DICARBOXYLATE GEMINI SURFACTANT
THAT FORMS A LYOTROPIC LIQUID
CRYSTAL

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ABSTRACT
Aliphatic dicarboxylate Gemini surfactants and lyotropic liquid
crystal compositions formed thereby are disclosed. The Gemini surfactants are capable of robustly forming Q phase
morphologies over broad ranges of temperature and concentration.

16 Claims, 9 Drawing Sheets
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FIG. 3

Impact of Na-74 concentration on diffraction patterns.

- 80.1 wt. % Na-74
- 65.0 wt. % Na-74
- 45.0 wt. % Na-74

Log(intensity) (a.u.) vs. q (Å⁻¹)

Key peaks:
- (100)
- (200)
- (211)
- (220)
- (321)
- (332)
- (400)
- (420)
- (110)
- (210)
FIG. 4
FIG. 5

Na-76

TEMPERATURE (°C)

WEIGHT FRACTION AMPHIPHILE
FIG. 6

K-74

TEMPERATURE (°C)

WEIGHT FRACTION AMPHIPHILE

Iso.  H₁  H₁ + G₁  Lα

G₁  G₁  Lα  Lα

+  X  +  X

*  *  *  *
FIG. 7

[Graph showing temperature versus weight fraction amphiphile with various phases labeled: Iso, H₁, G₁, Lα, X, etc.]
FIG. 8

Graph showing the phase behavior of Na-94 as a function of temperature and weight fraction of amphiphile.
FIG. 9

1.) LDA (2 eq.)
2.) THF/HMPA, -15°C
3.) Na₂CO₃, THF/MeOH

Na-74; x=7, y=4, M=Na
Na-76; x=7, y=6, M=Na
Na-94; x=9, y=4, M=Na
Na-96; x=9, y=6, M=Na
K-74; x=7, y=4, M=K
NMe₄-74; x=7, y=4, M=NMe₄
DICARBOXYLATE GEMINI SURFACTANT THAT FORMS A LyOTROPIC LIQUID CRYSTAL

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH & DEVELOPMENT

This invention was made with government support under 0902067 awarded by the National Science Foundation. The government has certain rights in the invention.

FIELD OF THE INVENTION

The field of the invention relates generally to anionic Gemini surfactants that form a lyotropic liquid crystal in an aqueous composition.

BACKGROUND OF THE INVENTION


BRIEF DESCRIPTION OF THE INVENTION

Briefly, therefore, the present invention is directed to a lyotropic liquid crystal composition. The LLC composition comprises a polar solvent such as water and an anionic Gemini surfactant, the anionic Gemini surfactant comprising at least one carboxylate moiety. The anionic Gemini surfactant forms a triply periodic phase over a range of concentrations from C1 to Cc, wherein the difference between C1 and Cc is at least 10 weight percent and over a range of temperatures from T1 to Tc, wherein the difference between T1 and Tc is at least 40°C. The present invention is further directed to a lyotropic liquid crystal composition. The LLC composition comprises a polar solvent such as water at a concentration of at least 10 weight percent; and an anionic Gemini surfactant at a concentration of at least 30 weight percent, the anionic Gemini surfactant having the following structure:

Herein X1 and X2 are each independently a substituted or unsubstituted aliphatic moiety having between four and 30 carbon atoms or a substituted or unsubstituted aryl-aliphatic moiety having between four and 30 carbon atoms; Y is a connecting moiety selected from the group consisting of a branched or unbranched hydrocarbyl moiety, a substituted or unsubstituted aryl or heteroaryl moiety, and a hydrophilic moiety; M is a counterion; and R1 through R6 are each inde-
dependently selected from the group consisting of hydrogen, fluoride, chloride, and bromide.

The present invention is still further directed to an anionic Gemini surfactant having the following structure:

Herein X₁ and X₂ are each independently a substituted or unsubstituted aliphatic moiety having between four and 30 carbon atoms or a substituted or unsubstituted aryl-aliphatic moiety having between four and 30 carbon atoms; Y is a connecting moiety selected from the group consisting of a branched or unbranched hydrocarbyl moiety, a substituted or unsubstituted aryl or heteroaryl moiety, and a hydrophilic moiety; M is a counterion; and R₁ through R₄ are each independently selected from the group consisting of hydrogen, fluoride, chloride, and bromide.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIGS. 1A through 1F are illustrations of the observed LLC morphologies formed by Gemini surfactants: hexagonal (H₃), lamellar (Lₐ), with flat interfaces (FIG. 1B), Double Gyroid (G₂) (FIG. 1C), Double Diamond (D₂) (FIG. 1D), Primitive (P₁) (FIG. 1E), and tetracatenaon hexagonal (H₋₋) (FIG. 1F) that require substantial positive and negative deviations from constant mean curvature.

FIGS. 2A through 2C are illustrations of the variety of possible curvatures adopted by Gemini surfactants with flexible hydrophobic alkyl spacers.

FIG. 3 is a graph depicting azimuthally integrated XRD patterns of Na₄-74 LLCs with various water contents at 25°C. Markers on each trace indicate calculated positions for Bragg reflections of the H₃ (○), G₂ (●), and Lₐ (■) morphologies. The broad low intensity peak at ~0.4 Å⁻¹ is an artifact due to the Kapton windows of the XRD sample holder.

FIG. 4 is a temperature v. concentration LLC phase diagram for hydrated sodium carboxylate Gemini surfactant Na₄-74. Isofluid isotropic phase, H₃-normal hexagonal, G₂-normal Double Gyroid, Lₐ—lamellar, X—crystalline, and +—unknown LLC phase.

FIG. 5 is a temperature v. concentration LLC phase diagram for hydrated sodium carboxylate Gemini surfactant Na₇-46. Isofluid isotropic phase, H₃-normal hexagonal, G₂-normal Double Gyroid, Lₐ—lamellar, P₁—normal primitive, X—crystalline, and +—unknown LLC phase.

FIG. 6 is a phase diagram for hydrated potassium carboxylate Gemini surfactant K₇-47. Isofluid isotropic phase, H₃-normal hexagonal, G₂-normal Double Gyroid, Lₐ—lamellar, X—crystalline.

FIG. 7 is a phase diagram for hydrated tetramethylammonium carboxylate Gemini surfactant NMe₄-74. Isofluid isotropic phase, H₃—normal hexagonal, G₂—normal Double Gyroid, Lₐ—lamellar, X—crystalline.

FIG. 8 is a phase diagram for hydrated sodium carboxylate Gemini surfactant Na₉-94. Isofluid isotropic phase, H₃—normal hexagonal, LC—normal tetracatenaon hexagonal, G₂—normal Double Gyroid, Lₐ—lamellar, X—crystalline.

