FERROELECTRIC LIQUID CRYSTALS FROM ACHIRAL MOLECULES

Stephanie L. Potisek   April 28, 2005

BACKGROUND

Liquid crystals (LCs) have properties of both solids and liquids. They can flow like liquids, but maintain order in a certain direction (i.e. positional, orientational, or bond orientational order). Ferroelectric liquid crystals (FLCs) exhibit the added property of spontaneous polarization – the macroscopic alignment of the molecular dipoles. The direction of the dipoles can be switched upon application of an electric field. This dipole switching is necessary for display applications and the high speed at which the FLC dipoles flip give them many advantages over standard LCs in display applications. Consequently, FLCs have been implemented into many commercial devices including high definition TVs, camera displays, auto instrument panels, head-mounted displays for training and simulation, holography, and medical imaging devices. Currently all the FLC technology uses chiral molecules.

The property of ferroelectricity was first discovered in the solid state (in Rochelle salt) by Valasek at the University of Minnesota in 1920.[1] In 1963, Williams at RCA in Princeton, NJ first proposed that this property existed in a LC.[2] Meyer then hypothesized in 1975 that ferroelectricity could exist in a chiral smectic C (smectic C[*]) LC phase made from chiral molecules.[3] It was thought that molecular chirality was needed to reduce the symmetry of a material and produce a polar superstructure. However, synthesizing chiral molecules for commercial devices is costly; therefore, achiral molecules are desirable to decrease production costs.

To produce FLCs from achiral molecules, scientists have exploited the polarity, shape, and intermolecular interactions of compounds to create organized polar phases. It is entropically unfavorable for molecules to arrange with a unidirectional dipole; however, the sh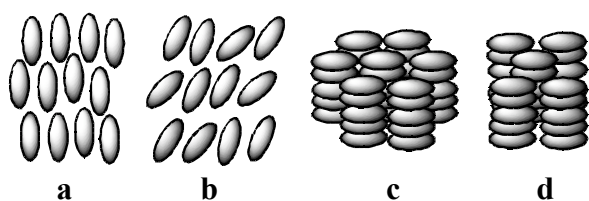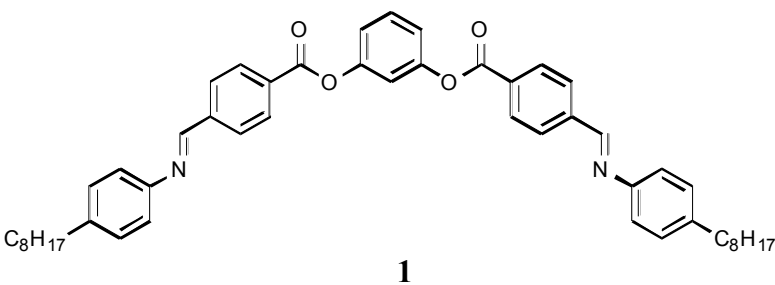ape and intermolecular interactions may stabilize these macromolecular arrangements. Overcoming the entropy barrier and promoting intermolecular interactions provides a unique challenge in the creation of new FLCs. Efforts toward the production of ferroelectric smectic and columnar phases (Figure 1) from achiral compounds will be discussed. These systems include banana-shaped, conical, disc-like, and rod-like molecules (Figure 2). W-shaped molecules have also been investigated.

Figure 1. Alignment of molecules in LC materials a) Smectic A phase b) Smectic C phase c) Columnar hexagonal (Col_h) d) Columnar rectangular (Col_r)

I. SMECTIC PHASES

Polar alignment of the smectic phase can be ferroelectric or antiferroelectric. To avoid unfavorable internal electric fields, most LC materials adopt a nonpolar antiferroelectric ground state in which the polar direction alternates from layer to layer. A macromolecular helical structure can also be formed, resulting in a bulk polarity of zero. In a ferroelectric LC however, a uniform dipole direction is adopted, creating a bulk polar material. Ferroelectric organization is required of LCs that are used in display applications and thus research has been focused on optimizing the properties of the ferroelectric smectic C^* phase.

