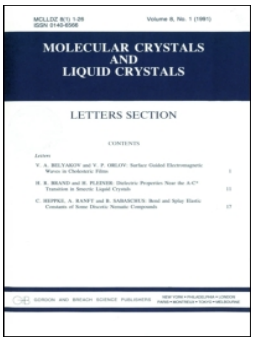

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Development of organic thin film devices based on Cu(II) complex with tetrathiafulvalene moieties in the ligands

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ABSTRACT
Paramagnetic metal complexes with tetrathiafulvalene moieties in its ligands, $[\mathrm{Cu^{II}(EDT\text{-}sae\text{-}TTF)_2}]$ (**1**) and two new derivatives were investigated towards the potential application to the organic thin film transistor (OTFT) with magnetic field responsiveness. The complex **1** and its benzene substituted derivative, $[\mathrm{Cu^{II}(Bz\text{-}sae\text{-}TTF)_2}]$ (**2**), gave semiconducting radical cation salts with fairly good electrical conductivity. A field effect transistor (FET) device fabricated with the spin-coated film of **1** was operative, but its performance was quite low. Atomic force microscopy (AFM) images revealed that the spin-coated film of **1** consists of very small grains with the size of about 10 nm, which can be responsible for the low device performance.

KEYWORDS
molecular conductor; paramagnetic metal complex; TTF-ligand; organic thin film transistor; spin-coated film

Introduction

Organic semiconductors have been attracting more and more interests because of their potential application as the practical electronic devices with unique features which cannot be seen in the conventional inorganic Si-based semiconductor devices. In order to explore new functionalities, introducing spin degree of freedom into the electronic devices is considered as a promising new class of approaches and semiconducting materials with spin-related functions, such as spin-valve, spin metal-oxide-semiconductor field effect transistor (spin MOSFET), and so on, have been extensively studied mainly with inorganic materials [1, 2]. In the spin-related devices, ferromagnetic metal contacts are used to inject the polarized electron spins into the semiconducting transport layer and retaining their polarization over the semiconducting channel is an important research issue for the application of such spin devices [3]. One of the possible approaches for preservation of the spin polarization may be utilizing an organic conductor with paramagnetic metal ion as the semiconducting layer.

Molecular magnetic conductors have generally been developed by the combination of organic donors, mainly tetrathiafulvalene (TTF) derivatives, and counter anions involving paramagnetic metal ions. Because the molecular conductors are radical salts, they are

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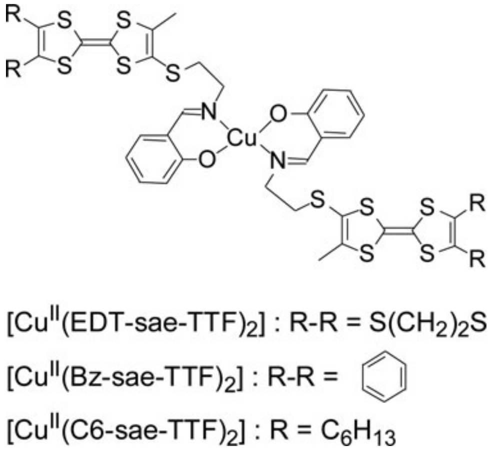
not suitable for the organic devices. On the other hand, we have synthesized a Schiff base type TTF-ligand, EDT-Hsae-TTF (4-(2-salicylideneiminoethylthio)-5- methyl-4′,5′-ethylenedithio-TTF), and its paramagnetic metal complex, [Cu^{II}(EDT-sae-TTF)$_2$] [4]. We have also succeeded in preparation of cation radical salts of [Cu^{II}(EDT-sae-TTF)$_2$], which are semiconductive with relatively high conductivities due to the partially oxidized states of the TTF moieties in the ligands [5]. Since the valence state of [Cu^{II}(EDT-sae-TTF)$_2$] is neutral, [Cu^{II}(EDT-sae-TTF)$_2$] is soluble to common organic solvents. In addition, substantial intermolecular interaction exists between TTF moieties through short sulfur contacts in the crystalline state. Therefore, [Cu^{II}(EDT-sae-TTF)$_2$] can be a possible material to provide a solution-processed organic thin film transistor (OTFT) device. In this paper, we investigated a preparation of the thin film [Cu^{II}(EDT-sae-TTF)$_2$] and a fabrication of the TFT devices. In addition to [Cu^{II}(EDT-sae-TTF)$_2$], we synthesized new derivatives substituted by benzene rings, [Cu^{II}(Bz-sae-TTF)$_2$], and long alkyl chains, [Cu^{II}(C6-sae-TTF)$_2$], in order to enhance the intermolecular interaction.



