Bent-Core Liquid Crystals Exhibiting Negative Gaussian Curvature

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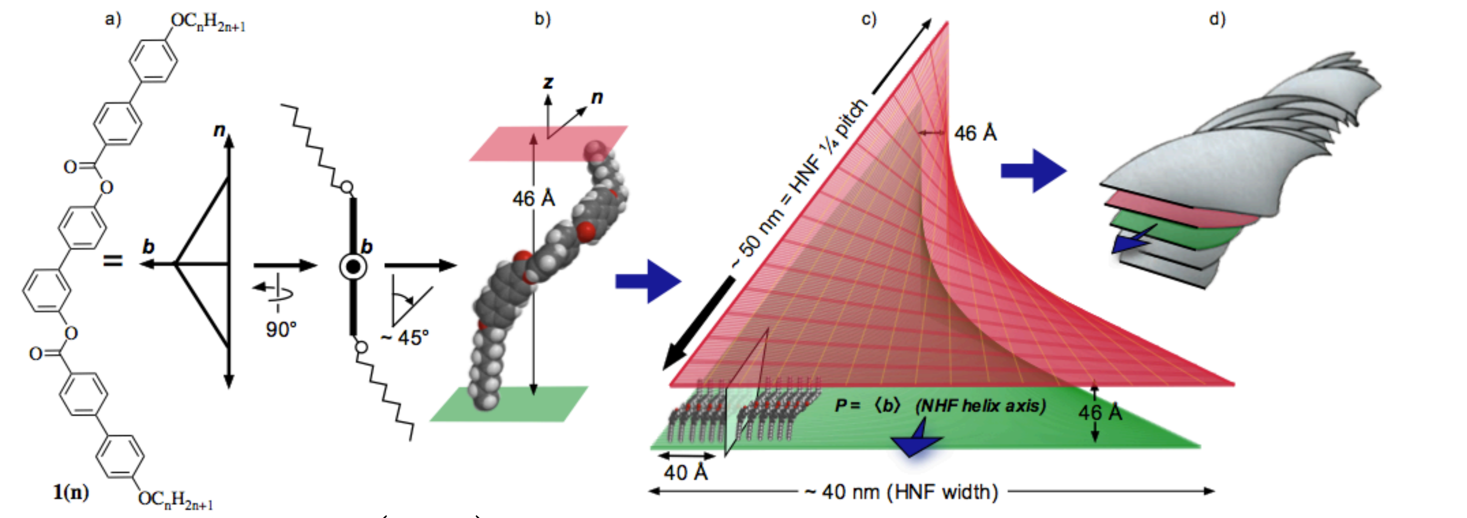
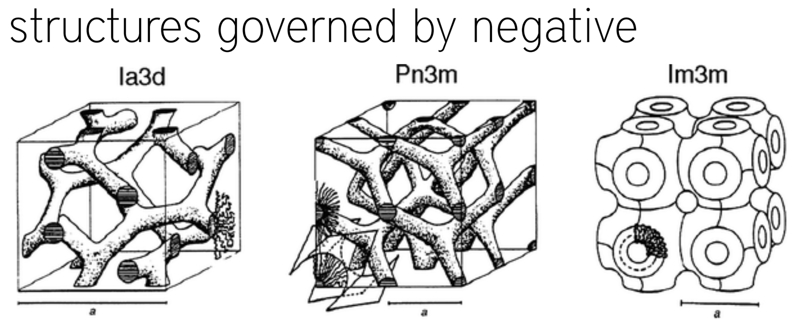
Abstract:

The goal of this research is to synthesize and characterize thermotropic bent-core liquid crystals of varying polyfluorinated tails to develop new phases of matter. Liquid crystalline phases exhibiting negative Gaussian curvature have potential in renewable energy applications, semi-conductor, and zeolite applications. The characterization of these novel liquid crystals assist in predicting mesogenic behavior and advancing applications for these unique materials. Phase structures currently being identified include bicontinuous cubic phases ("sponge phases"), isotropic chiral conglomerates, and helical nano-filament phases. The exploration of aforementioned molecules macromolecular form will give a greater insight and improved model of bent-core liquid crystalline behavior and introducing these phases into application.

