Anion-directed self-organization of thermotropic liquid crystalline materials containing a guanidinium moiety†

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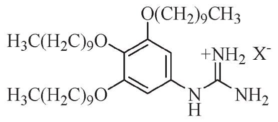
New wedge-shaped thermotropic liquid crystalline materials containing a guanidinium moiety at the apex organize into various supramolecular structures such as hexagonal columnar, rectangular columnar and *Pm*3*n* cubic mesophases depending on anions illustrating guest-directed self-organization in mesophases.

Self-organization of anisometric molecules into thermotropic columnar and cubic liquid crystals has been a subject of intense research in conjunction with development of new functional materials.[1] Recent studies demonstrated that the construction and manipulation of such interesting two-dimensionally and three-dimensionally ordered supramolecular structures on the nanometer scale can be achieved by careful design and covalent synthesis of anisometric building blocks including monodendrons, rod–coil block molecules, polyhydroxy amphiphiles and folic acid derivatives.[2] Another promising approach to manipulating such interesting supramolecular structures, however, may be to incorporate a binding motif into anisometric molecules, that can form a strong complex with various guest molecules through noncovalent interactions. One of the advantages of this noncovalent approach is that in principle, it allows us facile manipulation of their self-organized structures simply by altering the guest molecules. Our long interest in developing novel liquid crystalline materials and their applications[3] led us to explore the possibility of manipulating self-organized structures in mesophases using this noncovalent strategy, although similar approaches have been recently taken by others as well.[4] We decided to introduce a guanidinium moiety which is known to form a strong complex with a variety of anions such as sulfonate, nitrate, carboxylate or phosphate anions through electrostatic as well as hydrogen bonding interactions, at the apex of a wedge-shaped molecule and see how it assembles itself into an organized structure in the presence of various anionic guest molecules.[5] In this communication, we present new wedge-shaped thermotropic liquid crystalline materials containing a guanidinium moiety at the apex, which exhibit several different self-organized structures including hexagonal columnar, rectangular columnar and *Pm*3*n* cubic mesophases depending on guest anions. This system demonstrates that the noncovalent strategy is indeed a viable approach to the manipulation of self-organized structures in mesophases.



1^+X^-

$X^- = Cl^-, NO_3^-, BF_4^-, HCCCO_2^-$

The wedge-shaped compound 3,4,5-tridecyloxy-1-phenylguanidine **1** was synthesized by guanylation of 3,4,5-tridecyloxyaniline with 1*H*-pyrazole-1-(*N*,*N*′ -bis-Boc)-carboxamidine followed by deprotection of the Boc groups and basification of a guanidinium moiety.[6] The guanidinium complexes $\mathbf{1}^+X^-$ ($X^- = NO_3^-, BF_4^-, HCCCO_2^-$, and Cl^-) were synthesized by addition of the corresponding acid to **1**. The amphiphilic compounds $\mathbf{1}^+X^-$ show enantiotropic liquid crystalline behavior (Table 1), as confirmed by polarized optical microscopy, differential scanning calorimetry and X-ray diffraction studies. It is in sharp contrast to the fact that the parent free base compound **1** does not exhibit any liquid crystalline phase even though the guanidine moieties can also interact with each other through intermolecular hydrogen bonding interactions. Apparently, the charge introduced at the apex of the wedge-shaped molecule and the cooperative electrostatic interactions between the charged units successfully induce thermodynamically stable liquid crystalline phases. It is worth noting that **1** forms an organic gel in dodecane solution whereas under the same conditions $\mathbf{1}^+X^-$ does not,[7] which also indicates that the aggregation behavior is greatly affected by the introduction of a charge at the focal point of the molecule.

