Supporting Information for:

Discovery of a Tetracontinuous, Aqueous Lyotropic Network Phase with Unusual 3D-Hexagonal Symmetry

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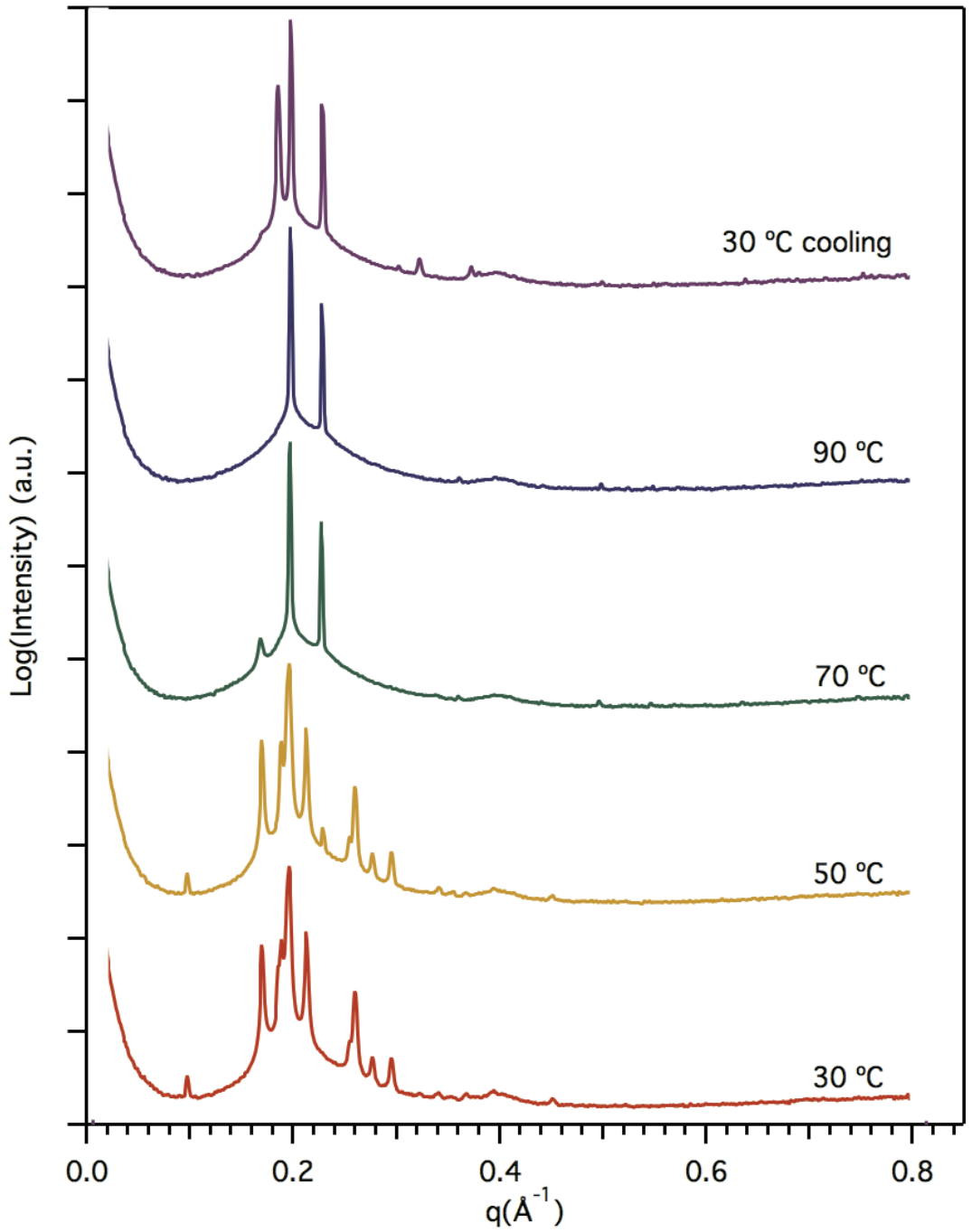

Fig. S1. Azimuthally-integrated synchrotron SAXS patterns for aqueous LLCs derived from 57.5 wt% **Na-94** in H_2O between T = 30-90 °C. A thermoreversible order-to-order transition is observed between 50-70 °C from the H_I^{193} to G_I. The kinetics of this transition are slow, as evidenced by only partial phase reversion upon cooling to 30 °C and annealing for 5 min.

