

Alkyl-bis(imidazolium) salts: a new amphiphile platform that forms thermotropic and non-aqueous lyotropic bicontinuous cubic phases†

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Lily A. Robertson, Magdalene R. Schenkel, Brian R. Wiesenauer and Douglas L. Gin*

New ionic amphiphiles with a hexyl-bridged bis(imidazolium) head-group; Br[−], BF₄[−], or Tf₂N[−] anions; and a long *n*-alkyl tail can form thermotropic bicontinuous cubic liquid crystal phases in neat form and/or lyotropic bicontinuous cubic phases with several non-aqueous solvents or water.

Bicontinuous cubic liquid crystal (LC) phases are an interesting class of ordered but fluid, self-organized assemblies formed by LC molecules. These phases consist of two chemically incompatible, 3D-nanoscale domains that are intertwined but physically separate from one another, with overall cubic symmetry.^{1,2} If such assemblies are formed by neat LCs as a function of temperature, they are categorized as *thermotropic* bicontinuous cubic (Cub_{bi}) phases (Fig. 1a).¹ If the LCs are strongly amphiphilic and self-assembly occurs in the presence of a solvent with affinity for one part of the amphiphile, then concentration- and temperature-dependent *lyotropic* bicontinuous cubic (Q) phases are formed in which one domain is open/solvent-filled (Fig. 1b).² Cub_{bi} and Q phases are highly sought-after because their ordered, 3D-interconnected nanodomains make them particularly useful for molecular transport and uptake/release applications.^{1,2}

Although molecules that form thermotropic Cub_{bi} phases can vary greatly in shape and structure,¹ they generally have two dissimilar regions in the same molecule (*e.g.*, rigid *vs.* flexible, or hydrophilic *vs.* hydrophobic), affording some level of phase-separation in their neat states.¹ Mesogens that form lyotropic Q phases are also biphilic but typically flexible and have an ionic or non-ionic hydrophilic head-group region plus a hydrophobic tail section. One region interacts preferentially with an added solvent to generate phase-separated, saddle-point structures in-between curved and non-curved phases.² Because of the interfacial curvature balance needed to form Cub_{bi} or Q phases, LC molecular shape and packing considerations are often not reliable predictors for their formation unlike in most thermotropic and lyotropic LC systems.^{1,2} Some amphiphilic molecules are also able to form both thermotropic and lyotropic LC phases, making them amphotropic in nature.³

Ionic Cub_{bi} and Q phases have recently been of interest because of the properties that result from one domain being intrinsically charged. For example, unpolymerized and polymerized ionic Cub_{bi} phases have been found to be excellent ion conductors and ion separation materials due to their interconnected nano-ion-channels.^{4–7} Cationic Cub_{bi} systems are useful for siRNA transfection applications.⁸ Nanoporous, cross-linked Q phases formed by ionic amphiphiles in water have been used as nanocomposite templates, heterogeneous catalysts, and membrane materials capable of molecular sieving.⁹ Non-aqueous, ionic Q phase polymers have been reported to be good ion-conducting membranes for potential battery applications.^{7,10} More recently, aqueous ionic Q phases containing strong acid have been found to be good proton-conducting materials.¹¹

Ionic thermotropic LCs that form Cub_{bi} phases have typically been based on a *single* ionic headgroup with a free counterion, and belong to two general structural types: (1) organic salts containing an ionic headgroup (*i.e.*, a cationic ammonium,⁴ phosphonium,⁵ or imidazolium⁸ unit, or an anionic metal phosphonate unit^{12,13}) connected to one or more flexible, hydrophobic tails; and (2) cationic metal-organic coordination complexes or salts containing one or more flexible alkyl tails.^{14,15} More recently, ionic mesogens containing *two* covalently bonded ionic units have been reported to form Cub_{bi} phases. These include (1) symmetric dicationic salts based on a rigidly connected arylbis(imidazolium) headgroup with

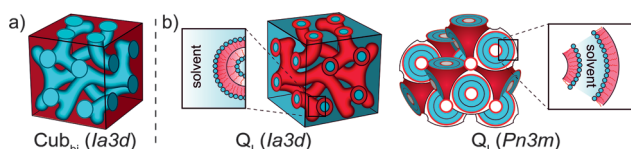


Fig. 1 Illustrations of bicontinuous cubic phases: (a) thermotropic *Ia3d* Cub_{bi} phase, and (b) two common lyotropic Q phases (type I).

