Hierarchy of Order in Liquid Crystalline Polycaps[**]

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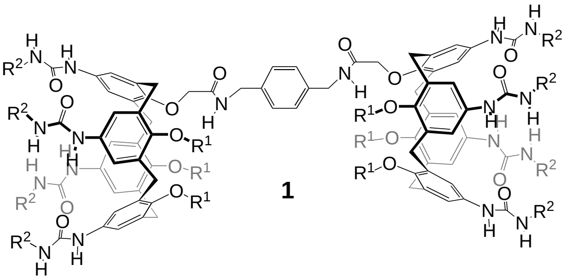
Calixarenes bearing urea groups on their upper (wider) rims dimerize by hydrogen bonding to form capsules.[1] When two such calixarene molecules are covalently linked at their lower rims, as in **1**, the recognition elements diverge, and assembly results in capsules along a polymer chain, or polycaps (Figure 1).[2] Unlike other main-chain, hydrogen-bonded polymers,[3–6] the polycaps are functional host units and form only when guests of proper size, shape, and chemical surface are present.[2] Polycap formation can be reversed or prevented by the addition of solvents that effectively compete for hydrogen bonds.[7] Here we explore the increasing order of certain polycaps as they spontaneously self-organize into polymeric liquid crystals[8] and then into micrometer-scale fibrous assemblies.



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It was discovered that mesogeneity could be induced by outfitting the monomers with long alkyl chains that can fill space, enhance solubility, and provide a liquidlike sheath around the polymer chains. When compound **1a** ($R^1 = n$-$C_{10}H_{21}$, $R^2 = p$-$CH_3C_6H_4$) is dissolved in chloroform (20–30% by weight), its solutions are notably viscous.[9] At higher concentrations of **1a** in chloroform ($\geq 36\%$ by weight),[10] the solutions become turbid.[11] When these more concentrated samples are viewed between crossed polarizers with a light microscope, the material is birefringent and produces the optical textures shown in Figure 2. These samples are liquid-like as they can be deformed with pressure and are self-healing, two characteristic properties of liquid crystals.

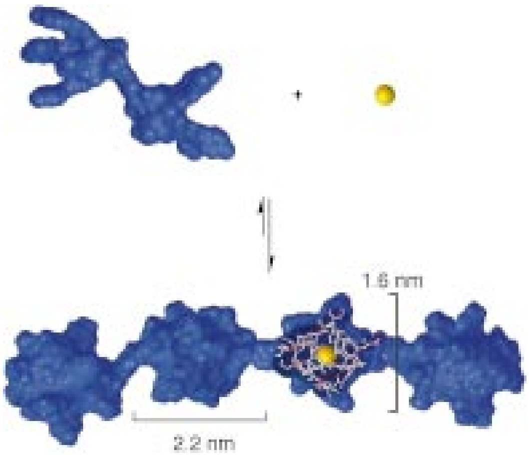

Figure 1. A molecular surface representation (AVS program) of polymeric capsule (polycap) formation. The side chains have been shortened for clarity.

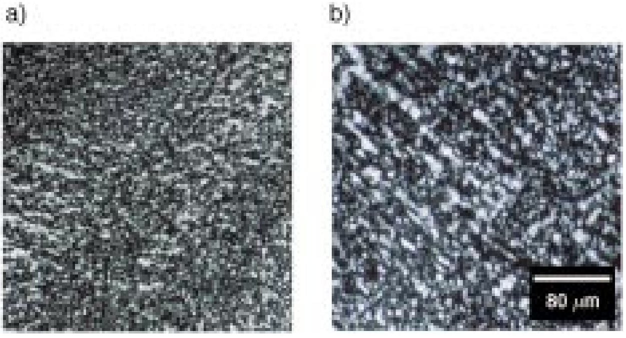

Figure 2. Photomicrographs of a typical Schlieren texture observed from **1a** in a) chloroform and b) *p*-difluorobenzene as viewed between crossed polarizers.

