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Structural and Electrical Properties of Organic Conducting Polymers Bearing Tetrathiafulvalene Backbone

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The structural and electrical properties of a new organic conducting polymer bearing a tetrathiafulvalene backbone whose termini are capped with the thioacetyl group were investigated. AFM observations indicated that on a gold surface, the polymers form rigid rod-like structures with a stretched length of about 50 nm, which is comparable to its average length (~60 nm). The current-voltage characteristic exhibited semiconducting behavior with a conductivity of 1.0×10^{-5} Scm^{-1}. *A doping measurement was also performed using iodine. The current was enhanced* 10^2–10^4 *times after doping indicating the highly electron-donating nature of the polymer.*

Keywords: current-voltage characteristic; doping effect; organic conducting polymer; rigid polymer; tetrathiafulvalene

INTRODUCTION

Tetrathiafulvalene (TTF) derivatives have been intensively studied for several decades because of their ability to form organic metals and superconductors with various acceptor species [1–3]. In such organic crystalline materials, the TTF molecules form one-dimensional (1D) columns in a face-to-face stacking manner. In addition, each 1D column interacts with neighboring columns anisotropically owing to widespread chalcogen orbitals and this results in a quasi

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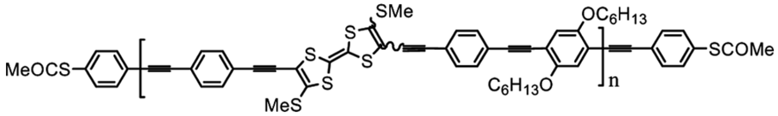

FIGURE 1 Chemical structure of TTF polymer **1**.

two-dimensional electrical property. Therefore, controlling the intermolecular interaction is one of the most important factors when designing molecules with the desired physical property. Although there have already been many studies based on TTF derivatives, most have been limited to small molecules because of low solubility and synthesis difficulties. The incorporation of a TTF unit into a polymer is attracting considerable interest with a view to developing a variety of organic conducting materials, however there have been few reports on this topic [4–6]. The published work can be divided into two approaches: (1) a pendant of the TTF unit is used as a side-chain in the polymer [5,6], (2) a TTF unit is introduced into the polymer backbone [6]. The introduction of a TTF unit into a conducting polymer is advantageous in two ways. First, the processability is improved by employing a solution process, which enables us to fabricate a high quality thin film with a large area. Second, in the latter case, the interchain interaction between neighboring polymers is enhanced by a side-by-side interaction with widespread sulfur orbitals in addition to the backbone conjugation. Taking the above advantages into account, we recently designed and synthesized a new organic conducting polymer **1** bearing a TTF backbone [7]. The chemical structure of the polymer is shown in Figure 1. This polymer has a π-conjugated electronic structure consisting of an alternating combination with a TTF unit and a phenyleneethynylene unit, and is expected to be rigid and conducting. In this paper, we investigate the molecular structure of **1** on solid surfaces using atomic force microscopy (AFM), and the electrical property of the thin film of **1**. Charge transfer complexes of **1** with iodine are also measured to evaluate the donor ability of the polymer.

EXPERIMENTAL

The synthesis procedure of the TTF polymer **1** is described in detail in our previous paper ($M_w = 2.28 \times 10^4$, $M_n = 7.25 \times 10^3$, $M_w/M_n = 3.1$) [7]. For the AFM study, we prepared samples on three different surfaces, namely Au(111), hydrogen-terminated Si(111) and SiO_2. A flat Au(111) surface was obtained by washing a gold substrate with pure water, acetone and ethanol, followed by three flame annealing treatments. A flat hydrogen-terminated Si(111) surface was obtained by treating Si(111) with NH_4F solution, and then drying it in a nitrogen gas stream. Samples of the polymer for the AFM measurements were prepared by casting a droplet of 10^{-1}–10^{-3} wt% toluene solution on a tilted substrate. For electrical measurements, interdigitated array electrodes with 5 digits on each electrode, a digit length of 100 μm and a channel length of 1 μm were fabricated on a silicon substrate with a 300 nm oxidized layer by conventional photolithography. Thin films were prepared by a spin coating method using 0.5 wt% toluene solution. Electrical measurements were performed in a vacuum to prevent the oxidation of the polymer.

