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Yoko Tatewaki [a], Shuji Okada [a], Junko Takizawa [b], Tatsuya Hatanaka [c], Mutsumi Kimura [b c] & Hirofusa Shirai [b c]

[a] Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan

[b] Collaborative Innovation Center for Nanotech FIBER, Shinshu University, Ueda, Japan

[c] Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Japan

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Structures in Langmuir-Blodgett Films of Amphiphilic Tetrathiafulvalenes and Tetrafluorotetracyanoquinodimethane CT Complex

YOKO TATEWAKI,[1] SHUJI OKADA,[1]
JUNKO TAKIZAWA,[2] TATSUYA HATANAKA,[3]
MUTSUMI KIMURA,[2,3] AND HIROFUSA SHIRAI[2,3]

[1]Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan
[2]Collaborative Innovation Center for Nanotech FIBER, Shinshu University, Ueda, Japan
[3]Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Japan

An asymmetric TTF derivative **1** *having two arms substituted by amide and chiral groups was synthesized and its CT complex with 2,3,5,6-tetrafluoro-7,7′,8,8′-tetracyano-*p*-quinodimethane (***1***-F_4TCNQ) were also prepared. Thin film formation at the air-water interface and the film deposition on substrates of* **1** *and* **1***-F_4TCNQ were investigated. When we deposited the film of* **1***-F_4TCNQ prepared on pure water onto a mica surface by a single upstroke withdrawal, curved nanowire structures were observed on the thin films. On the contrary,* **1** *without F_4TCNQ showed three-dimensional dome structures on the thin films, and the morphologies of the Langmuir-Blodgett (LB) films depended on the existence of F_4TCNQ. An average dimension of nanowire was 6.0 (height) × 500 (width) × 10000 (length) nm^3.*

Keywords Charge transfer; chirality; helical structures; hydrogen bonds; nanostructures

1. Introduction

Molecular-assembly nanostructures are interesting for the future technologies since they can be used as basic parts of electronic devices in a nanometer scale. Generally, such nanostructures are constructed by the combination of intermolecular interactions such as electrostatic, charge-transfer (CT), hydrogen-bonding and van der Waals interactions. For example, supramolecular approaches, which have a structural flexibility to form nanostructures with a variety of sizes and shapes [1], are effective methods to obtain novel low-dimensional molecular-assembly

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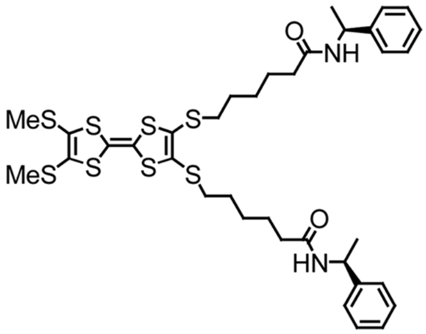
Address correspondence to Yoko Tatewaki, Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan. E-mail: ytatewa@yz.yamagata-u.ac.jp



Scheme 1. TTF derivative **1**.

nanostructures such as nanodots and nanowires [2]. The other approach is utilization of the LB technique. This technique provides a way of arranging the molecules by the orientational effect at the air-water interface as well as surface pressure applied. These characteristics of the LB method can give rise to well ordered monolayer packing in a two-dimensional (2D) layer [3]. In addition, the LB method using amphiphilic conducting molecules is promising for building conduction paths [4–8]. In the previous study, we have reported gel formation originated from molecular-assembly nanostructures composed of tetrathiafulvalene (TTF) derivatives, which have four arms substituted by amide and chiral groups, and 2,3,5,6-tetrafluoro-7,7′,8,8′-tetracyano-*p*-quinodimethane (F_4TCNQ) [7]. The intermolecular hydrogen bonding among chiral amide end-groups and the formation of CT complexes result in a long one-dimensional supramolecular stacking, and the chirality of the end-groups affects the molecular orientation of TTF cores within the stacks.

In the present study, we synthesized an asymmetric TTF derivative **1** having two arms substituted by amide and chiral groups as shown in Scheme 1. Its organization into supramolecular assemblies were investigated for **1** and its CT complex with F_4TCNQ (**1**-F_4TCNQ) by using the LB technique.

