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Synthesis, crystal structure, and charge-transfer complexes of TTF derivatives having two imidazole hydrogen-bonding units

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ABSTRACT

New hydrogen-bond functionalized tetrathiafulvalene (TTF) derivatives (**1** and **2**) having two imidazole moieties, which are attached to TTF at the 2- and 4-positions in the imidazole ring, respectively, were synthesized. Electrochemical measurements indicated that the introduction of imidazole moieties at 2- or 4-positions slightly reduced or enhanced the electron-donating ability of TTF. In the crystal structure of **1**, N–H⋯N hydrogen-bonds of the imidazole ring formed a two-dimensional sheet, and further π-stacks on the TTF skeleton built up a one-dimensional column. Mixing **1** with electron-acceptors afforded fully ionic charge-transfer complexes having a 1:1 donor–acceptor ratio, while complex formation of **2** with tetracyanoquinodimethane and *p*-chloranil yielded partial charge-transfer complexes showing semiconducting behaviors (room temperature conductivities$=10^{-3}$–10^{-2} S cm^{-1}).

1. Introduction

Hydrogen-bond (H-bond), a robust and directional intermolecular interaction, is widely utilized as a powerful tool to construct supramolecular assemblies in the recent development of molecule-based materials [1,2]. In the research field of conducting charge-transfer (CT) complexes [3,4], introduction of H-bond functional groups into tetrathiafulvalene (TTF) [5] and incorporation of H-bonding counter-parts [6–8] have been achieved to regulate molecular arrangement in the solid state.

To explore new conducting CT complexes whose crystal and electronic structures are modulated by H-bonds, we have previously designed an imidazole-substituted TTF derivative (TTF-Im) [9–11]. It was demonstrated for the first time that H-bonds between TTF-Im and electron-acceptor molecules can control the ionicity of CT complexes by site-selective molecular recognition and modulation of redox abilities of donor and acceptor molecules [11]. These electronic effects of H-bond provided highly conducting CT complexes. The imidazole-annelated TTF derivatives, which have been investigated from the viewpoint of cooperation between proton-transfer and CT, also construct H-bonded self-assemblies [12,13]. In addition to the investigations on H-bond functionalized TTF derivatives, we have also studied the synthesis of oligo(imidazole)s and CT complexes of their protonated species with tetracyanoquinodimethane (TCNQ) radical anions, in which the multi-dimensional H-bonds of oligo(imidazole)s constructed well-ordered structures to yield highly conducting complexes [14–17].

The combination between TTF-Im and oligo(imidazole)s is expected to give novel strategy to realize molecular materials exhibiting intriguing properties based on the electronic modulation effect and multi-dimensional H-bond network. In the present study, we newly synthesized two H-bond functionalized TTF derivatives having two imidazole moieties (**1** and **2**, Chart 1), in which imidazole rings are attached to TTF at the 2- and 4-positions, respectively. Their electrochemical measurements and crystal structure of **1** were investigated. Physical properties of their CT complexes are also presented in this article.

2. Experimental

2.1. Synthesis

Preparations of **1** and **2** were performed by the Stille-type cross coupling reactions between bis(tributylstannylated)TTF and *N*-[2-(trimethylsilyl)ethoxy]methyl (SEM)-protected 2- or 4-iodoimidazole, respectively, followed by the deprotection using tetrabutylammonium fluoride (Scheme 1) [18,19]. *E*- and *Z*-isomers were yielded in the reaction, and were not isolated since they change to each other due to rotation at the central C=C bond. Single crystals of **1** suitable for X-ray structure analysis were obtained by the vapor diffusion method using DMSO and MeCN [20]. CT complexes were prepared by mixing the solutions of donor and acceptor (TCNQ, *p*-chloranil (QCl_4), and

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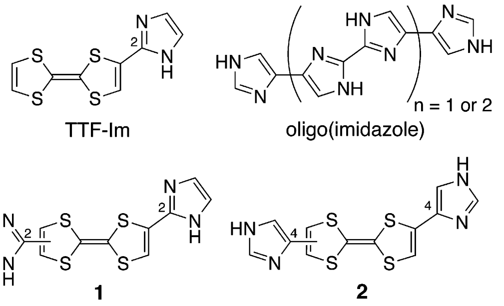
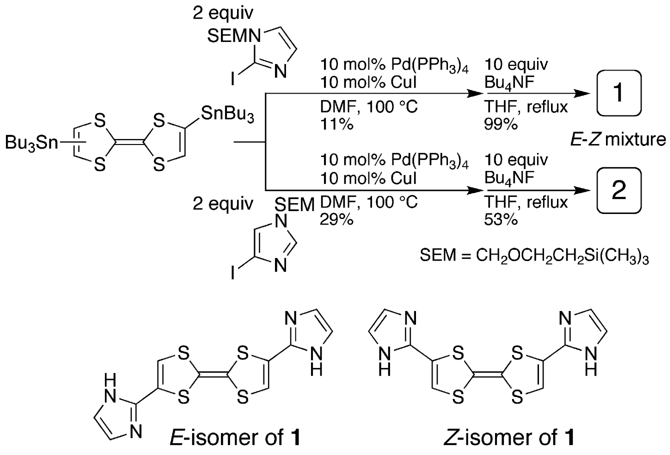


Chart 1. Molecular structures of TTF-Im, oligo(imidazole)s, **1**, and **2**.



