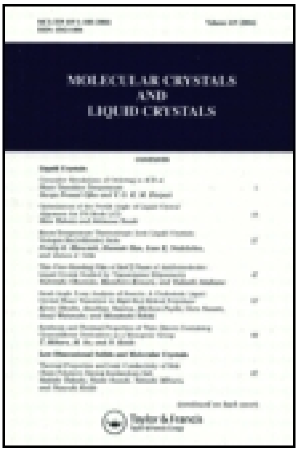

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# Synthesis and Solid-State Polymerization of Diacetylene with Tetrathiafulvalene and the Electronic Properties

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*We synthesized a new diacetylene monomer with urethane groups in the middle of the substituents and tetrathiafulvalene (TTF) moieties at both ends (BT). BT was found to form the CT complex with tetrafluorotetracyanoquinodimethane* ($F_4TCNQ$) *to be* $(BT)(F_4TCNQ)_2$. *BT could be polymerized in the solid state to give irregular conjugated structure by UV irradiation although the solid-state polymerization of the CT complex was not confirmed. Morphology of their cast films was observed by AFM. The films of* $(BT)(F_4TCNQ)_2$ *before and after UV irradiation showed semiconducting temperature dependence with activation energies of 0.19 and 0.16 eV, respectively, and the electrical conductivities at room temperature were found to be more than* $10^{-5}$ $Scm^{-1}$.

## 1. Introduction

It is known that polydiacetylene (PDA) single crystals have high carrier mobility, but most of polydiacetylene derivatives are insulators for their low carrier density [1,2]. In order to obtain conjugated polymers with high conductivities, chemical doping is necessary, i.e., giving electrons to the conduction band or accepting electrons from the valence band. Although polydiacetylene single crystals have 3D regular ordering and highly extended 1D $\pi$-conjugation system along the polymer chains in their solid state [3,4], their doping is not easy [5] because of the high crystallinity to avoid interaction between a $\pi$-conjugated backbone and dopant molecules. Therefore PDA is an insulator in general. Meanwhile, among the $\pi$-conjugated molecules, tetrathiafulvalene (TTF) derivatives have been widely investigated as molecular metals in the crystalline and supramolecular states [6–9]. TTFs have large electron donating properties and charge-transfer (CT) complexes composed of oxidized TTFs and electron-acceptor molecules show high electrical conductivities. In some cases, the complexes can be superconducting. Their conductivity strongly depends on the magnitude of the intermolecular CT interactions between the electron-donor and electron-acceptor molecules.

As the first step, we designed a new diacetylene monomer with TTF moieties (BT) and urethane groups in the side groups. Although a diacetylene derivative with one TTF unit in a molecule has been prepared previously [10], the diacetylene derivative with two TTF units

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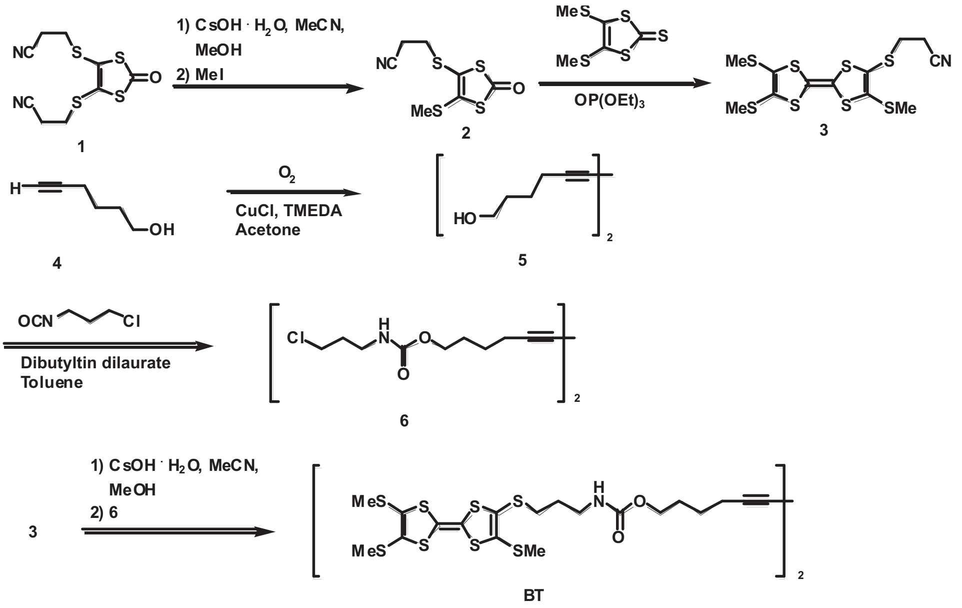