**FIG. 9** is a depiction of the synthesis of anionic Gemini dicarboxylate surfactants.

**DETAILED DESCRIPTION OF THE EMBODIMENT(S) OF THE INVENTION**

The present disclosure is directed to materials that form lyotropic liquid crystals. Lyotropic liquid crystals comprise materials that form phases having long-range translational order induced by the addition of a solvent. Stated another way, lyotropic liquid crystals comprise ordered phases in solvent, in which the structurally periodic phase that exists in the liquid crystal composition varies as a function of concentration of the surfactant in the solvent system, temperature, and pressure. A subset of these phases can be described as being triply periodic, since the phases comprise structures that repeat in three dimensions. LLC phases may be described in a phase diagram in which the X-axis (abscissa) is concentration and the Y-axis (ordinate) is temperature. The liquid crystalline phase that generally forms at low surfactant concentrations is the ‘micellar cubic’ or ‘discontinuous cubic’ phase comprising spherical micelles and which may be denoted by the symbol L₁. This is a viscous, optically n-birefringent phase in which the micelles are arranged on a cubic lattice. At higher concentrations, in general, the cylindrical micelles of indefinite length form and are arranged on a two-dimensional hexagonal lattice with long-range periodic order. This lyotropic liquid crystalline phase is known as the ‘hexagonal phase,’ or more specifically the ‘normal’ hexagonal phase and is generally denoted by the symbol H₃. At higher concentrations, the ‘lamellar phase’ generally forms. This phase is denoted by the symbol Lₐ. This phase consists of surfactant molecules arranged in bilayer sheets separated by layers of water. Some materials may form an intermediate phase at concentrations generally between those concentrations at which hexagonal and lamellar phases form. Some intermediate phases may be referred to as a bicontinuous cubic phases or Q-phases. Bicontinuous cubic phases include double gyroid phase (G₂, space group #230), the single gyroid phase (space group #214), the double diamond phase (space group #224), and the primitive cubic phase (space group #229). See FIGS. 1A through 1F. See also Seddon, J. M. *Biochimica et Biophysica Acta*, 1990, 1051, 1-69 and V. Luzzati, R. Vargas, P. Mariani, A. Gullik, H. Delacroix, J. Mol. Biol. 229 (1993) 540. FIGS. 1A through 1F depicts the Hexagonal (H₃) (FIG. 1A), Lamellar (Lₐ) (FIG. 1B), and Double Gyroid (G₂) (FIG. 1C through 1E) phases. FIG. 1F depicts a tetracatenaon hexagonal phase, which may be prepared using anionic Gemini surfactants of the present invention. The various phases that a lyotropic liquid crystal may assume are generally discussed as a function of concentration; however, phase transitions may occur as the temperature or pressure of the system increases. Surfactant concentrations at which a double gyroid phase, for example, may form at lower temperatures, e.g., 20°C, may shift or the range may narrow as the temperature of the system increases, e.g., to 100°C.

The present disclosure is directed to anionic Gemini surfactants comprising at least one carboxylate moiety, preferably two carboxylate moieties, that robustly form lyotropic liquid crystals upon the addition of a solvent. The anionic Gemini surfactants of the present disclosure form three dimensional multiply continuous lyotropic phases over broad ranges of concentration and temperature. These three dimensional multiply continuous phases encompass bicontinuous cubic phases known in the art, for example, the double gyroid...
phase (space group #230), single gyroid (space group #214),
double diamond phase (space group #224), or primitive cubic
phase (space group #229). The three dimensional multiply
continuous phases of the present disclosure additionally
encompass tetracontinuous phases, such as a novel hexagonal
tetracontinuous phase with percolating pores in three dimen-
sions. This phase is comprised of three distinct, interpenetrat-
ing, and unconnected hydrophobic networks each having P63/mmc (space group #194) symmetry to yield an overall
hydrophobic network structure with P63/mcm symmetry
(space group #193), in which the voids are filled with solvent.
This tetracontinuous phase is related yet distinct from that
described previously in connection with inorganic mesopo-
soric silicates (Han, Y.; Zhang, D.; Chung, L. L.; Sun, J.;

The anionic Gemini surfactants additionally comprise
multiple, preferably two, hydrophobic tail groups, the tail
groups being linked via a connecting moiety, generally
bonded to the carbon alpha to the headgroups. An anionic
Gemini surfactant according to the present disclosure may
have the following structure:

![Structure D](image)

In structure (I), X1 and X2 are each independently a substi-
tuted or unsubstituted aliphatic moiety having between four
and 30 carbon atoms or a substituted or unsubstituted aryl-
aliphatic moiety having between four and 30 carbon atoms,
preferably between four and 20 carbon atoms, even more
preferably between four and 16 carbon atoms, such as
between four and nine carbon atoms. The X1 and X2 aliphatic
groups may be saturated or may comprise unsaturated moi-
eties, such as alkenyl or alkynyl. That is, the X1 and X2
aliphatic groups may comprise one or more carbon-to-carbon
double bonds and/or one or more carbon-to-carbon triple
bonds. Additionally, the X1 and X2 aliphatic groups may
comprise cyclic moieties, i.e., cycloalkyl, either within the main
carbon chain or branched therefrom. X1 and X2 arylic aliphatic
groups may comprise arylic moieties either within the main
carbon chain or branched therefrom. The arylic moieties may
comprise two branching aliphatic moieties, which may be
positioned ortho, meta, or para. The X1 and X2 aliphatic
groups and aryl-aliphatic groups may comprise branching
moieties, e.g., alkyl, alkenyl, trialkylsilyl, phenyl, and substi-
tuted phenyl. The X1 and X2 aliphatic groups and aryl-al-
phatic groups may comprise hydrocarbaryl (i.e., the entirety
of the aryl-aliphatic group or aryl-aliphatic group comprises only
carbon-carbon or carbon-hydrogen bonds) or the aryl and
aliphatic groups may comprise heteroatom substituents, such
as halide atoms (e.g., fluoride, chloride, and bromide) or other
heteroatoms, such as oxygen, nitrogen, and sulfur within,
e.g., the aryl moiety, in heteroary groups. In some embodi-
ments, the aliphatic groups contain at least two fluorine
to atoms, such as at least four fluorine atoms. In some embodi-
ments, the aliphatic groups are perfluorinated, meaning that
all hydrogen atoms along the carbon chain are replaced with
fluoride atoms.

In some preferred embodiments, the X1 and X2 aliphatic
and arylic aliphatic moieties comprise at least one carbon-to-
carbon double bond. In some embodiments, each of the X1
and X2 aliphatic and arylic aliphatic moieties comprise at least
two carbon-to-carbon double bonds. In some embodiments,
the multiple carbon-to-carbon double bonds may be con-
jugated alkenes. In some embodiments, the multiple carbon-
to-carbon double bonds may be non-conjugated, for example,
separated by at least one intervening methylene. Anionic
Gemini surfactants comprising long, saturated aliphatic
chains tend to have a high degree of crystallinity, which may
shorten the concentration ranges over which the surfactants
form three dimensional multiply continuous phases. Double
bonded moieties advantageously disrupt the crystal-forming
tendencies of long aliphatic chain surfactants, thereby
extending the three dimensional multiply continuous phase
concentration range.

In structure (I), R1 through R6 are each independently
selected from the group consisting of hydrogen, fluoride,
chloride, and bromide. In some preferred embodiments, each
of R1 through R4 is hydrogen. In embodiments wherein the X1
and X2 aliphatic moieties are perfluorinated, each of R1
through R6 is fluoride.

