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# Organogelators Based on TTF Supramolecular Assemblies: Synthesis, Characterization, and Conductive Property

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A closely related family of organogelators 1-2 appended one or two electroactive tetrathiafulvalene (TTF) residues, has been designed and readily synthesized by Sonogashira reactions. These compounds can gelate a variety of organic solvents in view of multiple intermolecular interactions, and compounds 2 with two TTF subunits exhibit higher gelation ability than their corresponding 1. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigation of the xerogels from toluene gave a visual image showing that fibrillar aggregates are entangled in three-dimensional network structures. The columnar TTF cores stacking in the fiber, evidenced by the mixed-valence states absorption at around 2000 nm in ultraviolet-visible-near-infrared (UV-vis-NIR) spectra, provide an efficient pathway for the electron conduction. Upon oxidized by iodine, these xerogels exhibit semiconductive behaviors with moderate levels of conductivity. Additionally, the electrical conductivity of doped-xerogels 2 is 1 order of magnitude higher than that of 1 under identical conditions.

#### Introduction

The construction of one-dimensional (1D) conductive nanostructures is of great current interest for the fabrication of molecular electronic devices.<sup>1-4</sup> Self-assembly of organic  $\pi$ -conjugated molecules into low molecular mass organic gelators (LMOGs) via specific intermolecular interactions offers a simple and powerful approach to the spontaneous generation of various nanostructures, such as fibers, strands, and ribbons,<sup>5-14</sup> which have shown promise for use in many fields, such as fabrications of conductive nanowires,<sup>10-14</sup> light-harvesting and energy transfer,<sup>7,15,16</sup> sensing,<sup>9</sup> and noncopyable fluorescent imaging.<sup>17</sup> In particular, gelators as soft materials can be deposited on any surface, and the solvent immobilized upon gel formation can be removed by evaporation to leave the active nanostructures of xerogels for

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further study of a conducting nature. Hence, intense research has been devoted to build the family of conductive architectures from organogelators.<sup>10–14</sup> As one of the most famous organic  $\pi$ -donors, tetrathiafulvalene (TTF) derivatives have received intense scrutiny with a focus on fibrous gelators for electrically conducting materials.<sup>18–33</sup> In this context, for instance, Joergensen et al.<sup>20</sup> and Bryce et al.<sup>21</sup> introduced electroactive TTF residues into arborol scaffolds. Akutagawa et al.<sup>22,23</sup> constructed oriented nanowires and organogels based on amphiphilic TTF-substituted macrocycles. Zhang et al.<sup>24,25</sup> utilized the redox properties of TTF moiety to tune the gel–sol transition behaviors. Iyoda et al.<sup>26–29</sup> took advantage of the  $\pi$ -stacking behavior of TTF to build higher aggregates. Shinkai et al.<sup>30</sup> developed a TTF-based gelation

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Chart 1. Chemical Structures of the Gelators Studied Herein



system composed of 1D highly aligned fibers via  $\pi - \pi$  and hydrogen bonding interactions, and the mixed-valence state of the TTF stack was obtained after doping with iodine. Kato et al.<sup>31</sup> combined electroactive TTF-derived gelators with a liquid–crystal approach to generate oriented-gel fibers with electrical conductivity of  $10^{-5}$  S cm<sup>-1</sup>. Amabilino et al.<sup>32,33</sup> recently prepared electroactive fibrillar nanowires from an amide-functionalized TTF organogel with a bulk conductivity of  $3-5 \times 10^{-3}$  S cm<sup>-1</sup> at room temperature after doping with iodine and an irreversible phase transition after heating. All of the results indicate that the use of intermolecular noncovalent interactions via a gelation process to construct TTF-based conducting fibers is very appealing, although most of the fibers exhibit moderate to poor conductivities, presumably due to the poor ability to form a good conduction path between the TTF cores.

Particular interest in building 1D conductive nanostructures and understanding cooperative intermolecular interactions involved in self-assembly process prompted us to prepare the set of TTF derivatives 1-2 shown in Chart 1. Herein, 3,4,5-tris-(n-dodecyloxy)benzoylamide substituents a and cholesteryl group **b** as versatile gel-forming segments,  $^{6-9}$  the amide groups, and one or two electroactive TTF residues were readily introduced to examine the roles and extent of the  $\pi$ - $\pi$  stacking and S····S contacts among the TTF cores, the hydrogen-bonding, and the van der Waals forces among the amide groups and long alkyl chains or cholesteryl group as well (Chart 1). It is anticipated that with the cooperative multiple intermolecular interactions, such compounds can self-assemble into long fibers in organic solvents and entangle further to form gels. In these fibers, the more TTF residues may provide a more efficient conducting pathway. Comparison of the electrical conductivities of xerogels upon partial oxidization by iodine not only offers ideal TTF-based conductive nanostructures, but also provides valuable information as to what extent the TTF cores interact in these selfassembling fibers. The detailed results are presented below.

