Supporting Information

Path-dependent Preparation of Complex Micelle Packings of a Hydrated Diblock Oligomer

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Experimental Section

Materials. All reagents were purchased from the Sigma-Aldrich Chemical Co. (Milwaukee, WI) and used as received without further purification. C_{16}E_{20} was stored in a glovebox under an anhydrous argon atmosphere to avoid adventitious atmospheric moisture uptake. Ultra-pure water (18 MΩ●cm) obtained from Thermo Scientific™ Barnstead™ Smart2Pure 3 UV/UF water purification system was degassed by sparging N_2(g) for at least 30 min.

^1^H NMR Spectroscopy. ^1^H NMR spectra were acquired in CDCl_3 in the presence of excess trifluoroacetic anhydride, using a Bruker Avance 400 MHz spectrometer with Smartprobe with a pulse repetition delay time of 20 s. All spectra were referenced relative to the residual proton shift of CDCl_3 (δ 7.26 ppm). Carbon/Hydrogen (C/H) combustion elemental analysis were performed by Atlantic Microlab, Inc. (Norcross, GA, USA). M_n = 1074.2 g/mol was determined by end group analysis of the trifluoroacetylated C_{16}E_{20} (by treatment with excess trifluoroacetic anhydride in CDCl_3), based on quantitative integration of the ^1^H NMR spectrum based on the methyl group in the C_{16} hydrocarbon fragment (Figure S1).
Figure S1. $^1$H NMR of C$_{16}$E$_{20}$ in CDCl$_3$. The spectrum is calibrated such that there are three methyl protons ($a$). The integration of the protons on the PEO chain ($e$) are used to calculate the number of EO units. The integration of the hydrocarbon fragments ($a,b,c,d$) is consistent with a 16 carbon alkyl chain (33 protons). $M_n$ is calculated as the sum of masses of the hydrocarbon and PEO blocks.
**Size-Exclusion Chromatography (SEC).** SEC analyses in tetrahydrofuran (THF) were performed on a Viscotek GPCMax VE 2001 system equipped with three Agilent Technologies PLGel Mixed-B columns (350 mm × 7.5 mm) and a Viscotek VE 3580 refractive index detector, using an eluent flowrate of 1 mL/min. A polystyrene molecular weight calibration curve was constructed using 10 commercially available narrow molecular weight standards with $580 \leq M_n \leq 377400$ g/mol (Polymer Laboratories, Amherst, MA). For C16E20 with trifluoroacetate endgroup (by reaction with excess trifluoroacetic anhydride), $M_n = 1000$ g/mol and $D = M_w/M_n = 1.17$ (against polystyrene standards without correction) (Figure S2).

![SEC trace](image)

**Figure S2.** SEC trace obtained using differential refractive index detection for C16E20 in tetrahydrofuran. The dotted lines represent the bounds of the peak from the amphiphile.

**Lyotropic Liquid Crystal (LLC) sample Preparation.** LLC samples were prepared by massing desired amounts of C16E20 in 1 dram vials inside a glovebox under an argon atmosphere, followed by hydration using ultra-pure water (18 MΩ•cm). These mixtures were homogenized by three or more cycles of centrifugation (4950 × g for 10 min each) and hand-mixing to yield stiff and translucent, gel-like solids. Sample vials were capped and sealed using Parafilm to
prevent any loss of water. No expected or unusually high safety hazards were encountered during sample handling or preparation.

**Small-angle X-Ray Scattering (SAXS).** All LLC samples were allowed to equilibrate at 22 °C for at least 24 h prior to morphological analyses by synchrotron SAXS. Using an incident beam energy of either 13.3 or 14.0 keV (\(\lambda = 0.932\) or 0.886 Å) and a 3.617 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 1475 × 1679 pixel resolution (172 µm x 172 µm pixel size). The scattering wavevector (\(q = (4\pi \sin \theta)/\lambda\) scale in these patterns was 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 the desired temperature using a Linkam DSC hot–stage for at least 5 min prior to data collection (typical exposure times ~ 1 s). X-ray scattering analyses poses a significant safety hazard and all institutional radiation safety protocols were followed to mitigate exposure.

Lab source SAXS measurements were made using a SAXSLab Ganesha300XL instrument in the Characterization Facility, University of Minnesota. Cu Kα X-rays (\(\lambda = 1.54\) Å) generated by a Xenocs Geni3DX source were collimated through 2 or 3 sets of 4-bladed slits (JJ X-ray, A/S). 2D-SAXS patterns were acquired using a Dectris EIGER R 1M detector (7.72 cm × 7.99 cm rectangular area) with 1030 × 1065 pixels (75 µm × 75 µm pixel size) at a sample-to-detector distance of 46.8 cm. Samples were sealed in home-built sample holders with Kapton windows. They were mounted within an evacuated sample environment and equilibrated at the desired temperature on a Linkam hot-stage for ~20 min prior to data acquisition (typical exposure times
~10 min). X-ray scattering analyses poses a significant safety hazard and all institutional radiation safety protocols were followed to mitigate exposure.