In structure (I), Y is a connecting moiety. In some embodi-
ments, Y comprises an aliphatic moiety, which may be sub-
nstituted or unsubstituted and may be branched or unbranched,
the aliphatic moiety comprising between three carbon atoms
and 20 carbon atoms, such as between about three carbon
atoms and 8 carbon atoms. The aliphatic connecting moiety
may be saturated or may comprise unsaturated moieties, such
as alkenyl or alkynyl. That is, the aliphatic connector may
comprise one or more carbon-to-carbon double bonds and/or
one or more carbon-to-carbon triple bonds. In some embodi-
ments, Y comprises unsaturated carbon-to-carbon bonds.
Additionally, the aliphatic connector may comprise cyclic
moieties, i.e., cycloalkyl, either within the main carbon chain
or branched therefrom. In some preferred embodiments, Y
comprises the branched or unbranched hydrocarbaryl moiety
comprising between three carbon atoms and 20 carbon atoms,
such as between three carbon atoms and 12 carbon atoms,
such as between three carbon atoms and eight carbon atoms.
A hydrocarbaryl moiety comprises only carbon-carbon or
carbon-hydrogen bonds. Aliphatic and hydrocarbaryl
connecting moieties provide a large degree of flexibility to the
connection. Flexible hydrophobic spacers confer conformational
flexibility that enables the surfactant to accommodate the
substantial deviations from constant mean interfacial
curvature required for G-phase stabilization. See FIGS. 2A through
2C for illustrations of the curvatures afforded by flexible
aliphatic connecting moieties, including positive curvature
(FIG. 2A), flat curvature (FIG. 2B), and negative curvature
(FIG. 2C).

In some embodiments, Y comprises a substituted or unsub-
stituted aryl or heteroaryl moiety. An aryl moiety may impart
rigidity to the connecting moiety. Rigid moieties may stabi-
lize or destabilize various LLC phases, and thus allow
manipulation of the phase stability. Aryl group substituents
may include fluoride, chloride, bromide, methyl, ethyl, prop-
ynyl, butyl hydroxyl, alkoxy generally having from one to four
carbon atoms, nitro, and amines having the general structure
NH(R)n, wherein X has a value from 0 to 2, and R may be an
alkyl having from one to four carbon atoms. A heteroaryl
group may be selected from among pyridine, pyrazole, ferrar,
pyrrole, imidazole, imidazoliums, triazole, and triazolium.
Herein, the aryl moiety may comprise one or two aliphatic chains, which are bonded to the alpha carbons of the carboxylate. The aliphatic chains extending from the aryl moiety generally have from 0 to five carbon atoms, from one to five carbon atoms, or from one to three carbon atoms. The aliphatic chains may be located ortho, meta, or para to each other around the aromatic ring. In some embodiments, such a connecting moiety may have the structure:

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

wherein \( n_1 \) and \( n_2 \) are integers, each having an independent value between 0 and five, between one and five, or between one and three. The aliphatic chains herein may be located ortho, meta, or para to each other around the aromatic ring.

In some embodiments, \( Y \) comprises heteroatoms, such as oxygen, that increase the hydrophilicity of the connecting moiety. The hydrophilic moiety enables manipulation of the phase stability by manipulating curvative at the interface between hydrophobic and hydrophilic domains. In some embodiments, the hydrophilic moiety may comprise a polyalkylether moiety, for example, a short polyethylene oxide or polypropylene oxide, generally having from 1 to 4 repeat units. In some preferred embodiments, the hydrophilic moiety has the structure:

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

wherein \( n_1 \) is an integer having a value between one and four, such as one or two.

In some embodiments, the hydrophilic connecting moiety contains hydroxyl or alkoxy moieties. Such a connecting moiety may have the structure:

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

wherein \( R_1 \) and \( R_2 \) are each independently hydrogen, hydroxyl, alkyl having from one to five carbon atoms; and \( n_2 \) is an integer having a value between one and ten, such as between one and six, or between one and three. One such hydrophilic moiety may have the structure:

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

In structure (I), \( M \) is a counterion. Empirical results to date indicate that the counterion in the anionic carboxylate Gemini surfactants of the present invention also plays a role in enhancing the flexibility and the curvature of the surfactant.

Effective charge neutralization through counterion association allows the alkyl spacer between the carboxylate headgroups to relax, enabling the Gemini surfactant to adopt a wider range of interfacial curvatures over a broader range of headgroup hydration levels to stabilize the non-constant mean curvature \( G_f \)-phase. \( M \) counterions may be selected from among lithium ion; sodium ion; potassium ion; cesium ion; magnesium ion; calcium ion; zine ion; ammonium ion; alkylammonium ion having the structure \( H_xR_yN^+ \) wherein \( x \) is an integer having a value of 0 through 4 and \( R \) is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof; tetrakis(hydroxymethyl)phosphonium ion; tetramethylphosphonium ion; choline; imidazolium; and bis(quaternary ammonium) ion. Alkylammonium ions may include, for example, methylammonium ion, dimethylammonium ion, triethylammonium ion, ethylammonium ion, diethylammonium ion, triethylammonium ion, tetramethylammonium ion, and tetraethylammonium ion. Preferred \( M \) counterions include sodium ion, potassium ion, and tetramethylammonium ion.

In some embodiments of the present disclosure, the anionic Gemini surfactant has the following structure (II):

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

In structure (II), \( Z_1 \) and \( Z_2 \) are integers, each independently having a value between four and twenty; preferably between four and 12, such as between seven and 11, such as seven. \( Y \) is the connecting moiety, and \( M \) is the counterion. Each of \( Y \) and \( M \) are as defined above in connection with structure (I).

In some embodiments, the anionic Gemini surfactant has the following structure (III):

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

In structure (III), \( Z_1 \) and \( Z_2 \) are integers, each independently having a value between four and twenty; preferably between four and 12, such as between seven and 11, such as seven. \( Y_1 \) is an integer having a value between two and 12, preferably between four and eight. \( M \) counterions may be selected from among lithium ion; sodium ion; potassium ion; cesium ion; magnesium ion; calcium ion; zine ion; ammonium ion; alkylammonium ion having the structure \( H_xR_yN^+ \) wherein \( x \) is an integer having a value of 0 through 4 and \( R \) is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof; tetrakis(hydroxymethyl) phosphonium ion; tetramethylphosphonium ion; choline;
imidazolium; and bis(quaternary ammonium) ion. Alkylammonium ions may include, for example, methylammonium ion, dimethylammonium ion, trimethylammonium ion, ethylammonium ion, diethylammonium ion, triethylammonium ion, tetramethylammonium ion, and tetraethylammonium ion. Preferred M counterions include sodium, potassium ion, and tetramethylammonium ion.

In some preferred embodiments, the anionic Gemini surfactant has the structure (II) in which Z₁ and Z₂ are seven, Y₁ is four, and M is sodium ion. The surfactant is sodium docosane-9,14-dicarboxylate ("Na₇-74"). In some preferred embodiments, the anionic Gemini surfactant has the structure (III) in which Z₁ and Z₂ are seven, Y₁ is six, and M is sodium ion. The surfactant is sodium tetraicosane-9,16-dicarboxylate ("Na₇-76"). In some preferred embodiments, the anionic Gemini surfactant has the structure (III) in which Z₁ and Z₂ are seven, Y₁ is four, and M is tetramethylammonium ion. The surfactant is tetramethylammonium docosane-9,14-dicarboxylate ("NMMe₄-74"). In some preferred embodiments, the anionic Gemini surfactants have the structure (III) in which Z₁ and Z₂ are nine, Y₁ is four, and M is sodium ion. The surfactant is sodium hexacosane-11,16-dicarboxylate ("Na₉-94"). In some preferred embodiments, the anionic Gemini surfactants have the structure (III) in which Z₁ and Z₂ are nine, Y₁ is six, and M is sodium ion. The surfactant is sodium octacosane-11,18-dicarboxylate ("Na₉-96").