Figure 2. Shapes of achiral molecules for FLCs

BANANA-SHAPED FLCs

In 1992, Tournilhac *et al*. reported the first example of a FLC composed of an achiral molecule with an inherent dipole.[4] These achiral units assembled in a polar, asymmetric manner due to alternating polar and nonpolar segments within the molecule. Niori *et al*. then synthesized the achiral banana-shaped compound **1**[5] and established a new direction in the FLC field.[6]

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The polar order in banana-shaped FLCs can be produced by achiral molecules because of symmetry-breaking events.[7,8] The banana-shaped structure favors a steric packing of the molecules in which the "bows" point in the same direction, creating a layer with a uniform polar vector. An additional tilting of the molecules to form the smectic C phase further reduces the symmetry of the LC phase and creates chiral ordering within each layer. This architecture generates interesting properties such as chiral superstructures and ferroelectric phenomena. A recent publication by Tschierske and coworkers demonstrated a banana-shaped compound with a ferroelectric ground state.[9] Research on banana-shaped compounds is a field in and of itself and continuing efforts have focused on making these compounds more stable at room temperature. Although most banana-shaped compounds form smectic phases, these molecules have also been shown to form columnar phases.[10]

ROD-LIKE FLCs

Hird *et al.* later perturbed the banana-shaped structure and synthesized the rod-like 2,3,4,-trifluorophenyl compound **2** shown in figure 3.[11] This unsymmetrical molecule with a rod-like core formed a smectic C^* phase
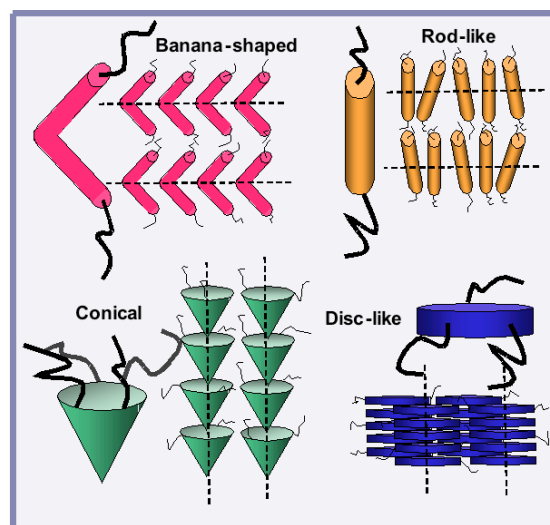
Figure 3. Rod-like LCs. R= C_8H_{17} or $C_{10}H_{21}$; R'=$C_{10}H_{21}$ or $C_{12}H_{25}$

containing left- and right-handed helices, which switched in the presence of an electric field. The chiral architectures were likely caused by the conformational flexibility of the ester groups. Rotation about the ester bonds in combination with the unsymmetrical bent structure produced a twist that occurred off the axis of the molecule, generating two mirror-image conformations. After the suggestion that rod-like molecules could produce ferroelectric phases, Stannarius *et al.* demonstrated a FLC that was formed by another achiral rod-like ester compound (**3**).[12] As was found with triflourophenyl **2**, the flexibility of the backbone in **3** likely caused the formation of a chiral LC and therefore the polar order.

Recently a more thorough investigation showed that the achiral rod-like compound **4** could produce a chiral liquid crystal.[13] The left- and right-handed helices randomly generated in different domains of the LC, were attributed to two conformations of the molecule formed by rotation about the Ar-O bond. The assembly of chiral domains was due to the affinity of one conformer to assemble with like conformers, a result of intermolecular dipole-dipole interactions. Although chiral LC superstructures with rod-like molecules have been reported, a bulk ferroelectric phase has not been realized.