Introduction:

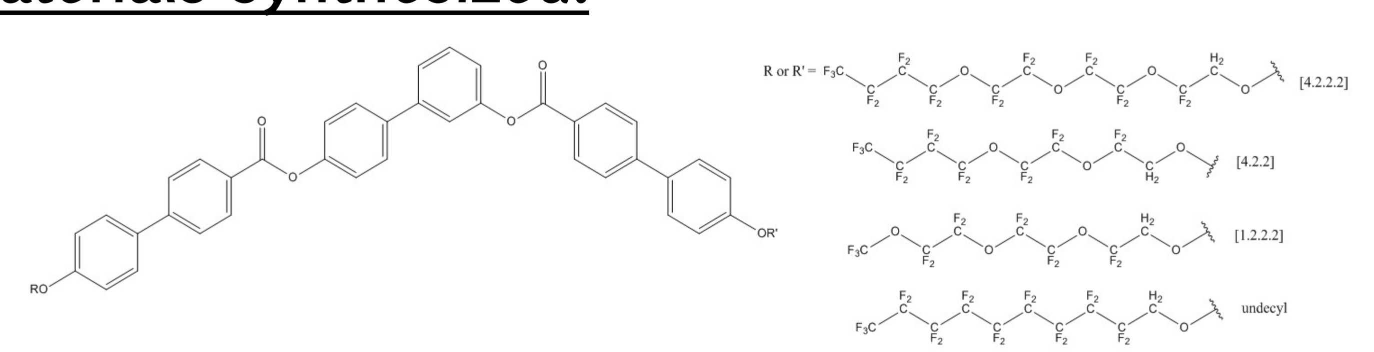


Helical nanofilament (HNF) phases in liquid crystalline materials exhibit incredible potential for a variety of mesomorphic applications. As seen in the diagram above, HNF phases are governed by the tendency to adopt a double-ruled saddle-splay architecture that has origins in the shape of the constiutent molecules and the need to create minimal surfaces due to free energy limitations in assembling such structures governed by negative Gaussian curvature.

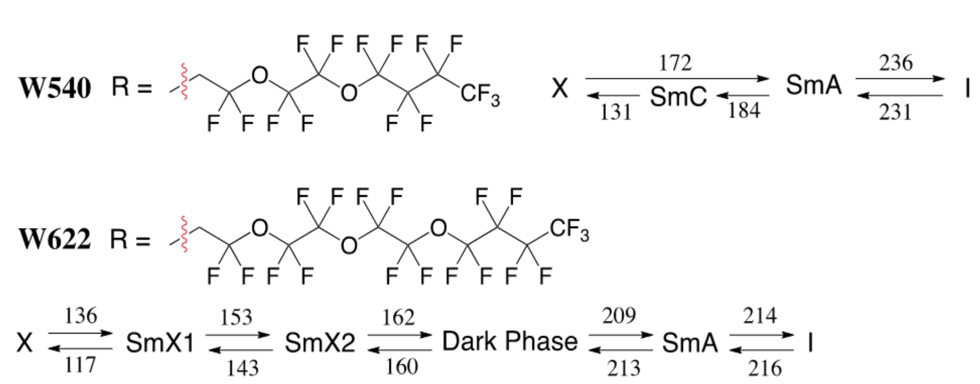


A logical extension of the HNF phase are the bicontinuous cubic phases (*right*). While similar to the HNF phase in that it is driven primarily by negative Gaussian curvature, these phases operate under a different free energy constraint, allowing for the formation of infinite minimal surfaces. This requires incredible chemical nanophase segregation to affect such phases – making these a primary target for the employ of perfluorinated aliphatics and perfluoropolyether moieties to enforce the desired level of nanophase segregation.