### **Experimental Section**

The synthesis of compounds 3-9 is described in the Supporting Information.

General Synthetic Procedures for 1 and 2. To the mixture of anhydrous tetrahydrofuran (THF; 30 mL) and triethylamine (TEA; 30 mL) were added 8 (0.50 mmol) or 9 (0.50 mmol), TTF-I (0.60 or 1.2 mmol), CuI (3.8 mg, 0.02 mmol), and Pd-(PPh<sub>3</sub>)<sub>4</sub> (12 mg, 0.01 mmol) under Ar. The reaction mixture was refluxed over 12 h under Ar atmosphere and was monitored by thin-layer chromatography (TLC). Upon completion, the solution was evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ EtOAc, 30/1) to give compound 1 or 2 as a red solid.

**1a** (0.36 g, 0.34 mmol, 68%): <sup>1</sup>H NMR (400 MHz, Pyr) δ 9.33–9.28 (m, 2H), 8.26 (d, J = 8.4 Hz, 2H), 7.78 (s, 2H), 7.61 (s, 1H), 7.16 (s, 1H), 6.63 (t, J = 6.6 Hz, 2H), 4.32 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 6.4 Hz, 4H), 3.80 (dd, J = 11.0, 5.3 Hz, 4H), 2.07–1.94 (m, 4H), 1.85–1.78 (m, 4H), 1.73–1.66 (m, 2H), 1.50–1.41 (m, 4H), 1.30 (br, 48H), 0.90 (t, J = 6.7 Hz, 9H). <sup>13</sup>C NMR (101 MHz, Pyr) δ 168.1, 167.4, 154.0, 141.7, 132.3, 131.0, 128.5, 128.1, 125.2, 120.5, 120.3, 115.8, 115.1, 107.8, 107.1, 93.7, 83.5, 74.0, 69.7, 37.8, 37.7, 32.6, 31.3, 30.8, 30.4, 30.2, 30.1, 27.0, 26.8, 23.4, 14.7. MALDI-TOF-MS: m/z calcd for C<sub>61</sub>H<sub>92</sub>N<sub>2</sub>O<sub>5</sub>S<sub>4</sub>: 1061.6; found: 1060.4 [M]<sup>+</sup>. Anal. calcd (%) for C<sub>61</sub>H<sub>92</sub>N<sub>2</sub>O<sub>5</sub>S<sub>4</sub>: C, 69.01; H, 8.73; N, 2.64; found: C, 69.07; H, 8.80; N, 2.82.

**1b** (0.23 g, 0.28 mmol, 56%): <sup>1</sup>H NMR (400 MHz, Pyr) δ 9.18 (t, J = 5.5 Hz, 1H), 8.22 (d, J = 8.2 Hz, 2H), 7.88 (t, J = 5.8 Hz, 1H), 7.17 (s, 1H), 6.63 (t, J = 6.8 Hz, 2H), 5.41 (d, J = 4.9 Hz, 1H), 4.97–4.84 (m, 1H), 3.80 (q, J = 6.2 Hz, 2H), 3.56 (dd, J = 12.1, 6.0 Hz, 2H), 2.64–2.44 (m, 2H), 2.05–0.91 (m, 40H, cholesterol and NHCH<sub>2</sub>*CH*<sub>2</sub>CH<sub>2</sub>NH), 0.68 (s, 3H, cholesteryl CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Pyr) δ 167.3, 157.7, 140.7, 132.3, 128.5, 128.1, 125.1, 123.0, 120.5, 120.3, 115.8, 115.1, 107.8, 93.7, 83.4, 74.5, 57.2, 56.8, 50.7, 42.9, 40.3, 40.1, 39.6, 39.1, 38.1, 37.7, 37.2, 36.9, 36.4, 32.6, 32.5, 31.2, 30.4, 29.1, 28.9, 28.6, 24.9, 24.6, 23.3, 23.1, 21.7, 19.8, 19.4, 12.4. MALDI-TOF-MS: m/z calcd for C<sub>46</sub>H<sub>60</sub>N<sub>2</sub>O<sub>3</sub>S<sub>4</sub>: 817.2; found: 816.4 [M]<sup>+</sup>, 839.4 [M+Na]<sup>+</sup>. Anal. calcd (%) for C<sub>46</sub>H<sub>60</sub>N<sub>2</sub>O<sub>3</sub>S<sub>4</sub>: C, 67.60; H, 7.40; N, 3.43; found: C, 67.62; H, 7.53; N, 3.49.

