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Solution Phase Epitaxial Self-Assembly and High Charge-Carrier Mobility Nanofibers of Semiconducting Molecular Gelators

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Self-assembly of semiconducting organic molecules in solution and solid substrates on a nanometer length scale is a priority research topic in the field of organic electronics.[1] In this context thiophene derived molecular systems have been extensively investigated for applications such as field effect transistors (FETs) and photovoltaics.[2] For optimum performance of such devices, microscopic alignment of hierarchically organized structures plays a crucial role.[3] Among different methods available, molecular beam or hot wall epitaxy has been shown to be useful for the alignment of thiophene derived molecules on substrates.[4] Herein we report a hither to unknown simple liquid-phase epitaxial self-assembly of an amide end-capped thienylenevinylene molecular gelator to aligned 1D fiber bundles. Further, we show that the charge carrier mobility is high for a sample from a decane gel when compared to that obtained from a chloroform solution, highlighting the importance of 1D self-assembly and gelation in improving the electronic properties.

Reports on conducting organogels are increasing, however restricted to a few systems such as tetrathiafulvalene (TTF) and oligothiophenes.[5,6] Notably, thienylenevinylene based conducting gels are not known even though a number of oligo(thieneylenevinylene)s are reported by Roncali and co-workers.[7] These observations and our interest in the self-assembly and gelation of linear π-systems[8] lead us to the synthesis of a few trithienylenevinylenes **TTV1−5** having different end functional groups (Figure 1a) which were synthesized by known procedures and characterized by FT-IR, NMR, FAB-MS, and MALDI-TOF spectral analyses (see Supporting Information).

While the absorption spectra of **TTV1−3** did not show any variation in chloroform and decane (Figure S1), **TTV4** and **TTV5** with amide end functional groups exhibited a considerable difference. For example a solution of **TTV4** in chloroform (1.5×10^{-4} M) showed the $\pi-\pi^*$ absorption maximum at 501 nm. However, in decane, λ_{max} is blue-shifted to 464 nm ($\Delta\lambda = 37$ nm) with a shoulder band at 550 nm (Figure 1c). This large blue shift in the λ_{max} points to a large oscillator strength and strong exciton coupling due to the 1D arrangement of the molecules in H-type aggregates. A variable temperature absorption spectral study indicated the reversible breaking of the aggregates to isotropic molecules with the λ_{max} shifting back to 491 nm at 70 °C through an isosbestic point at 550 nm (Figure 1d and Figure S2).

TTV4 and **TTV5** formed stable, red colored organogels from nonpolar solvents such as hexane, cyclohexane, and decane and weak gels from aromatic solvents such as benzene and toluene (Table S1). The critical gelator concentration (CGC) of **TTV4** in decane at 25 °C is 0.98 mM whereas that of **TTV5** is 0.69 mM. Upon heating, the nonflowing gel turned into a liquid which upon cooling regains the gel phase (Figure 1b). Plots of the gel melting temperature against the gelator concentration indicated better thermal stability for the **TTV5** gel (Figure S3). The FT-IR spectrum of the **TTV4** xerogel indicates hydrogen bonded C=O stretching and N−H bending modes of amide I and amide II bands at 1638 and 1544 cm^{-1} respectively (Figure S4).[5d]

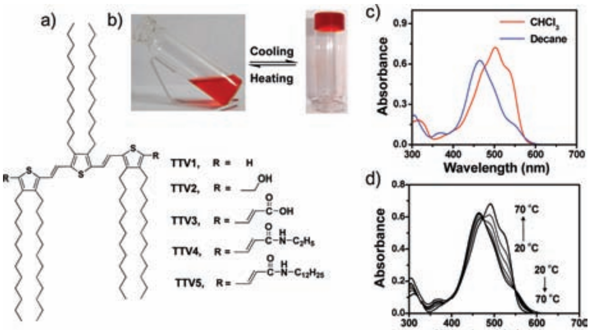

Figure 1. (a) Molecular structures of **TTV1−5**. (b) Photographs of **TTV4** gel in decane during heating and cooling. (c) Absorption spectra of **TTV4** in chloroform and decane (1.5×10^{-4} M) at 25 °C. (d) Temperature dependent absorption spectra of **TTV4** in decane from 20−70 °C.

TEM images of the xerogels of **TTV4** and **TTV5** obtained from 5×10^{-5} M decane solution are shown in Figure S5. These images reveal long and bundled fibers that form entangled network. The diameter of the fibers is in the range of 40−200 nm. In all cases the length of the fibers is on a micrometer scale. AFM images of **TTV4** and **TTV5** from decane (5×10^{-5} M) drop casted on freshly cleaved mica revealed the formation of oriented 1D fibers in the case of **TTV4** and interconnected short wires with T-junctions for **TTV5** (Figure 2a, b). This phenomenon was surprising to us since solution casting of π-gelators on a mica surface usually results in entangled fibrous structures. Cross section analysis of the **TTV4** assemblies showed an average width of 120 nm with a near uniform height of 10−15 nm and length of several micrometers. In the case of **TTV5**, the interconnected fibers have a width of 50−150 nm with a varying height of 4−10 nm and a varying length of 0.5−5 μm. The observed morphology clearly indicates epitaxial self-assembly which is known to be due to the exposed K^+ array on a mica surface (see Supporting Information).[9] It must be noted that epitaxial self-assembly of π-gelators is a rare phenomenon which makes the **TTV**s a unique gelator system.