The Schlieren textures displayed in Figure 2 pervade each of the samples and are characteristic of lyotropic, nematic, liquid crystalline phases,[12] and they are similar to those in other polymers that are also nematic mesogens.[13] The textures are present when either chloroform (Figure 2a) or *p*-difluorobenzene (Figure 2b)[14] is used as the solvent/guest for the capsule. Also, during evaporation of a dilute solution of **1a** in chloroform a typical two-phase, nematic and isotropic droplet texture was observed at the transition to the mesophase. Formation of a nematic phase implies that each self-assembled polymer chain is the individual mesogen and is correlated with its nearest neighbors by having an on-average, preferred orientation. The birefringent patterns persist if the solvent is evaporated completely, presumably because the

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[**] We are grateful to the Skaggs Research Foundation and the National Institutes of Health for financial support. R.K.C. thanks the American Chemical Society Division of Organic Chemistry and Schering-Plough for a graduate fellowship (1998–1999). C.N. thanks the National Institutes of Health for a postdoctoral fellowship (1999–2001). The authors thank Professor M. Reza Ghadiri (The Scripps Research Institute) for the use of his light microscope and for insightful discussions, Dr. Theresa Fassel for help with the freeze-fracture experiments, and Fraser Hof for assistance with the molecular graphics. We are grateful to Professor Timothy M. Swager (Massachusetts Institute of Technology) for the use of his equipment and for interpretive advice.

guest is still encapsulated. Other molecules that can serve as guests, such as nopinone (6,6-dimethylbicyclo[3.1.1]heptan-2-one), also form birefringent material, presumably representing a liquid crystalline phase.

Shown in Figure 3a is the X-ray diffraction pattern from a liquid crystalline sample of **1a** (ca. 67% by weight[15] in chloroform) at 50 °C. Two main peaks are observed at 2.4 and 1.6 nm that can be attributed to self-organization of the mesogen. Molecular modeling[16] suggests the origins of these diffraction maxima: The space-filling representation of the polycap in Figure 1 indicates that the 2.4-nm spacing matches the repeat unit along the polymer chain, and the 1.6-nm spacing corresponds to the distance between polymer chains. This correlates well with other nematic liquid crystal polymers which exhibit similar X-ray diffraction peaks.[17]

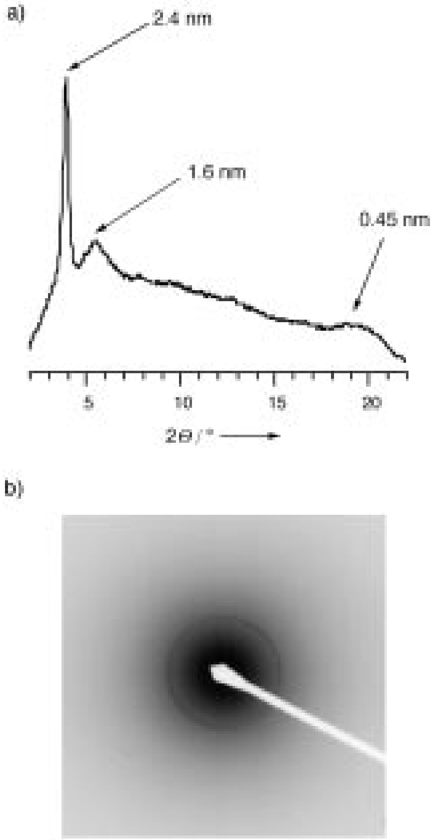

Figure 3. a) The X-ray diffraction pattern obtained from a liquid crystalline sample of **1a** in chloroform at 50 °C (2Θ = diffraction angle). b) Illustration of the extent of electron diffraction for a thin film of **1a** deposited from chloroform.

If instead the X-ray data is collected at 90 °C, the same two reflections appear but the intensity of the peak at 2.4 nm decreases relative to that of the other. At higher temperatures, the polycaps retain their liquid crystallinity but their fluidity increases, as evidenced by the greater intensity of the interchain diffraction maxima. However, at lower concentration (ca. 38% by weight), close to the transition to the isotropic solution, the reflection at 2.4 nm diminishes, whereas the peak at 1.6 nm remains albeit much broader and lower in intensity. Just as with heating, the more fluid, dilute samples also display a lyotropic, nematic mesophase. Shown in Figure 3b is the electron diffraction pattern of **1a** prepared as a thin-film following evaporation of chloroform. A similar, sharp reflection is observed at 2.2 nm, which can be associated with the repeat unit along the polymer chain, but the reflection for the interchain correlation (ca. 1.6 nm) is absent. Again, the polycaps retain their solution-phase ordering even after excess chloroform is removed. This is apparently due to the tight sequestering of solvent molecules within the capsules.

Replicas prepared from freeze-fractured samples of **1a** (ca. 10% in chloroform by weight)[18] were examined with a transmission electron microscope and produced micrographs like the one shown in Figure 4. Rounded structures are observed throughout the sample; they feature the dimensions of the calixarene capsules, about 1.6 nm × 2.2 nm, distances that match those from the diffraction data and molecular modeling. In some regions of Figure 4, extended structures can be seen that are identifiable as capsules along a polymeric chain, reminiscent of beads-on-a-string (white arrow in Figure 4). Since no external order was imparted to the polymer solution during the freeze-fracture deposition, the chains run randomly throughout the sample. Control experiments in the absence of monomer or with **1a** deposited from a solvent where assembly does not occur (tetrahydrofuran/methanol 9/1 v/v)[2] gave none of the rounded structures shown in Figure 4.