RESULTS AND DISCUSSION

Molecular Structure of 1 on Solid Surface

AFM topographies of the polymers on Au(111) are shown in Figure 2. When we used a dilute solution of the polymer (10^{-3} wt%) to prepare the sample, we observed rigid rod-like structures with a stretched length of ~50 nm, a typical width of 5–10 nm and a typical height of 2 nm in addition to the triangular structures of the Au(111) surface (Fig. 2(a)). This result indicates that most polymers tend to form a bundle consisting of a few polymer chains. In contrast, poly(*p*-phenyleneethynylene), in which the TTF units in the polymer are replaced by phenyl rings, tends to form stretched single polymer structures [8]. This difference is presumably due to an enhancement of the intermolecular interaction caused by the introduction of the TTF units. The length of the polymer is in good agreement with the average length estimated from ^{1}H-NMR (n ~ 20, 60 nm). If the density of the

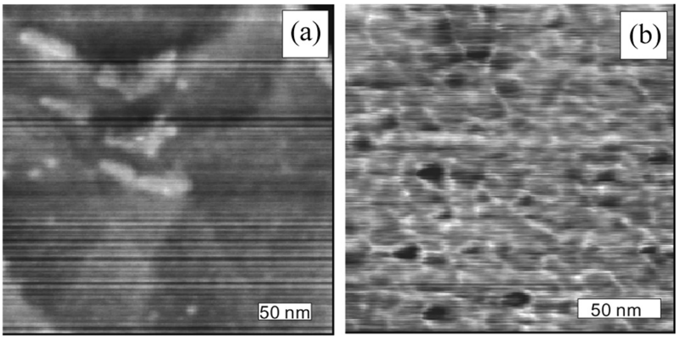

FIGURE 2 Tapping-mode AFM topographies of **1** on an Au(111) surface, (a) low density, (b) high density. Scale bar: 50 nm.

polymer increases (10^{-1} wt%), each bundle forms a network structure as shown in Figure 2(b).

Figure 3 shows an AFM topographic image of the polymer on hydrogen-terminated Si(111). Under this condition, most polymers form a lump-like structure by self-condensation that originates from a repulsive interaction with air [9]. However, in some cases we observed rigid chain-like structures as indicated by solid arrows. The stretched direction of the polymer corresponds to the flow direction of the solution during sample preparation. We assume this is due to the rigid nature of the TTF polymer. The TTF polymer has 6 sulfur atoms per TTF unit in addition to 2 sulfur atoms at each terminus. On a gold surface, the strong attractive interaction between the gold and sulfur atoms in the TTF polymer may cause the flat-on adsorption of the polymer. In such a situation, the polymers exhibit not an aggregation to form a lump-like structure, but an intrinsic nature of the polymer resulting in a stretch of the polymer backbone. On the other substrate, since the interaction between the polymer and surface is weakly attractive or repulsive, the strong repulsive interaction with air mainly contributes to the morphology. This is why lump-like structures are predominant on hydrogen-terminated Si(111). The

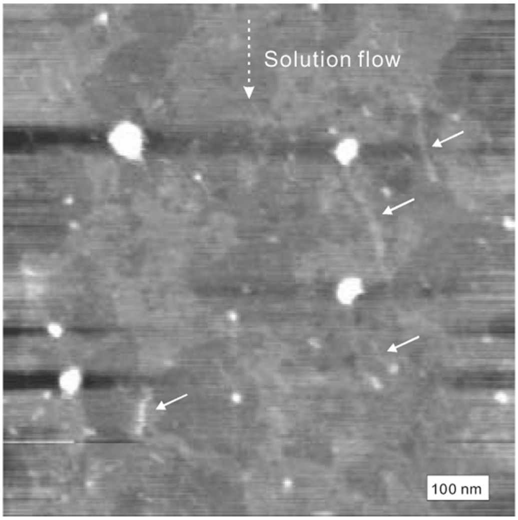

FIGURE 3 Tapping-mode AFM topography of **1** on a hydrogen-terminated Si(111) surface. A rigid rod-like structure was sometimes observed as indicated by the solid arrows. The stretched direction of the polymer corresponds to the flow direction of the solution as depicted by the dotted arrow. Scale bar: 100 nm.

polymer on a hydrophilic SiO_2 surface also exhibited a lump-like structure with a height of 10 nm.

