

A new class of gels

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Gels are soft solids containing a large volume of liquid and are commonly found in foods like jam and jelly, cosmetics, medicine, etc. They are formed by an interwined network of molecular assemblies, held together by weak interactions among molecules. These molecular interactions result in the self-organization of molecules to form architectures that can be several micrometres across. A group of researchers at the Regional Research Laboratory in Thiruvananthapuram has discovered a new class of gels made from rigid conjugated aromatic molecules. According to them, the spontaneous self-assembly of organic molecules to form gels is a method for creating nanoscopic and mesoscopic structures¹. In particular, the gelation of chiral molecules to form helical morphologies has received considerable attention².

Recently, through a serendipitous observation, it has been shown that the gelation of functionalized oligo(*p*-phenylenevinyls) (OPVs) takes place during the hierarchical self-assembly of a rigid pi-conjugated system to form coiled-coil helical ropes. This is an interesting case of gelation-assisted helix transition. Gelation-induced helix formation is promoted by a pair of remote chiral handles and assisted by weak hydrogen-bonding motifs and long hydrocarbon chains, thus allowing the molecules sufficient freedom to undergo self-assembly.

Three different OPVs with remote chiral handles, C-OPV1, C-OPV2, C-OPV3 (Scheme 1) were prepared by a reported procedure and fully characterized³.

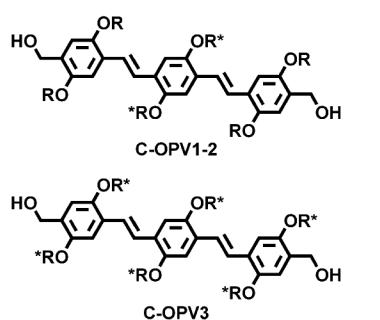
C-OPV2, with hexadecyl side chains, was able to form stable aggregates in solution. C-OPV1, with dodecyl side chains, was found to be a better gelator than C-OPV2, and formed yellow fluorescent gel in nonpolar solvents, such as dodecane, heptane and cyclohexane (critical gelator concentration in dodecane is 6.4×10^{-3} M). However, C-OPV3, which is substituted with six chiral side chains, failed to form a gel in any of the solvents. Optical polarizing microscopy revealed that C-OPV1 forms birefringent fibrous four-arm brushes when cooled from the isotropic dodecane solution, whereas neat C-OPV1 and C-OPV2 crystallize into spherulite textures when cooled from the isotropic melt. Field emission scanning electron microscope (FESEM) images of C-OPV1 from a dilute solution in dodecane (9×10^{-5} M) showed left-handed helical fibres of 20–50 nm diameter and a few micrometres in length, with a uniform helical pitch of approximately 150 nm. However, the FESEM image of C-OPV1 (partially gelled) from a more concentrated solution in dodecane (5×10^{-4} M) showed the formation of left-handed, coiled-coil, rope-like structures of 50–100 nm diameter, with an average pitch of 330 nm. These rope-like structures are formed by the twisting together of several helical fibres¹.

UV/Vis absorption, fluorescence emission and circular dichroism experiments were performed to obtain better insight into the self-assembly of chiral OPVs. The absorption and emission properties of C-OPV1 in chloroform are typical of molecularly dissolved OPVs⁴.

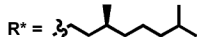
Concentration and temperature-dependent CD measurements of C-OPV1 in dodecane have provided insight into the hierarchical helical self-assembly and helix transition during gelation of the molecules. The characteristic UV/Vis absorption and fluorescence signals of C-OPV1 are a unique

observation associated with the gelation of chiral OPVs. In the initial levels, the molecules organize to form left-handed chiral aggregates, which are helical as indicated by the weak bisignated CD signal. At higher concentrations, these initial chiral assemblies grow further into helical fibres and coiled-coil ropes, thus resulting in a strong exciton-coupled CD signal.

The intriguing phenomenon of supramolecular assembly of biological molecules into helical nanostructures, such as DNA double helix, collagen triple helix, and alpha coiled-coil of myosin, has always fascinated scientists. In this context, the control of the supramolecular organization of pi-conjugated systems into helices of nanoscopic dimensions is of utmost importance, as the resulting structures could find application in the emerging area of supramolecular electronics, because of their unique optical and electronic properties. Although a few reports on helical self-assemblies of OPVs have appeared⁵, to the best of our knowledge this is the first example of a gelation-induced CD-signal change. The unusual transition observed in the CD signal is indicative of a helix transition during the hierarchical evolution of rope-like nanostructures via intermediate chiral assemblies and is reminiscent of the multistate folding and unfolding of the helical assemblies of biological macromolecules.



COPV1: R = C₁₂H₂₅
COPV2: R = C₁₆H₃₃



Scheme 1.

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4. Ajayaghosh, A. *et al.*, *Angew. Chem. Int. Ed. Engl.*, 2003, **42**, 332–335.
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