**2a** (0.46 g, 0.36 mmol, 72%): <sup>1</sup>H NMR (400 MHz, Pyr)  $\delta$  9.44 (t, J = 5.8 Hz, 1H), 9.27 (t, J = 5.8 Hz, 1H), 8.32 (d, J = 1.3 Hz, 2H), 7.77 (s, 2H), 7.64 (t, J = 1.4 Hz, 1H), 6.65 (d, J = 1.2 Hz, 4H), 4.31 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 6.4 Hz, 4H), 3.84 (d, J = 4.9 Hz, 4H), 2.16–2.09 (m, 2H), 2.01–1.94 (m, 2H), 1.86–1.80 (m, 4H), 1.73–1.65 (m, 2H), 1.52–1.49 (m, 4H), 1.30 (br, 48H), 0.90 (t, J = 6.8 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.9, 166.4, 154.0, 141.6, 136.9, 131.7, 131.1, 128.5, 120.5, 120.3, 115.5, 115.3, 107.7, 107.0, 92.5, 83.0, 74.0, 69.7, 38.2, 37.9, 32.6, 31.3, 30.7, 30.4, 30.2, 30.1, 30.1, 27.0, 26.9, 23.4, 14.7. MALDI-TOF-MS: m/z calcd for C<sub>69</sub>H<sub>94</sub>N<sub>2</sub>O<sub>5</sub>S<sub>8</sub>: C, 64.34; H, 7.36; N, 2.17; found: 64.72; H, 7.53; N, 2.28.

**2b** (0.25 g, 0.24 mmol, 48%): <sup>1</sup>H NMR (400 MHz, Pyr)  $\delta$  9.30 (t, J = 5.3 Hz, 1H), 8.32 (d, J = 1.3 Hz, 2H), 7.91 (t, J = 5.3 Hz, 1H), 7.63 (s, 1H), 6.67–6.63 (m, 4H), 5.43–5.41 (m, 1H), 4.90–4.85 (m, 1H), 3.84 (dd, J = 12.3, 6.2 Hz, 2H), 3.61 (dd, J = 12.1, 6.0 Hz, 2H), 2.66–2.62 (m, 1H), 2.48 (t, J = 11.7 Hz, 1H), 2.12–0.90 (m, 40H, cholesterol and NHCH<sub>2</sub>*CH*<sub>2</sub>CH<sub>2</sub>NH), 0.69 (s, 3H, cholesteryl CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Pyr)  $\delta$  166.1, 157.7, 140.7, 137.0, 136.8, 131.7, 128.5, 123.4, 123.0, 120.6, 120.3, 115.5, 115.2, 107.8, 92.6, 83.0, 74.5, 57.2, 56.8, 50.6, 42.9, 40.4, 40.1, 39.6, 39.3, 38.4, 37.7, 37.2, 36.9, 36.5, 32.6, 32.5, 31.0, 29.1, 28.9, 28.6, 24.9, 24.6, 23.4, 23.1, 21.7, 19.8, 19.4, 12.4. MALDI-TOF-MS: m/z calcd for C<sub>54</sub>H<sub>62</sub>N<sub>2</sub>O<sub>3</sub>S<sub>8</sub>: C, 62.15; H, 5.99; N, 2.68; found: C, 61.97; H, 6.08; N, 2.75.

#### **Results and Discussion**

Synthesis and Characterization. The synthesis of new gelators based on TTFs 1-2 were accomplished in high yields by using the Sonogashira reaction (Scheme 1). The starting compounds 3 with different R groups and gel-forming segments **a** and **b**, were directly coupled with iodo-substituted benzoic acid, with the aid of the coupling reagent benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) in a mixture of dimethylformamide (DMF) and CH<sub>2</sub>Cl<sub>2</sub>, to give compounds 4 and 5. The Sonogashira reactions of 4 and 5 with excess (trimethylsilyl)acetylene (TMSA) yielded 6 and 7, respectively, which were then deprotected by excess K<sub>2</sub>CO<sub>3</sub> in the mixture of CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub> to afford the terminal alkyne compounds **8** and **9**. Then, **8** and **9** were reacted with 2-iodotetrathiafulvalene in



<sup>*a*</sup>(a) 4-iodobenzoic acid or 3,5-diiodobenzoic acid, PyBOP, TEA, DMF, CH<sub>2</sub>Cl<sub>2</sub>; (b) TMSA, [Pd(PPh<sub>3</sub>)<sub>4</sub>], CuI, TEA, THF; c) K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>OH, CH<sub>2</sub>Cl<sub>2</sub>; (d) 2-iodotetrathiafulvalene, [Pd(PPh<sub>3</sub>)<sub>4</sub>], CuI, TEA, THF.

Table 1. UV-Vis Absorption and Electrochemical Properties of Compounds 1 and 2

	$(\varepsilon/\mathrm{dm}^{-3}\mathrm{mol}^{-1}\mathrm{cm}^{-1})^a$	$E^1_{1/2} \ /\mathrm{mV}^b$	$E_{1/2}^2 /\mathrm{mV}^b$
1a	299 (33131), 433 (4110)	605	856
1b	302 (31722), 434 (4115)	594	852
2a	296 (50954), 434 (7785)	591	895
2b	300 (48876), 435 (7877)	574	887

<sup>*a*</sup> Recorded at room temperature in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup> The data are given vs an SCE reference electrode in THF with *n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as the supporting electrolyte (100 mV s<sup>-1</sup>) at room temperature;  $E_{1/2} = (E_{pa} + E_{pc})/2$ ;  $E_{pa}$  and  $E_{pc}$  are the peak anodic and peak cathodic potentials, respectively.

the presence of triethylamine (TEA) in THF under typical Sonogashira reaction conditions to produce target compounds 1 and 2, which were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, matrixassisted laser desorption/ionization mass spectrometry (MALDI-TOF MS), and satisfactory elemental analysis.