Electrical Properties of Thin Films

The I_{sd}-V_{sd} characteristic of the thin film of **1** at room temperature is shown in Figure 4. The result demonstrates that the polymer thin film exhibits ohmic conduction in the low electric field region ($<2 \times 10^4$ Vcm^{-1}), and non-ohmic conduction in the high electric field region ($>2 \times 10^4 Vcm^{-1}$). Sometimes, current jumps were observed in the fairly high electric field region. The conductivity of the thin film is estimated to be $1.0 \times 10^{-5} Scm^{-1}$ from the ohmic region, which is a representative value for an organic semiconductor. In the high electric field region, the exponential values n estimated from the I_{sd}-$(V_{sd})^n$ relationship for all the samples were in the 1.4–2.5 range indicating that there is electric conduction resulting from a trap-controlled space charge limited current [10].

We attempted to inject carriers into the TTF polymer by using chemical doping with iodine. A neutral thin film was exposed in an iodine atmosphere for 10 hours and stored in a vacuum for several hours to remove excess iodine. As a result, the current increases 10^2–10^4 times. This large enhancement in conductivity can be explained by the effective reduction of the polymer that results from the introduction of the

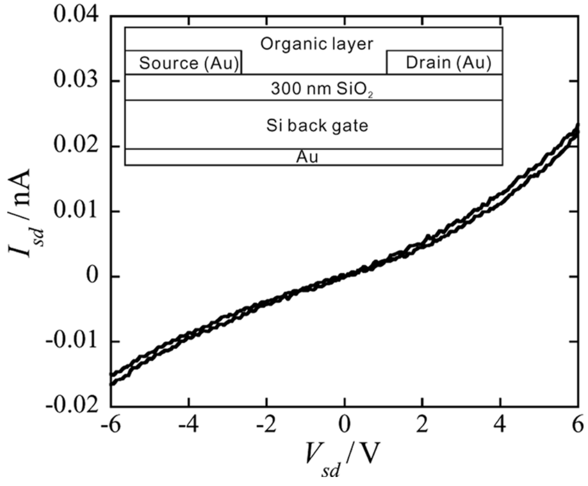

FIGURE 4 I_{sd}-V_{sd} characteristic of the thin film of **1** at room temperature. The inset shows a schematic cross-section of the device structure.

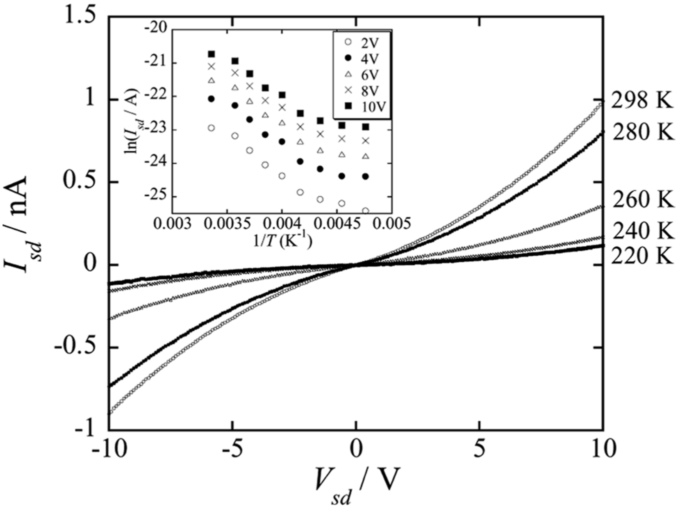

FIGURE 5 Temperature dependence of I_{sd}-V_{sd} characteristics of the iodine doped film. The inset shows $\ln(I_{sd}) \sim 1/T$ relationship at various V_{sd} values.

TTF unit into the polymer backbone. We investigated the temperature dependence of the I_{sd}-V_{sd} characteristic of the doped film as shown in Figure 5. This result is explained by a typical hopping conduction mechanism with an activation energy of 0.14 eV, which is an order of magnitude smaller than the HOMO-LUMO gap (~2.3 eV) [7].

CONCLUSION

We observed the structures and electrical properties of a newly designed and synthesized organic conducting polymer bearing a TTF backbone. This TTF polymer tends to form rigid rod-like structures especially on a gold surface owing to the strong affinity between the gold surface and the sulfur atoms in the polymer. Electrical measurement of the neutral thin film revealed semiconducting behavior that can be explained in terms of typical trap-controlled electric conduction. After iodine doping, the conductivity was enhanced 10^2–10^4 times. We conclude that the introduction of the TTF unit into the polymer backbone provides a new class of organic conducting polymers.

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