Self-assembly and Solvatochromic Fiber Formation of 4,5-Bis(dodecylthio)tetrathiafulvalene-4′-carboxylic Acid and Its Derivatives

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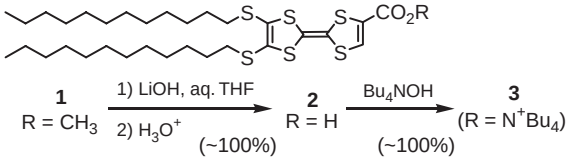
TTF-carboxylic acid **2** exhibits gelling ability for hexane and cyclohexane to form an orange fibrous material and shows solvatochromism both in solution and in the fiber formation to produce a reddish-purple fibrous material from acetonitrile. Moreover, the corresponding ester **1** forms yellow fibers from acetonitrile. However, the tetrabutylammonium salt **3** produces fine microcrystals without gel or fiber formation.

The synthetic chemistry of tetrathiafulvalenes (TTFs) has developed for the past 35 years,[1] and their attractive physical properties such as conductivity,[2] superconductivity,[3] and magnetic properties[4] have been extensively investigated by materials scientists. However, almost no attention has been paid to the self-assembling nanostructures, fiber, and other features of formation of TTFs except for the "fastner effect" of TTF derivatives with long alkyl chains.[5] Recently, several groups have reported that TTFs and their oligomers form nanostructures such as nanofibers, nanotapes, and nanotubes.[6] Moreover, we have shown the self-assembly of disc-like hexakis(tetrathiafulvalenylethynyl)benzene resulting in pronounced stacking in solution and in the formation of a hexagonal fiber in solid state.[7] The molecular framework of TTFs seems to be very effective for the formation of nanostructures.[8] We report here either the self-assembly or solvatochromic fiber formation of simple TTF derivatives.

The methyl ester **1** and the carboxylic acid **2** were prepared from the corresponding TTF-diester by a modification of a reported procedure (Scheme 1).[9] The tetrabutylammonium salt **3** was prepared by simply mixing **2** with an equimolar amount of Bu_4NOH in THF–methanol and then drying the mixture to remove solvents. The compounds **1**–**3** can be stored for a long time at 5 °C without decomposition.

The cyclic voltammetric (CV) analysis of **1** and **2** revealed fairly low oxidation potentials and hence good donor abilities; both **1** (5×10^{-3} M) and **2** (5×10^{-3} M) showed two reversible redox waves at 0.12 and 0.50 V and 0.10 and 0.47 V vs. Fc/Fc^+, respectively.[10] The first oxidation potentials of **1** and **2** are 0.20–0.18 V higher than that of TTF and comparable to that of BEDT-TTF ($E^1_{1/2} = 0.04$ V and $E^2_{1/2} = 0.37$ V vs. Fc/Fc^+ under similar conditions).

The ^{1}H NMR and UV–vis spectra of **1** and **3** in $CDCl_3$ showed no concentration dependence due to the lack of self-aggregation of these compounds in solution. As expected, **2** showed a monomer–dimer equilibrium in solution, and hence the ^{1}H NMR and UV–vis spectra of **2** showed a concentration dependence. Thus, the λ_{max} of 0.00908 mM cyclohexane solution of **2** is 440 nm ($\varepsilon = 1.99 \times 10^3\ M^{-1}\ cm^{-1}$), whereas that of 0.908 mM cyclohexane solution of **2** is 459 nm ($\varepsilon = 2.18 \times 10^3\ M^{-1}\ cm^{-1}$). The red shift by 19 nm is due to the monomer–dimer equilibrium of **2** in cyclohexane.[11]



Scheme 1. Synthesis of 4,5-bis(dodecylthio)tetrathiafulvalene-4′-carboxylic ester **1** and its derivatives **2** and **3**.

Interestingly, **2** gelated hexane (>10 mg cm^{-3}) and cyclohexane (>30 mg cm^{-3}) at room temperature to produce a reddish-orange gel (Figure 1a). The microscopic image (Figure 1b) of xerogel of **2** shows a fine fibrous structure. However, **2** did not gelate CH_3CN but formed reddish-violet fibrous precipitate having a thicker-wire structure (Figure 1c). In the case of **1**, no gelation was observed for the common organic solvents, but a yellow fibrous material was formed from CH_3CN. The microscopic and SEM images (Figures 1d and 1e) of the fibrous material of **1** show a tape-like morphology of 2–10-μm width and 100–1000-nm thickness. The ammonium salt **3** formed no gel or fibrous material from the common organic solvents and produced microcrystals from hexane, cyclohexane, or diisopropyl ether (Figure 1f). Although ionic amphiphilic systems often exhibit gel formation,[7,12] the ammonium carboxylate **3** shows no gelation or fiber formation. Similarly, the corresponding lithium salt showed no gelation or fiber formation.