The present invention is further directed to a lyotropic liquid crystal composition prepared by combining an anionic Gemini surfactant and a suitable polar solvent. Suitable polar solvents include water, ethylene glycol, diethylene glycol, glycerol, 2-butene-1,4-diol, propanediol, glycerol, formamide, N-methylformamide, N-ethylformamide, acetamide, N-methylacetamide, N-ethylacetamide, methanol, ethanol, propanol, ethylammonium nitrate, ethanolammonium nitrate, ethyl ammonium formate, ethanolammonium formate, ethylammonium acetate, ethanolammonium acetate, 1-ethyl-3-methyl-imidazolium acetate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium tetrafluoroborate, or any combination thereof, with water being particularly preferred. The lyotropic liquid crystal composition of the present invention is prepared by combining an anionic Gemini surfactant and a polar solvent capable of robustly forming a variety of lyotropic liquid crystal phases. The anionic Gemini surfactants of the present disclosure are capable of forming truly periodic phases over a broad range of concentrations and temperatures. These truly periodic phases encompass bicontinuous cubic phases, the double gyroid phase (space group #230), single gyroid phase (space group #214), double diamond phase (space group #224), or primitive cubic phase (space group #229). See Seddon, J. M. Biochimica et Biophysica Acta, 1990, 1031, 1-69 and V. Luzziati, R. Vargas, P. Mariani, A. Gulkik, H. Delacroix, J. Mol. Biol. 229 (1993) 540. The truly periodic phases of the present disclosure additionally encompass tetracontinuous phases, such as a novel hexagonal tetracontinuous phase with percolating pores in three dimensions. These pores in these materials may range from 5-100 Å.

In some embodiments, the anionic Gemini surfactant forms a truly periodic phase such as a double gyroid phase (space group #230), single gyroid (space group #214), double diamond phase (space group #224), primitive cubic phase (space group #229), or hexagonal tetracontinuous phase over a range of concentrations from C₁ to C₂, wherein the difference between C₁ and C₂ is at least 10 weight percent, at least 12 weight percent, at least 14 weight percent, at least 16 weight percent, at least 18 weight percent, or at least 20 weight percent. Advantageously, the truly periodic phase is stable over a broad range of temperatures from T₁ to T₂, wherein the difference between T₁ and T₂ is at least 40°C, at least 45°C, at least 50°C, at least 55°C, at least 60°C, or at least 65°C, or at least 70°C, or at least 75°C, or at least 80°C.

According to empirical results to date, the anionic Gemini surfactant generally forms a truly periodic phase at concentrations of at least 30 weight percent, at least 40 weight percent, at least 45 weight percent, or at least 50 weight percent. At these concentrations, the lyotropic liquid crystal phase generally transitions from hexagonal to Q-Phase. At anionic Gemini surfactant concentrations generally no greater than 90 weight percent, no greater than 85 weight percent, or no greater than 80 weight percent, the lyotropic liquid crystal phase generally transitions from Q-Phase to lamellar. The concentrations at which these phase transitions occur depend upon multiple factors, in addition to concentration. These factors include the structure of the anionic Gemini surfactant, the identity of the counterion, the temperature of the system, the pressure of the system, and the presence and identity of co-solvents, if any are added to the system. In view thereof, the concentrations of the phase transition may vary significantly from one surfactant to another. The anionic Gemini surfactants comprising at least one, and preferably two, carboxylate groups of the present disclosure advantageously provide robust LLC systems exhibiting truly periodic phases over broad concentration and temperature ranges.

The solvent concentration is generally at least 5 weight percent, preferably at least 10 weight percent, in order to prepare a lyotropic liquid crystal. At concentrations less than about 5 weight percent or less than about 10 weight percent, the anionic Gemini surfactant generally forms a crystalline phase. Suitable polar solvents include water, ethylene glycol, diethylene glycol, glycerol, 2-butene-1,4-diol, propanediol, glycerol, formamide, N-methylformamide, N-ethylformamide, acetamide, N-methylacetamide, N-ethylacetamide, methanol, ethanol, propanol, ethylammonium nitrate, ethanolammonium nitrate, ethyl ammonium formate, ethanolammonium formate, ethylammonium acetate, ethanolammonium acetate, 1-ethyl-3-methyl-imidazolium acetate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium tetrafluoroborate, or any combination thereof, with water being particularly preferred. The lyotropic liquid crystal composition of the present invention is prepared by combining an anionic Gemini surfactant and a polar solvent capable of robustly forming a variety of lyotropic liquid crystal phases. The anionic Gemini surfactants of the present disclosure are capable of forming truly periodic phases over a broad range of concentrations and temperatures. These truly periodic phases encompass bicontinuous cubic phases, the double gyroid phase (space group #230), single gyroid phase (space group #214), double diamond phase (space group #224), primitive cubic phase (space group #229). See Seddon, J. M. Biochimica et Biophysica Acta, 1990, 1031, 1-69 and V. Luzziati, R. Vargas, P. Mariani, A. Gulkik, H. Delacroix, J. Mol. Biol. 229 (1993) 540. The truly periodic phases of the present disclosure additionally encompass tetracontinuous phases, such as a novel hexagonal tetracontinuous phase with percolating pores in three dimensions. These pores in these materials may range from 5-100 Å.

In some embodiments, the anionic Gemini surfactant forms a truly periodic phase such as a double gyroid phase (space group #230), single gyroid (space group #214), double diamond phase (space group #224), primitive cubic phase (space group #229), or hexagonal tetracontinuous phase over a range of concentrations from C₁ to C₂, wherein the difference between C₁ and C₂ is at least 10 weight percent, at least 12 weight percent, at least 14 weight percent, at least 16 weight percent, at least 18 weight percent, or at least 20 weight percent. Advantageously, the truly periodic phase is stable over a broad range of temperatures from T₁ to T₂, wherein the difference between T₁ and T₂ is at least 40°C, at least 45°C, at least 50°C, at least 55°C, at least 60°C, or at least 65°C, or at least 70°C, or at least 75°C, or at least 80°C.

According to empirical results to date, the anionic Gemini surfactant generally forms a truly periodic phase at concentrations of at least 30 weight percent, at least 40 weight percent, at least 45 weight percent, or at least 50 weight percent. At these concentrations, the lyotropic liquid crystal phase generally transitions from hexagonal to Q-Phase. At anionic Gemini surfactant concentrations generally no greater than 90 weight percent, no greater than 85 weight percent, or no greater than 80 weight percent, the lyotropic liquid crystal phase generally transitions from Q-Phase to lamellar. The concentrations at which these phase transitions occur depend upon multiple factors, in addition to concentration. These factors include the structure of the anionic Gemini surfactant, the identity of the counterion, the temperature of the system, the pressure of the system, and the presence and identity of co-solvents, if any are added to the system. In view thereof, the concentrations of the phase transition may vary significantly from one surfactant to another. The anionic Gemini surfactants comprising at least one, and preferably two, carboxylate groups of the present disclosure advantageously provide robust LLC systems exhibiting truly periodic phases over broad concentration and temperature ranges.

