



## Molecular Crystals and Liquid Crystals

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### Structural Change in Langmuir-Blodgett Films of Bis-Tetrathiafulvalene Annelated Macrocycle-Tetrafluorotetracyanoc Charge Transfer Complex

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**STRUCTURAL CHANGE IN LANGMUIR-BLODGETT  
FILMS OF BIS-TETRATHIAFULVALENE  
ANNELATED MACROCYCLE–  
TETRAFLUOROTETRACYANOQUINODIMETHANE  
CHARGE TRANSFER COMPLEX**

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*We have already reported a nanowire structure of bis-tetrathiafulvalene (bis-TTF) annelated macrocycle – tetrafluorotetracyanoquinodimethane (F<sub>4</sub>TCNQ) charge transfer complex formed by Langmuir-Blodgett (LB) technique. Nanowires oriented on the mica substrates forming an angle of 60 degree to each other recognizing hexagonal potassium array of mica surface. In the present study, we examined the conditions for obtaining well oriented nanowires*

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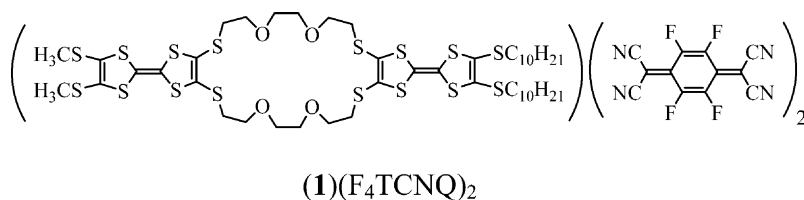
*and found that the nanowire orientation was quite sensitive to the temperature and potassium-ion concentration of subphase as well as the deposition speeds. By a slight change in conditions, a variety of nanowire morphology was observed on mica surface.*

**Keywords:** AFM; bis-TTF annulated macrocyclic; F<sub>4</sub>TCNQ; Langmuir-Blodgett techniques; nanowire

## 1. INTRODUCTION

Nanowires are considered to be the key materials for constructing nanostructures devices in recent years, and quite a few number of device prototypes have been reported, [1,2] which ranges from inorganic nanowires composed of GaAs or AlGaAs for quantum devices [3] to molecular nanowires composed of organic materials [4]. The present silicon-based technology is thought to be approaching its limit. As an alternative, molecular devices, especially single-molecule devices are extensively studied. For example, single-molecule devices exhibiting Kondo resonance have been already reported utilizing break junction of gold electrode [5]. On the other hand, the devices of molecular assembly has been studied for more than two decades, and a variety of electronic and optical devices has been reported [6]. One of the advantages of utilizing molecular assembly instead of single molecule is that we can expect functions arising from intermolecular interactions, which is never achieved by a single molecule. Nanowires composed of molecular assemblies are examples of such molecular assembly devices, whose electrical conduction is achieved by a band formation through the overlapping of  $\pi$ -orbitals. The band structure is dictated by intermolecular transfer integral,  $t$ , and the band width equals to  $4t$  in the case of one-dimensional system. Molecular assembly nanowires are easily derivatised to add functions advantageous for developing molecular devices based on molecular systems. Molecular assembly nanowires are thought to have difficulties to align compared to semiconductor nanowires, since the molecules merely oriented by self-assembly processes through weak intermolecular interactions. However, recent publications indicate that the molecular assembly nanowires also shows good orientation on substrates [7].

We already reported that the charge transfer (CT) complex between bis-tetrathiafulvalene (bis-TTF) annulated macrocycle (**1**) and tetrafluorotetracyanoquinodimethane (F<sub>4</sub>TCNQ) forms oriented nanowire structure on mica surface by applying Langmuir-Blodgett (LB) technique [8]. The molecule **1** was designed from the view points of supramolecular chemistry and molecular conductors, and have three functional units. TTF units are redox active and exhibit high conductivity by partial oxidation



## SCHEME 1

forming one-dimensional columnar structures. The one-dimensional column should be advantageous to construct a nanowire structure. Macrocyclic ring should have ion-recognition ability and is hydrophilic. CT units in ionic state should be also hydrophilic. By introducing long alkyl chains, the molecule and the CT complex become amphiphilic and therefore, we can apply LB method. In fact, when we deposited a monolayer of **(1)(F<sub>4</sub>TCNQ)<sub>2</sub>** on 0.01 mol dm<sup>-3</sup> KCl aqueous solution onto mica surface by a single upstroke withdrawal, oriented nanowire structure was obtained. The nanowire oriented along potassium site on mica surface forming an angle of 60 degree to each other. The nanowire network structure largely changed according to ionic species introduced in the subphase, which further supported the hypothesis that the nanowires orient by recognizing potassium ion array on mica surface. When we apply horizontal lifting method instead of ordinary vertical dipping method, different surface morphology with oriented structure of nanowires was also observed. However, the control of the nanowire orientation, which is thought to be one of the key steps for further application to device developments, has not been achieved. In the present study, we examined film deposition conditions for oriented nanowire network structure, towards the regulation of nanowire structures at substrate surface.