Materials Synthesized:



(above) The family of materials that were synthesized for characterization.



(left) Phase transition data for [4.2.2] and [4.2.2.2]. The phase of interest being the "Dark Phase" which has yet to be determined. The other materials have been syntheisized and results from those materials are pending.

Results:

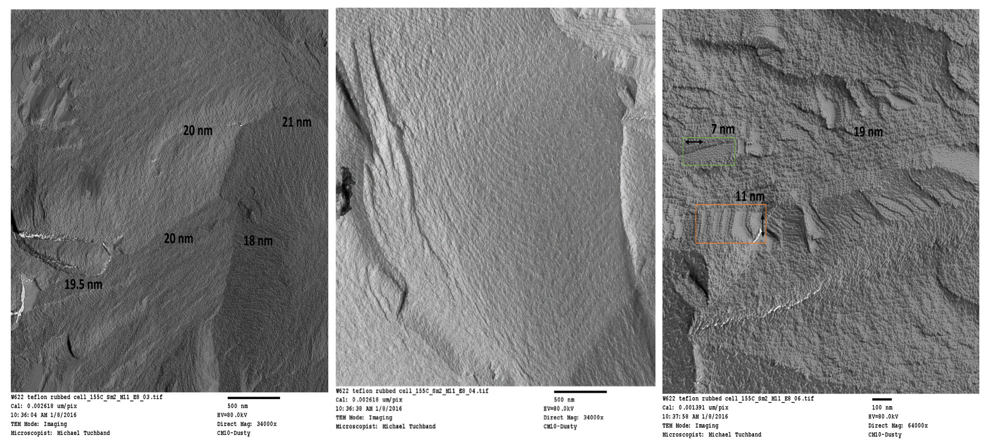
Polarized Light Microscopy (PLM)

PLM analysis of the [4.2.2.2] tail material (W622) has definitively shown that the "Dark Phase" which is of the highest characterization priority grows in at ~160 °C and melts at ~210 °C. The sample in this temperature range was analyzed while lying flat and at a slight tilt to show that the phase is absolutely isotropic.

(above) PLM data at 198.7 C° and 200 C° with tilt to show That the phase is truly isotropic

Freeze Fracture/TEM (FF-TEM)

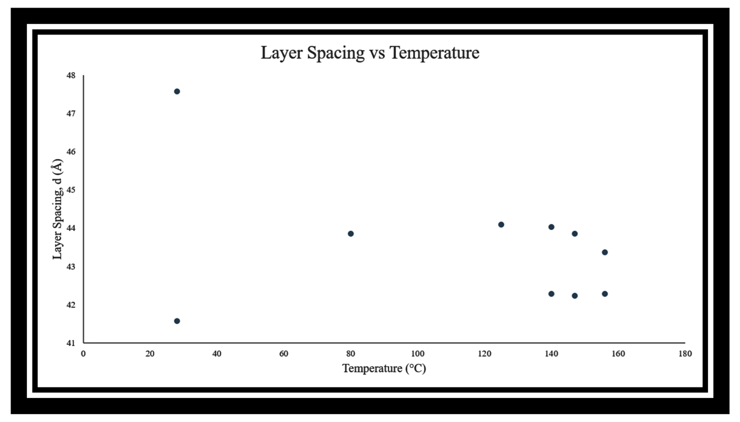
Freeze fracture experiments, analyzed by transmission electron microscopy (TEM), show periodicity in the material appearing as a striated type topography. These stripes occur with varying periodicity at 7, 11 and 20 nm and suggests that there is some ordered arrangement of molecules in the material's "Dark Phase".