The solvent concentration is generally at least 5 weight percent, preferably at least 10 weight percent, in order to prepare a lyotropic liquid crystal. At concentrations less than about 5 weight percent or less than about 10 weight percent, the anionic Gemini surfactant generally forms a crystalline phase. Suitable polar solvents include water, ethylene glycol, diethylene glycol, glycerol, 2-butene-1,4-diol, propanediol, glycerol, formamide, N-methylformamide, N-ethylformamide, acetamide, N-methylacetamide, N-ethylacetamide, methanol, ethanol, propanol, ethylammonium nitrate, ethanolammonium nitrate, ethyl ammonium formate, ethanolammonium formate, ethylammonium acetate, ethanolammonium acetate, 1-ethyl-3-methyl-imidazolium acetate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium tetrafluoroborate, or any combination thereof, with water being particularly preferred. The lyotropic liquid crystal composition of the present invention is prepared by combining an anionic Gemini surfactant and a polar solvent capable of robustly forming a variety of lyotropic liquid crystal phases. The anionic Gemini surfactants of the present disclosure are capable of forming truly periodic phases over a broad range of concentrations and temperatures. These truly periodic phases encompass bicontinuous cubic phases, the double gyroid phase (space group #230), single gyroid phase (space group #214), double diamond phase (space group #224), primitive cubic phase (space group #229).
The lack of observed optical birefringence upon examining this sample between crossed polarizers at 22°C is consistent with the cubic symmetry of this LLC phase. Since this G-phase window is situated at higher hydration levels than the L phase, it was assigned as a Type I (“normal”) G phase having interfacial curvature toward the hydrophobic domains. See Menger, P. M.; Keiper, J. S. Angew. Chem. Int. Ed. 2000, 39, 1906. Examination of samples having 40-50 wt % Na-74 indicate the formation of a “normal” hexagonal (H2) phase with a modest degree of long-range order, evidenced by XRD peaks that index as q\textsuperscript{\textast}v/1, q\textsuperscript{\textast}v/3, and q\textsuperscript{\textast}v/7 with a ~34 Å intercylinder spacing. From the complete temperature-dependent aqueous lyotropic phase diagram for Na-74 shown in Fig. 4, one sees that these ordered LLC phases persist up to 100°C.

Upon increasing the length of the alkyl spacer between the carboxylate headgroups in the decanoic acid-derivated Gemini surfactant as in Na-76, a large double gyroid phase window is observed in the midst of a different sequence of LLC phases upon hydration with ~15 wt% H2O. See Fig. 5. For samples hydrated in the range 75-85 wt % Na-76, stiff, optically non-birefringent gels characteristic of a Q-phase LLC formed with order-to-disorder (“clearing”) temperatures ~70°C. Synchrotron XRD patterns exhibit prominent scattering maxima at q\textsuperscript{\textast}v/2, q\textsuperscript{\textast}v/6, q\textsuperscript{\textast}v/8, and q\textsuperscript{\textast}v/10, consistent with either a single gyroid structure (Q\textsuperscript{14} space group symmetry) or a primitive (P) structure with a q\textsuperscript{\textast}v/4 extinction, which is comprised of a network of octahedral connectors (Q\textsuperscript{25}). See Hentz et al., Macromolecules 1999, 32, 5803. In accord with convention, the higher symmetry structure was tentatively assigned this cubic phase as a P\textsubscript{14} phase. Samples comprised of ~70 wt % Na-76 form stiff yet birefringent gels, which exhibit unusual X-ray scattering patterns that cannot be assigned to any of the classical LLC morphologies. Between ~50-65 wt % amphiphile, Na-76 unequivocally forms a G\textsubscript{2} phase. Thus Na-76 adopts double gyroid morphology with saddle curvature at substantially higher hydration levels than Na-74. By comparing XRD data for LLCs comprised of hydrated Na-74 and Na-76 at comparable water contents that adopt the same morphologies, the unit cell dimensions do not vary significantly in spite of the difference in spacer lengths.

The flexible, hydrophobic spacer connecting the ionic headgroups in the amionic Gemini surfactants of the present disclosure confers a degree of conformational flexibility that enables it to accommodate the substantial deviations from constant mean interfacial curvature required for G\textsubscript{2} phase stabilization (Fig. 1C). Additionally, counterion association with the carboxylate headgroup or protonation of the carboxylates (with attendant formation of hydroxide ions in the aqueous domains) can mitigate Coulombic repulsions between headgroups. Effective charge neutralization through one of these mechanisms allows the alkyl spacer between the carboxylate headgroups to relax, enabling the Gemini amphiphile to adopt a wider range of interfacial curvatures over a broader range of headgroup hydration levels to stabilize the non-constant mean curvature G\textsubscript{2} phase. The flexible spacer likely also pulls away from the aqueous interface to mitigate unfavorable hydrophobic/hydrophilic interactions, inducing alkyl tail chain splay that favors G\textsubscript{2} phase formation (Fig. 2). Lengthening the C\textsubscript{14} spacer to a C\textsubscript{18} spacer enhances the conformational flexibility of the surfactant and widens the G\textsubscript{2} phase window (Fig. 3), while also inducing a high degree of chain splay (greater hydrophobic volume) that permits the formation of a P\textsubscript{14} phase at lower hydration levels (Fig. 2).

Given that the curvature of a surface displaying densely packed carboxylic acids is known to affect the pH\textsubscript{pZC} of the acid functionality, the possibility for variable protonation states of the gemini carboxylate headgroups may also play an important role in stabilizing the observed G\textsubscript{2} phases. See Gao et al., Chem. Eur. J. 2008, 14, 11423.

Variable temperature XRD studies of the phase behavior of K-74 indicate that the H\textsubscript{2} phase window widens substantially and that the G\textsubscript{2} window widens and shifts to lower H\textsubscript{2}O contents as compared to sodium analog Na-74. The LLC phase diagram for NMe\textsubscript{4}-74 shows an even more pronounced widening of the H\textsubscript{2} phase composition window and a large shift in the G\textsubscript{2} phase toward lower hydration levels, such that L\textsubscript{a} phase completely vanishes. See Figs. 6 and 7.

The phase behavior of Na-94 (hexacosane-11,16-dicarboxylic acid disodium salt) was also observed. See Fig. 8. Na-94 exhibits a transition into the normal hexagonal (H\textsubscript{2}) in Fig. 8 at about 40 wt % surfactant in water and another transition to form the hexagonal tetracolumnar phase (I\textsubscript{C} in Fig. 8) at about 50-60 wt % surfactant in water, which is followed by a transition into the normal double gyroid (G\textsubscript{2}) phase.

Comparisons of the principal domain spacings for both the G\textsubscript{2} and H\textsubscript{2} phases at comparable hydration levels (λ = mol H\textsubscript{2}O/mol Gemini) indicate that the LLC unit cell dimensions are relatively constant at ~34 Å for H\textsubscript{2} phases and ~66 Å for G\textsubscript{2} phases with different counterions. See Table 1. These findings demonstrate that increased counterion dissociation favors the formation of LLCs with high curvature interfaces at constant water content, although the counterion size does not substantially alter the unit cell dimensions of the LLC at similar values of λ. Therefore, changing surfactant counterion provides a simple means of manipulating LLC phase stability in these Gemini surfactant liquid crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Weight percent</th>
<th>λ (nm)</th>
<th>δ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-74</td>
<td>H\textsubscript{2}</td>
<td>50.1</td>
<td>24.5</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>G\textsubscript{2}</td>
<td>69.3</td>
<td>10.9</td>
<td>6.58</td>
</tr>
<tr>
<td>K-74</td>
<td>H\textsubscript{2}</td>
<td>54.9</td>
<td>21.6</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>G\textsubscript{2}</td>
<td>69.9</td>
<td>11.3</td>
<td>6.58</td>
</tr>
<tr>
<td>NMe\textsubscript{4}-74</td>
<td>H\textsubscript{2}</td>
<td>55.0</td>
<td>24.7</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>G\textsubscript{2}</td>
<td>75.2</td>
<td>9.98</td>
<td>6.55</td>
</tr>
</tbody>
</table>

a) = mol H\textsubscript{2}O/mol Surfactant.
b) Unit cell dimensions (δ) were calculated from the position of the principle scattering maxima in azimuthally integrated XRD patterns; calculated values are estimates within ± 0.15 nm.