All 2D-SAXS patterns were azimuthally-integrated to obtain one-dimensional scattered intensity $I(q)$ versus $q$ plots, using the DataSqueeze software package (http://www.physics.upenn.edu/~heiney/datasqueeze/index.html). The 1D scattering intensity profiles were analyzed using customized Igor Pro procedure files developed by our group.

Using the JAN2006 crystallographic computing system software, Le Bail refinement of selected SAXS data sets was used to extract the structure factor intensities for each scattering maximum. These data were used as inputs for the charge flipping algorithms within the SUPERFLIP software package to reconstruct the electron density maps for various observed LLC phases. The resulting electron density contour maps (typically, 90% isosurfaces) were visualized using the VESTA software package. Details of these analyses along with the SUPERFLIP input files (in which the static structure factor intensities are listed) are provided on pages S9 and S19.
Figure S3. Temperature–dependent synchrotron SAXS patterns obtained from a LLC sample with 32.9 wt% $\text{C}_{16}\text{E}_{20}$ in water. This LLC sample transitions from a FCC micellar packing at 25 °C to BCC/FCC coexistence at 60 °C, which melts into a disordered solution of micelles at 74 °C. In the SAXS trace at 60 °C, the green marker indicates the peak corresponding to the coexisting BCC phase. At 68 °C, we observe an intervening window of two-phase coexistence between a micellar BCC phase and disordered micellar solution as expected based on Gibbs’ Phase Rule.
Figure S4. 1D-SAXS intensity profiles for the LLC formed at 46.5 wt% C$_{16}$E$_{20}$ showing the formation of a body-centered cubic (BCC) phase at $25 \leq T \leq 80$ °C, and H$_{1}$ + disordered micelles at 100 °C.
**SUPERFLIP** Input File for the A15 Phase formed at 58.9 wt% C\textsubscript{16}E\textsubscript{20} in H\textsubscript{2}O Used in Charge-Flipping Electron Density Reconstruction

The 1D-SAXS intensity \( I(q) \) versus scattering wavevector \( q \) profile for the as-made A15 phase at 25 °C with 58.9 wt% C\textsubscript{16}E\textsubscript{20} was scaled by multiplying the \( q \) values by 2, to halve the size of the unit cell to expedite the calculation and rendering of the electron density map with available computing resources. Le Bail refinement of the scaled SAXS data with a 10\textsuperscript{th} order polynomial fit for the X-ray background using the \textit{JANA2006} crystallographic computing software package enabled extraction of the static structure factor intensities for each peak in the pattern in the range \( q = 0.053−0.255 \text{ Å}^{-1} \) (in the original, unscaled pattern), the Miller indices of which were assigned using the \( Pm\bar{3}(−)n \) space group symmetry with a scaled cubic unit cell parameter \( a = 7.3081 \text{ nm} \). The structure factor intensities associated with each indexed SAXS peak are given in the text file below. Application of the SUPERFLIP charge-flipping algorithm using the input file below in 2000 trials yielded 11 converged electron density maps with excellent figures of merit (fm) < 6, starting from randomized initial conditions. The 11 converged maps were averaged and rendered using the VESTA software package to yield the 90% isosurface electron density maps shown in Figure 2A.