The absorption spectra of compounds 1 and 2 in  $CH_2Cl_2$ display two absorption bands at  $\lambda < 310$  nm and 430-440 nm, respectively (Table 1). With reference to our previous work on  $\pi$ -conjugated bond-bridged TTF- $\pi$ -A compounds,<sup>34-36</sup> the intense absorption band at high energy with extinction coefficients on the order of  $10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> is assigned to a local transition in the TTF moiety, while the low energy absorption band arises from intramolecular charge transfer. Additionally, the extinction coefficients of 2a and 2b were nearly twice those of 1a and 1b, in line with two TTFs units being involved in compounds 2a and 2b. It is well-known that TTF can be oxidized to its radical cation (TTF<sup>+•</sup>) and dication (TTF<sup>2+</sup>) sequentially and reversibly at low potentials ( $E_{1/2}^1 = 491$  mV and  $E_{1/2}^2 = 784$ mV vs saturated calomel electrode (SCE), in THF solution); we performed cyclic voltammetries (CV) to study the electrochemical properties of compounds 1 and 2 (Figure S1). As shown in Table 1, all of them exhibit two reversible redox waves. For 1a and 1b, the two oxidation potentials derive from two successive one-electron oxidation, corresponding to the formation of cation radical  $1^{+\bullet}$  and dication  $1^{2+}$ , while for **2a** and **2b** bearing two TTF units, these two redox waves correspond to the formation of

 
 Table 2. Gelation Properties of 1 and 2 in Selected Organic Solvents at Room Temperature<sup>a,b</sup>

solvents	1a	1b	2a	2b
Hexane	Ι	Ι	Ι	Ι
cyclohexane	Р	Ι	G (19.7)	Ι
dichloromethane	S	S	G (19.2)	G (16.9)
chloroform	S	S	G (17.6)	PG
benzene	G (25.2)	G (21.3)	G (14.9)	G (12.2)
chlorobenzene	G (28.1)	G (19.4)	G (14.2)	G (12.5)
toluene	G (26.3)	G (21.1)	G (14.4)	G (10.3)
o-xylene	G (24.8)	G (20.9)	G (13.1)	G (10.6)
<i>p</i> -xylene	G (26.6)	G (22.6)	G (14.1)	G (10.1)
pyridine	S	S	S	S
1,4-dioxane	PG	S	G (19.1)	S
ethanol	Ι	Ι	Ι	Ι
DMSO	G (15.3)	PG	Ι	S
DMF	PG	S	G (17.4)	S

<sup>*a*</sup>G: gel; PG: partial gel; P: precipitation; S: soluble; I: insoluble when heated. <sup>*b*</sup> The critical gelation concentrations [CGC, mg mL<sup>-1</sup>] of gelators are shown in the parentheses.

bis(cation-radical)  $2^{2+\bullet}$  and bis(dication)  $2^{4+}$ , originating from two two-electron oxidations of **2**. All of the potentials are shifted to higher positive values relative to the parent TTF, suggesting that the intramolecular charge transfer from the TTF unit to the amide acceptor moiety decreases the electron density of TTF and makes the oxidation of TTF cores less favorable.

Gelation Behavior. As described above, compounds 1 and 2 are expected to gelate some organic solvents with the aid of the cooperative multiple intermolecular interactions, including  $\pi - \pi$ stacking, hydrogen-bonding, van der Waals forces, and S···S interactions. To evaluate the gelation ability of 1 and 2, the "stable to inversion of a test tube" method was used in a selection of organic solvents (fore more detail, see the Experimental section in the Supporting Information). In general, all of the compounds can gel aromatic solvents, such as benzene, toluene, and *p*-xylene, while they are insoluble in protic solvent, such as water and ethanol, even after heating. The better gelations for aromatic solvents relative to the hydrocarbon or halogenated hydrocarbons shown in Table 2 is probably due to the enhancement of  $\pi - \pi$ interactions in aromatic solvents.<sup>6</sup> It was noted that heating the gel above the gel-to-sol phase transition temperature  $(T_{gel})$  disrupts the gel superstructure and reforms the isotropic solution. Upon cooling, the sol becomes the gel, and the whole process is reversible and can be repeated over a great number of cycles. Comparison of critical gelation concentration (CGC, the minimum amount of gelator required for immobilizing the solvent)

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among these gelators in organic aromatic solvents reveals that **1b** and **2b** with cholesteryl group **b** as the gel-forming segment has a better gelation ability than **1a** and **2a** bearing 3,4,5-tris(*n*-dode-cyloxy)benzoylamide substituents **a** in the given solvents, pre-sumably because the structure of cholesteryl **b** is more rigid than that of group **a**, and thereby increases van der Waals forces (Table 2). In contrast to **1a** and **1b** bearing one TTF unit, **2a** and **2b** having two TTF moieties exhibit a pronounced gelation ability as indicated by the lower CGC values, suggesting that  $\pi - \pi$  stacking and S···S interactions are crucial in mediating the gel formation.