Figure 1. Synthesis scheme of BT.

has not been reported so far. In this paper, we report synthesis and polymerizability of BT and its CT complex with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($F_4TCNQ$), i.e., $(BT)(F_4TCNQ)_2$. The temperature dependence of electrical conductivities of the cast films composed of $(BT)(F_4TCNQ)_2$ was investigated.

## 2. Experimental

5-Hexyne-1-ol, 3-chloropropyl isocyanate and $F_4TCNQ$ were purchased from Tokyo Chemical Industry Co., Ltd. BT was synthesized according to Fig. 1. TTF derivative **3** and diacetylene derivative **5** were prepared by the procedures described elsewhere [11–14]. The reaction of **5** and 3-chloropropyl isocyanate gave **6** in 99.3%. The coupling reaction of **3** and **6** resulted in BT in 23.9% yield. The chemical structure of BT was confirmed by the following NMR data: $^1$H-NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.57 (4H, m), 1.72 (4H, t, $J = 6.8$ Hz), 1.85 (4H, t, $J = 6.9$ Hz), 2.30 (4H, t, $J = 6.9$ Hz), 2.44 (9H, m), 2.84 (4H, t, $J = 6.9$ Hz), 3.31 (4H, m), 4.07 (4H, t, $J = 6.4$ Hz), 4.78 (2H, s); $^{13}$C-NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.88, 19.19 (overlapped three carbons), 24.75, 28.11, 29.74, 33.38, 39.47, 64.23, 65.67, 76.85, 110.65, 111.01, 124.35, 127.36, 127.50, 130.86, 156.56.

The CT complex solution of BT and $F_4TCNQ$ was prepared by mixing BT chloroform solution (1 mM) and $F_4TCNQ$ acetonitrile solution (1 mM) in 1:2 volume ratio. The cast films of the CT complex were prepared by depositing this solution on mica or quartz or glass substrates. Photoirradiation at 254 nm to the samples was carried out by using a 4-W lamp (UVG-11, UVP). The AFM images were taken using a Seiko SPA 400 scanning probe microscope with an SPI 3800 probe station operating at the dynamic force mode. Commercially available Si cantilevers with a force constant of 13 $Nm^{-1}$ were used. The redox potentials were obtained by using CV, and the experiment was carried out in dry degassed acetonitrile solutions of a compound and $n\mathrm{Bu_4NBF_4}$ (0.1 mM) was added as a supporting electrolyte. The temperature-dependent electrical conductivities of the cast films were measured using the DC two-probe method. Gold electrodes with an electrode gap of 500 $\mu$m were prepared by vacuum evaporation on a trichlorooctadecylsilane-treated hydrophobic glass substrate, and then the film was casted on the substrate. Electrical contacts were made using silver paste to attach the 25-$\mu$m$\phi$ gold wires. IR spectra were recorded by the ATR method on a Horiba FT-210 spectrometer. $^1$H- and $^{13}$C-NMR spectra were measured using a JEOL JNM-ECX 400 spectrometer. UV-visible-near-IR diffuse reflectance spectra were recorded on a JASCO V-570 spectrophotometer equipped with an ILN-472 integrating sphere. For the spectral measurements, the crystals were mixed with potassium bromide, ground and placed into a quartz-window cell.