2. Experimental

Compound **1** was prepared by referring the procedure for the similar compounds described in the literature 7. F_4TCNQ was purchased from Tokyo Chemical Industry Co., Ltd. The solution of the CT complex **1**-F_4TCNQ was prepared by mixing the same amount of solutions of **1** in $CHCl_3$ (1 mM) and F_4TCNQ in CH_3CN (1 mM). A conventional LB trough (USI, USI-3-22) was used for formation of the films and their depositions. Solution of **1** or **1**-F_4TCNQ was spread on the pure water as a subphase. The floating layer at the air-water interface was maintained for 20 min after spreading the solution. Surface pressure-area per molecule (π-A) isothermes were recorded at 291 K. Deposition surface pressures of **1** and the CT complex were 20 mNm^{-1} and 13 mNm^{-1}, respectively. For atomic force microscopy (AFM) observation, the films at the air-water interface were transferred onto a freshly-cleaved mica surface by the LB method with a single up-stroke withdrawal. AFM images were taken by a JSPM-5400 (JEOL) operating in a tapping mode by using microcantilevers of spring constant of 0.2 Nm^{-1}. For UV-Vis spectral measurements, 20 layers of the films were transferred by the horizontal lifting method on to quartz substrates ($30 \times 10 \times 1\,mm^3$), which were treated by hexamethyldisilazane (HMDS) vapour to be hydrophobic. UV-Vis spectra were recorded on a Hitachi U-4100. Column chromatography was performed with activated alumina (Wako, 200 mesh) or Wakogel C-200. Recycling preparative gel permeation chromatography was carried out by a JAI recycling preparative HPLC using $CHCl_3$. Analytical thin-layer chromatography was performed with commercial Merck plates coated with silica gel 60 F254 or aluminum oxide 60 F254.

Compound **1**: A solution of $CsOH \cdot H_2O$ (700 mg, 4.2 mmol) in methanol (10 mL) was added to a solution of 4,5-bis(2′-cyanoethylthio)-1,3-dithiole-2-thione (931 mg, 2.0 mmol) in acetonitrile (50 mL) over 10 min with stirring at room temperature. After stirring for 30 min, hexylbromide having (*S*)-methylbenzylamide end-group (3.0 g, 10.1 mmol) was added, and the reaction mixture was stirred for 24 h. The reaction mixture was concentrated in vacuo, and water (50 mL) was added. The aqueous solution was extracted with CH_2Cl_2 and the combined organic layer was washed with water. After drying with $NaSO_4$, the solvent was evaporated, and the residue was purified by column chromatography (silica, $CHCl_3$), to afford **1** as an orange powder (0.84 g, 53%). ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.28$ (m, 10H, Ar-***H***), 5.90 (q, $J = 8.0$ Hz, 2H, N-***H***), 5.10 (m, 2H, $-COCNHC\boldsymbol{H}CH_{3-}$), 2.81 (t, 4H, $J = 6.60$ Hz, $-SC\boldsymbol{H}_{2-}$), 2.42 (t, 4H, $J = 7.20$ Hz, $-C\boldsymbol{H}_2CONH-$), 2.15 (m, 6H, $-C\boldsymbol{H}_{3-}$), 1.62 (m, 10H, $-SCH_2C\boldsymbol{H}_{2-}$, $-CONHCHC\boldsymbol{H}_{3-}$), 1.52 ppm (m, 8H, $-SCH_2CH_2C\boldsymbol{H}_2C\boldsymbol{H}_{2-}$).

3. Result and Discussion

Figure 1 shows π-A isotherms of the Langmuir film of neutral donor **1** and the CT complex **1**-F_4TCNQ. Formations of stable floating layers were confirmed by sharp increases of the surface pressure during compression. The surface area extrapolated at $0\,mNm^{-1}$ of **1**-F_4TCNQ monolayer was $A_0 = 0.8\,nm^2$. A kink of the π-A isotherm was observed at around $20\,mNm^{-1}$. Compound **1** showed the same behavior on the

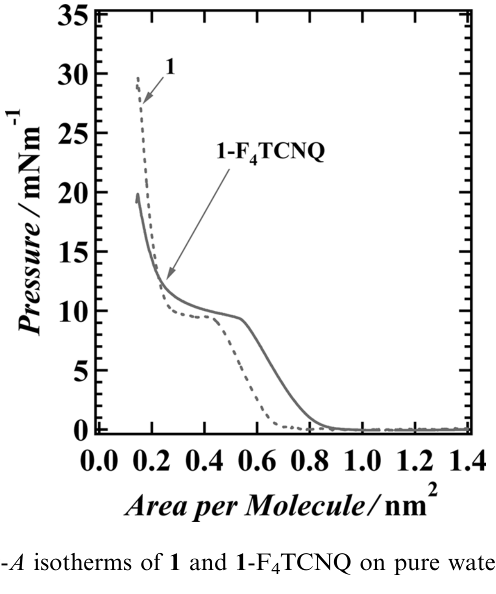


Figure 1. π-A isotherms of **1** and **1**-F_4TCNQ on pure water at 291 K.

