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# Morphological transition of a conductive molecular organization with non-covalent from nanonetwork to nanofiber



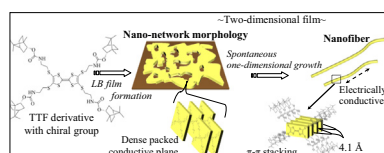
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## GRAPHICAL ABSTRACT



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## ABSTRACT

The formation of nanofiber morphology at a mesoscopic scale, and molecular level stacking of a tetrathiafulvalene (TTF) derivative with a chiral group were investigated by the one-dimensional growth method in interfacial molecular films. Monomolecular films of a TTF derivative with a chiral borneol group display a two-dimensional phase transition at the air/water interface. At high surface pressures, nanonetwork domains are formed, where the TTF molecular planes are densely packed with an interlayer distance of 4.1 Å. The formation of this network is attributed to the organized aggregation of the TTF derivatives, which is a result of strong intermolecular interactions. Subsequently, the growth of morphology is encouraged by the application of the one-dimensional growth method at low surface pressure conditions, varying compression speeds, and subphase temperatures. At low surface pressure and a subphase temperature of 15 °C, the TTF derivatives aggregated as nanofibers with close packing of molecules. Upon raising the subphase temperature, the thickness of the nanofibers was found to increase and hence, spontaneous morphogenesis at the air/water interface was achieved.

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## 1. Introduction

Although the development of the Langmuir–Blodgett (LB) film was first reported by Blodgett in 1934 [1], this technique has attracted a lot of attention in recent years, following its application in the formation of two-dimensional lamellae in linear polymers [2]. While there is a long history of development of this technique beginning with the studies on the optical and electronic properties of the LB films by Khun et al. [3,4], direct observation of the folding

of polymer chains in LB films using atomic force microscopy was a significant milestone, which revealed the phenomenon of “morphogenesis at the interface” [5,6]. For the several examples of “morphogenesis at the interface”, the formation of nanofibers [7], nanowires [8,9], nanospheres [10], nanocoils [11], nanoribbons [12], sea-island structures [13,14], rods [15], gyroids [16], lamellae [17], and honeycombs [18] are noteworthy. Simultaneous control of the mesoscopic morphology (at the sub-micron level) of a non-covalent molecular organization, along with control of the molecular arrangement and packing structure (at the sub-nanometer level) are essential for the construction of next-generation quantum devices and medical materials. In other words, the molecular arrangement and morphology need to be controlled at different dimensional scales.

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In this study, the formation of a nanofiber morphology at the mesoscopic scale and the molecular level stacking of a tetrathiafulvalene (TTF) derivative with a chiral group were investigated by the method of one-dimensional molecular film growth (Fig. 1a). In TTF derivatives, it achieves the stacking of the conductive plane for efficient expression of electrical conductivity, and these are organized into one-dimensional fiber shape [19,20]. In the case of the performing to the structural control as a two-dimensional film, although it is possible to ordering the molecules on the same plane, it does not lead to the formation of conductive fibers having anisotropy. Therefore, while maintaining the stacking of conductive molecular plane, the progression of one-dimensional growth will lead to the creation of new functional molecular devices. The fabrication of a nanometer-scale thin film having a fibril texture, which was achieved by incorporating a phenyl group in the TTF derivatives, has been reported previously [21]. However, the strong interactions between the molecules, which is a consequence of the competing forces of  $\pi$ - $\pi$  interactions (of TTFs and phenyl rings) and hydrogen-bonding (of urethane bonding units), inhibited accurate morphological control. Therefore, in our previous study, we attempted to substitute the phenyl ring with the bulky and chiral borneol group [22], in order to minimize these strong intermolecular interactions. However, since TTF derivatives containing borneol groups are amorphous, top-down fabrication of thin films and control of the molecular arrangement were quite difficult.