Details of the methodology were summarily described by Baez-Cotto \textit{et al.},\textsuperscript{4} and more details may be found in the original papers of Palatinus and co-workers.

```
title SAJB-47_00246_Try3_Superflip
perform CF
outputfile "SAJB-47_00246_Try3.xplor"
outputformat xplor

dimension 3

cell  73.0807  73.0807  73.0807  90.00  90.00  90.00

spacegroup Pm-3n
centro yes

centers
  0.000000  0.000000  0.000000

endcenters
```
symmetry
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-x1     -x2     x3
-x1     x2     -x3
 x3     x1     x2
 x3    -x1     -x2
-x3     -x1     x2
-x3     x1     -x2
 x2     x3     x1
-x2     x3     -x1
 x2   -x3     -x1
-x2   -x3     x1
 x2+1/2 x1+1/2 -x3+1/2
-x2+1/2 -x1+1/2 -x3+1/2
 x2+1/2 -x1+1/2 x3+1/2
-x2+1/2 x1+1/2 x3+1/2
 x1+1/2 x3+1/2 -x2+1/2
-x1+1/2 x3+1/2 x2+1/2
-x1+1/2 -x3+1/2 -x2+1/2
 x1+1/2 -x3+1/2 x2+1/2
 x3+1/2 x2+1/2 -x1+1/2
 x3+1/2 -x2+1/2 x1+1/2
-x3+1/2 x2+1/2 x1+1/2
-x3+1/2 -x2+1/2 -x1+1/2
 -x1     -x2     -x3
 x1     x2     -x3
 x1   -x2     x3
-x3     -x1     -x2
 -x3     x1     x2
 x3    -x1     x2
-x2   -x3     -x1
 x2   -x3     x1
-x2     x3     x1
 x2  -x3     -x1
-x2  -x3     x1
 x2+1/2 -x1+1/2 x3+1/2
 x2+1/2 x1+1/2 x3+1/2
-x2+1/2 x1+1/2 -x3+1/2
 x2+1/2 -x1+1/2 -x3+1/2
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-x3+1/2 x2+1/2 x1+1/2
.endsymmetry
composition C56 H114 O21
# Keywords for charge flipping
repeatmode 2000 sumgood
bestdensities 1 symmetry
polish yes
maxcycles 1000
delta AUTO
weakratio 0.000
Biso 0.000
randomseed AUTO
searchsymmetry average
derivesymmetry no
# End of keywords for charge flipping

# EDMA-specific keywords
inputfile SAJB-47_00246.Try3_Superflip.m81
outputbase SAJB-47_00246.Try3_Superflip
m40forjana yes
writem40 SAJB-47_00246.Try3_Superflip_tmp.m40
maxima all
fullcell no
scale fractional
plimit 0.3000 sigma
numberofatoms composition
centerofcharge yes
chlimit 0.2500
chlimlist 0.0375 relative
# End of EDMA-specific keywords