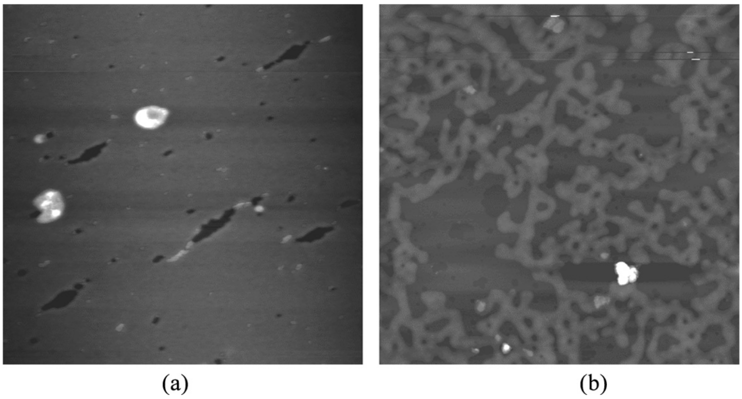


Figure 2. Surface morphologies of transferred films of (a) **1** and (b) **1**-F_4TCNQ by a single withdrawal from pure water.

π-A isotherm as **1**-F_4TCNQ although the film of **1** formed the hard film and the surface pressure arose over $30\,\mathrm{mNm}^{-1}$. The area per molecule at the deposition surface pressure of **1** was $0.18\,\mathrm{nm}^2$ at $20\,\mathrm{mNm}^{-1}$ (A_{20}) and that of **1**-F_4TCNQ was $0.22\,\mathrm{nm}^2$ at $\pi = 13\,\mathrm{mNm}^{-1}$ (A_{13}). Given that the A_{13} and A_{20} values are same as the areas of one close-packed alkyl chains ($0.20\,\mathrm{nm}^2$). The area per molecule of neutral donor **1** should be $0.4\,\mathrm{nm}^2$, because this compound has two alkyl chains ($0.20\,\mathrm{nm}^2 \times 2$). Our results indicate that the floating layers of **1** and **1**-F_4TCNQ didn't create the monolayers.

Figure 2 shows AFM images of LB film composed of **1** and **1**-F_4TCNQ transferred onto mica by a single withdrawal. The AFM image of **1** showed the thin films

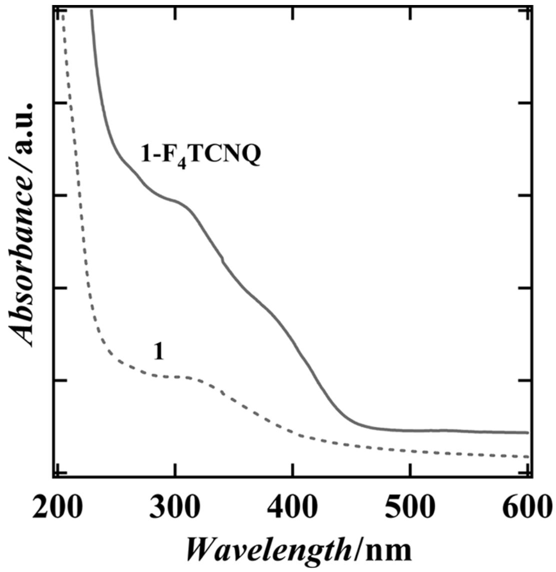


Figure 3. UV-Vis spectra of 20-layer multilayer films of **1** and **1**-F_4TCNQ transferred from pure water.

with thickness of about 4 nm and the three-dimensional (3D) dome-type aggregates with a typical dimension of $\sim 1.2 \times 1.2\,\mu m^2$ (Fig. 2a). The formation of nanowires wasn't observed for neutral donor **1**, the neutral **1** was assembled together and aggregated. On the other hand, **1**-F_4TCNQ formed the thin films with thickness of about 6 nm and the curved nanowires with an average dimension of 6.0 (height) × 500 (width) × 10000 (length) nm^3 were observed on the thin films (Fig. 2b). The nanowires were distributed randomly on the substrate. From these results, we can conclude that the molecular organization of synthesized TTF molecules is a combination of the formation of one-dimensional charge transfer stacks and hydrogen bonding among chiral amide groups.

UV-vis spectra of multilayer films (20 layers) of **1** and **1**-F_4TCNQ were measured from 200 to 600 nm (Fig. 3). The complex **1**-F_4TCNQ showed larger absorbance in the whole range measured than **1**. In particular, the shoulder band at 391 nm of **1**-F_4TCNQ is originated from the intramolecular charge transfer between TTF and TCNQ [9,10]. The absorption band at 320 nm for the LB film of the complex **1**-F_4TCNQ are assigned to the neutral TTF of **1** indicating the partial CT state.

4. Conclusion

Thin films of **1** and **1**-F_4TCNQ were formed on a pure water subphase and deposited on substrate surfaces by LB technique. The LB techniques were useful for arrangement of molecules. Both films deposited on to the mica surfaces showed 2D thin films. However, in addition to the thin films, **1** showed the 3D dome-type aggregates and **1**-F_4TCNQ showed the molecular-assembly curved nanowires. Large network structures of conductive nanowires will open new possibilities for the construction of soft electronic nanocircuits like neuronal networks, and **1**-F_4TCNQ and its derivatives may be used for such applications. Finally, large network structures of conductive nanowires will open new possibilities for the construction of soft electronic nano-circuits such as neuronal networks.

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