Experimental

Syntheses of Schiff base type TTF-ligands and their Cu(II) complexes were carried out according to the method reported previously [4]. Cyclic voltammetry was performed through the application of an electrochemical analyzer (ALS model 620A) at 25°C in dichloromethane containing n-Bu$_4$NPF$_6$ as a supporting electrolyte at a scan rate of 100 mV s^{-1}, using glassy carbon working and counter electrodes and a saturated calomel electrode (SCE) as a reference electrode. The solution was deaerated with N$_2$ bubbling before measurements.

Fabrication of the thin films of TTF-based Cu(II) complexes was performed by a spin-coating method from chloroform solution with rotating speed of 1500 rpm, onto a quartz substrate. The surface of the substrate was treated with hexamethyldisilazane before spin-coating. Morphology of the thin film was investigated by the atomic forth microscopy (AFM) using a Seiko Instruments, SPI 3800 and SPA 300. The FET devices were constructed by top-contact method on an n-type silicon wafer covered with SiO$_2$. Each chloroform solution of TTF-based Cu(II) complexes was spin-coated at 1500 rpm on the SiO$_2$ surface which was treated with hexamethyldisilazane before spin-coating. Gold source and drain electrodes were deposited on the films by using a resistive heating evaporation source. The FET properties were evaluated by using semiconductor characterization system (Keithley 4200) under nitrogen atmosphere.

Table 1. Redox potentials of TTF-metal complexes and their corresponding ligands.[a]

Compounds	E_1^{ox}	E_2^{ox}	$\Delta E\ (= E_2^{ox} - E_1^{ox})$
$[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$	0.45	0.83	0.38
EDT-Hsae-TTF	0.43	0.85	0.42
$[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]$	0.49	0.91	0.42
Bz-Hsae-TTF	0.48	0.95	0.47
$[Cu^{II}(C6\text{-}sae\text{-}TTF)_2]$	0.48	0.83	0.35
C6-Hsae-TTF	0.45	0.85	0.40

[a] Given in volt versus a SCE; 0.1 M n-Bu_4NPF_6 in CH_2Cl_2; glassy carbon electrode.

Results and discussion

Synthesis and electrochemical properties

New Cu(II) complexes were synthesized by the addition of methanol solution of copper chloride in the presence of triethylamine to dichloromethane solution of TTF-ligands which were prepared by our reported method [4].

Redox potentials of new TTF-based Cu(II) complexes, $[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]$ and $[Cu^{II}(C6\text{-}sae\text{-}TTF)_2]$, are summarized in Table 1, together with those of $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$ and the corresponding TTF-ligands. Similarly to $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$, all the new TTF-complexes exhibited two pairs of reversible redox waves corresponding to the oxidation from TTF moieties in the ligands. Compared with the redox potentials of TTF-ligands, the first oxidation potentials (E_1^{ox}) of all the TTF-complexes are higher, indicating that complexation with Cu(II) ion causes a decrease of the electron-donating ability. On the other hand, the ΔE ($= E_2^{ox} - E_1^{ox}$) values of the TTF-complexes are smaller than those of the corresponding TTF-ligands, meaning a decrease of on-site Coulombic repulsion involved in the formation of dicationic species. Since the TTF-complexes retain the redox ability of TTF, we examined preparation of a cation radical salt of $[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]$ by electrochemical crystallization with constant current in $CHCl_3$ and obtained a semiconducting partially oxidized radical salt, $[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]AsF_6$. The electrical conductivity of this salt was enhanced by two orders of magnitude compared with the radical salts of $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$ ($[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]AsF_6$: $\sigma(295K) = 0.37\ S\ cm^{-1}$; $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]PF_6$: $\sigma(295K) = 6.1 \times 10^{-3}\ S\ cm^{-1}$).

Thin films of TTF-based Cu(II) complexes

Absorption spectra of the spin-coated films of $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$ and $[Cu^{II}(C6\text{-}sae\text{-}TTF)_2]$ showed absorption peaks corresponding to TTF moieties at 300 – 400 nm, but no absorption peaks were observed for $[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]$. Because solubility of $[Cu^{II}(Bz\text{-}sae\text{-}TTF)_2]$ to $CHCl_3$ is very low, thin film with good quality could not be obtained for this complex. We also tried to prepare thin films by a vacuum deposition method, but thin films were not obtained for all the complexes probably due to decomposition of the complexes during the deposition process.

Top-contact FET devices fabricated using spin-coated films of $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$ exhibited p-channel characteristics corresponding to the TTF moieties being responsible for the hole mobility. Figure 1 shows the drain current (I_D)-drain voltage (V_D) and the I_D-gate voltage (V_G) characteristics of OTFT based on $[Cu^{II}(EDT\text{-}sae\text{-}TTF)_2]$. The values of hole mobility and on/off ratio were calculated to be $4.7 \times 10^{-7}\ cm^2\ V^{-1}\ s^{-1}$ and 9.7×10^2, respectively. In order to improve the device performance, the thin film was annealed at 40°C for