Table S1. Table of positions of the observed reflections (q_{obs}(Å^{-1}) and $2\theta_{obs}$(°)) from cell refinement of **Na-94** 57.5 wt% at 40 °C to *P6₃/mcm* symmetry and lattice constants of $a = b =$ 7.37 nm and c = 6.63 nm using the Jade 5 software package (Materials Data, Inc.), along with the angular residuals. For a three-dimensional hexagonal lattice, $q^2 = (4/3)(h^2 + k^2 + hk) + (1/R^2)l^2$, where $R = c/a$.*(21)*

hkl	q_{obs} (Å^{-1})	$2\theta_{obs}$ (°)	$2\theta_{cal}$ (°)	Residual = $2\theta_{calc} - 2\theta_{obs}$ (°)
100	0.0989	0.927	0.927	0
110	0.1715	1.607	1.606	-0.001
002	0.1906	1.786	1.785	0
111	0.1963	1.839	1.837	-0.002
200	0.1977	1.853	1.854	0.001
102	0.2146	2.011	2.012	0.001
112	0.2564	2.403	2.401	-0.001
210	0.2619	2.454	2.453	-0.001
202	0.2749	2.576	2.574	-0.002
211	0.2786	2.611	2.611	0
300	0.2969	2.782	2.782	0
212	---	---	3.034	
113	0.3330	3.121	3.123	0.001
220	0.3430	3.214	3.212	-0.002
302	0.3527	3.305	3.306	0
221	---	---	3.334	
310	0.3564	3.34	3.343	0.004
311	0.3693	3.461	3.461	-0.001
004	---	---	3.571	
213	---	---	3.632	
222	---	---	3.675	
104	---	---	3.689	
400	0.3958	3.709	3.709	0
312	---	---	3.79	
114	---	---	3.916	
204	0.4293	4.023	4.024	0
320	0.4314	4.043	4.042	0
402	---	---	4.117	
321	---	---	4.14	
223	---	---	4.183	
410	0.4535	4.25	4.25	0
313	---	---	4.284	

