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# Self-Assembly of Thienylenevinylene Molecular Wires to Semiconducting Gels with Doped Metallic Conductivity

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***Abstract:*** Oligo(thienylenevinylene) (OTV) based gelators with high conductivity are reported. When compared to **OTV1**, **OTV2** having an increased conjugation length forms relatively strong gels with a metallic conductivity of 4.8 S/cm upon doping which is the highest value reported for an organogelator. This new class of conducting gels is expected to be useful for organic electronics and photonics application, particularly for bulk heterojunction devices.

Self-assembled organic nanostructures of semiconducting molecules are important in the field of organic electronics.[1] The noncovalent, bottom-up self-assembly of functional molecules is a powerful tool to create 1D structures of organic semiconducting molecules.[2] Using this approach, organogels of semiconducting molecules comprising electronically active nanowire networks can be prepared for potential applications.[3] There are several reports on p-type and n-type semiconducting gels, based on tetrathiafulvalenes and perylene bisimides.[4,5] Surprisingly, organogelators based on thiophene derivatives are relatively very few despite the wide ranging application of this class of molecules in organic electronic devices.[6] Recently, we have shown that a trithienylenevinylene molecule exhibits high charge carrier mobility upon self-assembly;[7] however the bulk conductivity was found to be as low as 4.8 × $10^{-6}$ S/cm. Therefore, we were keen to explore utilizing oligo(thienylenevinylenes) (OTVs) in the search for organogelators with metallic conductivity, which are useful for electronic devices such as bulk heterojunction organic solar cells.

Herein we report organogelators derived from **OTV** molecular wires, **OTV1** and **OTV2**, having molecular lengths of ca. 3.7 and 4.9 nm with semiconductivity and metallic conductivity. These molecules were synthesized from the corresponding thiophene derivatives by multistep procedures as reported earlier by Roncali and co-workers[8] and characterized by $^1$H NMR, $^{13}$C NMR, MALDI-TOF-MS, and FT-IR techniques (see Supporting Information). At concentrations >0.4 mM, **OTV1** and **OTV2** resulted in the formation of gels in a variety of nonpolar solvents as shown in Table S1. **OTV1** gel shows a purple color whereas **OTV2** gels are black in color (Figure 1b). The critical gelator concentration (CGC) to form a stable gel of **OTV1** in decane is 0.66 mM, whereas that of **OTV2** is 0.44 mM; hence **OTV2** belongs to the class of supergelators.[9] The gel stabilities were determined from the plots of the gel melting temperature ($T_{gel}$) at different concentrations of the gelators and found to be 70 and 72 °C at 2 and 1.5 mM concentrations for **OTV1** and **OTV2**, respectively.

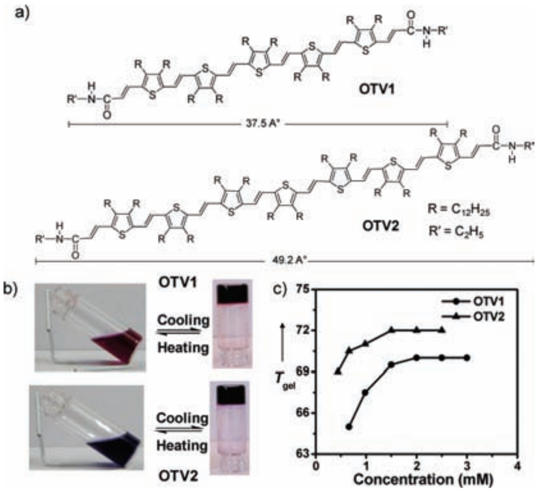

***Figure 1.*** (a) Chemical structures of **OTV1** and **OTV2**. (b) Photographs of **OTV1** and **OTV2** gels. (c) Plot of gel melting temperature against concentration of **OTV1** and **OTV2**.

Transmission electron microscopy (TEM) images of **OTV1** and **OTV2** (5 × $10^{-5}$ M) from a decane solution, placed on carbon coated grids, showed long fibrous network structures with dimensions ranging from 50 to 200 nm in width and several micrometers in length (Figure 2a,b). AFM images of **OTV1−2** drop casted from decane solutions ($c = 1 \times 10^{-5}$ M) on a highly ordered pyrolytic graphite (HOPG) surface showed entangled fibers (Figure 2c,d). Cross section analysis (Figure S1) of the fibers showed a height of 20−80 nm, width of 50−400 nm, and length in micrometers. A similar observation was made on a Si wafer (Figure S2). However, on a freshly cleaved mica surface, **OTV1** and **OTV2** showed epitaxially controlled assembly (Figure S3).

