

Porphyrin Liquid Crystals

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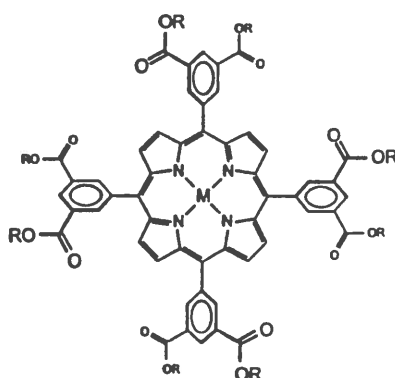
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Liquid crystalline phases, or *mesophases*, are commonly found in modern electronic devices (*e.g.* liquid crystal displays, LCDs) and in nature (*e.g.* the lipid bilayers that make up cell membranes) [1]. The liquid crystalline phase can occur in transition from the solid phase to the liquid phase. Most molecules, however, do not have mesophases; those that do are known as *mesogens*. Mesophases have some crystal-like properties (*e.g.* birefringence) and some liquid-like properties (*e.g.* fluidity). This unique combination of properties make liquid crystals well-suited for device applications as LCDs, ferroelectrics, optical data storage media [2], and non-linear optical (NLO) materials.

Liquid crystals were first discovered in 1888. From 1888 to 1977, all known mesogens were rod-like (*calamitic*) in shape. In 1977, S. Chandrasekhar and coworkers introduced a new class of mesogens that were discotic in shape [3]. These first discotic mesogens were hexa-*n*-alkanoyl benzene derivatives. Only three years later, the first porphyrin liquid crystal was reported by Goodby and coworkers [4]. Since 1980, several examples of porphyrin [5], phthalocyanine [6], and (alkylthio)tetraazaporphyrin [7] liquid crystals have been reported. With very rare exceptions [8], all of these molecules are flat, nonpolar molecules. In fact, the one example of a porphyrin with a dipole moment perpendicular to the porphine plane, an AlOH derivative, formed μ -oxo bridged species upon heating. Flat, non-polar molecules are not useful for most device applications because they cannot be aligned and manipulated on a macroscopic scale.

This thesis addresses the problem of creating versatile, robust porphyrin liquid crystals which can have permanent dipole moments without sacrificing mesogenic properties. The approach taken in this work involves creating a family of "bis-pocket" porphyrin mesogens. The ultimate goal is to prepare polar porphyrin mesogens which can potentially be used for device applications.