electrons 0.0000
dataitemwidths 4 15 15
dataformat intensity fwhm
fbegin
  1   0   1 22.0224  0.0101
  0   0   2 6987.5386  0.0110
  1   0   210000.0000  0.0117
  1   1   2 8136.5864  0.0125
  2   0   2 188.0041  0.0140
  1   0   3  56.9598  0.0154
  2   2   2 990.2704  0.0168
  2   0   3 475.1289  0.0174
  2   1   3 496.7450  0.0181
  0   0   4 1174.6332  0.0193
  1   0   4 357.6997  0.0200
  3   0   3  67.6408  0.0206
  1   1   4  67.6408  0.0206
  2   0   4  80.2654  0.0218
  2   1   4 20.9924  0.0224
  3   2   3 16.7596  0.0229
  2   2   4 77.5350  0.0241
  3   0   4 28.4030  0.0246
  3   1   4  8.7267  0.0252
  1   0   5  8.7267  0.0252
| v | w | z | 42.3261 | 0.0268 |
|---|---|---|---------|--------|
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| 3 | 2 | 4 | 42.3261 | 0.0268 |
| 2 | 1 | 5 | 32.1020 | 0.0273 |
| 4 | 0 | 4 | 172.2079 | 0.0283 |
| 3 | 3 | 4 | 21.1899 | 0.0293 |
| 3 | 0 | 5 | 21.1899 | 0.0293 |
| 3 | 1 | 5 | 1.4569 | 0.0298 |
| 6 | 2 | 7 | 0.0000 | 0.0511 |
| 3 | 0 | 9 | 0.0000 | 0.0514 |
| 5 | 1 | 8 | 0.0000 | 0.0514 |
| 5 | 4 | 7 | 0.0000 | 0.0514 |
| 3 | 1 | 9 | 0.0000 | 0.0517 |
| 5 | 2 | 8 | 0.0000 | 0.0524 |
| 6 | 3 | 7 | 0.0000 | 0.0527 |
| 3 | 2 | 9 | 0.0000 | 0.0527 |
| 4 | 4 | 8 | 0.0000 | 0.0533 |
| 4 | 0 | 9 | 0.0000 | 0.0537 |
| 7 | 0 | 7 | 0.0000 | 0.0540 |
| 4 | 1 | 9 | 0.0000 | 0.0540 |
| 5 | 3 | 8 | 0.0000 | 0.0540 |
| 0 | 0 | 10 | 0.0000 | 0.0546 |
| 6 | 0 | 8 | 0.0000 | 0.0546 |
| 4 | 2 | 9 | 0.0000 | 0.0549 |
| 6 | 4 | 7 | 0.0000 | 0.0549 |
| 6 | 1 | 8 | 0.0000 | 0.0549 |
| 1 | 0 | 10 | 0.0000 | 0.0549 |
| 1 | 1 | 10 | 0.0000 | 0.0552 |
| 7 | 2 | 7 | 0.0000 | 0.0552 |
| 6 | 2 | 8 | 0.0000 | 0.0558 |
| 2 | 0 | 10 | 0.0000 | 0.0558 |
| 2 | 1 | 10 | 0.0000 | 0.0561 |
| 5 | 4 | 8 | 0.0000 | 0.0561 |
| 4 | 3 | 9 | 0.0000 | 0.0564 |
| 5 | 0 | 9 | 0.0000 | 0.0564 |
| 5 | 1 | 9 | 0.0000 | 0.0567 |
| 6 | 6 | 6 | 0.0000 | 0.0570 |
| 2 | 2 | 10 | 0.0000 | 0.0570 |
| 3 | 0 | 10 | 0.0000 | 0.0573 |
| 6 | 3 | 8 | 0.0000 | 0.0573 |
| 6 | 5 | 7 | 0.0000 | 0.0576 |
| 5 | 2 | 9 | 0.0000 | 0.0576 |
| 3 | 1 | 10 | 0.0000 | 0.0576 |
| 7 | 0 | 8 | 0.0000 | 0.0585 |
| 3 | 2 | 10 | 0.0000 | 0.0585 |
| 7 | 4 | 7 | 0.0000 | 0.0588 |
| 7 | 1 | 8 | 0.0000 | 0.0588 |
| 5 | 5 | 8 | 0.0000 | 0.0588 |
| 5 | 3 | 9 | 0.0000 | 0.0591 |
| 4 | 0 | 10 | 0.0000 | 0.0594 |
|   |   |   |          |          |
|---|---|---|----------|----------|
| 6 | 4 | 8 | 0.0000   | 0.0594   |
| 4 | 1 | 10| 0.0000   | 0.0597   |
| 6 | 0 | 9 | 0.0000   | 0.0597   |
| 7 | 2 | 8 | 0.0000   | 0.0597   |
| 6 | 1 | 9 | 0.0000   | 0.0600   |
| 3 | 3 | 10| 0.0000   | 0.0600   |
| 4 | 2 | 10| 0.0000   | 0.0606   |
| 6 | 2 | 9 | 0.0000   | 0.0609   |
| 7 | 3 | 8 | 0.0000   | 0.0611   |
| 5 | 4 | 9 | 0.0000   | 0.0611   |
| 1 | 0 | 11| 0.0000   | 0.0611   |
| 4 | 3 | 10| 0.0000   | 0.0620   |
| 6 | 5 | 8 | 0.0000   | 0.0620   |
