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First Phenylenevinylene Based Organogels: Self-Assembled Nanostructures via Cooperative Hydrogen Bonding and π-Stacking

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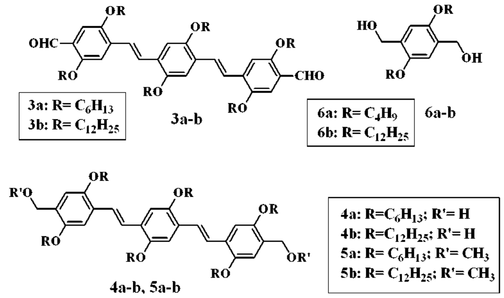
Control over supramolecular ordering of molecules to nanoscale dimension where hydrogen bonding, π-stacking, solvophobic, and donor−acceptor interactions are the main driving force is a challenging topic of research. Organogels which prevent the flowing of entrapped solvents are a novel class of materials that emerged from the self-association of small molecules.[1] Several examples of organogels are known in the literature,[2−6] among which, cholesterol based gels have been extensively studied for their use as templates for the designing of a variety of materials.[7] π-Conjugated systems are one of the least exploited classes of molecules in the designing of gels.[8] Herein we describe the first observation of the thermoreversible gelation of fluorescent *p*-phenylenevinylene derivatives **4a** and **4b** and the control of their gelation as a consequence of a cooperative hydrogen bond and π-stack induced self-assembly. The unique photophysical properties of phenylenevinylenes, particularly their strong emission characteristics, are of great advantage in providing insight into the role of self-assembly in the observed thermoreversible sol−gel phenomena. Even though there are several reports on the liquid crystalline behavior,[9] solid-state packing,[10] and self-assembly[11,12] of phenylenevinylene derivatives, there is no report pertaining to a phenylenevinylene based gelator.[1]

The *all-trans*-phenylenevinylenes **3a**,**b**, **4a**,**b**, and **5a**,**b** were prepared by a multistep synthetic scheme and characterized by spectral analyses (Supporting Information). Surprisingly, attempts to recrystallize **4a** and **4b** from various solvents resulted in the formation of a thick nonflowing mass, particularly in solvents such as hexane, cyclohexane, benzene, and toluene.[13] The thick gels thus obtained at room temperature were completely dissolved to form transparent homogeneous solutions at temperatures above 48 °C, and this thermoreversible sol−gel process was confirmed by several cycles of heating and cooling. Comparative study of compounds **3a**,**b**, **4a**,**b**, **5a**,**b**, and **6a**,**b** indicated the crucial role of the hydrogen bonding motifs, alkoxy side chains, and the conjugation length in controlling the gelation.[14]



The absorption and emission spectra of a hexane solution of **4b** at room temperature showed considerable resemblance to the spectra of a sheared film (Figure 1) indicating the possibility of self-assembled structures through H-bonding or π-stacking or both. To establish this possibility, we have recorded the absorption and emission spectra of **4b** in hexane at 50 °C, which resembled the spectra of **4b** in chloroform (Figure 1). These observations imply that **4b** forms self-assembled aggregates in hexane at room temperature whereas at elevated temperatures the self-assembly is disrupted to form isotropic solution as in chloroform. Variable-temperature absorption and emission spectral changes of **4b** between 20 and 50 °C in hexane indicated the possible existence of a cooperative thermoreversible self-assembly (Figure 1, insets). Addition of small amounts of H-bonding solvents such as methanol to a hexane solution of **4b** induces considerable blue shifting of their absorption and emission spectra similar to those in chloroform indicating the disruption of the molecular assembly.

The role of H-bonding to induce the π-stacked self-assembly and the consequent room-temperature gelation of **4a** and **4b** are further clarified by extending the studies to their methyl ether

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(13) The gelling was highly efficient in the sense that a dilute solution of **4b** (7 mM in hexane) in a 1 cm diameter glass vial on standing at room temperature could freeze the flow of the entrapped solvent when it was turned upside down. Statistically, each molecule of **4b** could entrap as many as 1160 molecules of hexane during gelation. Optical data and gel characteristics of **4b** are provided in Table 1 of the Supporting Information.

(14) Gelling efficiency of **4a** was less compared to **4b** revealing the role of alkyl chain length. **6a** and **6b** formed gelatinous precipitates even at very high concentration due to lack of conjugation and π-stacking.

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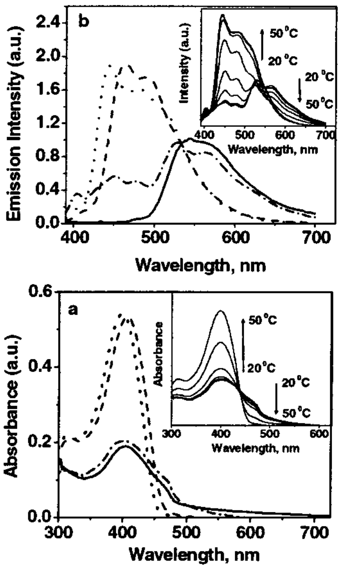

Figure 1. Absorption (a) and emission (b) spectra of **4b** in chloroform at 25 °C (- - -), hexane at 25 (• — •) and 50 °C (•••), and as a sheared film (—). Insets show changes in absorption and emission with temperature (excitation at 380 nm).