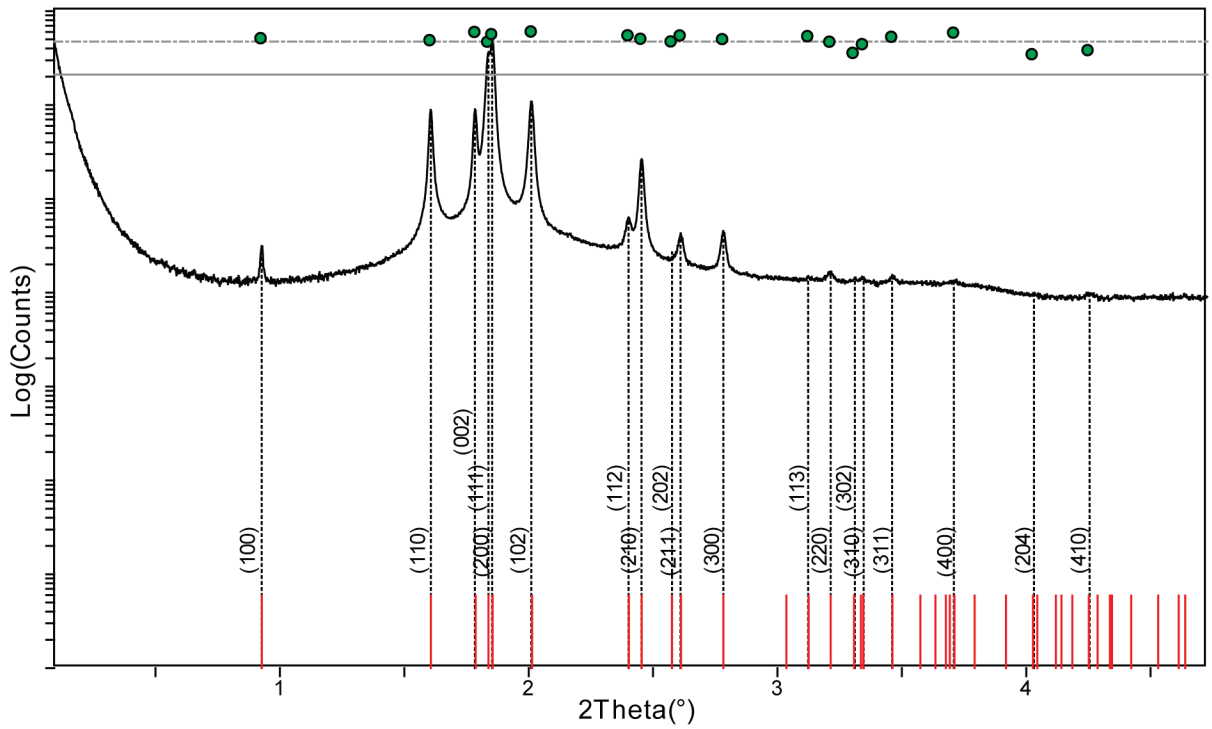

Fig. S2. Azimuthally integrated X-ray scattering pattern for 57.5 wt% **Na-94** in H_2O at 40 °C with observed reflections (---), calculated reflection positions (-), and (*hkl*) indices for a unit cell with $P6_3/mcm$ symmetry and lattice constants of $a = b = 7.37$ nm and $c = 6.63$ nm. Fitting was performed using the cell refinement function in Jade 5 software package (Materials Data, Inc.).

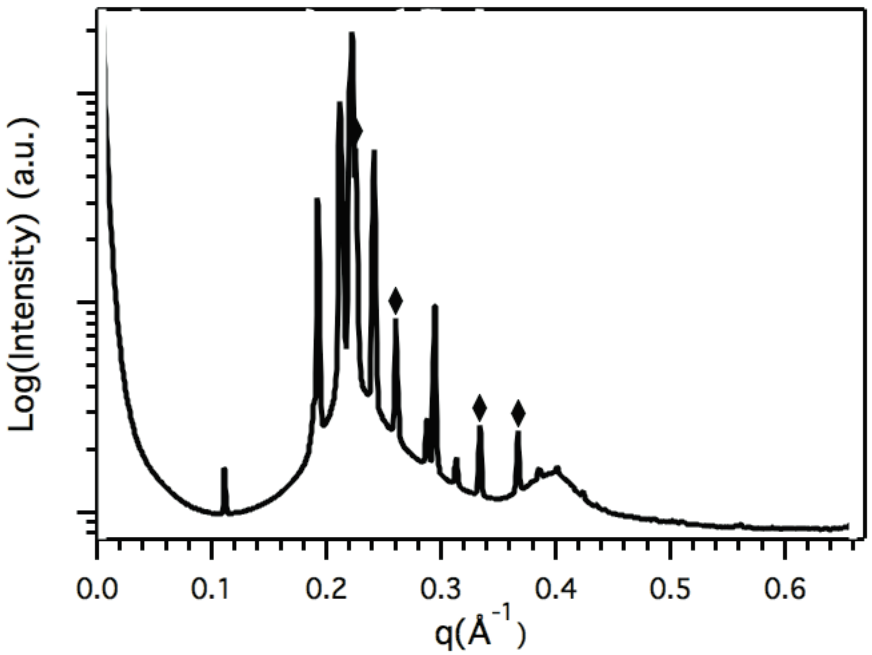

Fig. S3. Azimuthally-integrated X-ray scattering pattern for the aqueous LLC derived from 55.0 wt% **Na-74** in H_2O. Diamonds (♦) indicate the expected peak positions for the G_I phase that coexists with the H_I[193] phase.

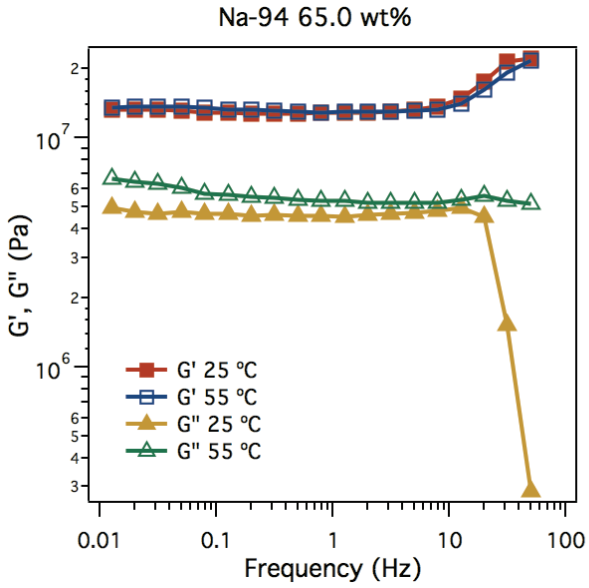

Fig. S4. Dynamic elastic storage (G') and loss (G") modulus as a function of shear frequency for the G_I-phase comprising 65.0 wt% **Na-94** in H_2O at 25 and 55 °C.