| 2 | 0 | 11| 0.0000   | 0.0620   |
| 5 | 0 | 10| 0.0000   | 0.0620   |
| 6 | 3 | 9 | 0.0000   | 0.0623   |
| 2 | 1 | 11| 0.0000   | 0.0623   |
| 5 | 1 | 10| 0.0000   | 0.0623   |
| 8 | 0 | 8 | 0.0000   | 0.0628   |
| 7 | 4 | 8 | 0.0000   | 0.0631   |
| 5 | 2 | 10| 0.0000   | 0.0631   |
| 3 | 0 | 11| 0.0000   | 0.0634   |
| 7 | 0 | 9 | 0.0000   | 0.0634   |
| 7 | 1 | 9 | 0.0000   | 0.0637   |
| 3 | 1 | 11| 0.0000   | 0.0637   |
| 4 | 4 | 10| 0.0000   | 0.0639   |
| 8 | 2 | 8 | 0.0000   | 0.0639   |
| 6 | 4 | 9 | 0.0000   | 0.0642   |
| 7 | 6 | 7 | 0.0000   | 0.0645   |
| 7 | 2 | 9 | 0.0000   | 0.0645   |
| 3 | 2 | 11| 0.0000   | 0.0645   |
| 5 | 3 | 10| 0.0000   | 0.0645   |
| 6 | 6 | 8 | 0.0000   | 0.0650   |
| 6 | 0 | 10| 0.0000   | 0.0650   |
| 4 | 0 | 11| 0.0000   | 0.0653   |
| 6 | 1 | 10| 0.0000   | 0.0653   |
| 7 | 5 | 8 | 0.0000   | 0.0656   |
| 4 | 1 | 11| 0.0000   | 0.0656   |
| 7 | 3 | 9 | 0.0000   | 0.0658   |
| 6 | 2 | 10| 0.0000   | 0.0661   |
| 4 | 2 | 11| 0.0000   | 0.0664   |
| 5 | 4 | 10| 0.0000   | 0.0664   |
| 6 | 5 | 9 | 0.0000   | 0.0666   |
| 8 | 4 | 8 | 0.0000   | 0.0672   |
| 0 | 0 | 12| 0.0000   | 0.0672   |
| 8 | 0 | 9 | 0.0000   | 0.0674   |
| 6 | 3 | 10| 0.0000   | 0.0674   |
| 1 | 0 | 12| 0.0000   | 0.0674   |
| 4 | 3 | 11| 0.0000   | 0.0677   |
| 8 | 1 | 9 | 0.0000   | 0.0677   |
| 7 | 4 | 9 | 0.0000   | 0.0677   |
| 1 | 1 | 12| 0.0000   | 0.0677   |
|   |   |   |   |   |
|---|---|---|---|---|
| 5 | 0 | 11 | 0.0000 | 0.0677 |
| 5 | 1 | 11 | 0.0000 | 0.0679 |
| 2 | 0 | 12 | 0.0000 | 0.0682 |
| 8 | 2 | 9  | 0.0000 | 0.0685 |
| 7 | 6 | 8  | 0.0000 | 0.0685 |
| 7 | 0 | 10 | 0.0000 | 0.0685 |
| 2 | 1 | 12 | 0.0000 | 0.0685 |
| 7 | 1 | 10 | 0.0000 | 0.0687 |
| 5 | 5 | 10 | 0.0000 | 0.0687 |
| 5 | 2 | 11 | 0.0000 | 0.0687 |
| 2 | 2 | 12 | 0.0000 | 0.0692 |
| 6 | 4 | 10 | 0.0000 | 0.0692 |
| 3 | 0 | 12 | 0.0000 | 0.0695 |
| 7 | 2 | 10 | 0.0000 | 0.0695 |
| 8 | 3 | 9  | 0.0000 | 0.0698 |
| 3 | 1 | 12 | 0.0000 | 0.0698 |
| 7 | 5 | 9  | 0.0000 | 0.0700 |
| 5 | 3 | 11 | 0.0000 | 0.0700 |
| 6 | 0 | 11 | 0.0000 | 0.0705 |
| 3 | 2 | 12 | 0.0000 | 0.0705 |
| 7 | 3 | 10 | 0.0000 | 0.0708 |
| 6 | 1 | 11 | 0.0000 | 0.0708 |
| 4 | 0 | 12 | 0.0000 | 0.0713 |
| 8 | 4 | 9  | 0.0000 | 0.0715 |
| 4 | 1 | 12 | 0.0000 | 0.0715 |
| 6 | 5 | 10 | 0.0000 | 0.0715 |
| 6 | 2 | 11 | 0.0000 | 0.0715 |
| 9 | 0 | 9  | 0.0000 | 0.0718 |
| 7 | 7 | 8  | 0.0000 | 0.0718 |
| 3 | 3 | 12 | 0.0000 | 0.0718 |
| 5 | 4 | 11 | 0.0000 | 0.0718 |
| 8 | 6 | 8  | 0.0000 | 0.0723 |
| 4 | 2 | 12 | 0.0000 | 0.0723 |
| 8 | 0 | 10 | 0.0000 | 0.0723 |
| 8 | 1 | 10 | 0.0000 | 0.0725 |
| 7 | 4 | 10 | 0.0000 | 0.0725 |
| 9 | 2 | 9  | 0.0000 | 0.0728 |
| 7 | 6 | 9  | 0.0000 | 0.0728 |
| 6 | 3 | 11 | 0.0000 | 0.0728 |
| 8 | 2 | 10 | 0.0000 | 0.0733 |
| 4 | 3 | 12 | 0.0000 | 0.0735 |
| 5 | 0 | 12 | 0.0000 | 0.0735 |