The  $T_{gel}$  values of gelators 1 and 2 at different concentrations in toluene were determined to examine their thermostabilities. Similar to that reported in the literature, <sup>5-9</sup>  $T_{gel}$  increased with the gelator concentrations (Figure 1). In relation to 1a and 1b, 2a and 2b show higher stability in a broad range of concentrations, with  $T_{gel}$  values around 26, 28, 42, and 44 °C for 1a, 1b, 2a, and 2b at 31 mg mL<sup>-1</sup>, respectively. Moreover, the organogels 2a and 2b in toluene can be stored for months without any sign of decomposition, while phase separation was observed in gels 1a and 1b under identical conditions after one week.

To gain insight into the gel-to-sol transition behavior and the reversibility of this process, we selected the gel of 2a in toluene as an example, to conduct the temperature-dependent UV-vis spectra in a 1 mm cuvette. The gel was subject to UV-vis measurement at temperature ranging from 5 to 90 °C, and the absorbance at 564 nm, the typical absorption of intramolecular charge transfer, was used to monitor the gel-to-sol transition



**Figure 1.** Gel-to-sol transition temperature  $(T_{gel})$  for gels 1 and 2 in toluene as a function of the concentration of the gelator.

process shown in Figure 2a. As temperature exceeded 40 °C, the rapidly decreased absorption intensity at 564 nm suggested the initial collapsing of the gel, i.e., the gel-to-sol transition. When the temperature was higher than 55 °C, the gel completely changed to a clear homogeneous solution. When the hot solution was placed in room temperature environment within a few minutes, the gel was reformed. The processes can be repeated by several cycles of heating and cooling (Figure 2b), indicative of the fully thermoreversible sol-to-gel conversion. In contrast, no spectral change was observed in the  $3.0 \times 10^{-5}$  M dilute solution. The fact that compound 2a in the gel state exhibited more intense color than its corresponding solution counterparts (see Figure 2a inset) is consistent with the red-shift of the typical intramolecular charge transfer absorption of these compounds in xerogels (Figure S2). Although 1b and 2b with chiral cholesterol units were totally circular dichroism silent in solution, their xerogel displayed two negative signals at 330 and 530 nm, respectively (Figure S3). All of the observations imply molecular aggregation in the gel state.

Self-Assembly Study. The morphology of xerogels obtained from different solvents (after evaporation of the solvent) was investigated by field-emission scanning electron microscopy (FE-SEM). In general, most of the gels show an entanglement of fibrous aggregates. Figure 3 shows the typical FE-SEM images of xerogels 1 and 2 upon depositing the gels in toluene on silicon wafers under identical conditions. The gelator molecules in the gel phase were self-assembling into 1D fibers with varying width and length in bundles that further extended to form a large



Figure 3. Typical FE-SEM images obtained from air-dried gels 1a (a), 1b (b), 2a (c), and 2b (d) from toluene.



**Figure 2.** (a) The absorbance changes at 564 nm of **2a** in toluene with a high concentration of  $1.6 \times 10^{-2}$  M ( $\blacktriangle$ ) and a low concentration of  $3.0 \times 10^{-5}$  M ( $\blacksquare$ ), respectively. Light-path length = 1 mm; inset shows the visual color changes of **2a** from the gel-to-sol transition. (b) The reversibility of the gel-to-sol transition processes of **2a** in toluene monitored at 564 nm.



**Figure 4.** Phase transition and thermochromic behavior of the sol (left) and gel (right) phases of **2a** (a) in toluene, and FE-SEM images of xerogels of **2a** in different solvents: (b) dichloromethane, (c) cyclohexane, (d) benzene, (e) *p*-xylene, (f) *o*-xylene, (g) chlorobenzene, (h) chloroform, (i) 1,4-dioxane, and (j) DMF. Samples were prepared by drop-casting the gels on a silicon substrate, drying under air, and coating with Au.

three-dimensional (3D) fibrous network. Close inspection of these fibers revealed that the fiber morphologies of **1b**, **2a**, and **2b** are more entangled in gels than that of **1a** (Figure 3a), which was also confirmed by transmission electron microscopy (TEM) images (Figure S4). The latter xerogel of **1a** fibers is thicker, larger, and shorter than the former three gels, consistent with its lower thermostability and transparent appearance in toluene (Figure S4a).