W-SHAPED FLCs

Another slight variation of the banana structure is the w-shaped compound. Kumar and coworkers synthesized w-shaped compound **5** (Figure 4) and showed that it displayed antiferroelectric ordering using DSC, microscopy, and spontaneous polarization experiments.[14] The π–π interactions between the fully conjugated structures caused ferroelectric ordering within the layers and an overall antiferroelectric material.
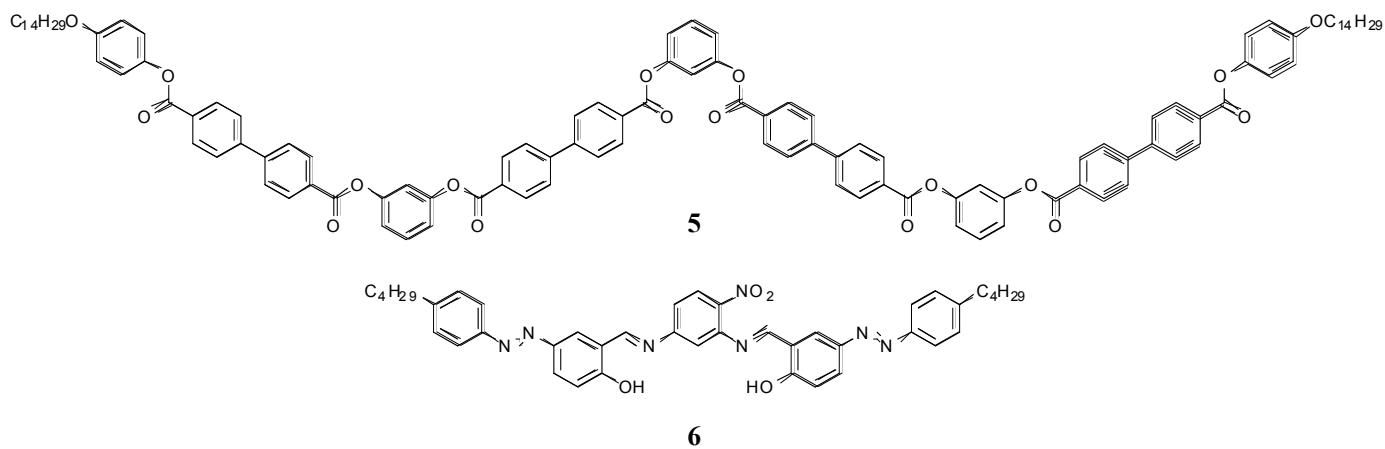

Figure 4. W-shaped FLCs

Rao and colleagues developed the w-shaped compound **6** (Figure 4) that self-organized into chiral LC phases.[15] The nitro group creates a lateral dipole at an angle to the molecular axis and facilitates chiral self-assembly. Additionally, H-bonding between the hydroxyl and imine groups aids in the association into a macromolecular helix. Although polar ordering produced chiral structures, application of an electric field showed no switching. An undefined tertiary structure was also found through x-ray crystallography experiments.

II. COLUMNAR PHASES

Since the development of the polar smectic phases, research efforts have also focused on the production of new ferroelectric columnar phases. Unlike the banana-shaped molecules which can easily form non-polar antiferroelectric materials, these columnar hexagonal lattices cannot readily accommodate antiferroelectric arrangements. Hexagonal phases cannot be organized so that each column is surrounded by columns of opposite polarity, thus allowing

Figure 5. Different possible polar orders in Col_h arrangements. Dark circles represent a dipole oriented out of the plane and light circles represent a dipole directed into the plane.

for new possible polar arrangements (Figure 5) that could be used for memory storage devices.[16]

