

# One-dimensional Stacks of Triphenylenes Stabilized by a Peripheral Hydrogen-bonding Network

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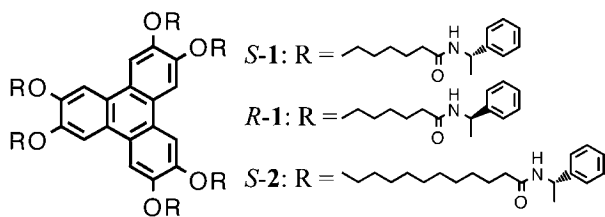
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Triphenylenes bearing chiral amide termini were found to form self-assembled nanofibers by the combination of  $\pi$ - $\pi$  stacking of triphenylene moieties with a hydrogen-bond network of amide terminates.

Since the discovery of discotic liquid crystals by Chandrasekhar,<sup>1</sup> self-assembled one-dimensional stacks composed of polyaromatic molecules have attracted increasing attention as potential molecular components in organic electronic and optoelectronic devices due to their fast one-dimensional charge- and energy-transfer capabilities.<sup>2</sup> Supramolecular conductors have great advantages in anisotropy, processibility, and self-healing characteristics of structural defects. The properties of organized states strongly depend on the ordering of aromatic disks in the stacks and the length of stacks. Shinkai et al. reported the eclipsed overlap formation of triphenylene moieties within the stacks due to hydrogen-bonding interactions among amides.<sup>3</sup> The combination of intermolecular noncovalent bonds with  $\pi$ - $\pi$  stacking between  $\pi$ -conjugated triphenylenes enables control of the ordering and molecular arrangement of triphenylenes within the stacks.<sup>4</sup> Here we describe the stabilization of one-dimensional stacks of triphenylenes by a peripheral hydrogen network.

Triphenylenes bearing six *R*- and *S*-methylbenzylamide termini were prepared from 2,3,6,7,10,11-hexahydroxytriphenylene in three synthetic steps (Scheme 1).<sup>5,10</sup> Compounds *R*-1, *S*-1, and *S*-2 were obtained by the reaction of hexa acids with chiral phenylethylamine in the presence of 1,1'-carbonylbis-1*H*-imidazole, and they were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and MALDI-TOF mass spectroscopy. The physical gels were formed when a mixture of powdered compound and organic solvent was heated to form a homogeneous fluid and then allowed to cool at 25 °C.<sup>6</sup> The gelation properties were investigated in various organic solvents. Compound *S*-1 can gelate in 2-methoxyethanol, anisole, DMSO, and NMP. The critical gelation concentrations of *S*-1 and *S*-2 for 2-methoxyethanol were 0.8 and 2.1 wt/vol %, suggesting that *S*-1, having shorter spacers, forms a more stable physical gel than *S*-2. In the FT-



Scheme 1.

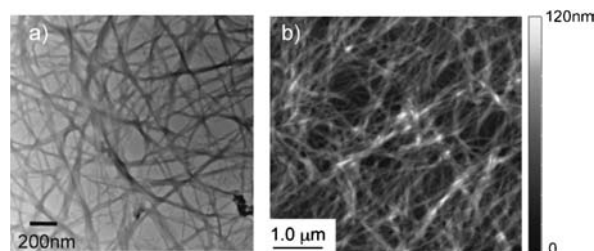
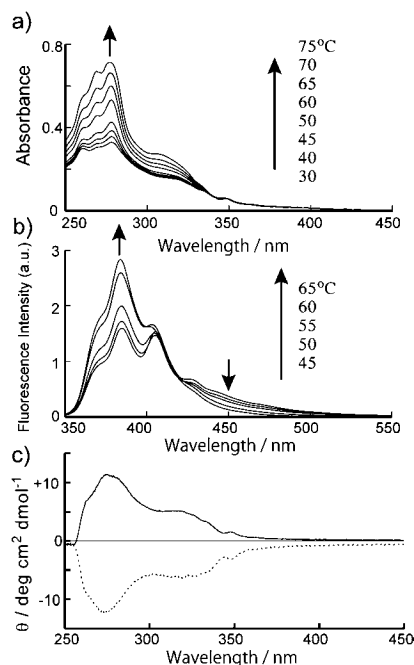


Figure 1. TEM (a) and AFM (b) images of fibrous aggregates made of *S*-1.

IR spectra, the characteristic peaks appeared at 3268 and 1658  $\text{cm}^{-1}$ , which are assignable to N-H and C=O intermolecular hydrogen-bonding stretching vibrations, respectively.<sup>5</sup> The formation of intermolecular hydrogen bonds between terminate amide units is one of the driving forces in gelation. Thermal properties were investigated using DSC and temperature-controlled polarized optical microscopy (TPOM). The DSC trace of *S*-1 and *S*-2 exhibited one transition peak at 171 and 124 °C, and *S*-1 and *S*-2 did not display any liquid crystalline textures in TPOM. Thus, the transition peaks observed in DSC correspond to the melting points of *S*-1 and *S*-2.

