Communication

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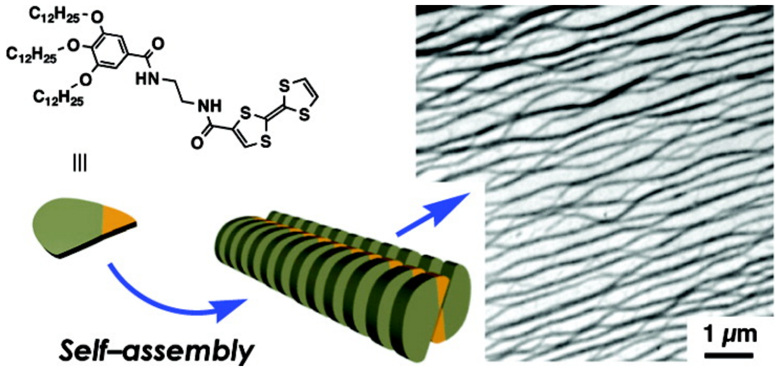

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Creation of a Mixed-Valence State from One-Dimensionally Aligned TTF Utilizing the Self-Assembling Nature of a Low Molecular-Weight Gel

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Tetrathiafulvalene (TTF)[1] is known as an organic conductive material whose high electron conductivity is originated from their π-stacked columnar structures in its single crystals.[2] Reducing the dimensional parameters of the bulk materials matrix from the three-dimensional crystal structure into the one-dimensional columnar structure gathers strong attention since this concept would furnish the functional nanowires[3] which are key materials in advanced nanosciences. Recently, we reported π-*block*-based low molecular-weight gelators that gave extremely elongated π-stacked assemblies through the strong $\pi-\pi$ interaction.[4] On the basis of this knowledge, we have developed a TTF-based low molecular-weight gel in which TTF cores stack with each other to give one-dimensional TTF aggregates, and upon I_2 doping, the one-dimensional aggregates show a characteristic near-infrared (NIR) absorption band at room temperature assignable to a mixed-valence state, which is known to be indispensable for constructing conductive nanowires.

We have newly designed a TTF gelator (**1**)[5] having a 3,4,5-trialkoxybenzoic acid backbone as a gel-forming segment[6] (Figure 1a). Compound **1** shows fine gelating properties in hydrocarbon solvents, such as hexane, decane, and cyclohexane, and their critical gelation concentrations are about 10 g dm^{-3} (Table S1). As **1** gives very transparent gels, they are very suitable for optical analyses without any light scattering effect (Figure 1b). In addition, the hexane gel of **1** has a very viscous property (Figure 1c) at high concentration unlike those of other stiff (sometimes fragile) low molecular-weight gels. This property is advantageous for preparing the elastic film in which the gel fibers are anisotropically arranged (vide post).[7]

To obtain visual images of the assembled **1**, we analyzed the samples with transmission electron microscopies (TEM). For the TEM observations, a carbon-coated copper grid was immersed in the hexane gel at relatively low concentration (50 g dm^{-3}) and dried for 12 h in a desiccator. As seen in Figure 2a, well-developed fibrous structures are observed in the TEM image. This morphology implies that TTF molecules stack with each other, forming one-dimensional wire-like superstructures. Next, the grid was immersed in the hexane gel of **1** at high concentration (100 g dm^{-3}) and pulled up vertically from the gel. After dried, the sample was examined by TEM. As seen in Figure 2b, the fibers are composed of the one-dimensionally assembled **1** with less than 20 nm in width and more than several micrometers in length. Very interestingly, the fibers are highly aligned into the one direction, in accord with that prepared at low concentration. Thus, this gel offers a very simple method to cover the large area with the parallel-oriented TTF-based nanowires, leading to production of thin films with anisotropic conductivity.

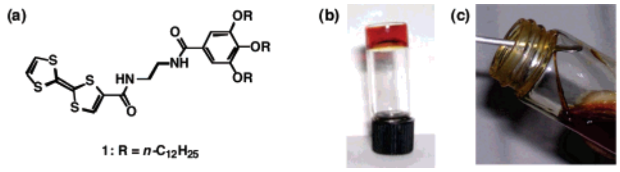

Figure 1. (a) Chemical structure of **1** and photographs showing (b) transparent and (c) viscous nature of the gel prepared from **1** with hexane (100 g dm^{-3}).

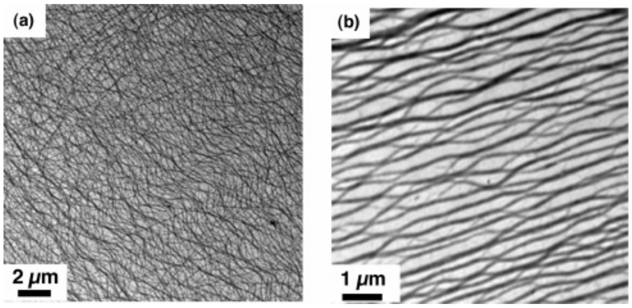

Figure 2. TEM images of the hexane gel of **1**; the samples were prepared at (a) 50 g dm^{-3} and (b) at 100 g dm^{-3}.