Organized molecular films [23] have been developed as potential candidates for the synthesis of biomimetic models [24] and molecular electronic devices [25–27], which are of considerable technological interest [28–32]. In addition to the interaction of

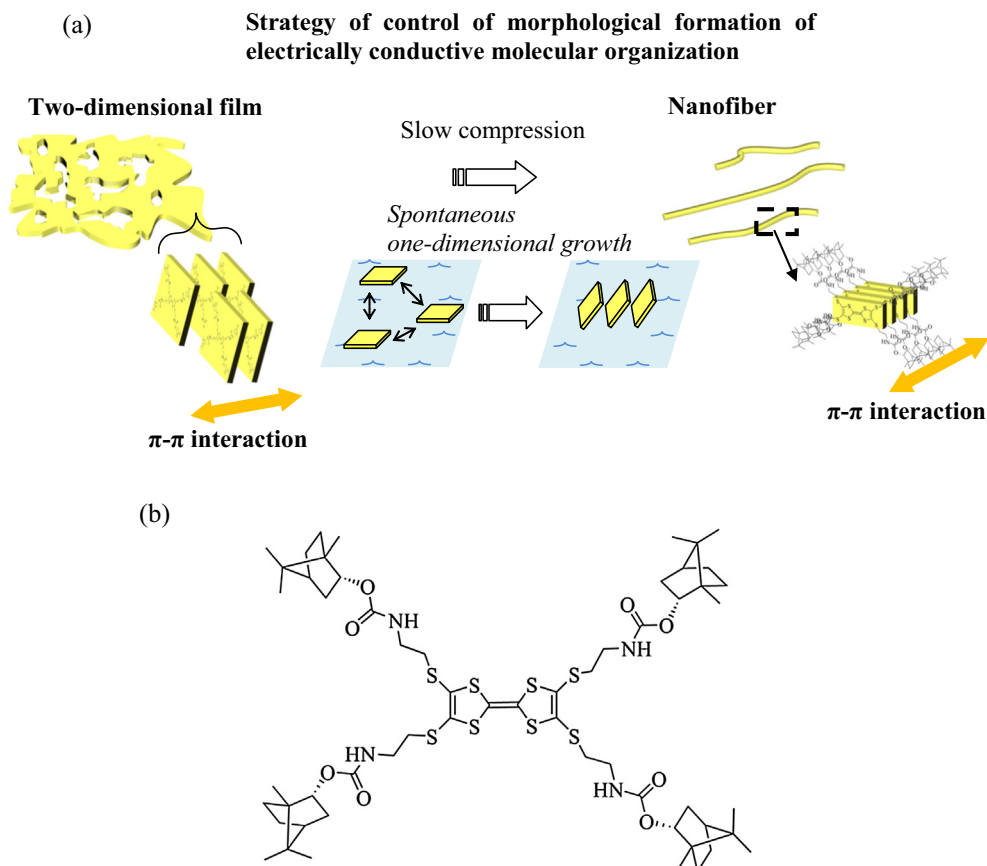
lipids and proteins with hydrocarbons, various amphiphiles containing functional groups (including  $\pi$ - and  $d$ -electron systems), and polymerizable groups have been synthesized to obtain monolayer assemblies with well-defined molecular arrangements [33]. Therefore, this technology could potentially provide an effective means for attaining hierarchically precise and regular structures.

In the present study, a new, conducting, four-armed amphiphilic compound (a TTF derivative with chiral borneol groups (TTF-4Bor, Fig. 1b) [22]) was synthesized. The monolayer behavior, molecular arrangement, and surface morphology of organized molecular films of TTF-4Bor were investigated by analysis of the surface pressure–area ( $\pi$ -A) isotherms, in-plane and out-of-plane X-ray diffraction (XRD) profiles, and atomic force microscopy (AFM) images. Further, morphogenesis was encouraged by applying the one-dimensional growth method to an LB film of TTF-4Bor in distilled water, under low surface pressure conditions. The size of the nanofibers thus obtained was controlled by variation of the subphase temperature. Since the internal structure of the mesoscopic nanofiber is comprised of stacked TTF planes at a molecular level, effective electrical conduction is expected along the direction of stacking.

## 2. Experimental section

### 2.1. Synthesis of TTF-4Bor

The synthesis of tetrathiafulvalene derivative with chiral borneol groups and urethane bond was performed in accordance with



**Fig. 1.** (a) Formation of nanofiber morphology at mesoscopic scale and molecular level stacking and (b) chemical structure of TTF-4Bor.

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