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Dodecagonal Quasicrystals of Oil-Swollen Ionic Surfactant Micelles

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A.J., C.M.B., T.J.M., and M.K.M. designed and performed the research and analyzed data; M.K.M. supervised the research; and A.J. and M.K.M. wrote the manuscript with input from all authors.

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Abstract

A delicate balance of non-covalent interactions directs the hierarchical self-assembly of molecular amphiphiles into spherical micelles that pack into 3D periodic arrays, which mimic intermetallic crystals. Herein, we report the discovery that adding water to a mixture of an ionic surfactant and *n*-decane induces aperiodic ordering of oil-swollen spherical micelles into previously unrecognized, aqueous lyotropic dodecagonal quasicrystals (DDQCs), which exhibit local 12-fold rotational symmetry and no long-range translational order. The emergence of these DDQCs at the nexus of dynamically arrested micellar glasses and a periodic Frank-Kasper (FK) σ phase approximant sensitively depends on the mixing order of molecular constituents in the assembly process and on sample thermal history. Addition of *n*-decane to mixtures of surfactant and water instead leads only to periodic FK A15 and σ approximants with no evidence for aperiodic order, while extended ambient temperature annealing of the DDQC also reveals its transformation into a σ phase. Thus, these lyotropic DDQCs are long-lived metastable morphologies, which nucleate and grow from a stochastic distribution of micelle sizes formed by abrupt segregation of varied amounts of oil into surfactant micelles on hydration. These findings indicate that molecular building block complexity is not a prerequisite for the formation of aperiodic supramolecular order, while also establishing the generic nature of quasicrystalline states across metal alloys and self-assembled micellar materials.

Significance Statement

Quasicrystals, which exhibit local rotational symmetries and infinite unit cells, are intermediate states of matter between glasses and periodic 3D crystals. Despite their ubiquity in metal alloys, self-assembled micellar quasicrystals have only serendipitously emerged from intricate molecular building blocks or complex materials processing protocols. We demonstrate that hydration of a simple oil and surfactant ("soap") mixture stimulates dodecagonal quasicrystalline ordering of oil-swollen spherical micelles, while oil addition to surfactant/water mixtures instead yields only periodic 3D crystals. Aperiodic order thus emerges as a scale-invariant feature of materials spanning metal alloys to self-assembled soft particles. The straightforward and path-dependent preparation of nonequilibrium quasicrystalline states from simple building blocks suggests that these complex sphere packings may often lurk in plain sight.

Main Text

Introduction

The 1984 discovery of Al-Mn alloys that form quasicrystals (QCs) (1), which display local rotational symmetry yet lack long-range translational order, forced a redefinition of crystals to include periodic and aperiodic structures that yield discrete X-ray diffraction patterns (2). Metal alloys are now known to form both polygonal QCs comprising periodic layers of 2D aperiodic particle arrangements with 5-, 8-, 10-, or 12-fold symmetries, as well as 3D aperiodic icosahedral QCs (3). A harbinger of the emergence of intermetallic quasicrystallinity is the observation of tetrahedrally close-packed crystalline approximants, known as Frank-Kasper (FK) phases, which exhibit large low-symmetry unit cells with average lattice coordination numbers $(CN)_{avg} > 13$ (4, 5).

Over the past 20 years, dodecagonal quasicrystals (DDQCs) have surfaced in supramolecular assemblies of particle-forming, charge-neutral thermotropic liquid crystalline dendrons (6), block polymers (7-11) and their aqueous dispersions (12), and giant shape amphiphiles (13). In a historical progression mirroring that of metal alloys (14), discoveries of these soft 12-fold QCs were often preceded by observations of spatially periodic, micellar FK A15 (Cr_3Si structure type with $Pm3(-)n$ symmetry) and σ (β-U structure with $P4_2/mnm$ symmetry) approximants in adjacent regions of phase space (6, 9, 13, 15, 16). However, these reports access soft DDQCs either by elaborate chemical syntheses (6, 7, 13) or complex materials-specific processing protocols (8, 10, 12), which severely curtail characterization of their detailed structures and dynamics. These serendipitous discoveries highlight the obscure physical origins of their aperiodic order and marked preference for 12-fold symmetry. The question of whether or not soft DDQCs are thermodynamic equilibrium or metastable states also remains debated (6, 8, 10, 17).

