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## PUBLICATION

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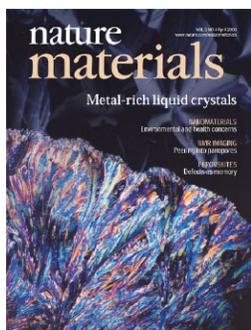
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## Metallo-tropic Liquid Crystals: Surfactant Induced Order in Molten Metal Halides

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*Liquid crystals consist of anisotropic molecular units, the majority of which are organic molecules. More recently, liquid crystals incorporating metals into anisotropic molecules have been prepared. Generally these require at least two long-chain organic ligands per metal center. In order to create liquid crystals with high metal content we have investigated the surfactant templated design of anisotropic structure in molten inorganic networks. Variable temperature x-ray diffraction (VTXRD) in conjunction with differential scanning calorimetry (DSC) and polarized light optical microscopy (POM) were used to determine the structural variation in metallo-tropic liquid crystals as the relative volume fraction of the inorganic block was increased from 33 to 80 mole percent.*

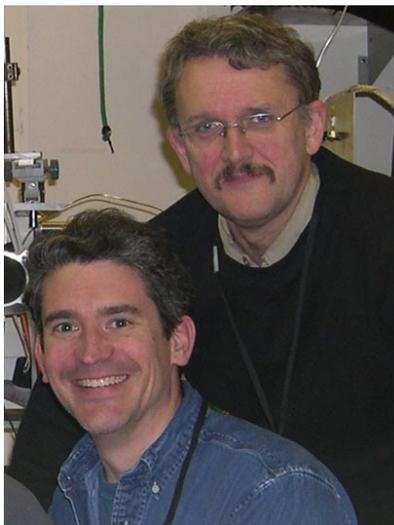


Using the cationic surfactants  $C_nTACl$  ( $C_n$  = alkyl chain with  $n = 8$  to 18, TA = trimethyl-ammonium) and divalent metal-halides (including Zn,

Cd, Cu, Ni, Co, Fe, and Mn) we have found a rich variety of liquid crystalline phases. The amphiphilic character of the inorganic/organic hybrid and the respective tunability of charge density of the inorganic anions are responsible for the observed variation in structure. Amphiphilic molecules and salts, as well as many diblock copolymers are well known to exhibit molecular scale phase segregation that results in the formation of lamellar, cubic, hexagonal columnar, and spherical micellar structural organizations depending on the nature and volume fraction of each block of the amphiphile. The majority of literature reports of  $[Surfactant]_2MCl_4$  salts exhibit a lamellar crystalline structure. However, reducing the relative volume of the organic block by re-

ducing the length of the surfactant tail to only an eight-carbon chain affords significantly increased curvature to the interface between the organic and inorganic blocks resulting in the columnar crystalline structure shown in **Figure 1a** for  $[C_8TA]_2ZnCl_4$ . In this work, we have also demonstrated that it is possible to control structural organization by variation of the volume fraction, and thus charge density, of the inorganic polar-block. The metal-halide fraction of these ma-

terials may consist of discrete molecular anions such as the relatively high charge density  $[MCl_4]^{2-}$  or low charge density oligomeric anionic networks,  $[M_nCl_{2n+m}]^{m-}$ , depending on the relative concentration of the inorganic component. An early stage of such oligomerization is observed in the crystal structure of  $[C_{16}TA]_2ZnCl_6$  shown in **Figure 1b**, for which the low charge density of the inorganic anion requires a severe canting of the surfactant chains. Any further decrease in the charge density of the inorganic anion requires a structure with a greater curvature than can be afforded by a lamellar structure.



Authors Jim Martin(left) and Jaap Folmer

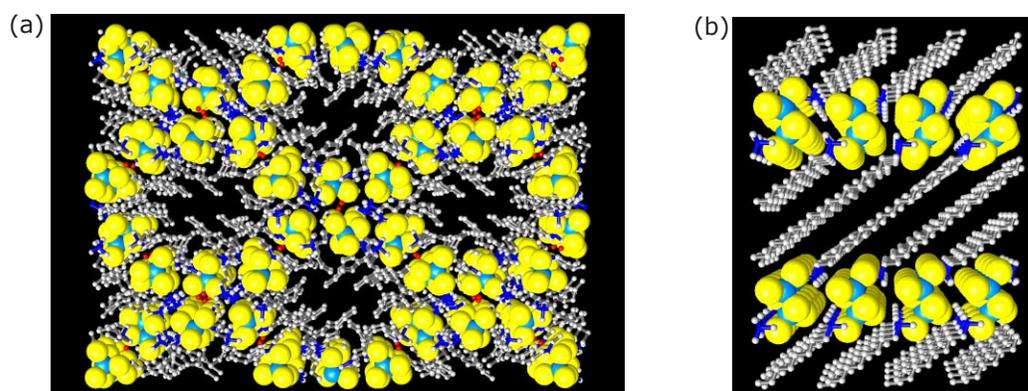
Each of the divalent metal halide systems studied exhibit relatively low melting points (below  $100^\circ C$ ). Furthermore, upon melting systems with surfactant chain lengths greater than  $C_{10}$  exhibit classic smectic, bicontinuous cubic, hexagonal columnar or spherical cubic liquid crystalline textures as observed by both x-ray diffraction, **Figure 2a**, and polarized optical microscopy (see the journal cover below). Because of the polymorphic nature of the parent binary metal halide, a greater structural diversity is observed for the zinc