The morphologies and textures of these xerogels were found to depend on the nature of the gelating solvents (Figure 4 and Figures S5-S7). Herein, the gel of 2a was selected as a representative example to show the morphologies of xerogels 2a obtained from different solvents, as illustrated in Figure 4. The samples of xerogels for FE-SEM imaging were prepared from the organic solvents at the same concentration by evaporating the solvent at ambient under identical conditions except for the DMF. In CH<sub>2</sub>Cl<sub>2</sub>, a loose packed network composed of long and thick fibers about 100 nm in diameter and even over 10 mm in length were observed (Figure 4b). In the case of cyclohexane, larger but shorter fibers were presented with some fusion (Figure 4c). In contrast, the xerogels derived from aromatic solvents such as benzene, *p*-xylene, and chlorobenzene exhibited a closely packed 3D network structure, which was composed of interlocked thinner and more uniform fibers with diameter in the range 50-90 nm extending over micrometers (Figure 4d-g). And a similar 3D network consisted of highly entangled fibers, was also observed in chloroform (Figure 4h). For the xerogel obtained from 1,4-dioxane, we could not observe any obvious fibrous structures even under high magnification, probably due to the serious fusion of the fibers during the evaporation of the solvent (Figure 4i). As for DMF, the solvent was evaporated in vacuum. The thicker and larger fibers were always obtained, in comparison with those derived from the aromatic solvents (Figure 4j). Although the drying process may influence the original structures of the gels, we found that these morphological features of xerogels from different solvents were highly reproducible in our cases. Similar solvent dependent morphologies were also observed in the other gels of 1a, 1b, and 2b (Figures S5-S7, Supporting Information). The precise roles of the solvents in governing the process of gelation and determining the morphologies of these gels are still ambiguous at the present stage; however, these results suggested that the microstructures of the xerogels could be tailored by the variation of solvents, one of the previously indicated important effects of solvent on gel structures.<sup>37,38</sup>

To probe the roles of TTF units as well as hydrogen bonding between the amide groups in the gelation process, temperaturedependent <sup>1</sup>H NMR studies of gel **2a** and **2b** were conducted in  $d_6$ benzene in the range of 20–80 °C (Figure 5). At a low temperature of 20–30 °C, broad and weak proton signals were observed due to extensive aggregation in the gel states of **2a** and **2b**. With

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Figure 5. Partial temperature-dependent <sup>1</sup>H NMR spectra (300 MHz) of 2a (a,  $2.5 \times 10^{-2}$  M) and 2b (b,  $2.8 \times 10^{-2}$  M) in benzene- $d_6$ .



Figure 6. FT-IR spectra of 2a (a) and 2b (b) in CHCl<sub>3</sub> solutions (dashed line) and xerogels (solid line) obtained from toluene, respectively.

temperature increasing to 80 °C by 10 °C steps, all of the signals in the <sup>1</sup>H NMR spectra became sharp and strong, along with the notable splitting. Meanwhile, the amide NH proton signal resonance shifted to upfield position, whereas the proton resonance of TTF units was downfield. The slightly downfield shift of aromatic proton neighboring the TTF units was also detected with warming. For **2b**, the signal of the amide  $NH^1$  and  $NH^2$  was shifted from  $\delta = 4.57$  to 4.44 ppm and from 6.73 to 6.44 ppm over the temperature range of 60 °C, respectively, evidencing the involvement of the NH protons in intermolecular hydrogen bond interactions. Additionally, the proton signal resonance of TTF residues shifted to downfield, from 5.88 to 6.04 ppm and from 5.39 to 5.56 ppm, respectively. The upfield shift of the amide NHprotons signal resonance and the downfield shift of the TTF and aromatic proton signals with increasing temperature indicate the weakening of intermolecular hydrogen bonding and aromatic  $\pi - \pi$  interactions as well as S···S interactions. In addition, we obtained concentration-dependent <sup>1</sup>H NMR spectra of 1 and 2 in  $d_6$ -benzene (Figure S8). The increase in the concentration resulted in the downfield shifts of amide NH and the slightly upfield shifts of the resonance signals for the aromatic and TTF protons, along with broadening of all signals. Evidently, the gel aggregates were indeed stabilized by the intermolecular interactions mentioned above.