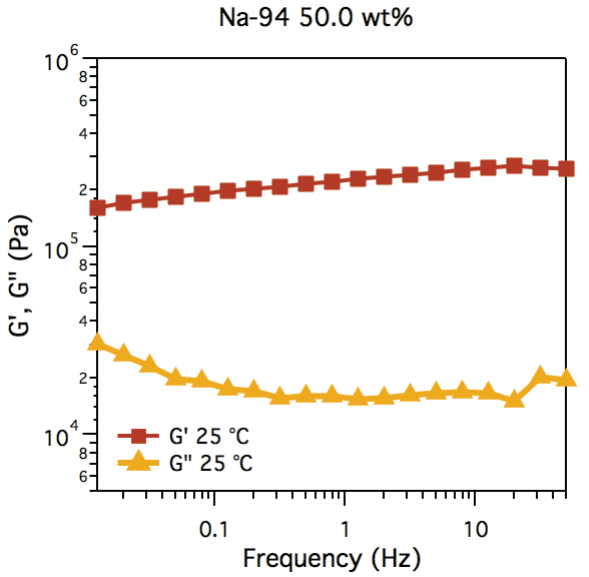

Fig. S5. Dynamic elastic storage (G') and loss (G") modulus as a function of shear frequency for the C_I-phase comprising 50.0 wt% **Na-94** in H_2O at 25 °C. Attempts to obtain rheological data for this sample at 55 °C failed due to sample dehydration at elevated temperatures.

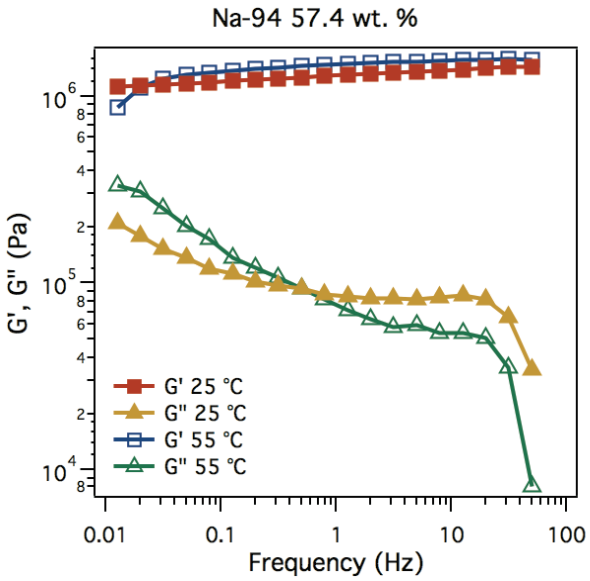

Fig. S6. Dynamic elastic storage (G') and loss (G") modulus as a function of shear frequency for the H_I^{193}-phase comprising 57.5 wt% **Na-94** in H_2O at 25 and 55 °C.

