheme 1) is well known as a good organic donor which affords many organic superconductors [2], but it is difficult to prepare good thin-films of ET because of the poor solubility in the usual solvents. Tetrathiafulvalene (TTF) molecules construct much larger bandwidth than such materials as polythiophene and pentacene usually used in thin film transistors, and if good thin films are formed, the large bandwidth is a great advantage in realizing high mobility. Many organic materials used as an active layer of electronic devices have alkyl chains to improve the solubility and orientation property. Along this line, we have attempted the replacement of one terminal hydrogen atom of ET by an alkyl chain (Scheme 1). Dimethyl-ET is known to form a superconductor [3], and diethyl-ET is also prepared [4], but the ET molecule with a single alkyl chain are scarcely explored, though the preparation of C1ET and C17ET has been reported [5]. In this paper, syntheses, structures, and chemical properties of CnET (n = 1–6) are reported.

2. Experiment

Synthesis of CnET (1a–1e) was achieved as shown in Schemes 2 (for n = 3–5) [6] and 3 (for n = 1, 2). In order to separate the asymmetric TTF in a pure form, cross coupling reactions by using cyanoethyl protecting groups were carried out.

Alkylated thiones (4) were prepared by the Diels–Alder reaction between oligo(4,5-dihydro-1,3-dithiole-2,4,5-trithione) (2) [7] and the corresponding 1-alkenes (3). 2,3-bis(cyanoethylthio)-6,7-ethylenedithiotetrathiafulvalenes (6) were obtained by triethyl phosphite-mediated cross coupling reactions between 4 and 5 [8]. Deprotection and treatment of 6 with dibromoethane provided the corresponding CnET (1) as orange solids [9]. All materials have chiral

Scheme 1. Molecular structures of ET and C1ET.
carbons at the bottom of the substituted alkyl chains, but these materials were obtained as racemic mixtures.

For C$_1$ET and C$_2$ET, the boiling points of the corresponding 1-alkenes are too low for the Diels–Alder reaction. Therefore, 8 was first obtained by triethyl phosphite-mediated cross coupling reactions between the thione (7) \cite{10} and 5, and the alkyl chain was introduced by using the corresponding 1,2-dibromoalkanes.

The electrochemical properties of C$_n$ET were investigated by cyclic voltammetry in benzonitrile in the presence of n-Bu$_4$PF$_6$ as a supporting electrolyte using a carbon glass electrode, a Pt counter electrode, and an Ag$^+/AgCl$ reference electrode at 25 °C, recorded on a Yanaco VMA-010 cyclic voltammogram.

The intensity data for X-ray crystal structure analysis were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation at room temperature. The structure was solved by the direct method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms).

AFM images were observed by an SPI3800 probe station and an SPA300 AFM unit with a Si$_3$N$_4$ cantilever.

3. Results and discussion

3.1. Melting points and redox properties

Melting points and the redox potentials of C$_n$ET together with the room-temperature electric conductivities are listed in Table 1. Fig. 1 shows the melting points of C$_n$ET. For $n = 1–3$, the melting point decreases as increasing the alkyl...
chain length. The melting point makes a minimum around \( n = 4–5 \), and turns up above \( n = 6 \). This upturn is attributable to the cohesive force of the long alkyl chains.

The donors display two redox waves corresponding to two-step one-electron transfers (Table 1). The redox potentials are almost the same as those of ET, suggesting that the replacement of a hydrogen atom with an alkyl chain does not change the electron donating ability.

### 3.2. Solubility of \( C_n\text{ET} \)

Solubility of \( C_n\text{ET} \) in the usual organic solvents such as CHCl3, CCl4, xylene, toluene, PhCN, \( n \)-hexane, cyclohexane and methanol was examined. When the alkyl chain is relatively short (\( n = 1 \) and 2), the solubility is slightly enhanced in comparison with ET. When the alkyl chain becomes longer (\( n > 3 \)) the solubility is remarkably improved, and these donors dissolve in all of the above polar and non-polar solvents. So we prepared the solution cast films of the present materials from the chloroform solution on a SiO2 substrate. Fig. 2 shows AFM images of the solution cast films of ET and \( C_4\text{ET} \). The thin film of ET consists of discrete microcrystals, whereas that of \( C_4\text{ET} \) is remarkably improved in the film quality.

### 3.3. Crystal structures of \( C_n\text{ET} \)

X-ray single crystal structure analysis is carried out for \( C_1\text{ET} \), \( C_2\text{ET} \), \( C_3\text{ET} \) and \( C_4\text{ET} \) [11]. The crystal structure of \( C_1\text{ET} \) is the same as ET as shown in Fig. 3 [12]. The molecules are strongly dimerized and they do not form a column structure (Fig. 3). The methyl carbon is attached to two ethylene carbons in a 50% probability with elongated temperature factors, because the compound is a racemic mixture. The intermolecular overlap integrals of ET and \( C_1\text{ET} \) are listed in Table 2 [13]. Though all lattice constants are larger than ET, the overlap integrals are not systematically changed.

The crystal structures of \( C_n\text{ET} \) (\( n = 2–4 \)) are entirely different from ET, but \( C_2\text{ET} \) and \( C_3\text{ET} \) are isostructural (Fig. 4). The molecules are stacked along the \( c \) axis, but the molecular long axes of the \( C_n\text{ET} \) molecules in a column are alternately tilted from each other (Fig. 4(a)). Consequently, the molecular long axes are tilted so as to form fourfold periodicity like down–up–down along the \( b \) axis (Fig. 4(a)). In addition, only the half of the TTF part overlaps in a chain, and these columns are considerably interpenetrated (Fig. 4(a) and (c)). Accordingly,
the calculated intrachain overlap integral \( c \) is much smaller than the interchain interactions, \( p_1 \), \( p_2 \) and \( p_3 \) (Table 2). Although, the alkyl chain is positionally ordered, an \( S \)-form makes an \( R \)-form by an inversion operation, and the crystal is a racemic mixture.

The crystal structure of \( C_4 \)ET is depicted in Fig. 5. The molecules construct interpenetrated columns similar to \( C_2 \)ET and \( C_3 \)ET, whereas all molecules are parallel to each other. The intrachain overlap integrals \( b_1 \) and \( b_2 \) are not larger than the interchain overlap integrals (\( p, q, \) and \( r \) in Table 2).

In ET and \( C_1 \)ET, the intradimer interaction is overwhelmingly large (\( >10 \times 10^{-3} \)), and the interdimer interactions are comparatively small (\( <1.5 \times 10^{-3} \)). By contrast, \( C_2 \)ET, \( C_3 \)ET, and \( C_4 \)ET have networks of relatively large interactions (\( 2–8 \times 10^{-3} \)), which are advantageous in carrier transport. The interactions along the stack are not very large, and major interactions run in the interstack directions.

### 4. Conclusion

In this work, syntheses and crystal structures of alkyl substituted ET are studied. The redox potentials represent that the substitution of alkyl chains does not change...
the electron donating ability of ET. The length of alkyl chains also improves the solubility of these molecules. The analysis of the intermolecular overlap integrals shows that the intermolecular interactions are improved as increasing the alkyl chain length. The device properties of this kind of materials will be reported shortly.

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