The XRD profile of **1** fiber showed a regular reflection pat-

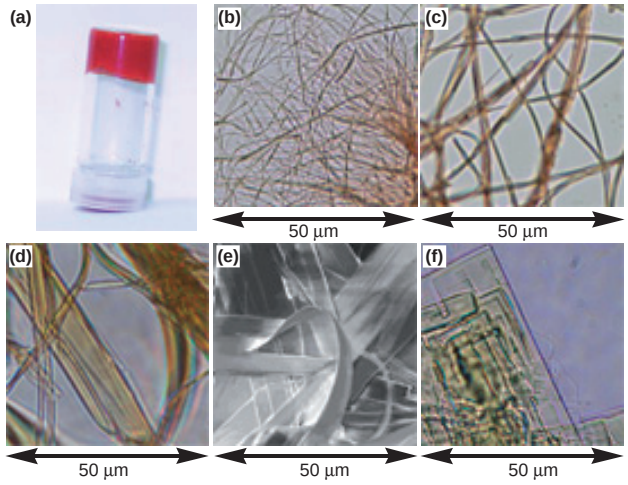


Figure 1. (a) Cyclohexane gel of **2**. (b) Optical micrograph of xerogel of **2**. (c) Optical micrograph of reddish-violet fibrous structure of **2**. (d) Optical micrograph of tape-like structure of **1** from CH_3CN. (e) SEM image of tape-like structure of **1**. (f) Microplates of **3** from cyclohexane.

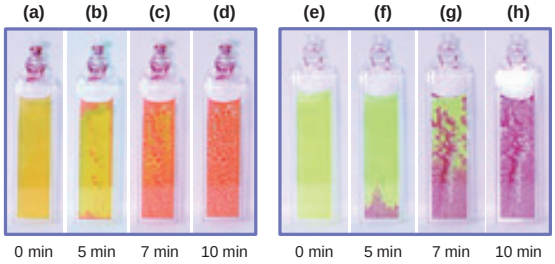


Figure 2. Solvatochromism of the TTF-carboxylic acid **2** in solution and the fibrous structure. (a)–(d) Fiber formation from hot hexane solution of **2** ($2\,mg\,cm^{-3}$). (e)–(h) Fiber formation from hot CH_3CN solution of **2** ($2\,mg\,cm^{-3}$).

tern and a distinct (100) peak at $2\theta = 2.05^\circ$ (4.31 nm) together with higher-order reflections observed in a small-angle region, indicating a considerably high crystallinity and the existence of a lamellar structure of 4.31-nm pitch.[13] Since the molecular size of **1** was estimated to be ca. 28 Å, a dimeric structure with a stacked head-to-head or head-to-tail arrangement could be expected.

It is noteworthy that the colors of **2** fibers prepared from hexane and CH_3CN are quite different. Thus, **2** shows solvatochromism both in solution and in the fiber formation. As indicated in Figures 2a–2d, a hot dilute solution of **2** in hexane ($2\,mg\,cm^{-3}$) was gradually cooled. First, a hot clear-orange solution (Figure 2a) showed UV–vis absorption at λ_{max} 456 nm. After 5 and 7 min, a reddish-orange fibrous material was gradually formed (Figures 2b and 2c), and the fiber formation was almost complete after 10 min (Figure 2d). The fibrous material showed UV–vis absorption at λ_{max} ca. 500 nm. In contrast, a hot dilute solution of **2** in CH_3CN exhibited a different behavior. A hot clear-yellow solution of **2** in CH_3CN ($2\,mg\,cm^{-3}$) (Figure 2e) shows UV–vis absorption at λ_{max} 418 nm. After 5 and 7 min, a reddish-violet fibrous material was gradually formed (Figures 2f and 2g), and the fiber precipitation was almost complete after 10 min (Figure 2h). This fibrous material showed absorption at λ_{max} ca. 580 nm. SEM and AFM images showed that the reddish-orange fiber was of 50–500-nm width and 20–100-nm thickness and that the reddish violet fiber was of 1–2-μm width and 100–1000-nm thickness.[14]

The XRD profile of the reddish-orange fiber as shown in Figure 2d revealed a regular reflection pattern and a distinct (100) peak at $2\theta = 2.34^\circ$ (3.77 nm) together with higher-order reflections; The reddish-violet fiber (Figure 2h) showed a similar regular reflection pattern with a distinct (100) peak at $2\theta = 2.40^\circ$ (3.56 nm) and higher-order reflections.[15] Thus, the XRD profiles of fibrous materials from hexane and CH_3CN indicate a fairly high crystallinity and lamellar structures of 3.77 and 3.56 nm, respectively. Since **2** forms a dimer in solid state, the size of the dimer is estimated to be ca. 5.6 nm. The alkyl–alkyl interaction in CH_3CN should be stronger than that in hexane and cyclohexane. Therefore, a stronger alkyl–alkyl overlap in a CH_3CN solution results in a shorter pitch of the lamellar structure, probably leading to a closer stacking of the TTF moiety. It is known that a J-type aggregation of chromophores results in a red shift, the lamellar structure prepared from a CH_3CN solution leads to a stronger face-to-face interdimer interaction of the TTF moiety. In summary, it is apparent that TTF-carboxylic acid and its derivatives with long alkylthio chains adopt various morphologies depending on their functional substituent and the solvent employed.

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10 The cyclic voltammetric analysis was carried out under the following conditions: 0.1 M $Bu^n_4NClO_4$, CH_2Cl_2, $100\,mV\,s^{-1}$, Pt working and counter electrodes, Ag/Ag^+ reference electrode, see Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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13 For the XRD reflactogram of fibrous material of **1**, see Supporting Information.

14 For the SEM and AFM images of reddish-orange fiber and reddish-violet fiber, see Supporting Information.

15 For the XRD reflactograms of fibrous materials of **2**, see Supporting Information.

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