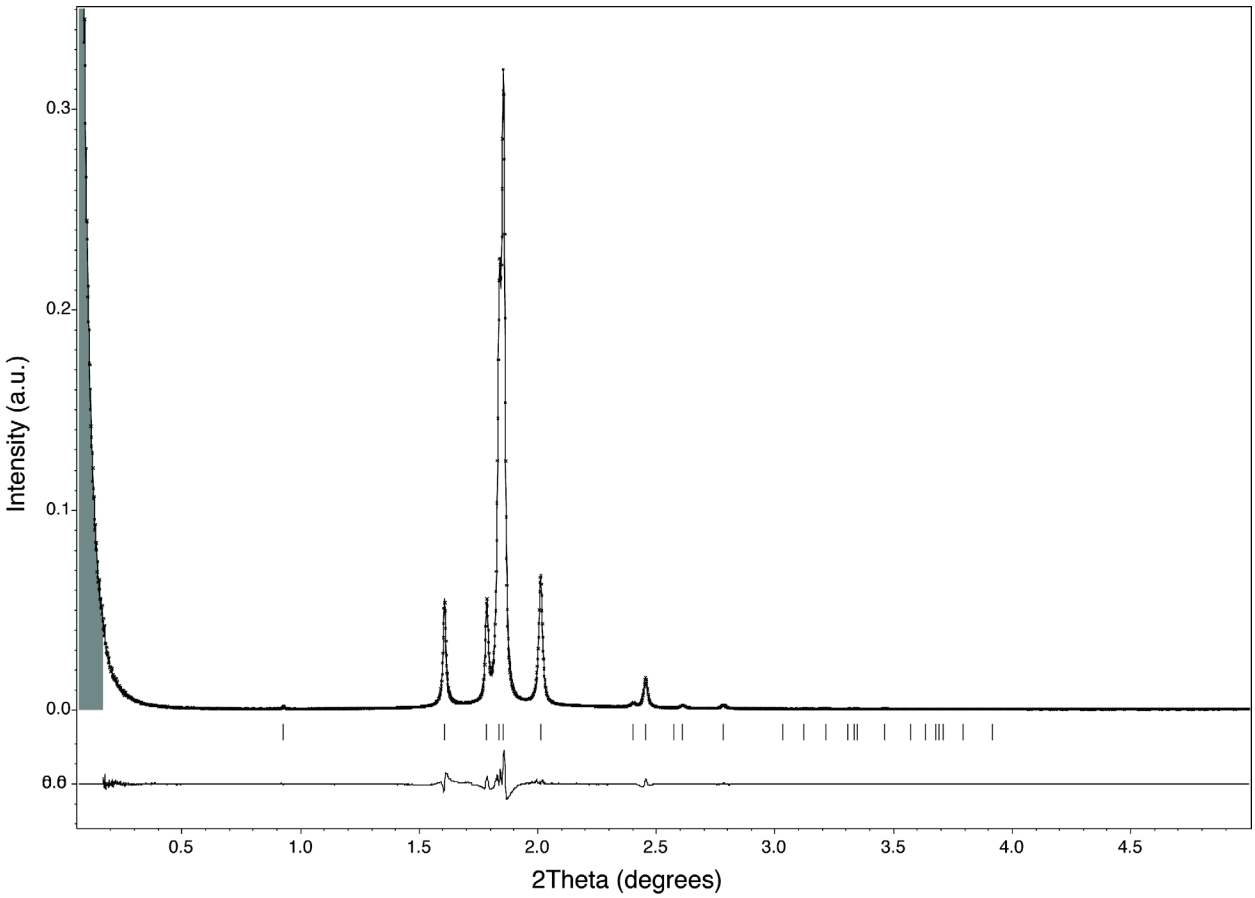

Fig. S7. Azimuthally-integrated X-ray scattering pattern for 57.5 wt% **Na-94** in H_2O at 40 °C overlaid with a simulated pattern from Rietveld refinement in *JANA2006*. Calculated peak positions and the fit residuals are displayed below the diffractogram. This fit assumes the $P6_3/mcm$ symmetry using lattice parameters $a = b = 7.34$ nm, $c = 6.60$ nm.

Table S2. List of structure factor intensities and peak full width at half maximum associated with each allowed reflection (*hkl*), derived from the fit shown in Fig. S7, as extracted by *JANA2006*.

(*hkl*)	Intensity	FWHM
1 0 0	4.4644	0.0074
1 1 0	1133.2637	0.0134
0 0 2	4084.4890	0.0156
1 1 1	3033.6406	0.0163
2 0 0	10000.0010	0.0165
1 0 2	1580.7277	0.0186
1 1 2	85.2785	0.0240
2 1 0	637.9702	0.0247
2 0 2	16.0249	0.0264
2 1 1	42.4498	0.0270
3 0 0	206.6376	0.0295
1 1 3	0.9880	0.0344
2 2 0	43.7681	0.0358
3 0 2	13.2740	0.0372
2 2 1	8.7943	0.0376
3 1 0	14.7810	0.0377
3 1 1	6.3111	0.0395
0 0 4	38.7469	0.0411
2 1 3	14.6813	0.0420
4 -2 2	17.3565	0.0427
1 0 4	18.1022	0.0429
4 0 0	47.1941	0.0432
3 1 2	0.1971	0.0444
1 1 4	52.9179	0.0463