endf
Figure S5. An enlarged and fully indexed SAXS pattern for the LLC FK σ phase obtained on quenching a sample comprising 58.7 wt% C₁₆E₂₀ from 70 °C to 25 °C and isothermally annealing it at 25 °C for 50 min. The complete assignment with indices for observed reflections are tabulated in Table S1 (see Page S14). Inset: 2D scattering pattern which was azimuthally integrated to give the 1D plot.
Table S1. List of the observed and calculated peak positions for the Frank-Kasper σ phase formed by quenching an aqueous LLC with 58.7 wt% C₁₆E₂₀ from 70 °C to 25 °C and annealing at 25 °C for 50 min. The corresponding tetragonal space group symmetry is \( P4_{2}/mnm \) (#136) and unit cell parameters are \( a = 28.37 \text{ nm} \) and \( c = 14.89 \text{ nm} \) \((c/a = 0.525)\). For a tetragonal lattice, the scattering wavevector modulus is given by:

\[
q^2 = (2\pi)^2 \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)
\]

| Miller indices | \(q_{\text{calc}} \text{ (Å}^{-1}\) | \(q_{\text{obs}} \text{ (Å}^{-1}\) | \(\% \text{ Residual} \) |
|----------------|---------------------------------|---------------------------------|----------------------------|
| (h k l)        | \(q_{\text{calc}} \text{ (Å}^{-1}\) | \(q_{\text{obs}} \text{ (Å}^{-1}\) | \(\Delta q/q_{\text{calc}} \times 100 \) |
| 3 1 0          | 0.0700                          | 0.0704                          | -0.52                      |
| 2 2 1          | 0.0755                          | 0.0760                          | -0.62                      |
| 3 0 1          | 0.0787                          | 0.0788                          | -0.11                      |
| 3 2 0          | 0.0799                          | 0.0803                          | -0.56                      |
| 3 1 1          | 0.0818                          | 0.0820                          | -0.28                      |
| 0 0 2          | 0.0844                          | 0.0844                          | 0.00                       |
| 4 0 0          | 0.0886                          | 0.0870                          | 1.79                       |
| 1 1 2          | 0.0900                          | 0.0885                          | 1.69                       |
| 3 2 1          | 0.0903                          | 0.0885                          | 2.01                       |
| 4 1 0          | 0.0913                          | 0.0918                          | -0.53                      |
| 3 3 0          | 0.0940                          | 0.0945                          | -0.57                      |
| 2 0 2          | 0.0953                          | 0.0952                          | 0.12                       |
| 2 1 2          | 0.0979                          | 0.0978                          | 0.06                       |
| 4 1 1          | 0.1006                          | 0.1010                          | -0.40                      |
| 3 3 1          | 0.1030                          | 0.1034                          | -0.38                      |
| 2 2 2          | 0.1051                          | 0.1046                          | 0.48                       |
| 4 2 1          | 0.1077                          | 0.1077                          | -0.04                      |
| 3 1 2          | 0.1097                          | 0.1096                          | 0.07                       |
| 5 1 0          | 0.1129                          | 0.1132                          | -0.24                      |
| 3 2 2          | 0.1162                          | 0.1161                          | 0.08                       |
| 4 3 1          | 0.1185                          | 0.1187                          | -0.16                      |
| 5 0 1          | 0.1185                          | 0.1187                          | -0.16                      |
| 5 1 1          | 0.1206                          | 0.1209                          | -0.28                      |
| 5 2 1          | 0.1265                          | 0.1269                          | -0.31                      |
| 4 3 2          | 0.1392                          | 0.1394                          | -0.12                      |
| 5 1 2          | 0.1410                          | 0.1411                          | -0.08                      |
| 2 2 3          | 0.1413                          | 0.1411                          | 0.11                       |
| 6 1 1          | 0.1412                          | 0.1411                          | 0.05                       |
| 3 1 3          | 0.1447                          | 0.1447                          | -0.01                      |
| 5 2 2          | 0.1461                          | 0.1466                          | -0.34                      |
| 6 2 1          | 0.1463                          | 0.1466                          | -0.21                      |
| 5 4 1          | 0.1480                          | 0.1478                          | 0.11                       |
| 6 3 0          | 0.1486                          | -                               | -                          |
|   |   |   |   |   |
|---|---|---|---|---|
| 5 | 3 | 2 | 0.1543 | 0.1545  | -0.15 |
| 6 | 3 | 1 | 0.1544 | 0.1545  | -0.04 |
| 4 | 1 | 3 | 0.1561 | 0.1565  | -0.26 |
| 7 | 1 | 0 | 0.1566 | 0.1565  | 0.07  |
| 5 | 5 | 0 | 0.1566 | 0.1565  | 0.07  |
| 6 | 0 | 2 | 0.1574 | 0.1577  | -0.18 |
| 3 | 3 | 3 | 0.1577 | 0.1577  | -0.03 |
| 6 | 1 | 2 | 0.1590 | 0.1593  | -0.21 |
| 7 | 2 | 0 | 0.1612 | 0.1620  | -0.47 |
| 7 | 1 | 1 | 0.1622 | 0.1625  | -0.19 |
| 5 | 5 | 1 | 0.1622 | 0.1625  | -0.19 |
| 6 | 2 | 2 | 0.1635 | 0.1630  | 0.33  |
| 5 | 4 | 2 | 0.1650 | 0.1654  | -0.23 |
| 6 | 4 | 1 | 0.1652 | 0.1654  | -0.13 |
| 7 | 2 | 1 | 0.1667 | 0.1673  | -0.38 |
| 0 | 0 | 4 | 0.1688 | 0.1685  | 0.18  |
| 7 | 3 | 0 | 0.1687 | 0.1685  | 0.10  |
| 5 | 1 | 3 | 0.1696 | -  | - |
| 2 | 0 | 4 | 0.1745 | 0.1740  | 0.30  |
| 2 | 1 | 4 | 0.1759 | 0.1759  | 0.01  |
| 8 | 1 | 0 | 0.1786 | 0.1791  | -0.30 |
| 7 | 4 | 0 | 0.1786 | 0.1791  | -0.30 |
| 3 | 1 | 4 | 0.1828 | 0.1827  | 0.03  |
| 8 | 2 | 0 | 0.1826 | 0.1827  | -0.04 |
| 6 | 6 | 0 | 0.1879 | 0.1884  | -0.25 |
| 8 | 2 | 1 | 0.1874 | 0.1884  | -0.51 |
| 6 | 5 | 2 | 0.1925 | 0.1918  | 0.35  |
| 6 | 6 | 1 | 0.1926 | 0.1918  | 0.42  |
| 7 | 5 | 0 | 0.1905 | 0.1918  | -0.67 |
| 9 | 2 | 2 | 0.2209 | 0.2218  | -0.39 |
| 7 | 6 | 2 | 0.2209 | 0.2218  | -0.39 |
| 3 | 1 | 5 | 0.2223 | -  | - |
| 8 | 2 | 3 | 0.2222 | -  | - |
| 9 | 4 | 1 | 0.2222 | -  | - |
| 9 | 3 | 2 | 0.2264 | 0.2266  | -0.08 |
| 6 | 6 | 3 | 0.2266 | 0.2266  | 0.00  |
| 10 | 1 | 1 | 0.2265 | 0.2266  | -0.03 |
| 4 | 1 | 5 | 0.2299 | 0.2298  | 0.05  |
| 10 | 2 | 1 | 0.2298 | 0.2298  | -0.01 |
| 7 | 1 | 4 | 0.2303 | 0.2298  | 0.20  |
| 5 | 5 | 4 | 0.2303 | 0.2298  | 0.20  |
| 7 | 2 | 4 | 0.2334 | 0.2334  | 0.01  |
| 9 | 2 | 3 | 0.2403 | -  | - |