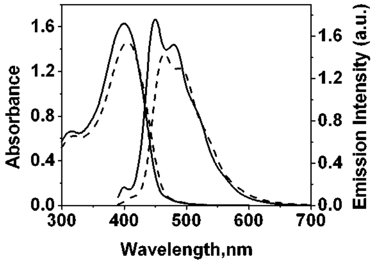

Figure 2. Absorption and emission spectra of **5b** in hexane (- - -) and chloroform (—) (excitation at 380 nm).

derivatives **5a** and **5b** and to the aldehydes **3a** and **3b**. In these cases, gelation could not be seen at room temperature even after considerable increase in concentration (6−7 times). Surprisingly, in the case of **5a** and **5b** gelation occurred at temperatures below 0 °C indicating that under extremely high concentrations and at low temperatures these molecules can induce stacking which leads to supramolecular ordering. Interestingly, the gelling efficiency of **4b** was considerably reduced by the addition of small amounts of H-bonding solvents such as methanol. The above observations clearly reveal that H-bonding moieties play a crucial role to assist π-stacking and thus the room-temperature gelation of **4a** and **4b** at relatively low critical gelator concentrations. This argument is further supported by comparing the absorption and emission spectra of **5b** in hexane and chloroform (Figure 2), which failed to show any evidence of the existence of aggregated species.

Differential scanning calorimetric (DSC) analysis of a gel of **4b** from *p*-xylene showed endothermic changes around 48 and 71 °C when heated to 80 °C and an exothermic phase transition around 20 °C, on cooling. Optical polarizing microscopic studies showed birefringent textures above the critical gelator concentrations revealing the presence of ordered structures. The scanning electron microscopic (SEM) image of a dried gel of **4b** revealed the formation of entangled nanostructures of approximately 100−150 nm width (Figure 3). X-ray diffraction (XRD) patterns of **4b** showed a *d*-spacing of 3.8 Å, which is characteristic of π-stacked lamellar packing and an intense signal at the small angle region corresponding to 23.4 Å due to the length of a repeat unit along the axis of the molecule. Variable-temperature ^{1}H NMR studies of **4b** in benzene-d_6 between 24 and 50 °C showed the appearance of well-resolved signals above 40 °C that correspond to the various protons indicating the disordering of the π-stacked self-assembly to the isotropic form (Supporting Information). The FT-IR spectrum of a toluene gel of **4b** showed a broad band around 3400 cm^{-1} revealing the presence of hydrogen-bonded OH groups in the gel state. A collective analysis of the available data supports the involvement of H-bond and π-stack assisted self-assembly as shown in Figure 4.

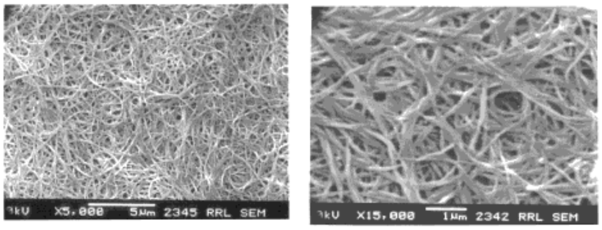

Figure 3. Scanning electron microscopic pictures of a dried gel of **4b** from toluene.

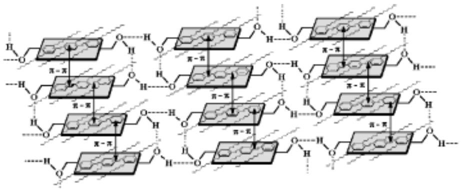

Figure 4. Probable self-assembly of the gel in hexane.

In conclusion, we are able to reveal the gelation, which was hitherto unknown for phenylenevinylenes, a class of molecules that are receiving immense attention in recent years. The cooperative effect of H-bonding and π-stacking in the formation of the supramolecular gel nanostructures of **4a** and **4b** at room temperature is established by the unique changes in their photophysical properties and by FT-IR, NMR, DSC, XRD, and SEM analyses. Detailed studies are under way to determine the role of conjugation and side chain lengths in controlling the self-assembly and gelation of phenylenevinylenes to tune their semiconducting and light emitting properties. Our findings hopefully will lead to the development of a novel class of gel-based luminescent and conducting materials.

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Supporting Information Available: Experimental procedures and characterization data of compounds **3a**,**b**, **4a**,**b**, and **5a**,**b**, a table containing optical data and gelation characteristics of **4b**, and variable-temperature ^{1}H NMR data and an optical polarizing micrograph (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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