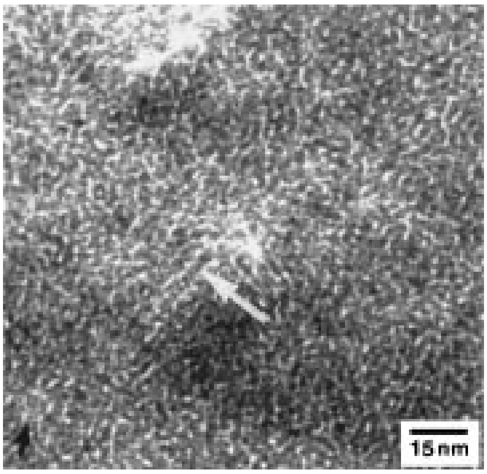

Figure 4. Transmission electron microscopy (TEM) image of **1a** prepared by freeze-fracture from a concentrated solution in chloroform. The black arrow indicates the direction of platinum shadowing. See text for further details.

Additional experiments addressed the relationship between the unique optical behavior of **1a** and its chemical structure. No liquid crystalline behavior was observed for compound **1b** ($R^1 = C_3H_7$, $R^2 = p\text{-}CH_3C_6H_4$) as concentrated solutions in chloroform. Apparently, the shorter alkyl chains do not impart a sufficiently liquidlike environment to the polymer. Also, simple tetraurea-calixarenes that cannot polymerize form only isotropic solutions in chloroform and *p*-difluorobenzene. Dissolution of **1a** in competitive solvents (that is, THF, DMF, or chloroform/methanol 9/1 v/v) predictably prevents liquid crystalline ordering. Finally, if methanol is allowed to diffuse into samples such as those shown in Figure 2, the birefringent texture erodes, and the sample becomes an isotropic liquid.

The covalent linker between the two calixarenes in the monomer **1** also contributes to the intermediate phase behavior. If the phenyl spacer is replaced by a flexible alkyl chain, the material no longer displays liquid crystallinity. The energy-minimized structure[16] of **1a** shows a hydrogen bond between the linker amide NH moiety and the adjacent phenolic ether oxygen atom of the calixarene lower rim.[19] This conformational rigidity[20] could impart a linear arrangement to the polycaps conducive to the formation of calamitic liquid crystals.[21]

External forces can be used to orient the liquid crystal formulations of **1a**. When samples like the one shown in Figure 2 are sheared, they display oriented fibrous assemblies.[3, 4, 6] A confocal microscope image of one such region is displayed in Figure 5a. The fibers are infinitely long and of approximately uniform width, about 6 μm, or on the order of thousands of molecules wide. Shown in Figure 5b is a confocal image of a fiber that was pulled with a needle from a liquid crystalline sample of **1a** in chloroform. These fibers could be pulled to centimeters in length, and their width (ca. 6 μm) was remarkably similar to those that resulted from shearing. When the fibers shown in Figure 5b are aligned colinearly with the polarizer or analyzer, they are extinguished; that is, each of the subunits within the fibers is mutually well aligned. The ability to pull fibrous structures from polymer liquid crystals is characteristic of other hydrogen-bonded polymers[4] and covalently linked polymers such as Kevlar (poly(*p*-phenylenterephthalamid)[11, 22] and spider silk.[23]

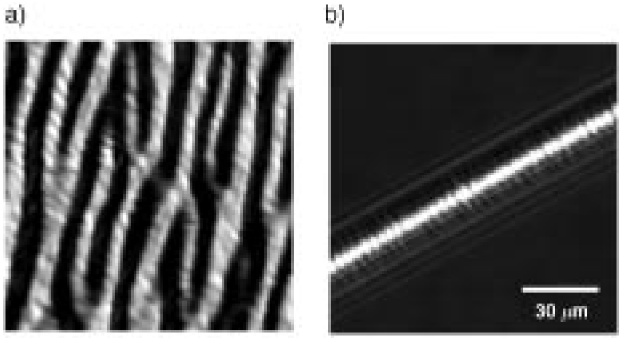

Figure 5. Laser confocal microscopy images of fibers formed from the liquid crystalline phases of **1a** in chloroform by a) shearing the sample or b) pulling a fiber from the sample.