S17
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 7 | 6 | 3 | 0.2403 | - | - |
| 8 | 2 | 4 | 0.2487 | 0.2487 | 0.00 |
**SUPERFLIP** Input File for Charge-Flipping Electron Density Reconstruction of the aqueous LLC FK σ Phase formed at 58.7 wt% C$_{16}$E$_{20}$

The 1D-SAXS intensity $I(q)$ versus scattering wavevector $q$ profile for the σ phase obtained upon quenching a sample comprising 58.7 wt% C$_{16}$E$_{20}$ from 70 °C to 25 °C followed by annealing at 25 °C for 2 days was scaled by multiplying the $q$ values by 3, to expedite the calculation and rendering of the electron density map with available computing resources. Le Bail refinement of the scaled SAXS data with a 10th order polynomial fit for the X–ray background using the *JANA2006* crystallographic computing software package enabled extraction of the static structure factor intensities for each peak in the pattern in the range $q = 0.0825–0.1300$ Å$^{-1}$ (in the unscaled pattern), the Miller indices of which were assigned using the $P4_2/mnm$ space group symmetry with a scaled cubic unit cell parameter $a = 9.4577$ nm and $c = 4.9837$ nm. The structure factor intensities associated with each indexed SAXS peak are given in the text file below. Application of the *SUPERFLIP* charge–flipping algorithm using the input file below in 2000 trials yielded 357 converged electron density maps with excellent figures of merit (fm) < 3, starting from randomized initial conditions. The 357 converged maps were averaged and rendered using the VESTA software package to yield the 90% isosurface electron density maps shown in Figure 4A.

```
**************start_file******************************
title B11_1_sigma_Superflip
perform CF
outputfile "B11_1_sigma_Superflip_Try13.xplor"
outputformat xplor
dimension 3
cell  94.5767  94.5767  49.8370  90.00  90.00  90.00
spacegroup P42/mnm
centro yes
centers  0.000000  0.000000  0.000000
endcenters
symmetry
    x1    x2    x3
```

S19
-x1   -x2   x3
-x2+1/2   x1+1/2   x3+1/2
x2+1/2   -x1+1/2   x3+1/2
-x1+1/2   x2+1/2   -x3+1/2
x1+1/2   -x2+1/2   -x3+1/2
x2   x1   -x3
-x2   -x1   -x3
-x1   -x2   -x3
x1   x2   -x3
x2+1/2   -x1+1/2   -x3+1/2
-x2+1/2   x1+1/2   -x3+1/2
x1+1/2   -x2+1/2   x3+1/2
-x1+1/2   x2+1/2   x3+1/2
-x2   -x1   x3
x2   x1   x3
endsymmetry

composition C13440 H27360 O5040

# Keywords for charge flipping
repeatmode 2000 sumgood
bestdensities 1 symmetry
polish yes
maxcycles 1000
delta AUTO
weakratio 0.000
Biso 0.000
randomseed AUTO
searchsymmetry average
derivesymmetry no
# End of keywords for charge flipping