CONICAL FLCs

Initial efforts to form a ferroelectric columnar phase exploited an achiral bowl shape. Based on preliminary research of an analogous chiral macrocycle,[17] an achiral bowl-shaped calixarene (**7**) was synthesized.[18] These molecules exhibited a dipole along the center axis of the bowl and it was thought that an electric field could switch the dipole vector upon an umbrella-like inversion of the core.[19] Although ferroelectric properties were not reported, this study demonstrated that achiral conical molecules could form a columnar phase.
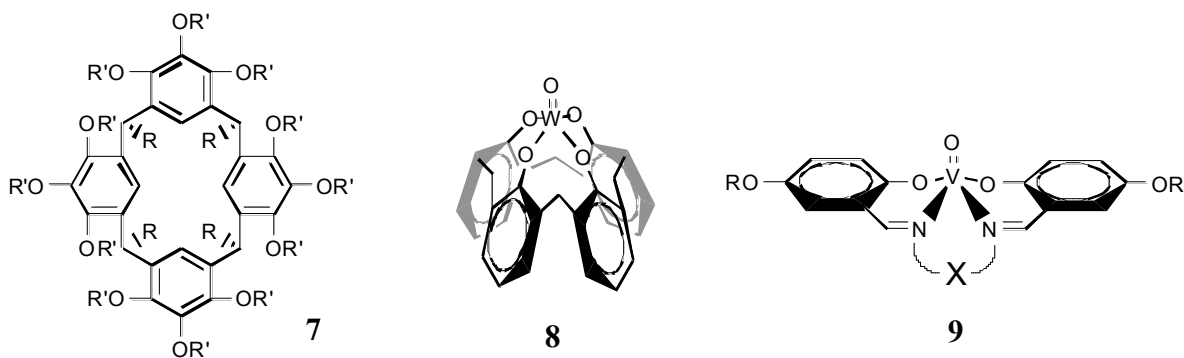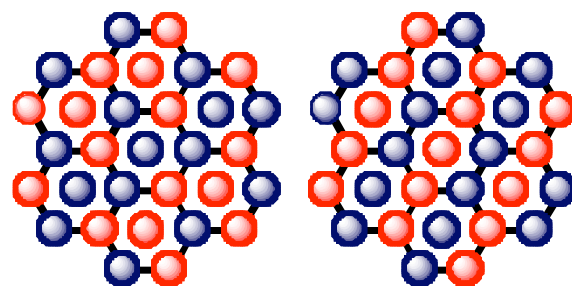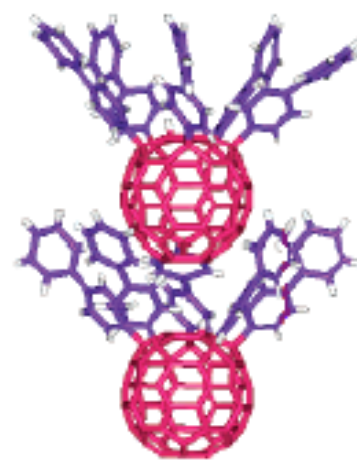
Figure 6. Conical LC. Compound **7** R=CH$_3$; R'=COC$_n$H$_{2n+1}$, n=12,13,15,17. Compound **9** R=(CH$_2$)$_n$H, n=4,5,6,7,8,10,12,14; X= CH$_2$C(CH$_3$)$_2$CH$_2$
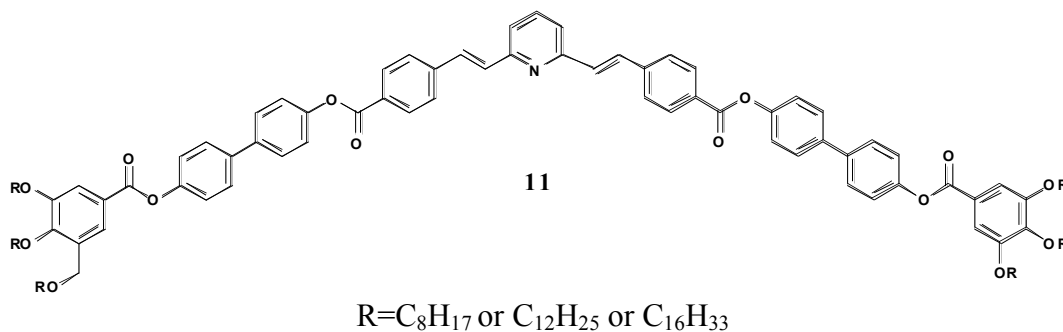
Swager and coworkers incorporated a transition metal into the conical molecule and developed the tungsten complex (**8**) shown in figure 6.[20] The rigid cone created by the calix[4]arene and the Lewis acidic nature of the square pyramidal tungsten resulted in an ideal situation for host-guest interaction with a Lewis base inside the cavity. These experiments suggested a polar head-to-tail stacking of the complexes in which the tungsten-oxo groups protruded into an adjacent calix[4]arene cavity. This research demonstrated that unidirectional stacking and axial polarity could occur within a columnar phase; however, the bulk properties of the material were not reported.