This study demonstrates that hierarchical ordering of molecules like **1a** can be accomplished through the presence of appropriate guests, substituents, and external forces such as shearing or pulling. Natural[23] and synthetic systems[3, 4, 6, 24] whose hydrogen-bonding forces work in concert with other noncovalent interactions lead to assemblies that are well defined over large volumes and possess properties and functions far removed from those of their constituent molecules.[25] The availability of capsules of an enormous diversity[26] augurs well for a new family of functional polymers. The concomitant order imposed on their encapsulated guests is expected to give these polycaps unique photophysical properties.[27]

Experimental Section

Compounds **1a**[28] and **1b**[2] were prepared as described in the literature.

Polarized light microscopy was performed on a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS46 camera. Selected samples were heated in a Linkam Scientific LTS350 hot stage controlled by a Linkam TP92 central processor. Fibrous samples were observed by polarized, laser-scanning confocal microscopy on a Bio-Rad MRC 1024 attached to a Zeiss Axiovert S100 TV microscope.

Freeze-fracture replicas were prepared by placing a few drops of a concentrated solution of **1a** in the appropriate solvent (1 mg μL^{-1}) between two aluminum plates. The sample was cooled in a bath of liquid nitrogen (−196 °C) and transferred to a Balzers BAF 400T freeze-fracture machine. The sample was fractured at −150 °C and a pressure of 10^{-7} Torr. Platinum was shadowed at a 45° angle to a depth of about 20 Å followed by a carbon support layer (250–300 Å) at normal incidence. The replicas were washed with chloroform/methanol (1/1) in the case of the chloroform samples and with tetrahydrofuran/methanol (9/1) for the control. After transfer to copper grids, the replicas were examined using a Philips CM100 transmission electron miscroscope.

The instrument used for the electron diffraction was a JEOL transmission electron microscope operating at 100 keV and equipped with a rotation-tilt stage. Samples were prepared by casting thin films of **1a** from a solution in chloroform onto a freshly exposed mica surface. The samples were obliquely shadowed with Pt evaporated at an angle of $\tan^{-1}0.5$ and coated with a patina of amorphous carbon to support them so they could resist distorting significantly under the impact of the electron beam. Finally the samples were floated off in water onto the Cu grids.

The sample for X-ray diffraction was prepared by filling a 1.5-mm Lindemann capillary tube with **1a** in chloroform (ca. 67% by weight) and placing it in a heating block whose temperature was controlled to ±1 °C by a Minco CT 137 controller. The X-ray diffractograms were recorded using Ni-filtered $\mathrm{Cu}_{K\alpha}$ radiation from a fine-focus X-ray tube and XRG 2000 generator. An Inel CPS 120 position-sensitive detector was calibrated using a mica standard from the National Bureau of Standards.

Received: April 28, 1999 [Z13327IE]
German version: *Angew. Chem.* **1999**, *111*, 2764–2768

Keywords: calixarenes · liquid crystals · molecular recognition · polymers · supramolecular chemistry

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A Mixed-Valence and Mixed-Spin Molecular Magnetic Material: $[Mn^{II}L]_6[Mo^{III}(CN)_7][Mo^{IV}(CN)_8]_2 \cdot 19.5\,H_2O$**

Amandeep Kaur Sra, Marius Andruh, Olivier Kahn,* Stéphane Golhen, Lahcène Ouahab, and J. V. Yakhmi

The cyano bridge in an efficient and versatile magnetic coupler can mediate both antiferromagnetic and ferromagnetic interactions. This ability is the clue to the remarkable magnetic properties of bimetallic Prussian blue phases.[1–7] These phases can behave as ferrimagnets or ferromagnets with critical temperatures reaching 340 K. These phases, however, have some drawbacks. In particular, they have a faced-centered cubic structure,[8] so that no magnetic anisotropy can be expected. That is why we recently decided to use a heptacyanometalate, $[Mo(CN)_7]^{4-}$, instead of a hexacyanometalate as a precursor. The heptacoordination is not compatible with cubic symmetry. The reaction of $[Mo(CN)_7]^{4-}$ with Mn^{2+} ions afforded two- and three-dimensional compounds whose structures and magnetic properties were investigated in great detail.[9–12] As expected, the symmetries of the metal sites as well as the symmetry of the lattice as a whole are low, which leads to very interesting magnetic anisotropy properties.

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[**] This work funded by the Indo-French Centre for the Promotion of Advanced Research (IFCPAR, project no. 1308–4). L = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene.