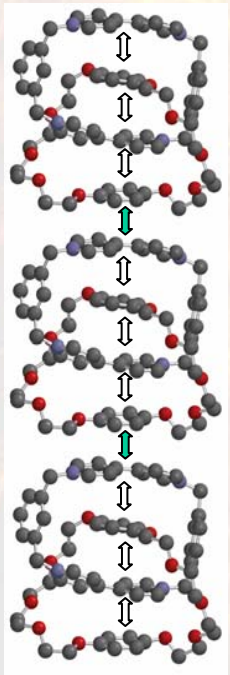
Amphiphilic Catenanes

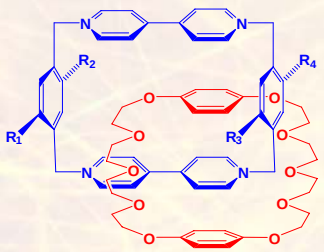
and related fiber-forming compounds

Kevin L. Caran, Department of Chemistry,
James Madison University, Harrisonburg, VA, 22807

Our lab's efforts to prepare high aspect ratio (fibrous) materials has continued to grow as has our understanding of these phenomena. We have synthesized and explored the utility of several amphiphilic catenanes as well as two related non-catenated amphiphiles. Several new biscationic, single-chained amphiphiles (prepared in one step from an intermediate in the catenane synthesis) exhibit surface activity and the ability to form needle-like fibers in an aqueous environment. In addition, a series of propargylic alcohols can be induced to form crystals or gels, as controlled by the nature of the liquid phase.

We have prepared three new amphiphilic catenanes (**1**-**3**), each bearing two or four hydrophobic chains on a central polar catenane. These molecules are designed to aggregate into fibers in non-polar media due to their amphiphilic nature, and π-π stacking of aromatic rings. Slow addition of a non-polar solvent to a chloroform solution of **1** leads to the formation fibrous aggregates, as shown in the SEM image below. Optimization of the formation of fibers, as well as similar studies on the derivatives with two or four branched chains (**2**, **3**) are underway.

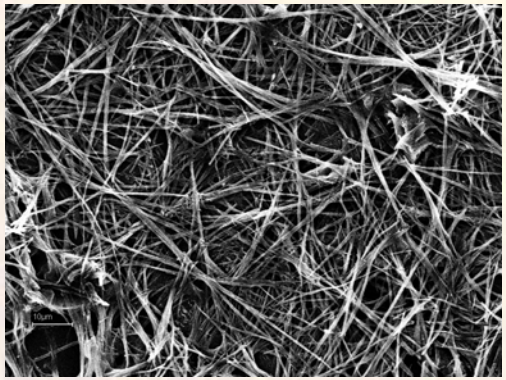


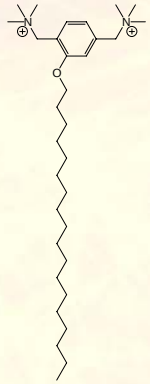


1 $R_1=R_3=OC_{14}H_{29}$, $R_2=R_4=H$

2 $R_1=R_2=$  $R_3=R_4=H$

3 $R_1=R_3=R_2=R_4=$ 

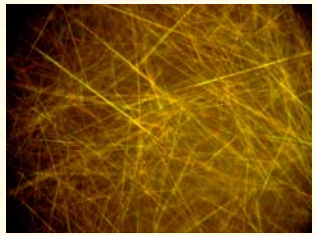




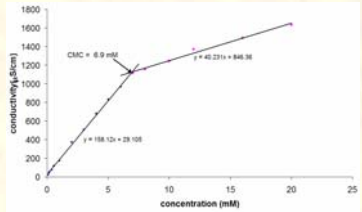
Chain length
$C_{10} - C_{18}$

Our novel double-headed amphiphiles form fibrous aggregates in water. These high-aspect ratio supramolecular structures suggest a high degree of either interdigitation or significant bending of the alkyl chains. Critical micelle concentrations (cmc) have been determined for several derivatives using conductivity.

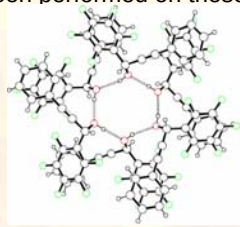
Self-assembled fibers in water



CMC study using conductivity

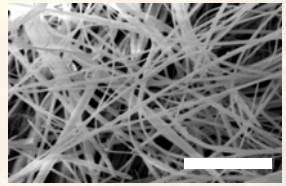


We have prepared and examined a series of propargylic alcohols, each with one electron-poor and one electron-rich aromatic ring flanking a propargylic alcohol core. While several of these compounds are known to form crystalline hexamers in the solid state, they can be induced to form stable gels in non-polar media. SEM of the dried gels reveals their fibrous nature. Additional structural characterization (powder XRD) and thermal stability tests (including DSC) have been performed on these gels.



Aggregation in the solid state, recrystalized from benzene

Gel and fibrous precipitate of two derivatives from $C_{12}H_{26}$



SEM of fibers from a desolvated C_6H_{12} gel