The intermolecular hydrogen-bonding between the amide groups was further investigated by Fourier transform infrared (FT-IR) spectroscopy, which is an important tool for studying the different noncovalent interactions involved in gelation.<sup>39,40</sup> The FT-IR spectra of the four gelators 1-2 both in dilute chloroform solution and in xerogel form prepared from toluene were measured (Figure 6 and Figure S9). In chloroform solution, all of the gelators exhibited a characteristic non-hydrogen-bonding transmittance band at 3420-3390, ~1650, and 1540-1565 cm<sup>-1</sup> for amide  $v_{N-H}$  (amide A), amide  $v_{C=O}$  (amide I), and  $\delta_{N-H}$  (amide II), respectively. A remarkable shift of the amide N-H stretching vibration  $(v_{N-H}, \text{ amide } A)$  to a lower wavenumber around  $3300 \text{ cm}^{-1}$  was observed in the xerogels 1–2. Additionally the C=O stretching ( $v_{C=O}$ , amide I) and N-H bending ( $\delta_{N-H}$ , amide II) bands for the xerogels respectively shifted to lower wavenumbers by  $10-25 \text{ cm}^{-1}$  and higher wavenumbers by  $15-25 \text{ cm}^{-1}$ , as

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Figure 7. Schematic representation of the postulated molecular

compared with those in the corresponding  $CHCl_3$  solution. The red shifts of amide N–H and C=O stretching as well as the blue shift of the N–H bending band demonstrated the presence of intermolecular hydrogen bonding between the amide groups in the gel state. As far as **2b** and **1b** were concerned, the stretching of ester carbonyl was found to shift to the lower wavenumber, further supporting the formation of the intermolecular hydrogen bonding.

packing model for xerogels 1-2.

To get an idea about the nature of the aggregate, wide-angle (WAXRD) and small-angle (SAXRD) X-ray diffractions of the xerogels 1-2 obtained from toluene were estimated (Figure S10-S11). All of the xerogels show a characteristic reflection peak in the wide-angle region at  $\sim$ 4.0 Å, which is related to the  $\pi - \pi$  stacking distance between TTF molecules.<sup>3,4,31</sup> In the lowangle range  $(0.8-8^{\circ})$ , the xerogel **1a** showed three reflection peaks at 7.42 nm, 3.02 nm, and 2.28 nm with a ratio of 1:1/2:1/ 3, illustrating that the molecules were packed into the lamellar structure. For xerogel 2a, a broad peak at 1.26° corresponding to a *d*-spacing of 7.01 nm was observed. The *d*-spacing 7.42 nm of **1a** and 7.01 nm of **2a** could be attributed to the distance of a stacked bilayer of 1a and 2a in a "tail-to-tail" fashion (Figure S12). Diffraction peaks were also observed for xerogel 1b and **2b**, indicating that the molecules are arranged orderly in the gel phase. The two reflection peaks at 2.05° (4.31 nm) and 4.32° (2.05 nm) in a ratio of 1:1/2 for xerogel 1b suggest a lamellar structure with a layer distance of 4.31 nm. As for xerogel 2b, a broad peak at 2.10° corresponding to the d-spacing of 4.21 nm was observed. The *d*-spacing 4.31 nm of 1b and 4.21 nm of 2b could be ascribed to the distance of a stacked single layer of 1b and **2b** in a "head-to-tail" fashion, which is different from xerogels 1a and 2a (Figure S13). On the basis of <sup>1</sup>H NMR, FT-IR, and SAXRD studies, it is clear that the cooperative interactions of the  $\pi - \pi$  stacking and S...S contacts among the TTF cores, the hydrogen-bonding, and the van der Waals forces among the amide groups and long alkyl chains or cholesteryl group can self-assemble molecules of 1-2 into long fibers in organic solvents and entangle further to form gels, as simulated in Figure 7.

**Conductive Property.** To examine whether more TTF residues involved in 1-2 could provide a more efficient conducting pathway, we performed the iodine-doping process for the xerogels of 1-2 derived from toluene under identical conditions. Typically, the xerogels of 1-2 were subject to iodine doping for 5 min, and then evaporated in vacuum for 1 day to remove excess iodine. UV–vis–NIR absorption of the xerogels in the oxidized state was





Figure 8. I-V curves measured on xerogel 2a prepared from toluene before and after doping with I<sub>2</sub>, respectively. The inset is a schematic representation of a top-contact device.

measured to investigate the assembled structure. New absorption bands appear at around 2000 nm, corresponding to the characteristic mixed-valence state of the stacked TTF cores13,14,18-33 (Figure S14). No significant variations could be detected in the UV-vis-NIR spectrum even after 1 week, suggesting that the mixed-valence state is quite stable. Electron spin resonance (ESR) spectroscopy of the doped-xerogels shows a broad peak with g values of about 2.008, whereas it was silent for the undopedxerogels. The results indicate the presence of TTF radical species in the partially oxidized fibers. The peak-to-peak line width  $(\Delta H_{\rm nn})$  in ESR around 4.0 G suggests the lower dimensional semiconductor-like  $\alpha$ -phase of as-prepared materials at room temperature (Figure S15).<sup>41</sup> Since no detectable changes in SEM images, XRD profiles, and even the N-H and C=O stretching bands of the amide groups in FT-IR spectroscopies before and after doping with iodine were observed, it is reasonable to think that this doping procedure did not have much influence on the structures and morphologies of these fibers (Figures S10, S11, S16, and S17).<sup>31,42</sup>