systems than any of the other transition metals. The phase diagram shown in **Figure 2b**, compiled by VTXRD, DSC and POM measurements demonstrates the diversity of structure based on the molecular scale segregation of surfactant and inorganic blocks of this hybrid system. Most of the crystalline phases melt congruently and have a relatively narrow homogeneity range. However, for compositions intermediate between crystalline phases, single homogeneous liquid crystalline phases with broad homogeneity ranges are observed

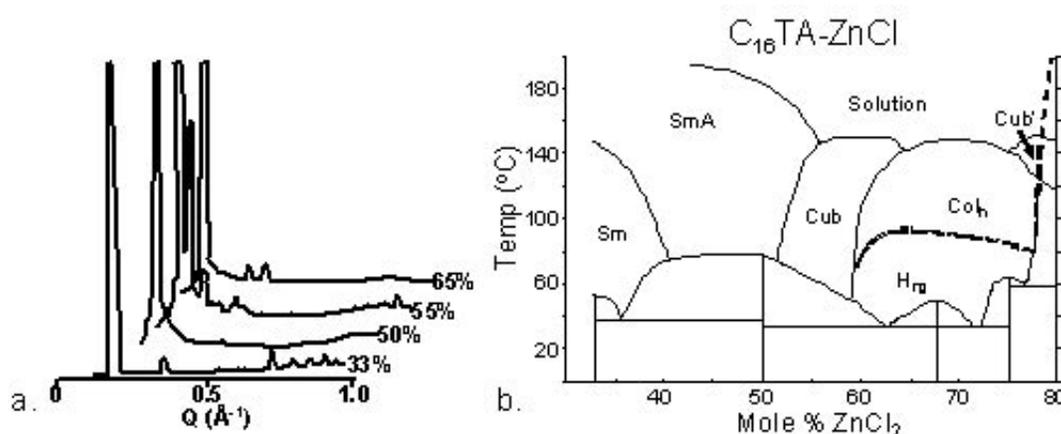
with no evidence of immiscible liquid crystalline phases except at compositions loaded as close to the phase boundary as possible. While the copper (II) system, for example yields somewhat less structural diversity than that of the zinc (II) system, the liquid crystalline organization of a relatively high concentration of  $d^9$  metals in  $C_{16}TA-CuCl$ -60 give evidence of ferromagnetic coupling between metal centers.

This demonstration of templating anisotropic structure into

liquid metal-halides, with length scales of organization sufficient to exhibit classic liquid crystalline birefringent optical textures, is a significant advance in the emerging field of amorphous materials engineering. The high metal content of these liquid crystalline systems significantly advances the field of metallomesogens, which seeks to combine magnetic, electronic, optical, redox and catalytic properties common to inorganic materials, with fluid properties of liquid crystals.



**Figure 1.** Drawing of the crystal structures of (a)  $[C_8TA]_2ZnCl_4$ , left (solved with the assistance of Dr. Jon Hanson using data from NSLS beamline X7B), and (b)  $[C_{16}TA]_2Zn_2Cl_6$ , right showing columnar and lamellar organization, respectively.



**Figure 2.** (a) XRD patterns for liquid crystalline  $C_{16}TA-ZnCl_2$ -# (# is the mole %  $ZnCl_2$ ) recorded at approximately 100 °C. Each pattern is offset by  $0.1 \text{ \AA}^{-1}$  for clarity. The 33% and 50% compositions exhibit lamellar structures, the 55% composition indexes to a  $Ia3d$  bi-continuous cubic phase, and the 65% composition indexes as a hexagonal columnar structure. (b) Phase diagram of the  $C_{16}TA/CuCl_2$  system. Crystalline phases are identified by solid vertical lines. Liquid crystalline phases include lamellar ( $SmA$ ) (also crystal smectic ( $Sm$ )),  $Ia3d$  bi-continuous cubic ( $Cub$ ), hexagonal non-geometric ( $H_{ng}$ ), hexagonal columnar ( $Col_h$ ) and cubic micelle ( $Cub'$ ). Dashed lines represent the composition boundary above which crystals of  $ZnCl_2$  are observed. The dotted line indicates the temperature of the  $H_{ng}-Col_h$  transition that is only observed by a change in the optical texture upon heating.