Minimal hydration of molecular amphiphiles induces their mesoscale self-assembly into 3D periodic, micellar lyotropic liquid crystals (LLCs). Scale-invariant hard sphere packing models anticipate the observed occurrence of high-symmetry body-centered cubic (BCC), face-centered cubic (FCC), and hexagonally closest-packed (HCP) micelle phases (18, 19). However, privileged amphiphiles form complex lyotropic FK A15 (20, 21) and σ phases (22, 23). The low-symmetry σ phase comprises a tetrahedral close packing of 30 ionic micelles of five discrete volumes in a large tetragonal unit cell. Recent theories and simulations (23-26) rationalize the parallel self-assembly behaviors of charge-neutral and ionic micellar materials in terms of frustrated free energy minimization at two distinct structural length scales. More explicitly, these structures simultaneously optimize the local spherical character of the micelles with minimal interfacial area and their ensemble cohesion, while filling space at uniform

density. In spite of apparent similarities across micellar materials self-assembly, lyotropic DDQCs remain conspicuously absent.

Herein, we describe the straightforward self-assembly of thus far elusive lyotropic DDQCs by hydration of mixtures of bis(tetramethylammonium) dodecylphosphonate (**C_{12}PA-TMA_2**) and *n*-decane. Synchrotron small-angle X-ray scattering (SAXS) analyses reveal the formation of DDQCs with high degrees of aperiodic order, which facilitates identification of their space group symmetry. By investigating the path-dependent formation of these micellar QC mimics and their time- and temperature-dependent evolution, we establish the nonequilibrium nature of this aperiodically ordered state.

Results & Analysis

C_{12}PA-Dec10 LLCs were prepared as transparent solids by controlled hydration of mixtures of **C_{12}PA-TMA_2** and 10 wt% *n*-decane relative to amphiphile by three successive iterations of hand-mixing and centrifugation (see *Materials and Methods* section). LLC water contents are reported as surfactant hydration numbers w_0 = (moles of H_2O)/(moles of **C_{12}PA-TMA_2**). The resulting soft solids were subsequently annealed at 50 °C for 30 min to ensure sample homogeneity. Attempts to prepare LLCs with higher *n*-decane loadings led to macrophase separation of the oil.

Figure 1A depicts synchrotron SAXS data for aqueous **C_{12}PA-Dec10** LLCs across the hydration range w_0 = 5−70, and a LLC phase diagram derived from temperature-dependent SAXS analyses is given in Figure 1B (see *Materials and Methods* for X-ray data acquisition details). While LLCs with $w_0 \geq 70$ are free-flowing disordered micelle solutions, an ordered BCC morphology forms at w_0 = 68 at 25 °C. Decreasing the hydration number to w_0 = 61–67 at 25 °C yields structured solids with sharp SAXS maxima at $(q/q^*)^2$ = 1, 4/3, 8/3, 11/3, 4, 19/3, and 20/3 (q^* = 0.1681 $Å^{-1}$ at w_0 = 66.1), corresponding to a FCC micelle packing with lattice parameter a = 6.47 nm. In the range $40 < w_0 \leq 45$ at 25 °C, the oil-swollen ionic micelles instead pack into a pure HCP structure. A SAXS pattern obtained from one such LLC with w_0 = 42.1 at 60 °C exhibits 15 sharp peaks consistent with the $P6_3/mmc$ symmetry and lattice constant a = 4.41 nm with a nearly ideal c/a = 1.629. In accord with Gibbs' Phase Rule, the pure FCC and HCP phases are separated by a two-phase coexistence window located at w_0 = 46–61 (*SI Appendix* Figure S1). Heating these close-packed LLCs drives thermoreversible transitions to micellar BCC phases, with (110), (200), (211), (220), (310), (222) and (321) SAXS reflections (*e.g.*, a = 4.89 nm for w_0 = 42.1 at 80 °C). These observed order-to-order transition (OOT) temperatures decrease with increasing w_0 (Figure 1B). Note that the high temperature BCC phases of **C_{12}PA-Dec10** with w_0 = 52−62 also reversibly melt into disordered micelle solutions at 100 °C.