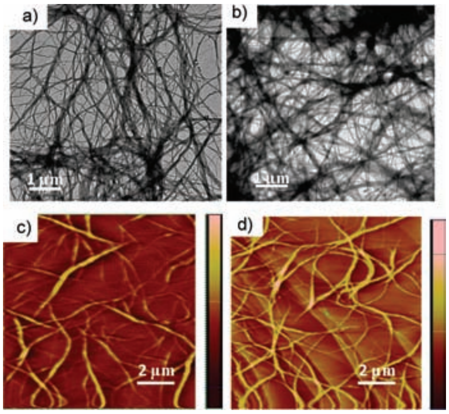

***Figure 2.*** TEM images of **OTV1** (a) and **OTV2** (b) drop casted on a carbon coated grid. AFM images of **OTV1** (c) and **OTV2** (d) drop casted on highly ordered pyrolytic graphite (HOPG). Samples were prepared from decane solutions at room temperature. *Z*-scale. (c) 120 nm and (d) 150 nm.

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These observations indicate that the nature of the substrate has a significant influence upon the morphology of the self-assembled structures.

The electrical conductivities of these fibers were measured using conducting probe atomic force microscopy (C-AFM).[10] The $I-V$ responses of **OTV1** and **OTV2** fibers indicate semiconductivity (Figure 3a). The highest conductance of the fiber bundles of the undoped **OTV2** was about 0.93 nS. Upon doping with iodine vapors, a significant increase in the $I-V$ response was observed (Figure 3b). The highest conductance obtained for **OTV2** gel fiber bundles after doping was ca. 7.1 nS which corresponds to 5.6 S/cm for a fiber height of 50−60 nm and tip contact radius of 70 nm.[11] For comparison, the reported conductance of the fiber bundles of doped bis(tetrathiafulvalene) gelator is about 0.03 nS.[4d] The metallic conductivity of the doped **OTV2** reflects a high concentration of the charge carriers upon iodine doping. AFM analysis of the xerogels after doping did not show any major change in the morphology (Figure S4), whereas the UV−vis−NIR spectra exhibited strong polaron/bipolaron bands in the range 800−2500 nm indicating mixed valence states responsible for the metallic conductivity (Figure S5).

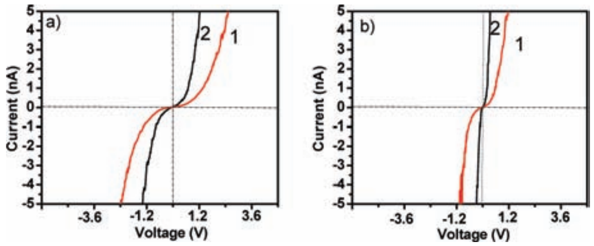

***Figure 3.*** (a) C-AFM measurements of **OTV1** and **OTV2** xerogels from decane solution drop casted on HOPG ($c = 1 \times 10^{-4}$ M). $I-V$ curves of undoped (a) and doped (b) xerogels of **OTV1** (1) and **OTV2** (2).

The room temperature bulk electrical conductivities ($\sigma$) of the as-prepared **OTV1** and **OTV2** films (four probe method) are $6.4 \times 10^{-4}$ and $4.9 \times 10^{-2}$ S/cm, respectively (Table 1). The conductivity has been significantly enhanced (an order of 2 magnitude) after doping with iodine vapors, $1.0 \times 10^{-2}$ and 4.8 S/cm for **OTV1** and **OTV2**, respectively which are close to the values obtained by C-AFM studies. These data reveal that **OTV2** xerogel behaves like metallic wires after doping with iodine which indicates that an extended conjugation length and strong gelation in **OTV2** have resulted in efficient charge carrier generation upon doping with iodine.

In summary, an increase in conjugation length of **OTV** molecular wires has a remarkable influence on the gelation and the conducting properties. The electrical conductivity of 4.8 S/cm observed for the iodine doped **OTV2** xerogel is one of the highest values reported for a molecular gelator.[4e,6b] This new class of metallic gels comprised of 1D nanowires are expected to generate interest among scientists working in the field of organic materials for electronics and photonics applications.

***Table 1.*** Four-Probe Conductivity (S/cm) Measurements of **OTV1** and **OTV2** Xerogels before and after Iodine Doping[a]

| Gelator | $\sigma$ | $\sigma$ ($I_2$) |
|---|---|---|
| **OTV1** | $6.45 \times 10^{-4}$ | $1.02 \times 10^{-2}$ |
| **OTV2** | $4.83 \times 10^{-2}$ | 4.83 |

[a] The values are the average of three independent measurements. The thickness of the films varied between 18 and 27 $\mu$m.

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**Supporting Information Available:** Details of synthesis, characterization, experimental procedures, and gelation studies. Absorption, C-AFM, and UV−vis−NIR data of **OTV1** and **OTV2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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