The bulk electrical conductivities of the doped-xerogels in the compressed pellets were examined by using a four-probe configuration in the Quantum Design Physics Property Measurement System (PPMS-9) at room temperature. The conductivities ( $\sigma_{rt} =$  $2.2 \times 10^{-5} \,\mathrm{S \, cm^{-1}} (1a, 4 \times 5 \times 0.1 \,\mathrm{mm}), 4.3 \times 10^{-5} \,\mathrm{S \, cm^{-1}} (1b, 6 \times 5 \times 10^{-5} \,\mathrm{S \, cm^{-1}})$ 0.1 mm),  $2.6 \times 10^{-4} \text{ S cm}^{-1}$  (2a,  $8 \times 7 \times 0.1 \text{ mm}$ ), and  $3.8 \times 10^{-4} \text{ S cm}^{-1}$ (2b,  $7 \times 6 \times 0.1$  mm), respectively) indicate that a significant degree of supramolecular order is present with  $\pi - \pi$  stacking of the TTF cores.<sup>13,14,18–33</sup> The temperature-dependent conductivity measurements in the range of 200-298 K revealed a semiconducting behavior (Figure S18). However, no signals were detected by this four-probe method for the undoped xerogels. Since the limiting value of the instrument with respect to the electrical resistivity measurement is  $2 \times 10^7 \Omega$ , the electrical conductivity  $\sigma_{rt}$  for the xerogels without doping must be smaller than  $10^{-7}$  S cm<sup>-1</sup>. These results indicate that the formation of the mixed-valence state is essential to acquire the electric conducting TTF assemblies. Evidently, the conductivity of as-prepared semiconducting xerogels 2 is 1 order of magnitude higher than that of 1, which can be rationalized by the fact that two TTF residues in close-packed gelator 2 provide a more efficient

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conducting pathway in these fibrous nanowires. From X-ray diffraction (XRD) analysis of the xerogels, the TTF stacking distance read from peak at 23.4° in 2 (3.8 Å) is smaller than that in xerogel 1, suggesting that there is an enhanced  $\pi - \pi$  stacking interaction and closer-packed arrangement in xerogel 2.<sup>40</sup> Moreover, the conductivity of the films prepared by drop-casting of 1-2 solution in THF with the same doping process were measured on the order of  $10^{-6}$  S cm<sup>-1</sup>, indicating that the gelation plays important roles on the electronic properties.<sup>10,11,43</sup>

Furthermore, a top-contact device with two Au-electrodes was constructed for xerogel 2a as a typical example to investigate current-voltage (I-V) characteristics without and with iodine-doping (for more detail, see the Experimental Section). All of the I-V measurements were performed under an air atmosphere, and the curve of the device was recorded by scanning the applied voltage from -10 to +10 V. As shown in Figure 8, the fibrous aggregates fabricated from 2a indeed display much higher conductivity upon doping with iodine, whereas the same sample without doping was hardly conductive with current in the range of pA. A distinct nonlinear dependence with a small threshold voltage was observed in the I-V characteristics of the doped sample, and no significant change was detected in the I-V curves after 1 week, reflecting its fairly high stabilities (Figure S19 in the Supporting Information). Several repeated measurements verified the reproducibility of I-V characteristics. Moreover, the conductivities of the xerogels estimated from I-V curves of the device before and after doping with iodine are on the order of  $10^{-8}$  and  $10^{-4}$  S  $cm^{-1}$ , respectively, in line with that measured for compressed pellets.

## Conclusion

In summary, we described the hierarchal self-assembly and conductive properties of supramolecular organogels 1-2 based on TTFs, which are easily prepared by Sonogashira reaction in relatively high yields. SEM investigations provide clear evidence for the formation of self-assembled nanofibers with the aid of the cooperative multiple intermolecular interactions. The fibers exhibit electrical conductivities upon doping with iodine, suggesting that the TTF cores interact with each other to a significant extent in these self-assembling fibers. Gelator 2 bearing two TTF units displays pronounced gelation ability as well as higher conductivity in relation to compound 1. These results demonstrate that the properties of the gelators, e.g., gelaion ability and conductivity, can be modulated by varying the number of TTF residues in the gel scaffolds to enhance their conductivity. The conductivity of the doped xerogels obtained in the present work is reproducible and stable at least for 1 week, implying a potential application in molecular electronic devices.

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**Supporting Information Available:** Experimental details, NMR and MS data of the compounds, SEM and TEM images, XRD, UV-vis-NIR, and ESR of these xerogels. This information is available free of charge via the Internet at http://pubs.acs.org.

<sup>(43)</sup>  $\sigma$ =1.2×10<sup>-6</sup> S cm<sup>-1</sup> (1a), 1.3×10<sup>-6</sup> S cm<sup>-1</sup> (1b), 2.6×10<sup>-6</sup> S cm<sup>-1</sup> (2a), and 2.8×10<sup>-6</sup> S cm<sup>-1</sup> (2b).