## 3. Results and Discussion

Colors of BT and (BT)($F_4$TCNQ)$_2$ in monomers were yellow and green, respectively. Their UV-visible-near-IR spectra obtained by changing the UV irradiation time are shown in Fig. 2. In Fig. 2(a), BT monomer showed broad absorption bands, whose cutoff wavelength was around 570 nm. The shoulder bands at around 430 and 330 nm are assigned to be neutral TTF moieties. When UV was irradiated to BT monomer, the absorption edge was shifted to longer wavelength. This indicated that diacetylene moiety was polymerized to some extent. Commonly, diacetylene monomers without $\pi$-conjugation to the substituents show no absorption in the visible region. On the other hands, for PDAs obtained by the regular 1,4-addition polymerization in the crystals, characteristic excitonic absorption of the $\pi$-conjugated backbone structure [3] is observed between about 500 and 700 nm. Since BT after UV irradiation did not show the excitonic band for typical PDA, polymerization of BT proceeded in an irregular manner, i.e., obtained PDA was distorted and/or polymerization other than regular 1,4-addition also occurred. In Fig. 2(b), the broad absorption band at around 386 nm of (BT)($F_4$TCNQ)$_2$ monomer are originated from overlapped intramolecular

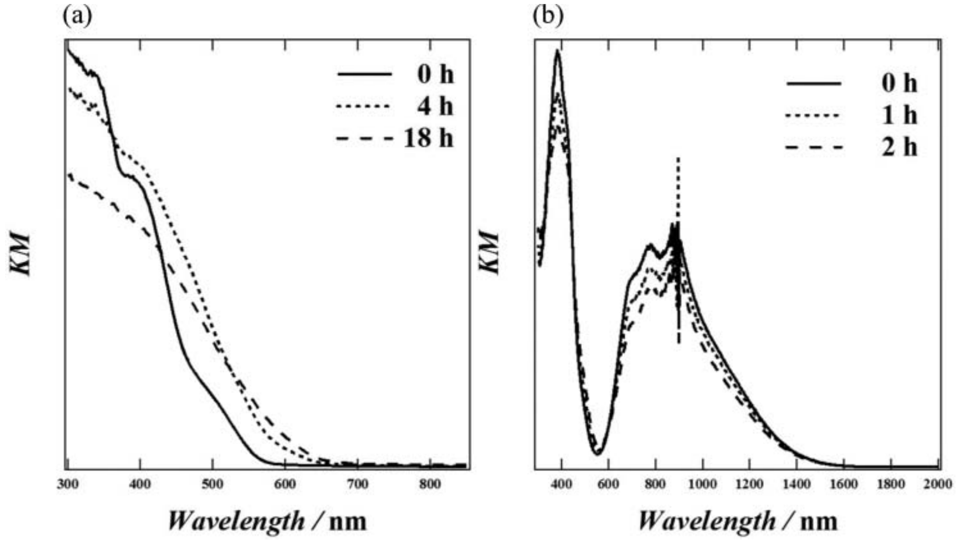

**Figure 2.** Spectral changes depending on UV irradiation time: (a) diffuse reflectance spectra of BT with UV irradiation time of 0 h, 4 h and 18 h. (b) diffuse reflectance spectra of (BT)($F_4$TCNQ)$_2$ with UV irradiation time of 0 h, 1 h and 2 h. The peaks and valleys at around 895 nm are noises.

transitions of $TTF^+$ and $F_4TCNQ^-$, and the two bands at 780 and 898 nm were assigned to radical anion of $F_4TCNQ$ [15–17]. These bands decreased when the UV irradiation time was increased. This indicates that the CT state of $(BT)(F_4TCNQ)_2$ was changed or degraded, and no polymerization was confirmed for the CT complex.