Insight into the charge carrier transport property of the gelators, **TTV4** and **TTV5** on smaller spatial scales, could be obtained from

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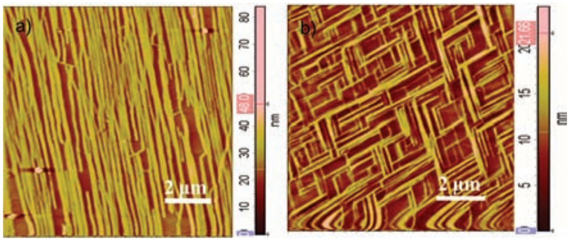

Figure 2. AFM images of (a) **TTV4** and (b) **TTV5** from decane drop casted on freshly cleaved mica surface ($c = 5 \times 10^{-5}$ M). *Z*-scales: (a) 40 nm and (b) 20 nm.

electrodeless flash-photolysis time-resolved microwave conductivity (FP-TRMC) studies.[10] Charge carriers were generated photolytically by adding *N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (PDI) as an electron acceptor.[11] The minimum charge carrier mobilities ($\Sigma\mu_{\min}$) of **TTV4** and **TTV5** films drop casted on quartz plates were determined by dividing $\phi\Sigma\mu$ of TRMC by ϕ, where ϕ (quantum efficiency of charge carrier generation) was estimated from the transient absorption spectra (TAS) of a PDI radical anion (Figure S7, Table S2).[12] The FP-TRMC transient conductivity profiles of **TTV4** and **TTV5** are shown in Figure 3. For **TTV4** films prepared by drop-casting of chloroform solutions, the $\Sigma\mu_{\min}$ was $\sim 1.5 \times 10^{-2}$ cm^2 V^{-1} s^{-1}. Once the films were prepared from *n*-decane/chloroform (1:1 v/v), the $\Sigma\mu_{\min}$ increased 6.0×10^{-2} cm^2 V^{-1} s^{-1}, due to the formation of hydrogen bonded 1D assemblies. **TTV5** which forms a relatively strong gel when compared to **TTV4** showed an enhanced $\Sigma\mu_{\min}$ of 4.0×10^{-2} cm^2 V^{-1} s^{-1} in chloroform and 7.4×10^{-2} cm^2 V^{-1} s^{-1} in the mixed solvent.

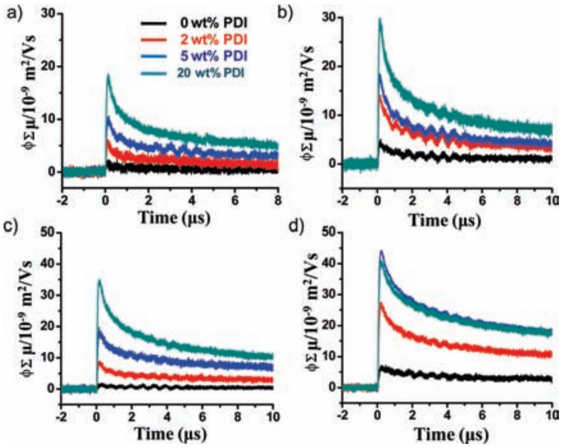

Figure 3. FP-TRMC transient conductivity profiles ($\lambda_{\mathrm{ex}} = 355$ nm) of **TTV4** (top) and **TTV5** (bottom) with **PDI** films prepared from (a,c) chloroform and (b,d) *n*-decane/chloroform (1:1 v/v) solutions. The color represents weight fraction of PDI relative to 100 wt % **TTV4**−**5**. The ϕ at the peak of each PDI fraction was estimated by TAS, giving 0.39−0.99% for (a), 0.24−0.33% for (b), 0.23−1.2% for (c), and 0.32−0.7% for (d).

In conclusion, described here is the first example for thienylenevinylene based gels that exhibit epitaxial self-assembly resulting in aligned supramolecular wires. Films of **TTV4** and **TTV5** prepared from decane−chloroform gels exhibited high charge carrier mobility when compared to films obtained from chloroform solutions, highlighting the role of self-assembly and gelation on the electronic properties. The finding that hydrogen bonded networks enhance the electrical properties would encourage the design of supramolecular gelators with high charge carrier mobility. Currently we are investigating a variety of thienylenevinylenes with different functional groups and conjugation lengths in search of metallic gelators for electronic devices such as organic solar cells.

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Supporting Information Available: Details of synthesis, characterization, experimental procedures, and gelation studies. Absorption studies of **TTV1**−**3** and TEM and AFM images and transient absorption spectra of **TTV4**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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