Distinctive scattering signatures of exceptionally well-ordered lyotropic FK σ mesophases with ≥ 50 resolution-limited synchrotron SAXS peaks are recorded for **C_{12}PA-Dec10** with w_0 = 33–35 between 25–100 °C (Figure 1A). Consistent with the initial report of σ LLCs of homologous ionic phosphonate amphiphiles in the absence of oil (23), the σ phase formed here at w_0 = 35.2 exhibits lattice parameters a = 15.24 nm and c = 8.01 nm with the expected c/a = 0.526 (see *SI Appendix* Figure S2 for an indexed X-ray pattern and Table S1 for peak positions and residuals). While a narrow σ/HCP two-phase coexistence window occurs in the range w_0 = 36–40 at 25 °C (*SI Appendix* Figure S1), these samples irreversibly transform into σ mesophases on heating to 60 °C. The last observation suggests that the initially formed, HCP phase is metastable with respect to the low-symmetry σ phase in this w_0-range.

LLCs of **C_{12}PA-Dec10** in the composition window $26 \leq w_0 < 30$ are clear and brittle solids that present unique SAXS signatures between 25–100 °C, which do not correspond to a periodic crystal structure (Figure 2A). These SAXS patterns instead display four closely spaced low q peaks (one relatively sharp and three considerably broader) with multiple, less well-defined maxima at higher q-values. These patterns qualitatively resemble those of DDQCs of charge-neutral, self-assembled soft materials (6, 8, 10, 11, 13), albeit with a larger number of higher order SAXS peaks. Given the sample composition proximity to that of a σ phase approximant, the last observation strongly suggests the emergence of a lyotropic DDQC of oil-swollen ionic micelles.

In spite of the polycrystalline nature of this LLC that precludes direct observation of its 12-fold rotational symmetry (6, 9, 12), the 10 well-resolved SAXS peaks in Figure 2A are readily indexed by a five-dimensional reflection scheme for DDQCs developed by Yamamoto (27) and validated by Ishimasa and co-workers in Mn-Cr-Ni-Si DDQC alloys (28, 29). The peak indices conform to the reflection condition ($h_1h_2h_10h_5$), [$h_5 = 2n$: $n \geq 0$, $n \in Z$] (see *SI Appendix* Table S2 for peak positions and residuals), consistent with the non-symmorphic 5D space group symmetry $P12_6/mmc$ (27) of this lyotropic QC. This observation concurs with a prediction by Lifshitz and Diamant of the generic structure of soft QCs (30).

Aqueous lyotropic DDQCs of **C_{12}PA-Dec10** thus comprise periodic layers, in which oil-swollen ionic micelles are aperiodically arranged at the vertices of a square-triangle tiling with local 12-fold rotational symmetry. A random Stampfli tiling (31) representing the aperiodic in-plane order for an ideal, defect-free DDQC is depicted in Figure 2B (32), in which the ratio of the number of triangles to squares is $4/\sqrt{3}$ (33). From the SAXS data in Figure 2A and *SI Appendix* Table S2, we deduce that the interlayer spacing is c = 8.02 nm with an in-plane intermicellar distance of a = 7.91 nm (the edge length in Figure 2B). The ratio c/a = 1.01 is consistent with those reported in metal alloys (28) and in less well-ordered diblock polymers and giant shape amphiphile DDQCs (8, 13).

SAXS analysis of the as-prepared lyotropic DDQC with w_0 = 29.1 after 953 days of ambient temperature annealing reveals a scattering signature consistent with a σ phase (Figure 3A). The apparent peak broadness in the 1D-SAXS intensity profile, arises from the anisotropic nature of the 2D-SAXS pattern (see *SI Appendix* Figure S3) that suggests the presence of large, ordered grains. The slow reorganization of this lyotropic DDQC into a σ LLC is reminiscent of that reported by Gillard et al. in diblock polymers (8). Consistent with the description of the σ phase as a specific, periodic square-triangle tiling (6), they found that the DDQC (00002) peak directly mapped to the σ (002) reflection implying near invariance in the interlayer spacing. In the lyotropic DDQC, we observe a similar reflection correspondence with a ~7% dilation in the σ interlayer spacing to c = 8.57 nm with the expected c/a = 0.523 Attempts to accelerate this LLC phase transformation by high temperature annealing for > 4 h resulted in sample decomposition due to the thermal instability of the $(CH_3)_4N^+$ ions. Nonetheless, these data directly demonstrate lyotropic DDQC metastability with respect to the periodic σ structure.