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Conical complexes containing an achiral vanadium oxide complex (n(Me$_2$salph)VO) (**9**) were also synthesized.[21] Intermolecular dative coordination of the oxygen and vanadium atoms drove the head-to-tail stacking of the compounds into columns. The V=O stretching frequency in the IR spectrum revealed the formation of a weak linear chain polymer and x-ray crystallography suggested that the intermolecular interactions led to an interdigited, layered structure with antiferroelectric ordering. The LC properties could be controlled by variations in the backbone of the complexes.[22] However, the switching observed was attributed to ions or charges present and it was hypothesized that bulk ferroelectricity did not occur because intercolumnar interactions were absent.[23,24]

Another class of achiral molecules is the badminton-shuttlecock compounds. Sawamura *et al.* recently functionalized C$_{60}$ fullerenes (**10**) (reprinted with permission from Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432-433. Copyright 2004 American Chemical Society.) and showed that these compounds stack head-to-tail to form a polar hexagonal columnar LC.[25] The attachment of 5 biphenyl groups to a C$_{60}$ fullerene using an organocopper-based strategy yielded an aromatic pentadiene at the base of a concave cavity. The π–π interaction of this aromatic moiety with the base of an adjacent fullerene drove the macromolecular columnar assembly. An additional incompatibility between C$_{60}$ and the flexible aliphatic chains on the biphenyl rings provided microphase separation and the necessary mobility to form a liquid crystalline material. The badminton compounds were later modified to improve their structural mobility.[26] The addition of an (aryl)-(dimethyl)silylmethyl linker created a broader and larger cup-shaped cavity allowing for

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R=C$_8$H$_{17}$ or C$_{12}$H$_{25}$ or C$_{16}$H$_{33}$

more flexibility and improved interaction with the fullerene and the neighboring cavity. Unlike the other conical molecules, these LCs were well-characterized and the Col$_h$ packing was elucidated with x-ray crystallography. The orientation of the molecules and the dipoles alternated from row to row. Despite the uniqueness of this system, the mechanism for switching between the polar states seems difficult.

Greater potential for switching is seen with the polycatenar molecule (molecules composed of a rigid core flanked by numerous alkyl chains) (**11**). Due to the banana shape, compound **11** is expected
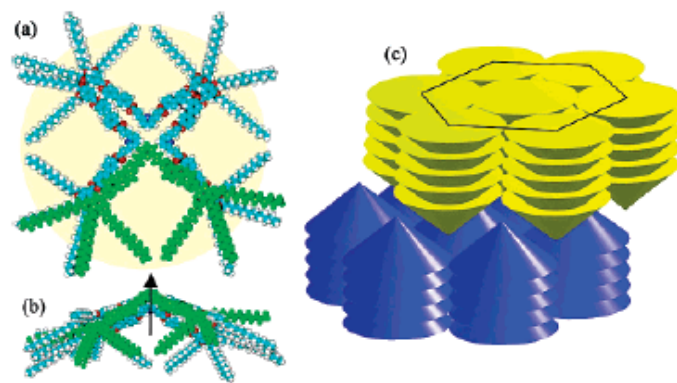