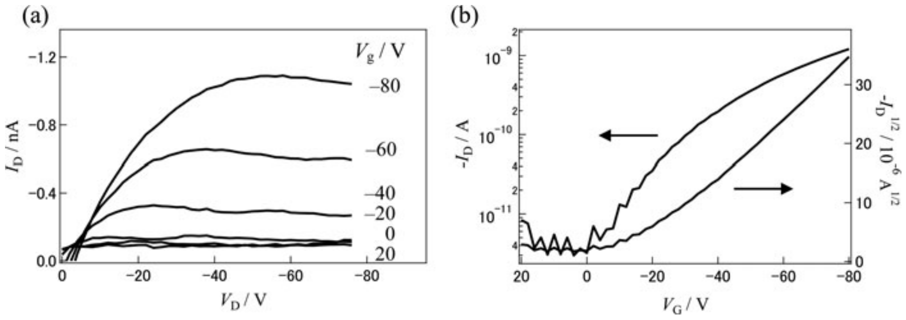


Figure 1. (a) I_D-V_D and I_D-V_G characteristics of OTFT based on [Cu^{II}(EDT-sae-TTF)$_2$].

1.5 h under a N_2 atmosphere, but no remarkable change was observed. The device using spin-coated film of [Cu^{II}(C6-sae-TTF)$_2$] did not show any FET performance.

In order to investigate the structure of the spin-coated films of TTF-metal complexes, AFM images of the TTF-complexes were measured for [Cu^{II}(EDT-sae-TTF)$_2$] and [Cu^{II}(C6-sae-TTF)$_2$]. As shown in Figure 2, the spin-coated film of [Cu^{II}(EDT-sae-TTF)$_2$] was composed of a relatively uniform film with very small grains (less than 10 nm). It is known that the grain size affects the FET performance; thin films with the larger grain size show the better device performance [6]. Thus, the small grain size is likely the cause of the bad FET performance of the [Cu^{II}(EDT-sae-TTF)$_2$] thin film. The AFM images of the spin-coated film of [Cu^{II}(C6-sae-TTF)$_2$] showed that the film morphology is also relatively smooth but the grain size is smaller than that of the [Cu^{II}(EDT-sae-TTF)$_2$] thin film.

In summary, we investigated preparation of thin films by spin-coating method and fabricated the FET device of spin-coated films of TTF-based paramagnetic metal complexes. Among the TTF-complexes, only the thin film of [Cu^{II}(EDT-sae-TTF)$_2$] showed FET properties, although the device performance was very low. It is reported that the FET devices based on single crystals of dibenzo-TTF showed high field-effect mobilities in the rage of 0.1 – 1 cm^2 V^{-1} s^{-1} [7]. Therefore, benzo-derivative of TTF-complex, [Cu^{II}(Bz-sae-TTF)$_2$], may have a potential to give OTFTs with higher performance than [Cu^{II}(EDT-sae-TTF)$_2$]. Also, solution-processed OTFTs using zone-casting or spin-coating methods of TTF derivatives with long alkyl chain substituents exhibited relatively high FET performance [8, 9]. In these cases, the lengths of the alkyl groups are longer than *n*-dodecyl group. Thus, substituting *n*-hexyl groups of [Cu^{II}(C6-sae-TTF)$_2$] with much longer alkyl groups could provide solution-processible OTFTs with higher performance than [Cu^{II}(EDT-sae-TTF)$_2$]. Because the present FET device

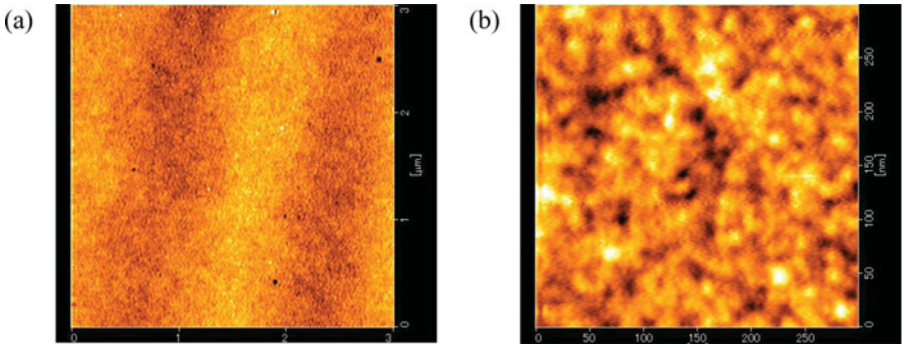


Figure 2. AFM images of [Cu^{II}(EDT-sae-TTF)$_2$] thin film (a) 3 × 3 μm (b) 300 × 300 nm.

involves the local magnetic spin in the semiconducting active layer, the FET properties can be controlled by the application of an external magnetic field. Thus, improvement of the device performance should be significant to investigate the spin-related functionality. Further works on investigation of processing conditions of spin-coated films for [Cu^{II}(Bz-sae-TTF)$_2$] and development of new TTF-complexes with longer alkyl groups are ongoing.

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