As-prepared **C_{12}PA-Dec10** LLCs with 30 ≤ w_0 < 33 exhibit σ/DDQC phase coexistence at 25 °C, evidenced by the superposition of noticeable shoulders on the four prominent low q-value DDQC SAXS peaks (Figure 3B). Heating these samples to 100 °C triggers their irreversible transformation into pure σ phases that do not further evolve on cooling to 25 °C. X-ray analyses of different sample regions demonstrate complete DDQC reorganization into a periodic σ phase. Again, the location of the σ (002) peak thus obtained nearly matches that of the initial DDQC (00002) reflection.

SAXS intensity profiles for **C_{12}PA-Dec10** LLCs with w_0 = 11–23 are devoid of sharp peaks (Figure 1A). They are instead characterized by a broad yet intense peak at q = 0.17 Å^{-1}, flanked by broad, low-intensity correlations at q = 0.07–0.09 Å^{-1} and 0.28–0.35 Å^{-1}. Some of these samples exhibit SAXS patterns with a low-q shoulder on the most intense peak, which coincides with the DDQC (00002) peak position (see *SI Appendix* Figure S4). The lack of sharp Bragg peaks suggests the absence of order in these solid samples, consistent with a dynamically arrested, supercooled micelle liquid or a micellar glass that is stable up to 100 °C. Bates and co-workers described similarly correlated block polymer melts as non-ergodic, liquid-like packings (LLP) of micelles (8, 10). The composition window bounded by the LLP and DDQC states at 23 ≤ w_0 < 26 is populated by LLCs that exhibit two-phase coexistence (see *SI Appendix* Figure S4). Further reduction in LLC hydration to w_0 = 10.2 yields SAXS patterns with four discernable scattering maxima superposed on a broad correlation peak. These SAXS maxima are located at q/q^* = √2, √4, √5, and √6 (q^* = 0.1024 Å^{-1} at 25 °C), which we tentatively ascribe to a poorly ordered FK A15 LLC, possibly coexisting with a LLP. Note that Su et al. reported similarly broad SAXS signatures for intermediates in OOTs between the FK A15 and a new FK Z-phase (Zr_4Al_3 intermetallic mimic with *P6*/*mmm* symmetry) of giant-shape amphiphiles (34), which alternatively could suggest slow

formation of an as yet unidentified FK phase. Finally, LLCs with w_0 = 6.1 form hexagonally-packed cylindrical micelles (H_I) (see *SI Appendix* Figure S5).

We subsequently sought to confirm metastability of the DDQC by assessing the sample preparation path dependence of **C_{12}PA-Dec10** LLC morphologies. The appearance of a non-ergodic LLP state at low w_0 coupled with the DDQC ➞ σ OOTs triggered by sample annealing hint that "normal" water addition to surfactant/oil mixtures generally yields nonequilibrium LLCs. In this vein, we prepared LLC samples **C_{12}PA-Dec10-I** of the same compositions by an "inverse" order of addition. More specifically, we pre-mixed **C_{12}PA-TMA_2** and H_2O via three cycles of centrifugation and hand-mixing to form aqueous LLCs, after which 10 wt% *n*-decane relative to **C_{12}PA-TMA_2** was added by three additional centrifugation and hand-mixing cycles (see *Materials and Methods* for details). Isothermal sample annealing at 50 °C for 30 min subsequently effected complete oil uptake to yield clear, homogeneous **C_{12}PA-Dec10-I** LLCs.

The **C_{12}PA-Dec10-I** LLC phase portrait in Figure 4 diverges significantly from that in Figure 1B obtained by the "normal" order of component addition. The inverse addition order extinguishes the DDQC and LLP states of **C_{12}PA-Dec10**, in favor of pure FK σ and A15 approximants (see *SI Appendix* Figure S6) when w_0 = 31–41 and w_0 = 7–27, respectively. SAXS traces for the A15 LLCs additionally exhibit up to 18 sharp peaks, indicative of high degrees of long-range translational order (see *SI Appendix* Figure S7 for a representative SAXS pattern and Table S3 for a listing of peak positions and residuals). Note that the lyotropic DDQC composition that evolves into a σ LLC forms coexisting A15 and σ morphologies by the inverse addition protocol, affirming that the path-independent equilibrium state is a periodic FK phase.