Figure 7. a)Arrangement of 4 polycatenar-type molecules into a conical structure b) Dipole directed along the axis of the cone c) Tertiary assembly of polycatenars. Reprinted with permission from Gorecka, E.; Pociecha, D.; Mieczkowski, J.; Matraszek, J.; Guillon, D.; Donnio, B. *J. Am. Chem. Soc.* **2004**, *126*, 15946-15947. Copyright 2004 American Chemical Society.
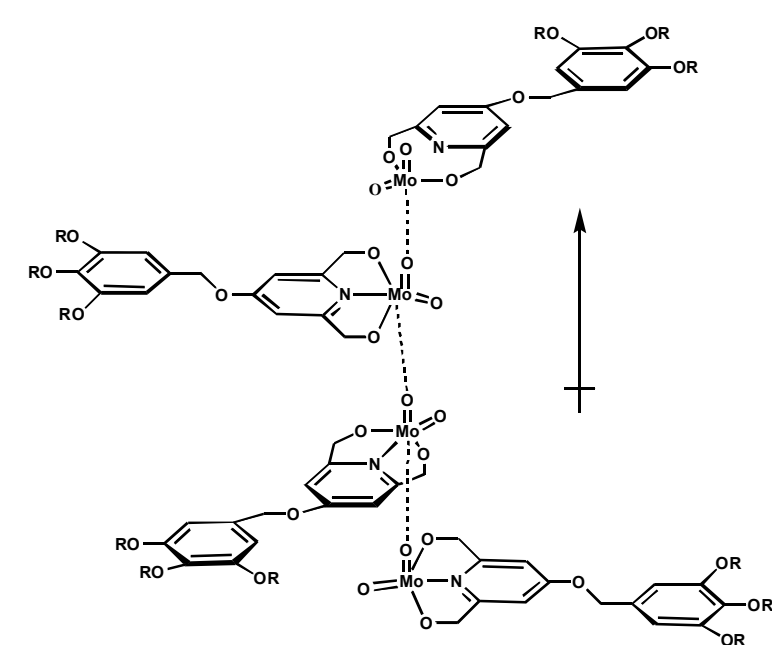
to exhibit ferroelectric properties, while the polycatenar design is known to form a columnar mesophase. Gorecka and coworkers hypothesized that the combination of the banana shape and the polycatenar structure would produce a ferroelectric columnar phase.[27] Using this theory, it was shown that 4 polycatenar molecules associated to form a cone-like structure with a dipole present along the cone axis (Figure 7a, 7b). The cone structure was a result of the favorable packing of the aromatic rings, as well as reduced steric interactions between the alkyl chains. The cones further assemble into a Col$_h$ LC with antiferroelectric properties. It was proposed that anitferroelectric ordering arose either from a quasihexagonal structure (randomly oriented dipoles in the hexagonal lattice) or from a 3-dimensional arrangement in which the hexagonal lattice was shifted in adjacent layers of alternate polarity (Figure 7c).

DISC-LIKE FLCs

Disc-like entities have also been examined. Another route to FLCs depends upon metal-oxygen coordination as the driving force for macromolecular organization. Dioxomolybdenum complexes formed linear chains in which
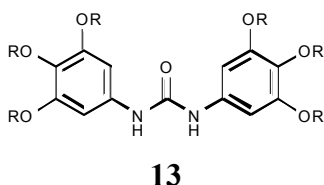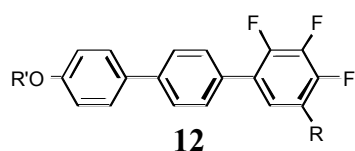

Figure 7. Four dioxomolybdenum complexes stack to form a disc-like entity. R= (CH$_2$)$_n$H, n=8,10,12,14,16

Figure 9. Molecules that form disc-like units and assemble into columnar phases. Compound **12a.** R= $C_8H_{17}O$; R'=C_7H_{15} **12b.** R= $C_{10}H_{21}O$; R'=C_5H_{11} Compound **13.** R= $C_{12}H_{25}$ or $C_{14}H_{29}$

Mo ligands rotated about a center axis to form a columnar superstructure (Figure 7).[28] The weak (Mo=O--Mo=O--)$_n$ bond associations promoted the organization of the molecules into columns with a uniform dipole vector along the center axis. The organization of into a Col$_h$ phase demonstrates the ability of disc-like molecules to assemble into a columnar phase.