Most interestingly, however, several different self-organized structures were observed depending on guest anions. When polyatomic anions such as NO_3^- and BF_4^- are employed as guest anions, only a hexagonal columnar mesophase is observed. For example, $\mathbf{1}^+NO_3^-$ shows a *pseudo*-focal conic texture under a polarized microscope (Fig. 1a), which is characteristic of a hexagonal columnar mesophase. The X-ray pattern of the mesophase of $\mathbf{1}^+NO_3^-$ taken at 105 °C displays a strong peak and two weak peaks in the small-angle region with reciprocal Bragg spacings in a ratio of $1 : \sqrt{3} : 2$, which can be assigned as the (100), (110) and (200) reflections of a hexagonal arrangement with a lattice constant $a = 33.6$ Å (Fig. 2a). Similarly $\mathbf{1}^+BF_4^-$ also

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Table 1 Thermal transitions of compounds

Comp.	Heating [$T/^\circ C$ (H/J g^{-1})]	Cooling [$T/^\circ C$ (H/J g^{-1})]
1	K 97 (24.0) I	I 75 (−26.6) K
$\mathbf{1}^+HCCCO_2^-$	Col$_{rec}$ 93 (1.50) I	I 91 (−1.38) Col$_{rec}$
$\mathbf{1}^+BF_4^-$	K 37 (23.1) Col$_h$ 173 (1.06) I	I 170 (−1.05) Col$_h$ 27 (−19.9) K
$\mathbf{1}^+NO_3^-$	K 97 (13.5) Col$_h$ 140 (1.01) I	I 138 (−0.97) Col$_h$ 86 (−12.2) K
$\mathbf{1}^+Cl^-$	K 78 (15.2) Col$_h$ 114 (1.38) Cub 165 (0.47) I	I 160 (−0.32) Cub 106 (−1.70) Col$_h$

[a] K = crystalline phase; Col$_{rec}$ = rectangular columnar phase; Col$_h$ = hexagonal columnar phase; Cub = *Pm*3*n* cubic phase; I = isotropic phase.

shows a hexagonal columnar mesophase with a lattice constant a = 34.2 Å at 100 °C. The larger lattice parameter compared with that for $\mathbf{1}^+NO_3^-$ may be due to the larger size of BF_4^- ion.

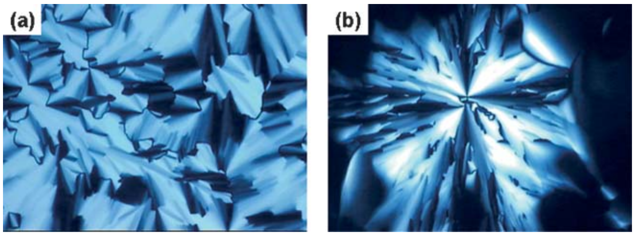

Fig. 1 Polarized optical micrograph of a) the texture exhibited by the hexagonal columnar mesophase of $\mathbf{1}^+NO_3^-$ at 105 °C in the cooling scan and b) the texture exhibited by the rectangular columnar mesophase of $\mathbf{1}^+HCCCO_2^-$ at room temperature in the cooling scan.