When w_0 = 41–65, closest-packed FCC and HCP structures result regardless of preparation method with thermally-induced OOTs to BCC phases on heating to 40–80 °C. Although hard sphere FCC packings are typically entropically favored over HCP phases (35), the free energy differences between these phases are minute so that the observed packing likely arises from nucleation-limited growth (36). In spite of this commonality between the sample preparation method outcomes, **C_{12}PA-Dec10-I** LLCs form BCC morphologies when 65 < w_0 < 70 in opposition to the FCC and BCC phases formed by normal order of component addition. Beyond this morphology difference, we also find that **C_{12}PA-Dec10-I** forms a BCC phase at w_0 = 70, while the normal order of addition yields only disordered micelle solutions.

Discussion

The path-dependent preparation of decane-swollen aqueous LLCs of **C_{12}PA-TMA_2** indicates that the order of molecular component addition variably induces amorphous, quasicrystalline, and periodic

micelle packings. As compared to binary LLCs comprising water and amphiphile, oil incorporation furnishes an extra degree of freedom that enables access to new phases. Thus, we surmise that the sample preparation method controls characteristics of the underlying micelle size distribution that guides nucleation and growth of variously ordered mesophases.

To gain deeper insights into **C_{12}PADec10-I** LLC formation by the inverse order of addition, we mapped the aqueous lyotropic phase behavior of **C_{12}PA-TMA_2** in the absence of *n*-decane (see *SI Appendix* Figure S8). With increasing hydration over the range w_0 = 11–72, SAXS analyses of **C_{12}PA-TMA_2** aqueous LLCs revealed the lyotropic phase sequence H_I ➞ A15 ➞ A15/σ ➞ σ ➞ σ/HCP ➞ HCP with a lyotropic order-to-disorder transition at $w_0 > 72$. This phase progression emulates that reported for related dianionic surfactants (22, 23). Kim et al. previously used SAXS-based electron density reconstructions and atomistic simulations to elucidate the discrete micelle size distributions in low-symmetry FK LLCs, which emerge from frustrated two length scale optimization of global lattice cohesion and local ionic sphericity of the micelles (23). While there are detailed differences between the A15 and σ LLC phase window locations and widths for **C_{12}PA-TMA_2** and its 10-carbon analogue (23), such tail length-dependent effects are expected (22).

In lyotropic mesophases formed by the inverse order of addition, *n*-decane infiltrates a pre-formed **C_{12}PA-TMA_2** aqueous LLC with a pre-determined, discrete micelle size distribution. Consequently, micelle swelling by oil partitioning into the particle cores is templated by the existing structure. Upon modest particle swelling to accommodate the 10 wt% *n*-decane relative to surfactant, the micelles reoptimize both their lattice arrangements and preferred surfactant aggregation numbers by interparticle chain exchange to maximize micelle ionic sphericity and lattice cohesion. Established structural relationships between the A15 and σ phases suggest possible mechanisms for such transitions (37).

Templated oil uptake by the micelles of **C_{12}PA-Dec10-I** LLCs is regulated by the degree of counterion-headgroup dissociation specified by w_0, since particle swelling occurs at constant interfacial area per surfactant to minimize intermolecular headgroup repulsions within each micelle (38, 39). The latter constraint drives the formation of higher mean interfacial curvature aggregates at lower w_0 values, consistent with the observed phase window shifts of $\Delta w_0 \approx 8–10$ in **C_{12}PADec10-I** microemulsions (Figure 4) as compared to **C_{12}PA-TMA_2** aqueous LLCs (*SI Appendix* Figure S8). Oil addition also increases the hydrophobic volume at each lattice position, which amplifies ionic sphericity deviations and widens the overall FK LLC phase windows. Conceptually similar arguments explain the emergence of σ, C14, and C15 micelle packings in homopolymer-swollen sphere-forming diblock polymer melts (40).