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, USA. E-mail: gin@spot.colorado.edu; Fax: +1-303-492-8595; Tel: +1-303-735-1107

† Electronic supplementary information (ESI) available: Synthesis procedures, characterization data (including ¹H and ¹³C NMR spectra) for synthesized CnX compounds. PLM, DSC, and XRD data for CnX compounds with thermotropic LC behaviour. SAXS data for selected Cub_{bi} phases. PLM penetration scan data, phase diagrams, and XRD data of CnX-solvent systems with lyotropic LC behaviour. Thermotropic and lyotropic phase identification procedures. See DOI: 10.1039/c3cc44452j

multiple alkyl tails,^{16,17} and (2) zwitterionic pyridinium salts tethered to their anions and a single long alkyl tail.¹¹ Ionic lyotropic LCs that form Q phases with water or other solvents have typically been (1) organic salts containing a single cationic or anionic headgroup connected to one to three long alkyl tails with a free counterion,^{2b,10} (2) organic salts containing a single zwitterionic headgroup and two long alkyl tails,¹⁸ or (3) gemini surfactants containing two bridged cationic or anionic units, each with an attached long alkyl tail.^{19–22} An ionic, amphotropic LC platform that can form Cub_{bi} and Q phases has not been reported.

Herein, we report a new amphiphilic, ionic LC platform based on a hexyl-bridged bis(imidazolium) headgroup connected to a single alkyl tail that can form both Cub_{bi} and Q phases (*i.e.*, amphotropic behaviour) (Fig. 1). A homologous series of 15 compounds of this type (denoted **CnX**) with 10, 14, 16, 18, and 20 total carbons in the tail (**Cn**) and **X** = Br, BF₄, or Tf₂N for the anion (Fig. 2) were synthesized and analyzed for thermotropic and lyotropic LC behaviour. It was found that four homologues (generally with C18 and C20 tails) exhibit Cub_{bi} phases in neat form or Q phases with several non-aqueous solvents or H₂O. One other homologue was also found to be able to form both Cub_{bi} and Q phases.

The **CnBr** compounds were synthesized by reacting the appropriate *n*-alkyl imidazole with 1-(6-bromohexyl)-3-methylimidazolium bromide. The analogous **CnBF₄** and **CnTf₂N** salts were prepared by ion-exchange of the **CnBr** compounds with NaBF₄/AgBF₄ and lithium bis(trifluoromethylsulfonyl)imide, respectively. After purification, the structures and purities of the synthesized compounds were verified by ¹H NMR, ¹³C NMR, and HRMS analyses (see the ESI†). Elemental analysis was attempted on the final compounds, but most did not completely combust, yielding unreliable composition data as previously observed for oligo(imidazolium) compounds.²³ The purity of these compounds is confirmed by HRMS data and inclusion of their ¹H and ¹³C NMR spectra in the ESI.†

The **CnX** compounds were analysed for thermotropic and lyotropic LC behaviour using a combination of variable-temperature polarized light microscopy (PLM) and powder X-ray diffraction (XRD). Differential scanning calorimetry (DSC) was also used to characterize compounds that exhibited thermotropic LC phases. Small-angle X-ray scattering (SAXS) was performed on specific samples as needed to aid in LC phase identification.

The 15 **CnX** salts were first screened for thermotropic LC phase behaviour by (1) observing the PLM optical textures of the neat compounds as a function of temperature and (2) detecting any phase transitions *via* DSC (see ESI†). The compounds that exhibited bright PLM optical textures (indicative of anisotropic/non-cubic, thermotropic LC phases),¹ black PLM textures with high sample viscosity (possible Cub_{bi} phase),¹ and multiple transition peaks in their DSC profiles were subsequently analyzed by XRD to confirm LC phase identity (see ESI† for detailed procedure). Table 1 lists the **CnX** salts found to exhibit thermotropic LC phases and their phase behaviour.