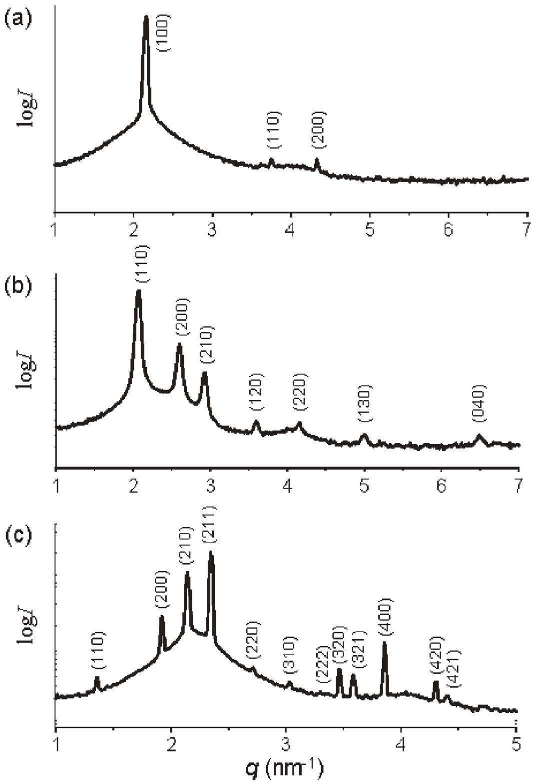

Fig. 2 X-ray diffraction patterns of a) the hexagonal columnar mesophase exhibited by $\mathbf{1}^+NO_3^-$ at 105 °C, b) the rectangular columnar mesophase exhibited by $\mathbf{1}^+HCCCO_2^-$ at room temperature and c) of the *Pm*3*n* cubic mesophase exhibited by $\mathbf{1}^+Cl^-$ at 140 °C.

On the other hand, $\mathbf{1}^+HCCCO_2^-$ containing a cylindrical carboxylate as a guest anion has a rectangular columnar phase. Under a polarized microscope the mesophase of $\mathbf{1}^+HCCCO_2^-$ at room temperature in the cooling scan exhibits the texture shown in Fig. 1b. The small-angle X-ray pattern of $\mathbf{1}^+HCCCO_2^-$ taken at room temperature (Fig. 2b) shows three strong peaks at 30.2 Å, 24.1 Å, and 21.4 Å which have been assigned to the (110), (200) and (210) reflections, respectively, of a rectangular columnar structure with lattice parameters of a = 48.2 Å and b = 38.7 Å. These observations indicate that the shape of guest anions also affects the arrangement of the columns in liquid crystalline state.

Finally, $\mathbf{1}^+Cl^-$ forms not only a columnar mesophase but also a micellar cubic mesophase. The amphiphilic compound shows a *pseudo*-focal conic texture from 78 °C to 114 °C between crossed polarizers, whereas the birefringence disappears from 114 °C to 165 °C indicating the formation of a 3-D cubic liquid crystalline phase. The mesophases and phase transition have been confirmed by small-angle X-ray diffraction studies using synchrotron

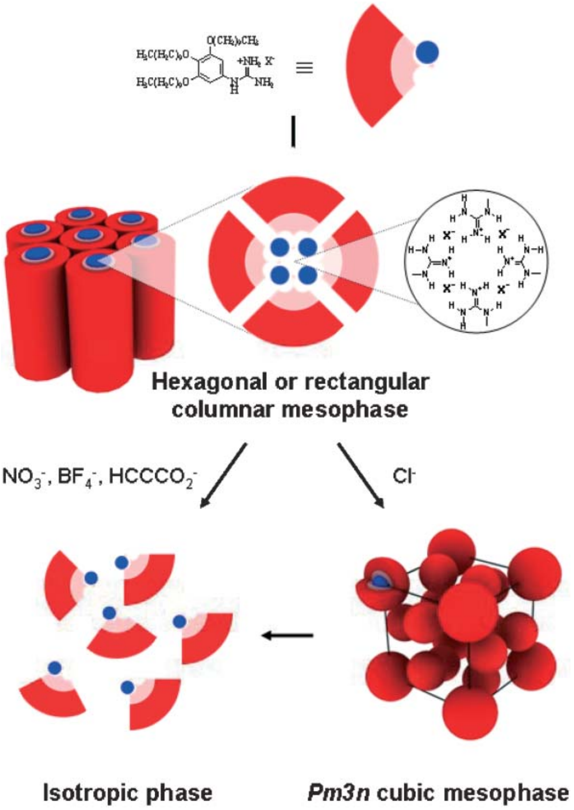

Fig. 3 Schematic illustration of the formation of hexagonal columnar mesophase and *Pm*3*n* cubic mesophase in $\mathbf{1}^+X^-$.