Addition of water to *n*-decane and **C_{12}PA-TMA$_2$** mixtures instead yields non-ergodic LLP and QC states, indicating that the method of component addition frustrates periodic FK LLC nucleation. In this case, we speculate that water addition induces rapid and stochastic *n*-decane partitioning into the micelle cores to yield a broad, nonequilibrium particle size distribution incommensurate with periodic ordering. At low w_0 values, the large interfacial tension between the ionic and hydrophobic microdomains impedes particle size equilibration through interparticle oil and amphiphile chain exchange, leading to a non-ergodic state with solid-like properties associated with a dynamically arrested LLP or micellar glass. At slightly higher w_0 values, the decrease in the average number of micelles per unit volume unjams the glassy LLP state to enable micelle rearrangement and DDQC nucleation. While the appearance of higher order SAXS peaks suggests substantially better long-range aperiodic order in this DDQC as compared to other soft quasicrystals, phason strain and small grain sizes likely cause broadening of the observed SAXS peaks (29). However, the DDQC formed at w_0 = 29.1 eventually evolves at ambient temperature into a periodic σ phase on a time scale of many months. Although the **C_{12}PA-Dec10-I** phase diagram (Figure 4) suggests that the final equilibrium morphology should be A15/σ coexistence, prior work indicates that OOTs between these closely related FK phases can be exceedingly slow (19). The observation of long-lived, metastable supramolecular assemblies of small molecules that only slowly transform into equilibrium structures is surprising, as it significantly defies the conventional wisdom that the kinetics of such transformations are fast.

Further hydration of **C_{12}PA-Dec10** to w_0 > 33 reduces the interfacial tension between the microdomains to allow faster interparticle exchange of oil and amphiphile, since water compatibilizes the hydrophobic and ionic LLC microdomains. The micelle size distribution thus approaches equilibrium, resulting in greater similarities in the phase diagrams for the normal and inverse order of addition in this w_0 range (Figures 1B and 4, respectively). Signatures of incomplete oil-swollen micelle size equilibration nonetheless persist. For example, irreversible OOTs to pure σ phases on heating two-phase coexisting DDQC/σ and σ/HCP LLCs from normal order of addition, coupled with exclusive formation of σ phases in **C_{12}PA-Dec10-I** with w_0 = 31-40, suggest that heating facilitates micelle size relaxation toward equilibrium σ mesophases. However, the σ LLC unit cell volume from normal order of addition is ~5% larger than that obtained from **C_{12}PA-Dec10-I** at w_0 = 32.1, consistent with nonequilibrium behavior. Finally, narrow dispersity particle size formation that allows facile BCC ordering at w_0 = 70 is also inhibited, in contrast to the **C_{12}PA-Dec10-I** LLCs. This persistence of nonequilibrium signatures across all examined hydrations defies the conventional wisdom that OOTs in oil-swollen, ordered LLC morphologies of low molecular weight amphiphiles are fast. These transformation timescales are likely governed by a convolution of activation barriers associated with micelle-size equilibration by interparticle

surfactant and oil exchange, ordered phase nucleation, and micelle diffusion into the lattice positions of the new phase.

Therefore, LLP and DDQC states obtained from the normal order of addition are long-lived, metastable states with respect to the periodic FK approximants formed by **C_{12}PA-Dec10-I** LLCs. The three broad peaks in the LLP SAXS pattern (Figure 1A) indicate a strongly correlated micelle glass, with characteristic length scales that may reflect either tetrahedral or icosahedral clustering widely observed in particle-based liquid simulations (41-43). Simulations by Keyes and Glotzer (44) suggest the intermediacy of such clusters in the nucleation and growth of DDQCs and their approximants. In diblock polymers, Gillard et al. reported that rapid thermal quenching of a disordered, particle-forming diblock polymer melt drove the formation of a LLP state, from which a DDQC emerges and slowly reverts to a periodic, equilibrium σ phase upon extended isothermal annealing (8). By geometric analogy to intermetallic QC formation (33), the broad and possibly continuous distribution of micelle sizes in the diblock polymer and LLC LLPs seemingly lead to a lower DDQC nucleation barrier as compared to that of its equilibrium σ approximant that requires a discrete particle size distribution (15, 23).

Conclusion

The discovery of previously unrecognized lyotropic DDQC mesophases of oil-swollen micelles establishes the universality of 12-fold aperiodic order in particle-forming self-assembled soft materials. The scalable preparation of this nonequilibrium DDQC from simple molecular constituents may expedite new studies of their detailed structures and dynamics. The identification of the $P12_6/mmc$ space group symmetry of the DDQC may also enable theoretical studies of the origins of 12-fold aperiodic order in soft materials (42, 43). The path-dependent formation of the oil-swollen micellar DDQC also complements reports of kinetically-controlled, multi-component syntheses of mesoporous silicate quasicrystals templated by ionic surfactants under controlled reaction conditions (45, 46).