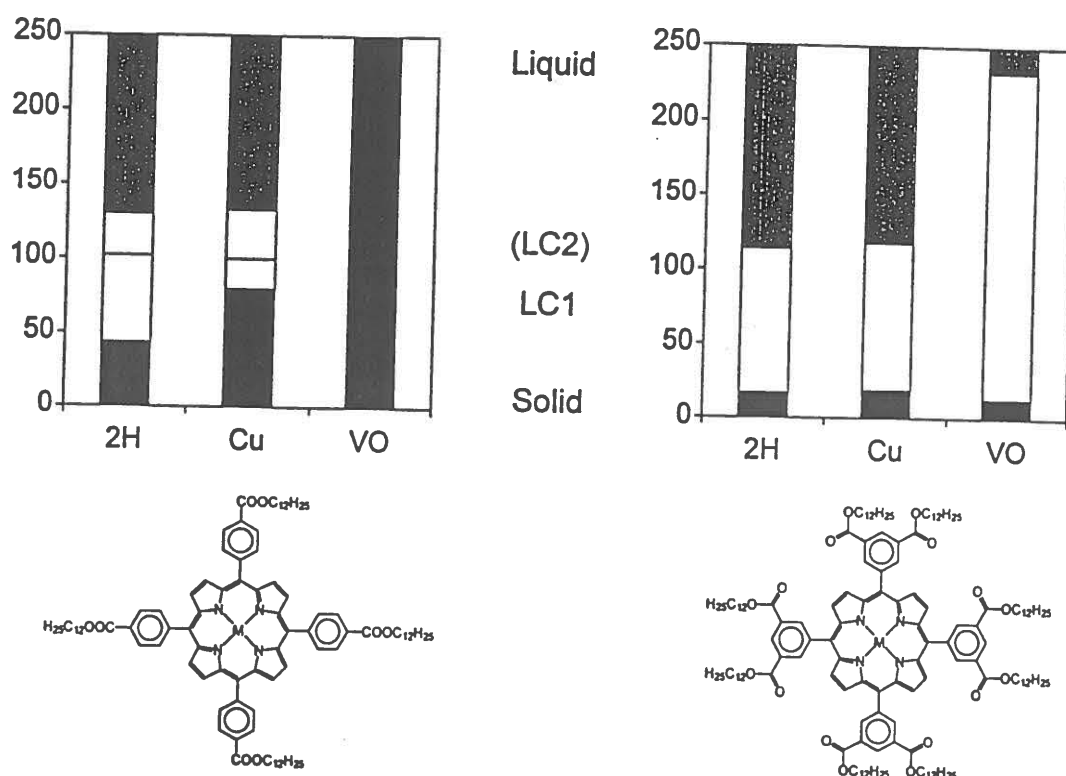


$H_2DCarPP$: $R = H$; $M = 2H$

Alkyl DiCarPP: $R = n-C_nH_{2n+1}$ ($n = 2, 8, 10, 12, 14, 16, 18, 20, 22$)
 $M = 2H, Cu, VO, FeX$

The family of porphyrin liquid crystals we studied comprises *n*-alkyl esters of 5,10,15,20-tetrakis(3',5'-dicarboxyphenyl)porphyrin ($H_2DCarPP$). The synthesis and characterization of $H_2DCarPP$ starting with mesitylene will be described, followed by its esterification to form the octa-*n*-alkyl $H_2DCarPP$ liquid crystals. Unlike its predecessors in the literature, this family of alkyl $H_2DCarPP$ liquid crystals was specifically designed *not* to be flat in shape.

The "bis-pocket" shape arises from the fact that the phenyl groups are not coplanar with the porphine core. Substituents at the eight *meta* positions project out and away from the center of the porphyrin in three-dimensions. The C_{10} through C_{22} derivatives are mesogenic, as determined by differential scanning calorimetry and polarized microscopy. In fact, the C_{10} and C_{12} derivatives are liquid crystals at room temperature. Structural characterization has been conducted using polarized microscopy and small-angle X-ray diffraction (SAXS). A model for the mesophase structure will be presented. The proposed mesophase structure involves the stacking of the porphyrins into columns. The columns, in turn, are layered in an A-B-A packing motif to form discotic hexagonal columnar phases (D_h). For some derivatives, the columns are disordered within the layers, resulting in a discotic lamellar columnar phase (D_L).



Phase Transitions of C_{12} H₂TCPP and C_{12} H₂DCarPP and Metalloderivatives

In order to prove the effectiveness of the bis-pocket concept, copper and vanadyl derivatives of C_{12} H₂DCarPP were compared with copper and vanadyl derivatives of C_{12} 5,10,15,20-tetrakis(*p*-carboxyphenyl)porphyrin (H₂TCPP). C_{12} H₂TCPP is a much flatter porphyrin that lacks pockets. The results are shown in the histogram above. C_{12} H₂TCPP and C_{12} H₂DCarPP are both mesogenic. The four-coordinate, relatively planar copper derivatives are also mesogenic. When the porphyrins are metalated with a five-coordinate vanadyl species, the results are dramatic: (C_{12} DCarPP)VO has an expanded mesophase range, whereas (C_{12} TCPP)VO loses its mesogenicity.

EPR spectra of undiluted (C_{12} TCPP)VO and (C_{12} DCarPP)VO at room temperature reveal an interesting difference between the two materials. The (C_{12} TCPP)VO sample shows axial symmetry typical of vanadyl porphyrins. The (C_{12} DCarPP)VO complex, on the other hand, gives an isotropic signal, indicating that the unpaired electron in V^{4+} is mobile on the EPR time scale for this porphyrin liquid crystal.

The alkyl H₂DCarPP liquid crystals have unique and interesting properties. The (C₁₂DCarPP)VO complex shows that robust discotic liquid crystals with permanent dipole moments can be made, given the right mesogen shape. Further studies should reveal whether the materials are truly viable for device applications.

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