The gelation in organic solvents suggests that supramolecular aggregates form through weak intermolecular interactions.<sup>7</sup> The morphology of the aggregates was examined by TEM and AFM (Figure 1). TEM and AFM images of *S*-1 gel showed twisted fibrous structures with a length of several micrometers and a minimum width of about 30 nm. The gels of *R*-1 and *S*-2 had a similar morphology. The XRD pattern of dried *S*-1 gel was characterized by a broad reflection of 1.8 nm, which could be attributed to the average distance between one-dimensional stacks. In addition, there was a weak peak at 0.35 nm due to the stacking between triphenylene moieties within the stacks.

To obtain detailed information about the molecular arrangement of triphenylene within the aggregates, the temperature-dependent UV-vis, fluorescence, and CD spectra of *S*-1 were measured in 2-methoxyethanol at a concentration of 6.1 mM (1.0 wt/vol %). The gel was subjected to UV-vis, fluorescence, and CD spectra at temperatures ranging from 25 to 75 °C. With heating, the intensity of the absorption bands from 250 to 340 nm increased (Figure 2a). The fluorescence spectrum of *S*-1 in 2-methoxyethanol at 25 °C exhibited two maxima at  $\lambda = 380$  and 405 nm with a red-shifted shoulder between 425–550 nm. Upon increasing temperature, the fluorescence intensity of the emission at 380 nm increased and the intensity of the shoulder decreased (Figure 2b). These spectral changes are attributed to the stacks of triphenylene rings through intermolecular  $\pi$ - $\pi$  interaction within the fibrous aggregates observed in TEM and



**Figure 2.** a) Absorption and b) fluorescence spectra of *S*-1 in 2-methoxyethanol recorded at various temperature ( $[S-1] = 6.1$  mM). c) CD spectra of *S*-1 (solid line) and *R*-1 (dotted line) in 2-methoxyethanol at 25 °C.

AFM.<sup>3</sup> While *S*-2 formed fibrous aggregates, *S*-2 did not show a change of absorption and fluorescence spectra with varying temperature and these spectra in the gel were the virtually same as those of DMF solution. Longer alkyl spacers between triphenylene and chiral amide termini inhibit the formation of triphenylene stacks.

The formation of a hydrogen-bond network among the chiral amide termini may affect the molecular arrangement of triphenylene stacks.<sup>8</sup> Although the CD spectrum of DMF solution of *S*-1 showed weak peaks, 2-methoxyethanol gel of *S*-1 exhibited an intense CD spectrum corresponding to the absorption band (Figure 2c). The CD activity in the gel state suggests the formation of helical stacks. The intensity of the CD spectra decreased with increasing temperature due to the collapse of the helical stacks. The gel of *R*-1 showed a mirror CD spectrum to that of *S*-1, revealing the opposite molecular arrangement of triphenylene rings within the stacks. The gel of *S*-2 showed weak CD activity compared to *S*-1. From the results of the temperature-dependent spectral changes of *S*-2, the hydrogen bond among chiral amide terminates is a main driving force for the formation of fibrous aggregates lacking stacking of triphenylenes. On the other hand, *S*-1 assembles due to the combination between the peripheral hydrogen-bond network and  $\pi$ - $\pi$  stacks of triphenylenes.

Aromatic disks can form charge-transfer (CT) complexes by the addition of electron acceptors. The columnar liquid crystalline phase of triphenylene derivatives can be stabilized by the formation of CT stacks.<sup>9</sup> When 2,4,7-trinitro-9-fluorenone (TNF) solution was added to 2-methoxyethanol gel of *S*-1 (1:1 molar ratio), the absorption spectra and the color of the gel remained unaltered at room temperature. After heating above 70 °C and cooling to room temperature, a brown-colored gel

was formed, indicating the formation of CT complexes.<sup>10</sup> The hydrogen-bond network around a triphenylene stack prevents the penetration of TNF at room temperature, and the dissociation of hydrogen bonds by heating induces the formation of CT complexes. A TEM image of CT complexed *S*-1 with TNF was similar to that of *S*-1. The gel-sol dissociation temperature ( $T_g$ ) of *S*-1 with TNF was enhanced by 30 °C from that of *S*-1 gel ( $T_g = 52$  °C). The enhancement of  $T_g$  suggests the stabilization of aggregates through the formation of CT stacks. In contrast, the 2-methoxyethanol gel of *S*-2 exhibited a pale brown color upon addition of TNF at room temperature.

We demonstrated the formation of long and flexible nanoscopic fibrous assemblies made of triphenylenes with chiral amide termini in solvents by the combination of a hydrogen-bond network with  $\pi$ - $\pi$  stacking of triphenylenes. The spacer length affected the ordering of triphenylenes. We believe that one-dimensional stacks of triphenylenes stabilized by a peripheral hydrogen-bond network have good potential for the development of conductive molecular wires.

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