radiation. In the lower temperature region three peaks corresponding to the (100), (110) and (010) reflections appeared in the small-angle X-ray pattern, which is consistent with a hexagonal columnar mesophase with a lattice parameter of a = 33.4 Å at 90 °C. On the other hand, the small-angle X-ray diffraction pattern of the highly viscous isotropic mesophase at 140 °C shows 12 peaks with a reciprocal spacing ratio of $\sqrt{2} : \sqrt{4} : \sqrt{5} : \sqrt{6} : \sqrt{8} : \sqrt{10} : \sqrt{12} : \sqrt{13} : \sqrt{14} : \sqrt{16} : \sqrt{20} : \sqrt{21}$ (Fig. 2c). On the basis of the extinction rule and its position in the phase sequence located between hexagonal columnar phase and isotropic liquid, the cubic phase is best described as an inverted micellar cubic phase with *Pm*3*n* symmetry and a lattice parameter of a = 65.5 Å.

The anion-dependent formation of the self-organized structures in $\mathbf{1}^+X^-$ may be understood based on the self-assembly behavior of guanidinium complexes which are known to form various supramolecular architectures such as *quasi*-hexagonal hydrogen-bonded sheet, tube and rosette *via* cooperative hydrogen bonding as well as electrostatic interactions in the solid state.[5] Approximately four $\mathbf{1}^+X^-$ molecules form a disk with the anions at the core, which is in turn stacked to form an infinite column through favorable intermolecular interactions in a columnar mesophase (Fig. 3).[8] While spherical (Cl^-) or highly symmetrical (BF_4^-, NO_3^-) anions prefer a hexagonal arrangement of the columns, the less symmetrical and linear anion $HCCCO_2^-$ leads to a rectangular arrangement. When the temperature increases, the infinite cylindrical assemblies collapse or reorganize into spherical aggregates, mainly depending on the stability of the resulting spherical aggregates. Although the stability of the self-organized structures is affected by a number of factors including the size and shape of guest anions as well as their binding mode and affinity to guanidinium moieties, the observation of a three-dimensionally ordered mesophase only with Cl^- seems to indicate that a small and spherical anion with no preferred binding directionality favors the formation of the spherical assembly. A systematic study is, however, needed to better understand the interesting anion-dependent self-assembly.

In conclusion, we present novel supramolecular liquid crystalline materials containing guanidinium moieties which demonstrate that a variety of supramolecular structures can be constructed simply by varying guest anions. This approach can be extended to the introduction of functional guest molecules such as anionic metal complexes and polyelectrolytes into the inner region of ordered cylindrical and spherical assemblies. Such materials may be further utilized in preparation of ordered nanocomposite arrays by the combination with *in-situ* polymerization methods.[3d,9] Our current efforts are directed along these lines.

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7 A 5 wt% solution of **1** in dodecane forms an organic gel at 37 °C with a transition enthalpy change of 1.53 J g^{-1} on cooling, which is transformed to sol at 53 °C on heating with a transition enthalpy change of 1.79 J g^{-1}.

8 The number per unit cell in hexagonal columnar mesophase of $\mathbf{1}^+Cl^-$ was calculated using the formula $n = (\sqrt{3}/2)a_{hex}{}^2h_{hex}\ (N_A/M)\rho$ (N_A = Avogadro constant, M = molecular mass), a density ρ = 0.97 g cm^{-3} and a height h_{hex} = 4.1 Å (the XRD pattern of the hexagonal columnar mesophase of $\mathbf{1}^+Cl^-$ taken at 30 °C in the cooling scan shows a small and sharp peak at q = 15.4 nm^{-1} corresponding to an interplanar spacing of ∼ 4.1 Å, which can be assigned as (001) in hexagonal columnar mesophase) to give ∼4 molecules per unit cell. Similarly, the number of molecules per unit cell in *Pm*3*n* cubic mesophase is calculated to be ∼267 molecules, which indicates that each sphere in unit cell is composed of average 33 molecules at 140 °C.

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