It is well-known that conductivity of TTF assemblies is due to its aggregation manner; that is, TTF molecules should stack with each other and form the one-dimensional columnar structure. To obtain the structural insight into the assembled **1** in the gel phase, XRD analyses were applied to this gel system. The cyclohexane gel of **1** (150 g dm^{-3}) was freeze-dried, and the resultant xerogel of **1** was subjected to XRD analyses. An XRD profile of the xerogel shows the appearance of strong peaks at $2\theta = 3.0°$ (100), 6.0° (110 and 200), and 7.8° (210), which are reasonably assigned to a rectangular structure whose cell parameter is $a = 29.5$ Å, $b = 17$ Å, and $c = 4.4$ Å (Figure S1). Each cell consists of two molecules of **1**, and their alkyl substituents, solvophilic with cyclohexane, occupy the outer phase and the TTF molecules occupy the core due to the solvophobicity against cyclohexane. Actually, the AFM image (Figure S2) of the assembled **1** cast on HOPG by spin-coating shows the thinnest fibers having a height of 14 Å, which is consistent with a single fiber composed of dimeric **1**s ($d = 17$ Å). Figure 3a shows a simulation of a stack of 12 TTF gelators (**1**) by means of force field calculations (MMFF, vacuum, TNCG minimization to gradient below 0.001 kJ/mol). In the simulated structure, one can find reasonable TTF stacks, which is consistent with the XRD profile and the AFM observations of **1** gel.

With such assembled **1** in hand, we estimated the electropotential of the gel fibers. The hexane gel of **1** was cast on an ITO electrode and dried for 10 days under ambient conditions to remove the solvent. The resultant gel fibers on the ITO electrode were subjected to the analyses by cyclic voltammetry (tetrabutylammonium

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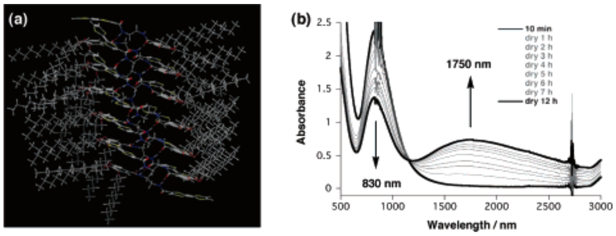

Figure 3. (a) Force field calculations of 12 molecules of **1** and (b) NIR spectra of the assembled **1** prepared from hexane gel of **1** (1.0 g dm^{-3}).

phosphate: 50 mM, reference electrode: Ag/AgCl, counter electrode: Pt wire, scan rate: 100 mV/s, Figures S3 and S4). The obtained cyclic voltammogram of the assembled **1** shows the first oxidation potential at 0.62 V (vs SHE) and the second oxidation potential at 0.96 V (vs SHE)[8] in acetonitrile. Meanwhile, oxidation potentials of naked TTF (15 mM) in acetonitrile are observed at 0.62 and 1.1 V (vs SHE) for the first and the second oxidation potentials, respectively. Although **1** has an amide substituent which may act as an electron-withdrawing group, the first oxidation potential of the assembled **1** is the as same as that of naked TTF, and the second one is observed at the slightly lower potential. In solution, **1** (6.0 mM in benzonitrile) possesses oxidation potentials at 0.66 and 1.2 V (vs SHE) for the first and second oxidation potentials, respectively, which are higher than those of naked TTF under the same conditions (0.57 and 1.1 V vs SHE for the first and second oxidation potentials, respectively). These results clearly show that the oxidation potentials of the assembled **1** become lower owing to the stabilization effect arising from the strong $\pi-\pi$ interaction. Such π-stacked TTF aggregates are expected to show a mixed-valence state upon appropriate doping with oxidation reagents. It is known that I_2 acts as a suitable oxidation reagent because it has reduction potentials at 0.615 V (for I^-, vs SHE) and 0.784 (for I_3^-, vs SHE).[9] One can expect, therefore, that the assembled **1** would undergo the one-electron oxidation to generate the radical cation species of **1**.

To construct TTF nanowires composed of **1** in the gel phase, the hexane gel of **1** (10 g dm^{-3}) was placed on the sidewall of a quartz cell and dried for 5 min. Then, the dried **1** gel was subjected to I_2 doping in an I_2-saturated desiccator for 10 min. The NIR−UV−vis absorption spectral analyses of this sample revealed that the I_2-doped nanowires show a characteristic absorption band at 850 nm, which is assignable to the dimeric radical cation species of the TTF core (π-dimers). Interestingly, the I_2-doped nanowires composed of **1** show a characteristic absorption band at 1750 nm at room temperature after removing the excess I_2 in vacuo, which is assignable to the mixed-valence state of the stacked TTF core.[10] Time-dependence NIR−UV−vis absorption spectral analyses during the removal of I_2 process clearly show that the absorbance at around 1750 nm gradually increases with the decrease in the absorption band at around 850 nm (Figure 3b). This striking observation supports the view that the TTF cores of **1** are assembled through the strong $\pi-\pi$ stacking to give one-dimensional columnar structures, and the assembled TTF cores form the mixed-valence state.

In summary, we have demonstrated that the one-dimensional columnar structure, characteristic of a low molecular-weight gel system, is useful as a potential strategy for construction of TTF nanowires. An unexpected result is that the obtained gel possesses the high viscosity, which has enabled us to prepare the highly aligned self-assembled TTF fibers on the surface. In addition, the mixed-valence state of the TTF stack was observed upon I_2 doping as a characteristic absorption band at the NIR region, which is indispensable to the conductivity generation. These findings consistently indicate that the low molecular-weight gel system is able to provide novel soft materials for electrochemistry.

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Supporting Information Available: Synthesis and gelation properties of **1**. Cyclic voltammogram, XRD analyses, and AFM observation of **1** gel. This material is available free of charge via the Internet at http://pubs.acs.org.

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