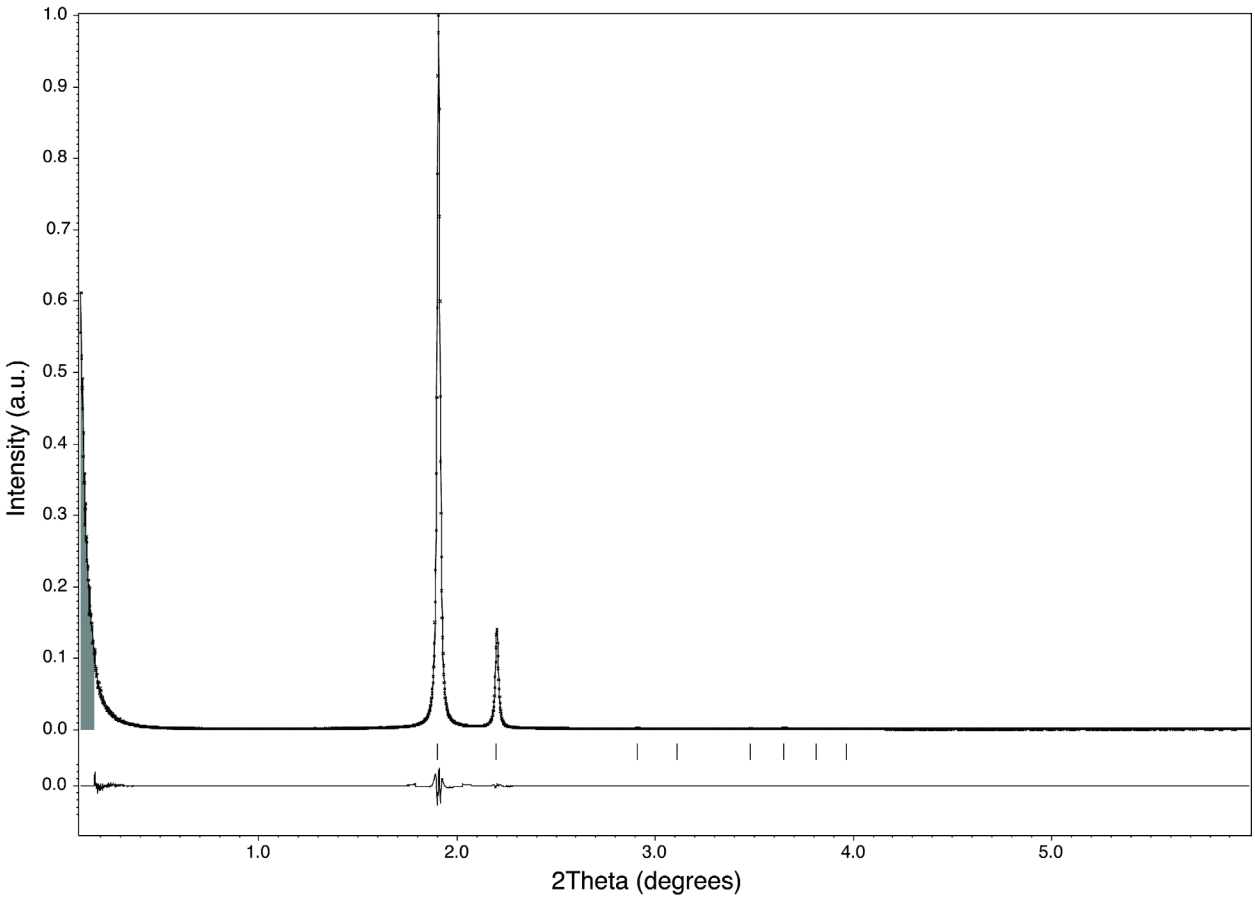

Fig. S8. Azimuthally-integrated X-ray scattering pattern for 62.5 wt% **Na-94** in H_2O at 40 °C overlaid with a simulated pattern from Rietveld refinement in *JANA2006*. Calculated peak positions and fit residual are displayed below the diffractogram. The fit was performed using *JANA2006* assuming $Ia\bar{3}d$ symmetry and resulting lattice parameters are $a = b = c = 7.53$ nm.