A CV study of BT was performed. The solution of BT displayed two reversible one-electron-oxidation waves at $E_{1/2} = +0.53$ and $+0.89$ V versus SCE in the anodic

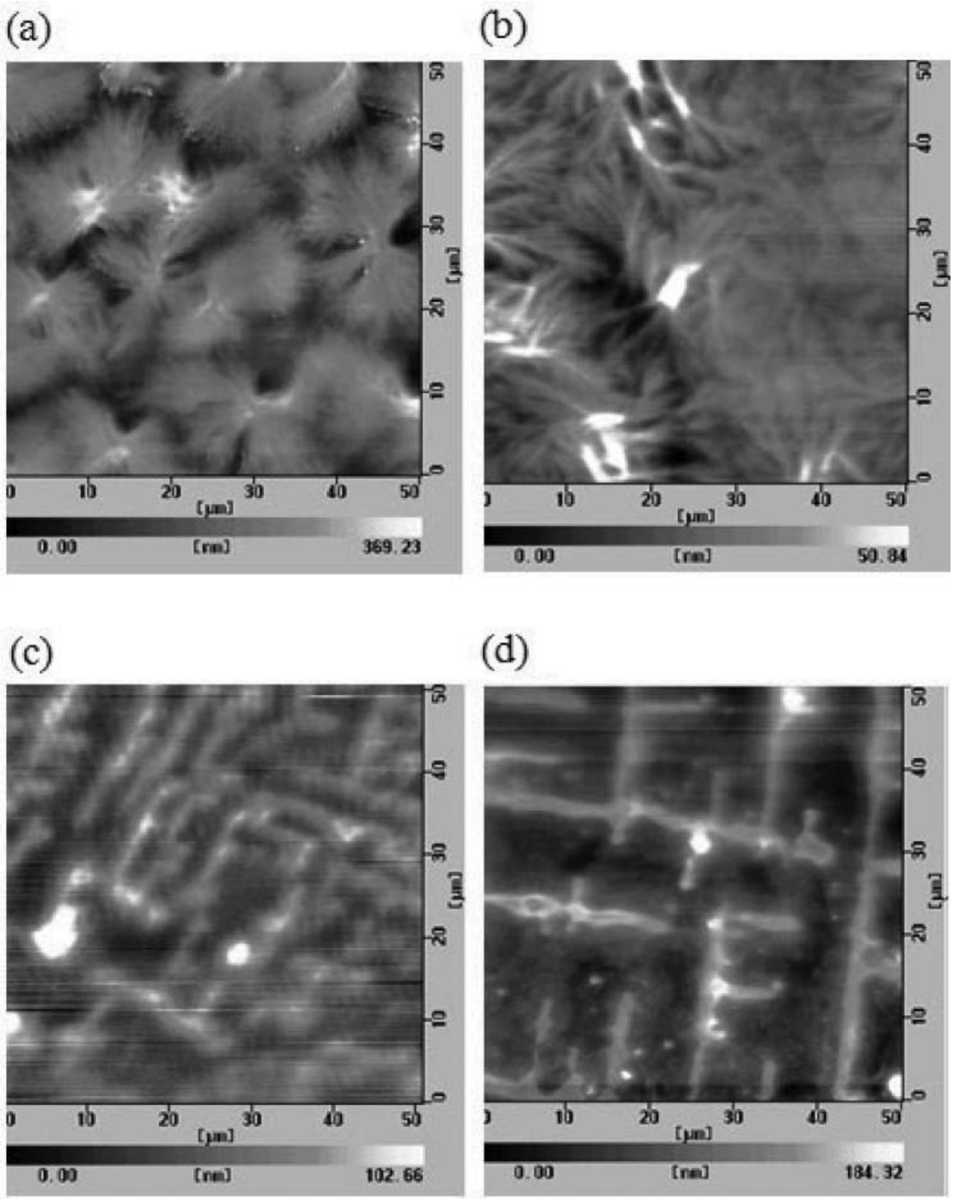

**Figure 3.** Surface morphology of cast films on mica substrates: (a) BT before UV irradiation, (b) BT after UV irradiation, (c) $(BT)(F_4TCNQ)_2$ before UV irradiation and (d) $(BT)(F_4TCNQ)_2$ after UV irradiation.

window, which indicated the formation of the stable radical cations. Because the redox potential for reduction of $F_4$TCNQ (+0.70 V vs. SCE) was higher than the first oxidation potential of BT, the TTF segments could be oxidized to the radical cation by the addition of $F_4$TCNQ. The $\nu_{CN}$ bands were observed at 2192 and 2173 $cm^{-1}$ in the FTIR spectrum of (BT)($F_4$TCNQ)$_2$. Since the $\nu_{CN}$ bands of $F_4$TCNQ and $F_4$TCNQ$^-$ is observed at 2227 and 2193 $cm^{-1}$, respectively, the observed electronic ground state of (BT)($F_4$TCNQ)$_2$ is concluded to be close to the complete ionic state [18–21].