The formation of DDQCs and their periodic approximants in both lyotropic and thermotropic liquid crystals (6), diblock polymers (8, 40), and giant shape amphiphiles (13) suggests the existence of overarching, scale-invariant self-assembly principles that guide the formation of periodic and aperiodic order in supramolecular soft materials. In regions of phase space proximal to A15 and σ structures, past and present studies apparently indicate that sample processing paths that furnish broad micelle-size distributions enable nucleation and growth of nonequilibrium DDQCs. However, the reasons for soft DDQC metastability remain obscure at this time. In block polymer (40) and LLC assemblies, judicious

design of core-swelling additives offers an enticing strategy for controlling the average particle size and its distribution breadth that permits formation of new periodic and aperiodic mesoscale crystals. We speculate that the preference for 6D icosahedral QCs in intermetallics as compared to 5D DDQCs of soft materials stems from differences in the number of available degrees of freedom in each system, which set the sphere size distributions and their interparticle correlations from which aperiodic order develops. Understanding and harnessing these principles may enable scale up of aperiodic order to technologically-relevant length scales as useful hyperuniform structures (47) with unusual photonic bandgap behaviors (48-50).

Materials and Methods

Materials. All reagents were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI) and used as received. $(CH_3)_4NOH$ (1.007 M in H_2O) was titrated with standardized 1.000 N HCl (*aq*). Ultra-pure water (> 18 MΩ●cm) obtained from a Thermo Scientific™ Barnstead™ Smart2Pure 3 UV/UF water purification system was degassed by sparging with $N_2(g)$ for at least 30 min.

Molecular Characterization. ^1H and ^{13}C NMR spectra were recorded in CD_3OD on a Bruker Avance 400 MHz spectrometer with Smartprobe and referenced relative to the residual protiated solvent (δ 3.31 ppm). Combustion analysis (C, H, and N) was performed by Atlantic Microlab, Inc. (Norcross, GA).

Bis(tetramethylammonium) dodecylphosphonate (C_{12}PA-TMA_2) Synthesis. A suspension of dodecylphosphonic acid (3.029 g, 12.10 mmol) in MeOH (50 mL) was treated with $(CH_3)_4NOH$ (*aq*) (24.05 mL, 1.007 M in H_2O, 24.20 mmol). This mixture was stirred at 22 °C for an additional 2 h after it became homogeneous, after which all volatiles were removed under vacuum. The resulting solid was freeze-dried twice under reduced pressure from benzene (20 mL). ^1H NMR (400.18 MHz, CD_3OD-d4, 24 °C): δ (ppm) 3.23 (N−CH_3, s, 24H), 1.70−1.64 (P−CH_2, m, 2H), 1.51−1.42 (CH_2−CH_2, m, 2H), 1.36−1.30 (CH_2, m, 18H), 0.93−0.90 (CH_2−CH_3, t, 3H). ^{13}C NMR (100.62 MHz, CD_3OD, 24 °C): δ (ppm) 54.59 ($N(CH_3)4$), 32.14 (CH_2), 31.96 (CH_2), 31.96 (CH_2), 31.68 (CH_2), 31.41 (CH_2), 30.11 (CH2), 29.54 (CH_2), 29.43 (CH_2), 29.10 (CH_2), 24.83 (CH_2), 22.35 (CH_2), 13.06 (CH_3). Anal. calc for $C_{20}H_{49}PN_2O_3 \cdot 5.07\ H_2O$: C, 49.22; H, 12.24; N, 5.74. Found: C, 49.22; H, 12.29; N, 5.62.

LLC sample preparation. In the normal order of addition protocol, desired masses of **C_{12}PA-TMA_2** were weighed into one dram vials followed by 10 wt% *n*-decane (relative to surfactant mass), and they were mixed by three cycles of centrifugation (4950 × *g* for 10 min) and hand-mixing. LLCs were then prepared by addition of ultrapure water, homogenization by three additional cycles of centrifugation and hand-mixing, followed by isothermal annealing at 50 °C for 30 min.