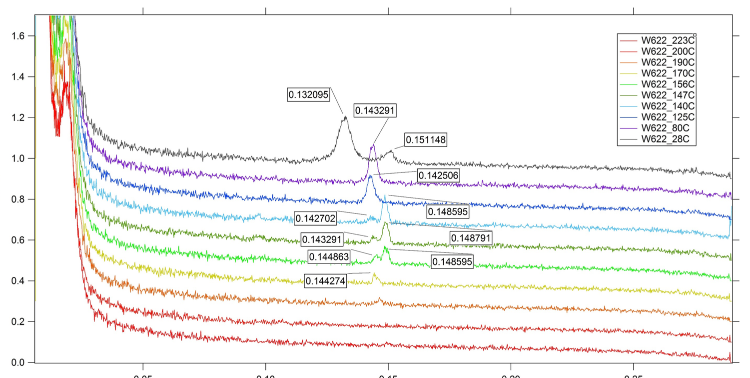


(left) TEM image for W622 ([4.2.2.2] bent –core material). Striations in the material reflect periodicity forming within the bulk material. This data does not support results from PLM which reflected a completely isotropic phase structure along all molecular oreientations.

X-Ray Diffraction (XRD)

Powder x-ray experiments show weakly periodic behavior at approximately 4 nm. The data shows strong periodicity that exists within the materials crystalline phase and appears to diminish as the material is heated. The peak is still present during the "Dark Phase" which has a phase temperature ranging from 160 °C to 210 °C. The x-ray data shows the existence of the signal from 170 °C to 180 °C.





(top) correlation distance vs. temperatur eplot(below) X-ray diffraction data for W622 at its mesogenic phase range temperatures.

Discussion:

The results from analysis of this compound from PLM, freeze fracture/TEM, and x-ray diffraction have provided little insight into the true nature of the "Dark Phase". While the PLM data suggest that there is a complete lack of anisotropy within the phase, both the Freeze fracture/TEM and XRD suggest a range of periodicities present in the material. Furthermore, the periodicities that are observed in the FF-TEM and XRD data sets are not in agreement. The presence of three distinct periodic regions in FF-TEM at 7, 11, and 20 nm cannot be explained or verified with the consideration of alternative data. The main peak within the XRD data correlates to periodicity at ~4 nm which is shorter than the molecular length of the material.

Conclusion & Future Work:

Bent-core liquid crystals with perfluorinated aliphatic and perfluoropolyether moieties were synthesized and analyzed using PLM, FF-TEM, and SAXS XRD. The material has several liquid-crystalline phases including an uncharacterized phase that exists from 160 °C to 210 °C which is of interest. The results from the implemented analytical methods do not reveal any details as to the structure colloquially known as the "Dark Phase". While the FF-TEM data suggests a possible 2D lamellar structure the isotropy observed in PLM suggests that this is not the case. Furthermore, the periodicities observed at 7 nm, 11 nm, and 20 nm in the FF-TEM data are in disagreement with the large peak at ~4 nm seen in the XRD data set. In total, every set of data acquired for this material has provided a different result leading to the conclusion that more analysis is required to make a statement about the "Dark Phase" structure.

Further analysis includes synchotron small angle x-ray diffraction, and resonant x-ray diffraction to double check higher order at extremely small Q values. Current theories suggest that the small ranges which higher order structural assembly may be existing in is not being probed effectively. These experiments will be performed at the Lawrence Berkeley National Lab during the summer of 2016.

The data for the other materials synthesized for this research are still pending and will be arriving soon. It is uncertain if other perfluorinated bent-core materials will shed light on the "Dark Phase" or if any of the other materials will actually exhibit a similar phase. Further studies within the homologous group are focused on creating "asymmetrically substituted bent-core materials with "mixed and matched" perfluorinated aliphatic and polyether moieties.

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References: Richardson, J.; Chapter 3: Exploring the B1 and B4 Phases; Bent-core molecules without schiff base moieties. Ph.D. Dissertation, University of Colorado, Boulder, CO, 2010.