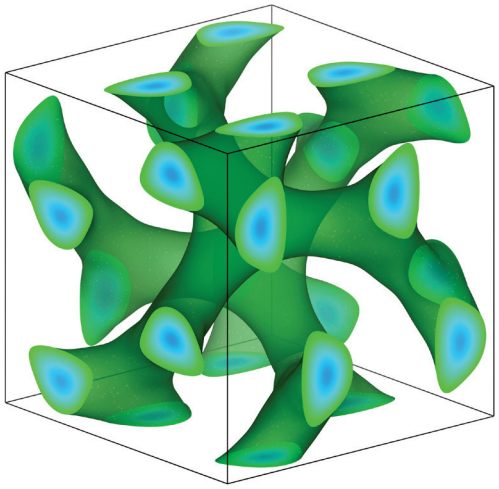

Fig. S9. Electron density reconstruction for G_I-phase comprising 62.5 wt% **Na-94** in H_2O at 40 °C using the Superflip charge flipping algorithm, derived from the fit shown in Fig. S8 with the lattice parameters $a = b = c = 7.53$ nm. This reconstruction serves to validate our use of the *SUPERFLIP* charge flipping algorithm for the reconstruction of the electron density maps for LLCs derived from gemini surfactants.

Figure S10. *SUPERFLIP* Text File Input for the generation of the electron density contrast map for the H_I^{193} phase shown in Fig. 3A is given below this line. *SUPERFLIP* implements a computer algorithm described in references 19 and 26 of the main article to generate an electron density reconstruction from the SAXS data by: (1) randomly assigning the initial phases associated with each observed reflection and generating a structure, (2) transforming the resulting structure into reciprocal space for comparison with the experimentally observed X-ray data, and (3) iteratively permuting the phases and comparing the results to the observed X-ray data, until a user defined convergence criterion is attained.The figure of merit associated with this electron density reconstruction was fm = 15, which is considered an excellent fit.

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perform CF
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centro yes
centers
 0.000000  0.000000  0.000000
endcenters

symmetry
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       -x2    x1-x2        x3
  -x1+x2        -x1        x3
       -x1        -x2  x3+1/2
        x2  -x1+x2  x3+1/2
    x1-x2        x1   x3+1/2
        x2        x1 - x3+1/2
    x1-x2       - x2 -x3+1/2
       -x1 -x1+x2 -x3+1/2
       -x2        -x1       -x3
  -x1+x2         x2       -x3
        x1    x1-x2       -x3
       -x1        -x2       -x3
        x2  -x1+x2       -x3
    x1-x2         x1       -x3
        x1         x2 -x3+1/2
       -x2    x1-x2 -x3+1/2
  -x1+x2        -x1 -x3+1/2
       -x2        -x1   x3+1/2
  -x1+x2         x2   x3+1/2
        x1    x1-x2   x3+1/2
        x2         x1         x3
```

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      -x1   -x1+x2         x3

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voxel auto
maxcycles 200000
delta AUTO
weakratio 0.000
Biso   0.000
randomseed AUTO
searchsymmetry average
derivesymmetry no
# End of keywords for charge flipping

# EDMA-specific keywords
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fullcell no
scale fractional
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numberofatoms composition
centerofcharge yes
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chlimlist    0.1884 relative
# End of EDMA-specific keywords

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dataitemwidths 4 15 15
dataformat intensity fwhm
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2  -1   0     1133.2637         0.0134
0   0   2     4084.4890         0.0156
2  -1   1     3033.6406         0.0163
2   0   0    10000.0010         0.0165
1   0   2     1580.7277         0.0186
2  -1   2       85.2785         0.0240
```

3	-1	0	637.9702	0.0247
2	0	2	16.0249	0.0264
3	-1	1	42.4498	0.0270
3	0	0	206.6376	0.0295
2	-1	3	0.9080	0.0344
4	-2	0	43.7681	0.0358
3	0	2	13.2740	0.0372
4	-2	1	8.7943	0.0376
4	-1	0	14.7810	0.0377
4	-1	1	6.3111	0.0395
0	0	4	38.7469	0.0411
3	-1	3	14.6813	0.0420
4	-2	2	17.3565	0.0427
1	0	4	18.1022	0.0429
4	0	0	47.1941	0.0432
4	-1	2	0.1971	0.0444
2	-1	4	52.9179	0.0463

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