In the inverse order of component addition method, aqueous LLCs of **C_{12}PA-TMA_2** were first prepared by three cycles of centrifugation (4950 × *g* for 10 min) and hand-mixing to yield transparent

samples. *n*-Decane (10 wt% with respect to **C_{12}PA-TMA_2**) was then added and mixed by three additional cycles of centrifugation and hand-mixing. Isothermal annealing for 30 min at 50 °C effected complete oil sorption and ensured **C_{12}PA-Dec10-I** LLC homogeneity.

Small-angle X-ray Scattering (SAXS). Prior to temperature-dependent synchrotron SAXS analyses, LLCs were quiescently equilibrated at 22 °C for ≥ 24 h to relax any shear stresses induced by sample preparation. Using an incident beam energy of either 13.3 or 14.0 keV (λ = 0.932 or 0.886 Å) and a 2.011 m sample-to-detector distance at the 12-ID-B beamline of the Advanced Photon Source (Argonne, IL), synchrotron 2D-SAXS patterns were recorded on a Pilatus 2M detector (25.4 cm × 28.9 cm rectangular area with 172 x 172 μm^2 pixel resolution) and calibrated using a silver behenate standard (d = 58.38 Å). LLC samples were hermetically sealed in alodined aluminum DSC pans (TA Instruments, Newcastle, DE), which were equilibrated at each stated temperature on a custom-built multiple-sample array stage for at least 10 min prior to X-ray exposure for ~ 0.1 s. Sample homogeneity was assessed by acquiring X-ray data at a minimum of three different sample positions.

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Figure Legends

Figure 1. Phase behavior of **C_{12}PA-Dec10** aqueous LLCs. (A) Synchrotron 1D-SAXS intensity profiles for aqueous LLCs prepared by hydration of **C_{12}PA-Dec10**, illustrating formation of high-symmetry FCC, HCP, and BCC micelle packings, FK σ and A15 phases, and an amorphous LLP state. All data was acquired at 25 °C, except where noted. (B) Temperature *versus* amphiphile hydration number w_0 morphology diagram for **C_{12}PA-Dec10** aqueous LLCs, derived from SAXS analyses of samples on first heating. Solid lines indicate approximate phase boundary locations.

Figure 2. Discovery of a lyotropic dodecagonal quasicrystal. (A) 1D-SAXS intensity profile and 2D-SAXS pattern (*inset*) of a well-ordered DDQC formed by **C_{12}PA-Dec10** at w_0 = 29.1 and 25 °C with interlayer spacing c = 8.02 nm and in-plane intermicellar distance a = 7.91 nm. Miller indices mark the first ten peaks corresponding to the 5D space group symmetry $P12_6/mmc$; higher order peaks could not be unambiguously indexed (*red lines*). (B) Stampfli tiling depiction of the in-plane aperiodic order of micelles in an ideal, defect-free DDQC, where the markers indicate the relative micelle positions along the *z*-axis perpendicular to the plane.

Figure 3. Metastability of the lyotropic DDQC. (A) Comparison of 1D-SAXS patterns obtained from a **C_{12}PA-Dec10** lyotropic DDQC (w_0 = 29.1) as-made and after ambient temperature annealing for 953 d, illustrating its transformation into a FK σ phase. The apparent breadth of the peaks arises from the anisotropic nature of the 2D-SAXS pattern, which contains large ordered grains (see *SI Appendix* Figure S3). (B) Temperature-dependent SAXS demonstration of **C_{12}PA-Dec10** lyotropic DDQC (w_0 = 32.1) metastability with respect to a σ approximant on heating, with a ≥ 10 min thermal equilibration at each temperature. The as-made sample exhibits DDQC/σ two-phase coexistence, with σ phase peaks marked by dashed lines near 0.17 $Å^{-1}$, that irreversibly transforms into a pure σ phase on heating to 100 °C and is unchanged on cooling to 25 °C. The respective (00002) and (002) spacings of the DDQC and the σ phase at 25 °C nearly coincide (*dashed line*).

Figure 4. Temperature *versus* w_0 LLC phase diagram for **C_{12}PA-Dec10-I** LLCs formed by the inverse order of component addition protocol, in which *n*-decane is introduced into aqueous LLCs of **C_{12}PA-TMA_2**. This sample preparation technique does not generate LLP or aperiodic DDQC states.