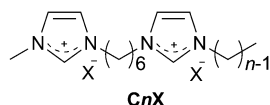


Fig. 2 Structure of new alkyl-bis(imidazolium) salts **CnX** ($n = 10, 14, 16, 18, 20$; **X** = Br, BF₄, Tf₂N).

Table 1 **CnX** compounds that exhibit thermotropic LC behavior

Compound	Thermotropic LC behaviour (°C) ^a
C20Br	Cr → 66 → SmX → 225 → Decomp
C18Br	Cr → 57 → SmX → 192 → Decomp
C16Br	Cr → 40 → LC → 63 → Cub _{bi} → 189 → Decomp
C14Br	Cr → 18 → SmX → 184 → Iso
C20BF₄	Cr → (64 → LC) → 67 → Cub _{bi} → 210 → Decomp
C18BF₄	Cr → (57 → LC) → 58 → Cub _{bi} → 220 → Decomp
C16BF₄	Cr → 40 → SmX → 180 → Iso
C14BF₄	Cr → 19 → SmX → 146 → Iso
C20Tf₂N	Cr → 52 → SmX → 71 → Iso → 67 → SmX → 29 → Cr
C18Tf₂N	Cr → 47 → Iso → 39 → SmX → 17 → Cr

^a Cr = crystalline phase; SmX = as-yet unidentified Sm phase; LC = as-yet unidentified LC phase; Iso = isotropic melt.

C10Br, **C10BF₄**, **C10Tf₂N**, **C14Tf₂N**, and **C16Tf₂N** were liquid or crystalline upon analysis and had no thermotropic mesomorphism (see ESI†).

As can be seen in Table 1, three compounds, **C16Br**, **C20BF₄**, and **C18BF₄** form Cub_{bi} phases. In all three cases, the samples display black PLM textures and two XRD peaks that have the characteristic $1/\sqrt{6} : 1/\sqrt{8}$ *d*-spacing ratio (*i.e.*, d_{211} and d_{220}) of a Cub_{bi} phase with *Ia3d* symmetry (Fig. 3).^{1,4–7}

The *Ia3d* structure is the most prevalent one reported for Cub_{bi} phases for rodlike mesogens.^{1,4–7,24} Other cubic unit cells (such as *Pn3m*, which has the same $1/\sqrt{6} : 1/\sqrt{8}$ *d*-spacing ratio) have rarely been seen for Cub_{bi} materials.²⁴ Consequently, we have tentatively assigned the Cub_{bi} phases for **C16Br**, **C20BF₄**, and **C18BF₄** as *Ia3d*. In order to help verify that the cubic phases of **C16Br**, **C20BF₄**, and **C18BF₄** are Cub_{bi} phases and not discontinuous micellar cubic phases,^{25,26} we examined their small-angle regions using SAXS. Micellar cubic phases typically show d_{110} , d_{200} , and d_{210} SAXS reflections in addition to the d_{211} and d_{220} reflections, denoting a *Pm3n* structure.^{25,27} SAXS analysis of the Cub_{bi} phases of **C16Br**, **C20BF₄**, and **C18BF₄** only revealed d_{211} and d_{220} peaks and the absence of d_{110} , d_{200} , or d_{210} reflections, suggesting that a *Pm3n* micellar cubic phase is not present (see ESI,† Fig. S12–S17).

The **CnX** compounds were then screened for lyotropic LC behaviour (specifically for Q phases) in several organic solvents and H₂O using the PLM penetration scan technique.^{13,21} This method involves wicking in a solvent to one edge of a neat **CnX** film and then using PLM to observe all of the lyotropic LC phases formed after a solvent gradient forms across the sample. Under PLM, a Q phase appears as a viscous, black band between two birefringent areas of the gradient sample.¹³ Phase diagrams were then prepared of **CnX**-solvent systems that showed evidence of Q phases by the

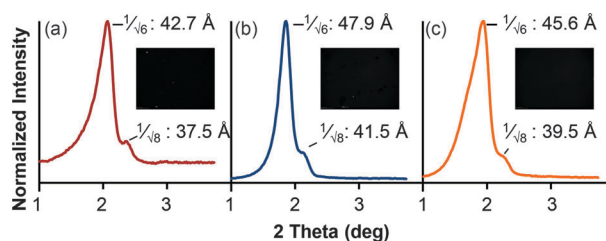


Fig. 3 XRD profiles of: (a) neat **C16Br** at 140 °C (no anneal), (b) neat **C20BF₄** at 140 °C (annealed), and (c) neat **C18BF₄** at 140 °C (annealed). Insets: PLM textures (mag. = 40×).