Hird and coworkers showed that compounds containing terphenyl cores (**12**) could also form polar Col$_h$ mesophases.[11] Although these rod-like molecules would be expected to form a smectic phase, the rigid structure likely restricts molecular conformations and promotes organization into a Col$_h$ phase. It was proposed that phenyl-fluorophenyl stacking facilitated the formation of disc-shaped aggregates that assembled into columns. Electrooptic experiments showed different LC regions of unidirectional polar alignment. Although the bulk material displayed a zero dipole, switching was observed within the polar domains, demonstrating that switching is possible in Col$_h$ phases composed of disk-like compounds.

Kishikawa and coworkers, recently reported the first ferroelectrically switchable liquid crystalline Col$_h$ phase using N,N'-diarylureas (**13**).[29] Unidirectional stacking of **13** and polar packing into columns were promoted by intermolecular hydrogen bonding. Rotation of the benzene rings decreased the steric repulsion between molecules within the columns (Figure 10a). The long alkyl chains effectively shield the polar axis located at the center of the molecule, preventing repulsive intercolumnar dipole-dipole interactions. In an electric field, the polarity of all columns became uniform and a ferroelectric material was obtained (Figure 10b, 10c). Although a low energy barrier prevented the polar organization from being maintained, this research showed that switchable bulk ferroelectric ordering of a Col$_h$ is possible.

CONCLUSION

FLCs are of interest to a variety of fields including chemistry, physics, optoelectronics, and nonlinear optics.
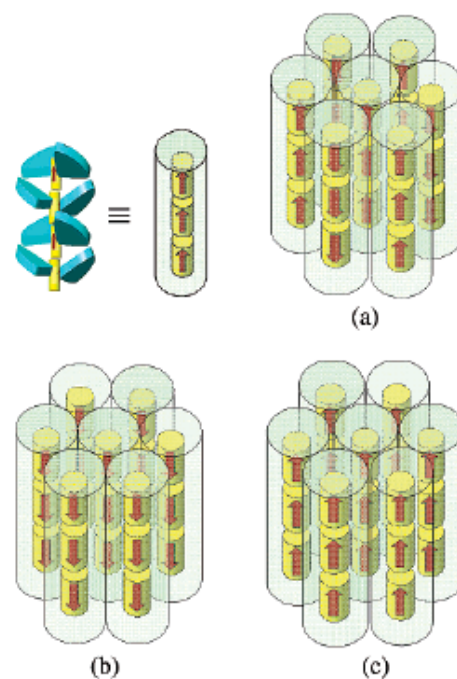

Figure 10. a) Columnar stacking of urea-based compounds b) antiferroelectric state c) and d) 2 ferroelectric states with unidirectional dipole alignment. Reprinted with permission from Kishikawa, K.; Nakahara, S.; Nishikawa, Y.; Kohmoto, S.; Yamamoto, M. *J. Am. Chem. Soc.* **2005**, *127*, 2565-2571. Copyright 2005 American Chemical Society

The shapes of molecules and their molecular interactions have been exploited in the production of new FLC phases. Although it has been suggested that the shape of the molecules dictates the LC phase formed, it appears that the intermolecular interactions are more important in determining the macromolecular organization of the molecules. Since the field is young, much investigation is still needed to understand the molecular requirements to form ferroelectric phasse and to realize the potential of these materials. Not only are the scientific implications of forming chiral superstructures from achiral molecules scientifically novel, but these materials also have great potential in display technology.

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