Scheme 1. Synthetic procedures of **1** and **2**, and molecular structures of *E*- and *Z*-isomers of **1**.

2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)) in PhCN–DMF–CH_2Cl_2 for **1** and in THF for **2** [21,22].

2.2. Measurements

Cyclic voltammetry measurements were made with an ALS Electrochemical Analyzer model 612A in the DMF solution containing tetraethylammonium perchlorate at room temperature. The results were calibrated with ferrocene/ferrocenium couple (Fc/Fc^+). X-ray crystallographic measurement was performed on a Rigaku Saturn CCD area detector with a graphite monochromated Mo Kα radiation (λ=0.71070 Å). Structure was determined by a direct method (SIR-92 [23]), and refined with a full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. Positional parameters of hydrogen atoms were calculated and included in the final refinement with isotropic thermal factors. Direct current electrical conductivity measurements were made on compressed powder pellets by a conventional two- or four-probe method using gold paint and gold wires.

3. Results and discussions

3.1. Electrochemical measurements

Both **1** and **2** exhibited reversible two-stage redox processes in the cyclic voltammetry measurements. Table 1 summarizes the oxidation potentials (E^{ox}) of **1**, **2** and TTF. E^{ox1} of **1** and **2** (-0.05 and -0.12 V, respectively) indicate that these molecules possess comparable electron-donating abilities to that of TTF. Substitution of TTF with imidazole moieties at the 2- and 4-positions resulted in the slight positive and negative shifts from that of TTF, respectively. This behavior was also observed in the mono-substituted derivatives [9] (Table 1).

Table 1
Oxidation potentials (E^{ox}) of **1**, **2**, and TTF (V vs. Fc/Fc^+)[a].

	E^{ox1} (V)	E^{ox2} (V)	ΔE (V)
1	-0.05	+0.25	0.30
2	-0.12	+0.15	0.27
TTF	-0.09	+0.15	0.24

[a] Conditions: solvent, DMF (0.1 M Et_4NClO_4); counter/working/reference electrodes, Pt wire/glassy carbon/Ag/$AgNO_3$ (0.01 M in MeCN).

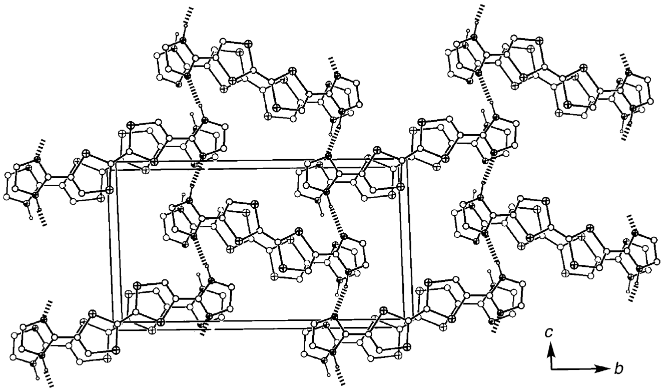


Fig. 1. Crystal structure of **1** viewed nearly along the *a*-axis showing the two-dimensional H-bond network and π-stacking column.

3.2. Crystal structure of 1

Crystal structure of **1** consisted only of the *E*-isomer. A half of the molecule was crystallographically independent, and the inversion center located at the central C=C bond. The TTF skeleton was planar, and the imidazole ring showed a twisted configuration to the TTF moiety by 12.6°. The imidazole moiety was connected through N–H···N H-bonds (2.97 Å) along the *c*-axis to form a two-dimensional sheet (Fig. 1). The molecules were stacked with a face-to-face distance of 3.50 Å to construct a one-dimensional column along the *a*-axis.

3.3. Properties of CT complexes

Fig. 2 presents the electronic spectra of CT complexes of **1** and **2** with TCNQ, DDQ and QCl_4. Table 2 summarizes donor–acceptor (D:A) ratios estimated by elemental analyses, the lowest CT absorption bands, and transport properties of CT complexes [21,22]. The protonation on the imidazole moiety in the CT complex formation is hardly expected because the proton-accepting abilities of **1** and **2** should be too weak to withdraw proton from the reaction system (H_2O, etc.) considering the small pK_a value (3.6) of protonated species of TTF-Im [24]. The complexes of **1** were characterized as 1:1 fully ionic CT complexes from the elemental analyses and intermolecular CT absorption bands at 9000–13 000 cm^{-1} (Fig. 2a, gray lines) [25–27]. Fully ionic states of the acceptor moieties were also suggested by the resemblances in IR spectra with their radical anion salts. The complexes were insulators with room temperature conductivities (σ_{RT}) of 10^{-7}–10^{-6} S cm^{-1} and activation energies (E_a) of 0.35–0.53 eV. From the formation of D–A–D 2:1 H-bond triad in the CT complexes of mono-substituted