Figure 3 shows AFM images of the films of BT and (BT)($F_4$TCNQ)$_2$ on freshly cleaved mica. BT before UV irradiation formed the spherulite-like domains with a typical dimension of $\sim 20 \times 20\ \mu m^2$ (Fig. 3(a)) while radial 1D nanowire structures were intensively observed after UV irradiation (Fig. 3(b)). As shown in Figs 3(c) and (d), (BT)($F_4$TCNQ)$_2$ formed the 1D structures before and after UV irradiation with typical height, width and length of 60 nm, 5 nm and more than 50 nm, respectively. Since scanned areas were different between Figs 3(a) and (b) and between Figs 3(c) and (d), density of the materials cannot be compared. However, morphology of each nanostructure before and after UV irradiation was generally maintained.

Figure 4 shows the temperature dependent electrical conductivities of the (BT)($F_4$TCNQ)$_2$ cast films before and after UV irradiation. Increase of resistivity after UV irradiation corresponded to decrease in absorption bands related to CT after UV irradiation. Both cast films showed semiconducting temperature dependence. The activation energies ($E_a$) of (BT)($F_4$TCNQ)$_2$ before and after UV irradiation were 0.19 and 0.16 eV, respectively. The conductivities of the cast films could not estimate exactly because there are many openings in the films on the mica substrates, as shown in Figs 3(c) and (d). However, when we postulated that the film thickness was fully occupied by the material, we could estimate the electrical conductivities at room temperature ($\sigma_{RT}$) for (BT)($F_4$TCNQ)$_2$ before and after UV irradiation to be not less than $10^{-5}$ $Scm^{-1}$. Since the conductivity of the cast films of BT could not be measured, it is clear that CT complex formation resulted in conducting properties. The conductivities of cast films composed of CT complexes based on TTF derivatives become up to $10^{-3}$ S/cm [22]. Lower conductivity of (BT)($F_4$TCNQ)$_2$ is due to overestimation of the fill factor of the material in the film and maybe unoptimized packing structure of the CT complex parts.

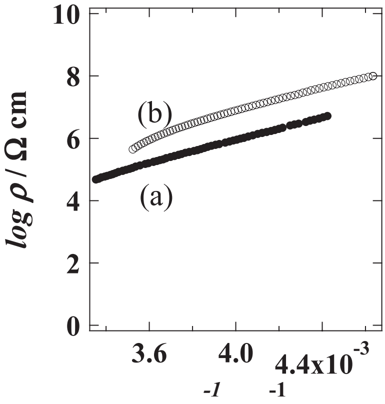

**Figure 4.** log $\rho$ / Ωcm vs. $T^{-1}$/ $K^{-1}$ plots of cast films: (a) (BT)($F_4$TCNQ)$_2$ before UV irradiation and (b) (BT)($F_4$TCNQ)$_2$ after UV irradiation.

## 4. Conclusion

We synthesized BT as a new diacetylene compound with two TTF moieties and its CT complex of (BT)($F_4$TCNQ)$_2$. Irregular solid-state polymerization was observed for BT although the polymerization could not be confirmed for the CT complex. Structures of the cast films on mica substrates were spherulite-like domains with radial nanowires for BT and linear aggregates for (BT)($F_4$TCNQ)$_2$. The temperature-dependent conductivities of (BT)($F_4$TCNQ)$_2$ before and after UV irradiation showed the semiconducting behaviors. Although their bulk conductivities at room temperature was obtained to be $10^{-5}$ Scm$^{-1}$ as the lowest limit, much higher conductivities are expected for their individual linear nanostructures. Extension of the compounds with diacetylene and CT-complex moieties are in progress.

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