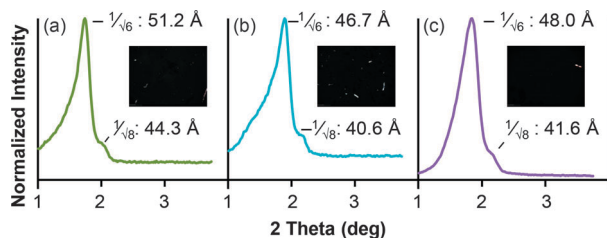


Fig. 4 XRD spectra of the Q phases of: (a) a 90:10 w/w sample of **C20Br**–glycerol at 120 °C (annealed to 120 °C); (b) a 95:05 w/w sample of **C18Br**–glycerol at 100 °C (annealed to 100 °C); and (c) a 95:05 w/w sample of **C20BF₄**–EMIM BF₄ at 140 °C (annealed to 140 °C). Insets: PLM textures of the samples (mag. = 40×).

penetration scan method. XRD analysis was performed on the observed lyotropic LC phases to confirm their identities (see ESI† for detailed procedures). Although H₂O is the usual solvent for lyotropic phase studies, Q phase formation in non-aqueous solvents was of primary interest to us because of the novelty and importance of non-aqueous ionic Q systems in several engineering applications.^{10,21}

Using this procedure, it was found that compounds **C14Br**–**C20Br** and **C14BF₄**–**C20BF₄** showed definitive lyotropic LC behavior in water, glycerol, and the ionic liquid (IL) ethyl-methylimidazolium tetrafluoroborate (EMIM BF₄) (see ESI†). Since these compounds also show thermotropic LC behaviour, they are notably amphotropic. **C20Br**, **C18Br**, and **C20BF₄** were found to form Q phases with glycerol, EMIM BF₄, and water. Fig. 4 shows representative XRD profiles and PLM textures of the Q phases formed by **C20Br**–glycerol, **C18Br**–glycerol, and **C20BF₄**–EMIM BF₄. Each of these Q phases has two XRD *d*-spacings with the $1/\sqrt{6} : 1/\sqrt{8}$ ratio and black PLM images indicative of a *la3d* or *Pn3m* Q phase.^{2,21} However, there are insufficient XRD peaks to distinguish between these two most common Q structures.² Full phase diagrams for these three systems are included in the ESI† (Fig. S18, S20, and S22). The high viscosity of these phases and the position of one of them on the solvent-rich side of a lamellar phase and solvent-deficient side of a hexagonal phase (see **C20Br**–glycerol phase diagram) suggest that they are type I (*i.e.*, normal) Q phases and not discontinuous/micellar lyotropic cubic phases.² Although **C20Br** and **C18Br** have possible Q phases in EMIM BF₄, phase diagrams of these systems were not elucidated at this point because of concerns of Br[−]–BF₄[−] exchange between the salts and IL affecting the phases. Q phase formation of **C20Br**, **C18Br**, and **C20BF₄** with H₂O was confirmed by PLM analysis (ESI† Fig. S24).

In summary, of a series of 15 new alkyl-bis(imidazolium) salts, four were found to form Cub_{bi} phases in neat form or Q phases with glycerol, EMIM BF₄, or water; and one (**C20BF₄**) was found to do both (*i.e.*, amphotropic bicontinuous cubic behaviour). On-going work with these materials includes more detailed analysis of their Cub_{bi} and Q phases and measurement of their ion conductivity. Future work will involve design of polymerizable analogues to generate stabilized Cub_{bi} and non-aqueous Q phases for applications exploration.

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