According to empirical results to date, the lyotropic liquid crystal comprising amionic surfactants having any of structures (I), (II), and (III), wherein M comprises a sodium ion generally exhibit a hexagonal phase at concentrations between 30 weight percent and about 50 weight percent, a bicontinuous cubic phase (Q\textsubscript{2} phase) at concentrations between about 45 weight percent and about 70 weight percent, and a lamellar phase at concentrations between about 65 weight percent and about 95 weight percent. When M is the potassium ion, the lyotropic liquid crystal generally exhibits a hexagonal phase at concentrations between 30 weight percent and about 60 weight percent, a bicontinuous cubic phase (Q\textsubscript{2} phase) at concentrations between about 55 weight percent and about 85 weight percent, and a lamellar phase at concentrations between about 80 weight percent and about 95 weight percent. When M is the tetramethylammonium ion, the lyotropic liquid generally exhibits a hexagonal phase at concentrations between 30 weight percent and about 80 weight percent, and a bicontinuous cubic phase (Q\textsubscript{2} phase) at concentrations between about 75 weight percent and about 95 weight percent. The stated concentrations ranges are general and may vary depending upon the identity of the aliphatic tails and connecting groups.
The counterion-dependent self-assembly of anionic Gemini dicarboxylate surfactant in water may be rationalized by considering the level of cation dissociation from the anionic carboxylate headgroup. Consistent with Hofmeister series trends, Brun et al. have shown that the association of cations with single tail allyl carboxylates in dilute solutions increases in the order (CH₃)₄N⁺<K⁺<Na⁺. See Brun, T. S., et al., *J. Colloid Interface Sci.* 1978, 63, 590. In the case of the counterions that strongly associate with the carboxylate headgroups, cation association with the interface reduces the repulsive Coulombic interactions between the headgroups to stabilize the G₄-phase over a large concentration window. Since the (CH₃)₄N⁺ cation is highly dissociated, the lack of charge screening causes the alkyl spacer to extend in a manner that accommodates only very small deviations from constant mean curvature. Therefore, the G₄-phase window shrinks in size at the expense of the more stable H₄-phase.

The anionic Gemini dicarboxylate surfactant may be prepared by contacting a carboxylic acid with at least two equivalents of a sufficiently strong base capable of deprotonating the alpha carbon of the carboxylic acid. Deprotonation of the alpha carbon of the carboxylic acid yields a carbanion that is reactive with compound comprising leaving groups. Suitable bases include alkyl lithiums, alkyl magnesium reagents, lithium diisopropylamide, lithium tetramethylpiperidine, dialkylamide base, sodium hydride, and potassium hydride, among other suitable strong bases. The reaction suitably occurs in aprotic solvent, e.g., tetrahydrofuran, diethyl ether, any carbonate solvent, any aromatic solvent, alkylamine solvents, alkyl diamine solvents, alkyl phosphoramidite solvents.

The carboxylic acid component containing the reactive carbanion is then contacted with a compound comprising the Y moiety terminated with leaving groups, which may be depicted:

\[
\begin{align*}
L_1^+ &\rightarrow Y \rightarrow L_2
\end{align*}
\]

wherein L₁ and L₂ comprise leaving groups, Y comprises a connecting moiety. The molar ratio is generally about 2 moles deprotonated carboxylate to 1 mole compound containing the Y moiety. Appropriate leaving groups include bromide, iodide, chloride, tosylate, mesylate, trflate, and benzene-sulfonate and p-toluene sulphonate. This contact thereby yields an Gemini dicarboxylate salt, e.g., a lithium Gemini dicarboxylate if an lithium reagent is used to deprotonate the alpha carbon. Upon workup and isolation, this yields a dicarboxylic acid. This dicarboxylic acid may be deprotonated with a base (e.g., sodium hydroxide, potassium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide, etc.) to thereby prepare a variety of Gemini dicarboxylates with a desired charge balancing counterion. A general synthesis may be illustrated as shown in FIG. 9.

The following examples illustrate specific embodiments with the scope of the present disclosure. The examples are provided for the purpose of illustration and are not to be construed as limitations of the present disclosure.

**EXPERIMENTAL**

**Materials.**

All materials and reagent grade solvents were purchased from Sigma–Aldrich Chemical Co. (Milwaukee, Wis.) and used as received unless otherwise noted. 1,4-dibromobutane and 1,6-dibromohexane were distilled and stored under nitrogen. Dimethylamine (Sigma–Aldrich) was distilled from CaH₂ and stored under nitrogen. Hexamethyldisilazane (HMPA) was distilled from CaH₂ and stored over 4 Å molecular sieves. 2.5 M n-Butyllithium in hexanes was titrated according to diethylacetic acid in THF. Anhydrous and anaerobic THF was obtained by sparging analytical grade solvent with nitrogen for 30 minutes followed by cycling through a column of activated alumina in a Vacuum Atmospheres solvent purification system.

¹H NMR and ¹³C NMR spectra were recorded in DMSO-d₆ or methanol-d₄ at 25°C on both Varian MercuryPlus 300 and Bruker AC+300 spectrometers and were referenced to residual protiated solvent peaks in the samples.

Mass Spectrometry was performed using a Waters MicroMass LCT® electrospray ionization time-of-flight mass spectrometer operating in negative ion detection mode. Samples dissolved in methanol were sprayed with a sample cone voltage of 20 V.

**General Gemini Surfactant Synthesis.** We employed a procedure adapted from Pfeffer et al. See Pfeffer, P. E.; Silbert, L. S.; Chirinko, J. M. *J Org Chem* 1972, 37, 451. A 500 mL 2-necked round bottom flask fitted with an addition funnel was charged with a stir bar, THF (104 mL) and dimethylamine (17.05 mL, 121 mmol) under nitrogen. This solution was cooled to ~15°C in an ethanol/water/dry ice bath and n-BuLi (42.7 mL of a 2.71 M solution in hexanes, 115 mmol) was added dropwise via addition funnel. The reaction mixture was stirred for 30 min, after which a solution of decanoic acid (10.0027 g, 58.07 mmol) in THF (58 mL) was added dropwise via addition funnel. HMPS (10.1 mL) was the added, and the stirred reaction mixture was warmed to 22°C for 30 min. The reaction mixture was again cooled to ~15°C, and 1,4-dibromobutane (3.45 mL, 29.0 mmol) was added dropwise. The reaction was then allowed to warm to room temperature and stirred for 4 h. The reaction was quenched by the addition of cold 10% HCl (aq) (100 mL), transferred to a separatory funnel, and the aqueous and organic layers were separated. The aqueous layer was extracted with ether (3×50 mL) and the combined organic layers were washed with 10% HCl (3×50 mL), water (50 mL), and saturated NaCl(aq) (50 mL). After drying over MgSO₄(s), all volatiles were removed under vacuum. The crude solid was purified by recrystallization from EtOH.