## 2. EXPERIMENTAL

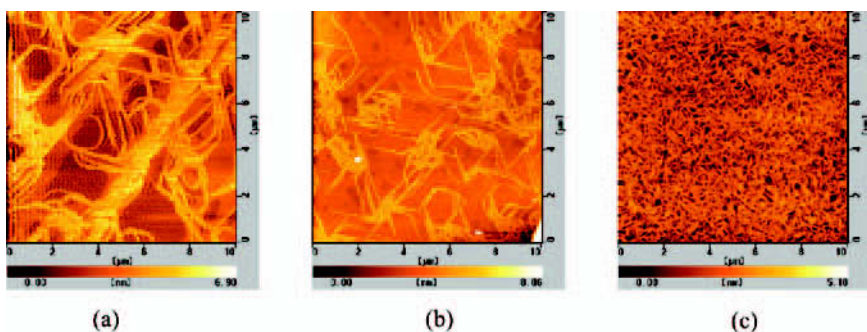
A conventional LB trough (NIMA 5152D) was used for monolayer formation and LB film depositions. CHCl<sub>3</sub>–CH<sub>3</sub>CN (9:1) was used as a spreading solvent and the concentration of spreading solutions was adjusted to 1 × 10<sup>-3</sup> mol dm<sup>-3</sup> with respect to **1**. The complex **(1)(F<sub>4</sub>TCNQ)<sub>2</sub>** was prepared *in-situ* by mixing **1** and two equivalents of F<sub>4</sub>TCNQ in a spreading solution. Atomic force microscopy (AFM) images were taken by SPA400 (Seiko Instruments) operating in tapping mode by using microcantilevers of spring constant of 13 N/m.

### 3. RESULTS AND DISCUSSION

In the previous work, [9] we preliminary checked the conditions of film deposition for oriented nanowire formation. For example, besides the change in deposition method and ionic species introduced in the subphase, we checked the effect of surface pressure upon deposition. The surface pressure of  $10 \text{ mNm}^{-1}$  gave a well oriented network structure, whereas a cyclic domains and extended nanowires were observed at lower pressures. The whole substrate was covered with small fibrils when we deposited above  $20 \text{ mN/m}$  [10].

The conditions with the subphase temperature of  $291 \text{ K}$ ,  $\text{KCl}$  concentration of  $0.01 \text{ mol dm}^{-3}$  and the deposition speed of  $10 \text{ mm min}^{-1}$  give nanowire network structure. For the regulation of nanowire morphology on mica substrate, we changed the subphase temperature,  $\text{KCl}$  concentration and deposition speed, and examined the morphology of the film by AFM measurements.

First, we examined effects of subphase temperature. Figure 1 shows the AFM images of films deposited on mica surface at  $289$ ,  $291$  and  $293 \text{ K}$ . Dipping speed and  $\text{KCl}$  concentration were adjusted at  $10 \text{ mm min}^{-1}$  and  $0.01 \text{ mol dm}^{-3}$ , respectively. As seen in the Figure 1, a slight change in the subphase temperature largely affected the film morphology. At  $289 \text{ K}$ , the orientation of nanowires disappeared in part, forming a bundle of nanowires. The film deposited at  $291 \text{ K}$  showed a well oriented nanowire structure as reported previously [10]. On the other hand, the film deposited at  $293 \text{ K}$  was composed of small fibrils, which were seen in the film deposited at higher pressures at  $291 \text{ K}$ . It should be noted that the height of the nanowires was around  $3 \text{ nm}$  in all cases. Unexpectedly large change in morphology with respect to subphase temperature may be related to the

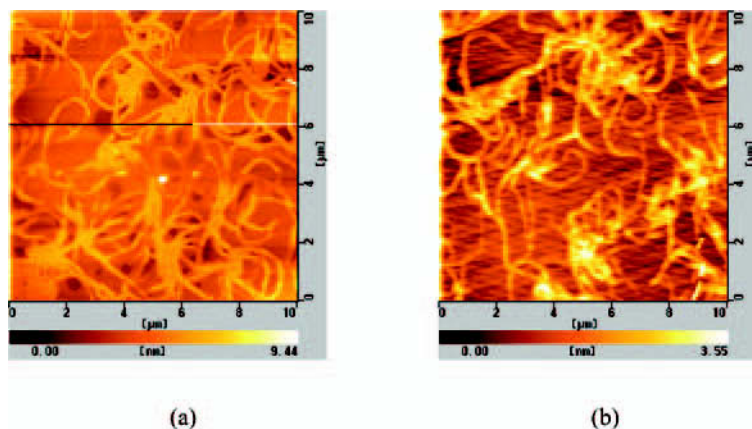


**FIGURE 1** Morphology of the films on mica surface deposited at (a)  $289 \text{ K}$ , (b)  $291 \text{ K}$ , and (c)  $293 \text{ K}$ .