# EDMA-specific keywords
inputfile B11_1_sigma_Superflip.m81
outputbase B11_1_sigma_Superflip
m40forjana yes
writem40 B11_1_sigma_Superflip_tmp.m40
maxima all
fullcell no
scale fractional
plimit 0.3000 sigma
numberofatoms composition
centerofcharge yes
chlimit 0.2500
chlimlist 0.0375 relative
# End of EDMA-specific keywords

electrons 0.0000
dataitemwidths 4 15 15
dataformat intensity fwhm
fbegin
  2   2   0       1.7759       0.0153
  2   1   1       0.6081       0.0160
| 3 | 1 | 0 | 50.7322 | 0.0175 |
| 2 | 2 | 1 | 27.6748 | 0.0191 |
| 3 | 0 | 1 | 24.8614 | 0.0201 |
| 3 | 2 | 0 | 42.5197 | 0.0204 |
| 3 | 1 | 1 | 243.3518 | 0.0210 |
| 0 | 0 | 2 | 7667.8828 | 0.0217 |
| 4 | 0 | 0 | 25.9448 | 0.0230 |
| 1 | 1 | 2 | 214.5956 | 0.0233 |
| 3 | 2 | 1 | 183.7736 | 0.0235 |
| 4 | 1 | 0 | 8860.2031 | 0.0238 |
| 3 | 3 | 0 | 10000.0010 | 0.0245 |
| 2 | 0 | 2 | 7899.1997 | 0.0248 |
| 2 | 1 | 2 | 5575.9712 | 0.0256 |
| 4 | 2 | 0 | 38.2897 | 0.0260 |
| 4 | 1 | 1 | 8456.5996 | 0.0264 |
| 3 | 3 | 1 | 9312.3828 | 0.0271 |
| 2 | 2 | 2 | 2624.2578 | 0.0277 |
| 4 | 2 | 1 | 78.2934 | 0.0285 |
| 3 | 1 | 2 | 948.7307 | 0.0290 |
| 4 | 3 | 0 | 33.5163 | 0.0294 |
| 5 | 1 | 0 | 72.1135 | 0.0300 |
| 3 | 2 | 2 | 157.2879 | 0.0309 |
| 4 | 3 | 1 | 138.2182 | 0.0316 |
| 5 | 0 | 1 | 138.2182 | 0.0316 |
| 5 | 2 | 0 | 94.8668 | 0.0318 |
| 5 | 1 | 1 | 305.8773 | 0.0322 |
| 4 | 0 | 2 | 240.2753 | 0.0326 |

endf
Figure S6. 1D-SAXS intensity profiles obtained every 2 °C, on heating the aqueous LLC with 58.7 wt% C_{16}E_{20} heated from 25 °C to 70 °C. Samples were equilibrated at each temperature for at least 5 min. A LLC BCC phase nucleates at 37 °C and it completely transforms to H_{I} at 60 °C. The σ phase is notably absent on heating, and it can only be accessed upon cooling the H_{I} phase.
Figure S7. Time-resolved 1D-SAXS patterns obtained upon quenching LLC sample with 58.7 wt% C₁₆E₂₀ from 70 °C to 50 °C. H₁ rapidly transforms into a BCC morphology on quenching, the latter of which remains stable for up to 10 h after annealing at 50 °C with no signs of either FK A15 or σ phase nucleation. Changes in the peak intensities with time upon extended monitoring suggest changes in the average micelle aggregation number ($N_{agg}$) within the BCC phase.
Figure S8. 1D-SAXS patterns obtained upon quenching an LLC with 58.7 wt% C_{16}E_{20} from 70 °C to 40 °C after various 40 °C isothermal annealing times. Prolonged annealing at 40 °C leads to decreased intensities of the “forest” or peaks which correspond to σ phase, and the peaks corresponding to BCC remain intense even after a long annealing time.
Figure S9. SAXS analyses of an aqueous LLC sample comprising 58.7 wt% $C_{16}E$ quenched from 70 °C to 0 °C demonstrate the lack of nucleation of either FK $\sigma$ or A15 phases upon annealing at 0 °C for > 3 days. The Miller indices corresponding to the observed peaks are marked on the plot.
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