**Docosane-9,14-dicarboxylic acid**
Synthesized from decanoic acid (10.0027 g) and 1,4-dibromobutane (3.45 ml); Yield: 9.2816 g (80.4%); $^1$H-NMR: (299.7 MHz, DMSO-d$_6$) δ 11.968 (COOH, s, 2H), 2.158 (CH—COOH, m, 2H), 1.557-1.018 (CH$_2$, m, 36H), 0.849 (CH$_3$-CH$_2$, t, J=7.0 Hz, 6H). $^{13}$C-NMR: (75.4 MHz, DMSO-d$_6$) δ 177.32 (C==O), 45.18 (CH), 32.21 (CH$_2$), 32.09 (CH$_3$), 31.67 (CH$_2$), 29.37 (CH$_2$), 29.26 (CH$_2$), 29.04 (CH$_2$), 27.25 (CH$_2$), 27.20 (CH$_2$), 22.48 (CH$_2$), 14.30 (CH$_3$). MS (ESI-TOF) calcld. m/z for C$_{24}$H$_{34}$O$_4$+: 397.3, found: 397.4.

Tetracosane-9,16-dicarboxylic acid

Synthesized from decanoic acid (10.0021 g) and 1,6-dibromohexadecane (4.42 ml); Yield: 8.3526 g (68.2%); $^1$H-NMR (299.7 MHz, DMSO-d$_6$): δ 11.951 (COOH, s, 2H), 2.160 (CH—COOH, m, 2H), 1.557-1.018 (CH$_2$, m, 36H), 0.847 (CH$_3$-CH$_2$, t, J=7.0 Hz, 6H). $^{13}$C-NMR (75.4 MHz, DMSO-d$_6$): δ 177.34 (C==O), 45.26 (CH), 32.25 (CH$_2$, x2), 31.68 (CH$_3$), 29.39 (CH$_2$), 29.27 (CH$_2$), 29.04 (CH$_2$), 27.27 (CH$_2$), 27.21 (CH$_2$), 22.49 (CH$_2$), 14.28 (CH$_3$). MS (ESI-TOF) calcld. m/z for C$_{30}$H$_{46}$O$_4$+: 425.4, found: 425.4.

General Procedure for Gemini Dicarboxylic Salt Synthesis. See Hoag, B. P.; Gin, D. L. Macromolecules 2000, 33, 8549. In a flask equipped with a stirrer, the Gemini diacid (1 mol eq.) and alkali carbonate were suspended in methanol (0.1-0.2M). The mixture was stirred at ambient temperature until it became homogeneous, and then stirring was continued for one additional hour. All volatiles were removed under vacuum and residual water and methanol azeotropically distilled using benzene three times under vacuum. All yields were quantitative.

Sodium Docosane-9,14-dicarboxylate (Na-74)

$^1$H-NMR (299.7 MHz, CD$_3$OD): δ 2.144 (CH—COO), m, 2H), 1.529 (CH—CH$_3$, m, 4H), 1.431-1.158 (CH$_2$, m, 32H), 0.889 (CH$_2$-CH$_3$, t, J=7.1 Hz, 6H). $^{13}$C-NMR (75.4 MHz, CD$_3$OD): δ 184.09 (C==O), 49.49 (CH), 33.41 (CH$_2$), 33.26 (CH$_2$), 31.60 (CH$_2$), 29.59 (CH$_2$), 29.30 (CH$_2$), 28.99 (CH$_2$), 28.19 (CH$_2$), 27.70 (CH$_2$), 22.24 (CH$_2$), 12.96 (CH$_3$).

Potassium Docosane-9,14-dicarboxylate (K-74)
17

1H-NMR (299.7 MHz, CD3OD): δ 2.141 (CH—COO—, m, 2H), 1.526 (CH—CH2, m, 4H), 1.427-1.160 (CH2, m, 32H), 0.890 (CH3—CH2, t, J=7.1 Hz, 6H). 13C-NMR (75.4 MHz, CD3OD): δ 184.02 (CO—O), 49.50 (CH3), 33.40 (CH2), 33.28 (CH2), 31.60 (CH2), 29.59 (CH2), 29.29 (CH2), 28.99 (CH2), 28.19 (CH2), 27.70 (CH2), 22.25 (CH2), 12.95 (CH3).

Tetramethylammonium Docosane-9,14-dicarboxylate (NMe4-74)

18

Synthesized from dodecanoic acid (10.0102 g) and 1,4-dibromobutane (2.90 ml); Yield: 9.2849 g (83.8%); 1H-NMR: (299.7 MHz, DMSO-d6) δ 11.964 (COOH, s, 2H), 2.154 (CH—COOH, m, 2H), 1.557-1.082 (CH2, m, 44H), 0.848 (CH3—CH2, t, J=7.0 Hz, 6H); 13C-NMR: (75.4 MHz, DMSO-d6) δ 177.29 (C=O), 54.14 (CH), 32.21 (CH2), 32.17 (CH2), 32.04 (CH2), 31.72 (CH2), 29.39 (CH2), 29.31 (CH2), 29.13 (CH2), 27.24 (CH2), 27.18 (CH2), 22.50 (CH2), 14.28 (CH3); MS (ESI-TOF) calc. m/z for C29H50O5− 453.4. found 453.4.

1H-NMR (299.7 MHz, CD3OD): δ 3.194 (s, 24H), 2.143 (CH—COO—, m, 2H), 1.532 (CH—CH2, m, 4H), 1.432-1.148 (CH2, m, 32H), 0.891 (CH3—CH2, t, J=7.1 Hz, 6H).

13C-NMR (75.4 MHz, CD3OD): δ 183.82 (C=O), 54.39 (CH), 53.46 (CH2), 33.40 (CH2), 33.27 (CH2), 31.60 (CH2), 29.61 (CH2), 29.31 (CH2), 29.00 (CH2), 28.28 (CH2), 27.73 (CH2), 22.25 (CH2), 12.96 (CH3).

Sodium Tetracosane-9,16-dicarboxylate (Na-76)

1H-NMR (299.7 MHz, CD3OD): δ 2.148 (CH—COO—, m, 2H), 1.519 (CH—CH2, m, 4H), 1.423-1.150 (CH2, m, 36H), 0.891 (CH3—CH2, t, J=7.1 Hz, 6H). 13C-NMR (75.4 MHz, CD3OD): δ 184.08 (C=O), 49.39 (CH), 33.40 (CH2), 33.29 (CH2), 31.60 (CH2), 29.73 (CH2), 29.58 (CH2), 29.29 (CH2), 28.99 (CH2), 27.83 (CH2), 27.70 (CH2), 22.24 (CH2), 12.94 (CH3).

Hexacosane-11,16-dicarboxylic acid
Octacosane-11,18-dicarboxylic acid

Synthesized from dodecanoic acid (8.0060 g) and 1,6-dibromohexane (3.05 ml); Yield: 7.0712 g (73.96%); ^1H-NMR: (299.9 MHz, DMSO-d_6) δ 12.003 (COOH, s, 2H), 2.159 (CH-CH(CH_2), t, J=6.9 Hz, 6H); 13C-NMR: (75.4 MHz, DMSO-d_6) δ 177.50 (C=O), 45.31 (CH), 32.31 (CH_2), 31.80 (CH_3), 29.47 (CH_2), 29.38 (CH_2), 29.28 (CH_2), 29.21 (CH_2), 27.33 (CH_2), 27.28 (CH_2), 22.59 (CH_2), 14.42 (CH_3); MS (ESI-TOF) caleld m/z for C_{36}H_{70}O_2: 481.4, found 481.4.