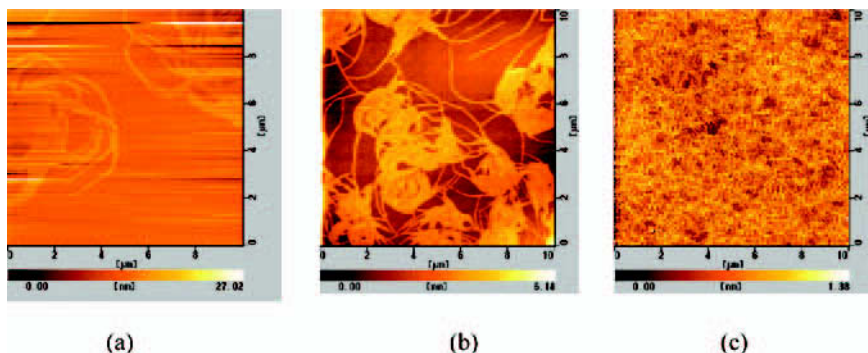
mesogen-like molecular structure of **1**. Structural change of molecular assembly is thought to occur at around room temperature.

Next we examined the structural change in nanowire upon the KCl concentration in the subphase. The temperature and deposition speed was 290 K and  $10 \text{ mm min}^{-1}$ , respectively. Figure 2 shows the morphology of the film deposited from aqueous subphase containing 0.001 and 0.1  $\text{mol dm}^{-3}$  KCl. In the case of 0.001  $\text{mol dm}^{-3}$  KCl aqueous solution as a subphase, the orientation of the nanowires disappeared largely. As described previously, the nanowires deposited from 0.01  $\text{mol dm}^{-3}$  KCl aqueous solution oriented on mica forming an angle of 60 degree to each other through recognizing potassium ion array on the surface. Freshly cleaved mica surface has potassium ion sites on its outermost layer, which are filled with potassium ions upon immersing the mica substrate in the subphase prior to the deposition process. The potassium sites have a six-fold symmetry and the nanowires orient on the surface through recognizing the potassium array. The small correlation between the directions of potassium ion array and nanowires suggests that the filling of potassium ions on the mica surface is insufficient.

When we increased the KCl concentration up to 0.1  $\text{mol dm}^{-3}$ , again the orientation of nanowires with respect to potassium ion sites was interrupted. This is probably due to the additional physical adsorption of potassium ions on mica surface. The phenomenon is thought to be related to the disappearance of the orientation of nanowires deposited from  $\text{BaCl}_2$  containing subphase. Matching between the electric potential motif generated by ion array on the surface and that of nanowires should be the origin of nanowire orientation on mica substrates.



**FIGURE 2** Morphology of the film on mica surface deposited from (a) 0.001 and (b) 0.1  $\text{mol dm}^{-3}$  KCl aqueous solution.



**FIGURE 3** Morphology of the films on mica surface deposited at the dipper speed of (a) 1, (b) 5 and (c) 20 mm min<sup>-1</sup>.

Finally we checked the morphology change of the film with respect to the deposition speed. The subphase temperature and KCl concentration was adjusted to 291 K and 0.01 mol dm<sup>-3</sup>, respectively. Figure 3 shows the deposition speed dependence of the morphology of the film on mica surface. When we deposited the film at lower deposition speeds, 1 and 5 mm min<sup>-1</sup>, the orientation of the nanowires disappeared. The morphology rather resembles those deposited from the monolayers on pure water subphase. The equilibrium process of adsorption and desorption of potassium ions at the mica-water interface at lower deposition speeds is thought to be one possible explanation of the disappearance of nanowire orientation. Such dynamic process of potassium ions should affect the potential motif of the mica surface and then the morphology of the film. However, further investigation is necessary to obtain a solid evidence of such process.

In the case of higher deposition speed of 20 mm min<sup>-1</sup>, the nanowire orientation was retained to some extent but each nanowire was much shorter than those observed for the films deposited at 10 mm min<sup>-1</sup>. The larger shear stress upon the high speed deposition process should be responsible for the formation of short-length nanowires.

## 4. CONCLUSION

We examined the effect of subphase temperature, KCl concentration of the subphase, and the deposition speed on the surface morphology of (1)(F<sub>4</sub>TCNQ)<sub>2</sub> films on mica surface. The effect was unexpectedly large, probably because the mesogen-like molecular structure of **1** on one hand, and the ionic nature of nanowires sensitive to potential motif on the mica surface on the other. Such sensitivity, however, is thought to be a clue to



the regulation and control of nanowire structure on the surface, which is one of the most important steps to the practical application to the device formation. The studies on this line are in progress.

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