Sodium Hexacosane-11,16-dicarboxylate

Sodium Octacosane-11,18-dicarboxylate

1475x1679 pixel resolution. Samples were placed in aluminum DSC pans with Kapton windows and placed in a Linkam DSC stage. Samples were heated to the desired temperature in a Linkam DSC and allowed to equilibrate for 5 min before data collection (exposure time = 1 s). 2D patterns were azimuthally integrated to obtain intensity I(q) vs. q plots using DataSqueeze software package (http://www.datasqueeze-software.com/).

Laboratory SAXS measurements were performed in the Materials Science Center at the University of Wisconsin-Madison. Cu-Kα X-rays generated by a Rigaku Micromax 002+ microfocus source were collimated using a Max-Flux multilayer confocal optic (Osmic, Inc.) followed by passage through three pinholes to collimate and trim the final beam diameter to <0.5 mm. Samples were mounted in a vacuum chamber on a Linkam temperature-controlled hot-stage with a 10 min thermal equilibration time (typical exposure times ~3-5 min). Two-dimensional XRD patterns were recorded on a Gabriel X-ray detector (150 mm diameter active circular area) using a sample-to-detector distance of 31.19 cm (calibrated using a silver behenate standard sample with d=58.38 Å).

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including
making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

What is claimed is:

1. A lyotropic liquid crystal composition comprising:
   a polar solvent and an anionic Gemini surfactant, the anionic Gemini surfactant comprising at least one carboxylate moiety;
   wherein the anionic Gemini surfactant forms a triply periodic phase over a range of concentrations from C_l to C_u, wherein the difference between C_l and C_u is at least 10 weight percent and over a range of temperatures from T_l to T_u wherein the difference between T_l and T_u is at least 40°C.

2. The lyotropic liquid crystal composition of claim 1 wherein the difference between C_l and C_u is at least 12 weight percent.

3. The lyotropic liquid crystal composition of claim 1 wherein the difference between T_l and T_u is at least 45°C.

4. The lyotropic liquid crystal composition of claim 1 wherein the triply periodic phase comprises a gyroid phase (space group #230), a double diamond phase (space group #224), a primitive cubic phase (space group #229), or a tetracontinuous hexagonal phase (space group #193).

5. The lyotropic liquid crystal composition of claim 1 wherein the polar solvent is selected from the group consisting of water, acetone, tetrahydrofuran, diethyl ether, ethylene glycol, diethylene glycol, glycerol, 2-butene-1,4-diol, propanediol, glycerol, formamide, N-methylformamide, N-ethylformamide, acetamide, N-methylacetamide, N-ethylacetamide, methanol, ethanol, propanol, ethylammonium nitrate, ethanolammonium nitrate, ethyl ammonium formate, ethanolammonium formate, ethylammonium acetate, ethanolammonium acetate, 1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium tetrafluoroborate, and any combination thereof.

6. The lyotropic liquid crystal composition of claim 1 wherein the anionic Gemini surfactant is present at a concentration of at least 30 weight percent; and the anionic Gemini surfactant is present at a concentration of no greater than 95 weight percent.

7. A lyotropic liquid crystal composition comprising a polar solvent and an anionic Gemini surfactant, the anionic Gemini surfactant comprising at least one carboxylate moiety;
   wherein the anionic Gemini surfactant forms a triply periodic phase over a range of concentrations from C_l to C_u, wherein the difference between C_l and C_u is at least 10 weight percent and over a range of temperatures from T_l to T_u wherein the difference between T_l and T_u is at least 40°C.

8. The lyotropic liquid crystal composition of claim 7 wherein X_1 and X_2 are each independently a substituted or unsubstituted aliphatic moiety having between four and 30 carbon atoms or a substituted or unsubstituted aryl-aliphatic moiety having between four and 30 carbon atoms;
   Y is a connecting moiety;
   M is a counterion; and
   R_1 through R_6 are each independently selected from the group consisting of hydrogen, fluoride, chloride, and bromide.

9. The lyotropic liquid crystal composition of claim 7 wherein Y comprises an aliphatic moiety, which may be substituted or unsubstituted and may be branched or unbranched, the aliphatic moiety comprising between three carbon atoms and 20 carbon atoms.

10. A lyotropic liquid crystal composition comprising a polar solvent and an anionic Gemini surfactant, the anionic Gemini surfactant comprising at least one carboxylate moiety;
   wherein the anionic Gemini surfactant forms a triply periodic phase over a range of concentrations from C_l to C_u, wherein the difference between C_l and C_u is at least 10 weight percent and over a range of temperatures from T_l to T_u wherein the difference between T_l and T_u is at least 40°C.

wherein the anionic Gemini surfactant has the following structure:

\[
\text{H}_3\text{C}\quad \begin{array}{c}
\text{O} \\
\text{M}^+
\end{array}
\]

wherein Z_1 and Z_2 are integers, each independently having a value between four and 20;
Y is a connecting moiety; and
M is a counterion.
11. A lyotropic liquid crystal composition comprising: a polar solvent at a concentration of at least 10 weight percent; and an anionic Gemini surfactant at a concentration of least 30 weight percent, the anionic Gemini surfactant having the following structure:

wherein \( X_1 \) and \( X_2 \) are each independently a substituted or unsubstituted aliphatic moiety having between four and 30 carbon atoms or a substituted or unsubstituted aryl-alkyl moiety having between four and 30 carbon atoms;

\( Y \) is a connecting moiety selected from the group consisting of a branched or unbranched hydrocarbyl moiety, a substituted or unsubstituted aryl or heteroaryl moiety, and a hydrophilic moiety;

\( M \) is a counterion; and

\( R_1 \) through \( R_5 \) are each independently selected from the group consisting of hydrogen, fluoride, chloride, and bromide.

12. The lyotropic liquid crystal composition of claim 11 wherein the polar solvent is selected from the group consisting of water, acetone, tetrahydrofuran, diethyl ether, ethylene glycol, diethylene glycol, glycerol, 2-butene-1,4-diol, propanediol, glycerol, formamide, N-methylformamide, N-ethylformamide, acetamide, N-methylacetamide, N-ethylacetamide, methanol, ethanol, propanol, ethylammonium nitrate, ethanoammonium nitrate, ethyl ammonium formate, ethylammonium acetate, ethanoammonium acetate, 1-ethyl-3-methyl-imidazolium acetate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, 1-ethyl-3-methylimidazolium tetrafluoroborate, and any combination thereof.

13. The lyotropic liquid crystal composition of claim 11 wherein each \( M \) is selected from the group consisting of lithium ion; sodium ion; potassium ion; cesium ion; magnesium ion; calcium ion; zinc ion; ammonium ion; alkylammonium ion having the structure \( \text{H}_4\text{R}_x\text{N}^+ \) wherein \( x \) is an integer having a value of 0 through 4 and \( R \) is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof; tetrakis(hydroxymethyl)phosphonium ion; tetramethylphosphonium ion; choline; imidazolium; bis(quinuclidinyl ammonium) ion; and combinations thereof.

14. The lyotropic liquid crystal composition of claim 11 wherein \( Y \) comprises the substituted or unsubstituted aryl or heteroaryl moiety.

15. The lyotropic liquid crystal composition of claim 11 wherein \( Y \) comprises the hydrophilic moiety.

16. The lyotropic liquid crystal composition of claim 11 wherein the anionic Gemini surfactant has the following structure:

wherein \( Z_1 \) and \( Z_2 \) are integers, each independently having a value between four and twenty; \( Y \) is the connecting moiety; and \( M \) is the counterion.

* * * *