Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Designer lyotropic liquid-crystalline systems containing amino acid ionic liquids as self-organization media of amphiphiles

Takahiro Ichikawa,[a,b] Kanae Fujimura,[a,b] Masafumi Yoshio,[c] Takashi Kato[c] and Hiroyuki Ohno*[a,b]

1. General Procedures and Materials

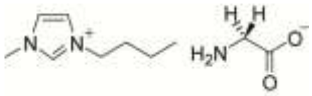
General Procedures. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-ECX400 at 400 and 100 MHz in DMSO, respectively. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to $(CH_3)_4Si$ (δ = 0.00) and DMSO (δ = 39.5) as internal standards, respectively. Elemental analyses were carried out on an Elementar Analytical vario EL3. The viscosity of amino acid ionic liquids was measured by a cone/plate viscometer (LVDV-1+, Brookfield). The thermal properties of amino acid ionic liquids were measured using a differential scanning calorimeter (DSC-6220, Seiko Instruments). The thermal properties of the liquid-crystalline mixtures were examined by a DSC using a Netzsch DSC204 *Phoenix*. The heating and cooling rates were 5 °C min^{-1}. A polarizing optical microscope Olympus BX51 equipped with a Linkam LK-600 hot stage was used for visual observation. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Rigaku RINT-2500 diffractometer with CuKα radiation. Two-dimensional small-angle X-ray scattering (2D SAXS) patterns of the materials were also recorded using an image plate detector (R-AXIS DS3C).

Materials. All chemical reagents and solvents were obtained from commercial sources and used without purification. All reactions were carried out under an argon atmosphere in anhydrous solvents.

2. Synthesis

Four types of amino acid ionic liquids, [bmim][X] (X = Gly, Ala, and Leu), were prepared through neutralization of 1-butyl-3-methylimidazolium hydroxide with corresponding natural amino acids according to the literature.[1] Amphiphile **1** was synthesized according to the literature.[2]

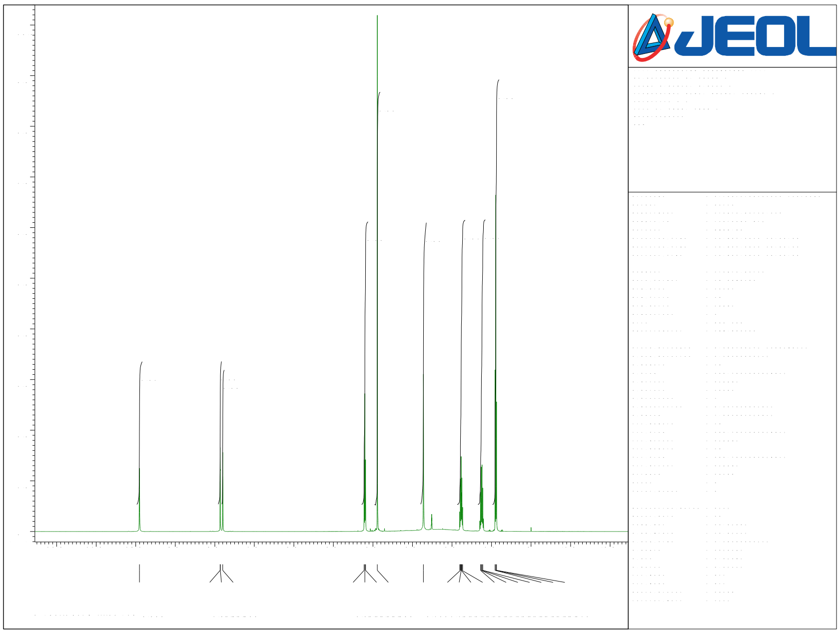
3. Characterization of Amino Acid Ionic Liquids [bmim][X]



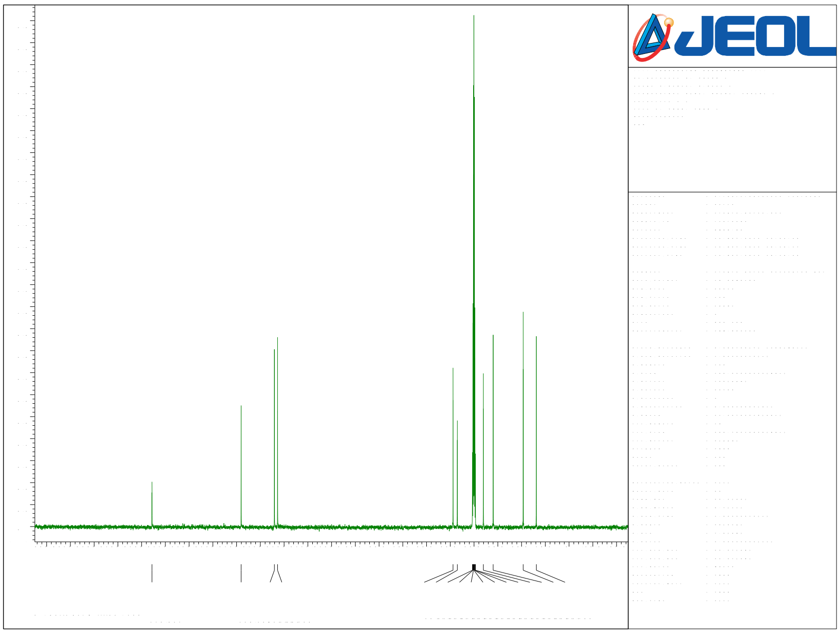
[bmim][Gly]

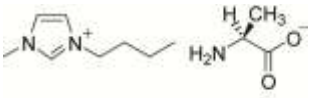
^{1}H-NMR (400MHz, DMSO, δ/ppm relative to TMS): 0.89 (3H, t, *J* = 4.6 Hz), 1.24 (2H, m), 1.76 (2H, m), 2.72 (2H, s), 3.89 (3H, s), 4.20 (2H, t, *J* = 7.0 Hz), 7.80 (1H, d, *J* = 1.8 Hz), 7.86 (1H, d, *J* = 2.0 Hz), 9.90 (1H, s), ^{13}C-NMR (100 MHz, DMSO): δ= 175.65, 138.10, 124.08, 122.76, 48.85, 47.05, 36.08, 31.95, 19.30, 13.79.

^{1}H-NMR Spetcrum



^{13}C-NMR Spetcrum

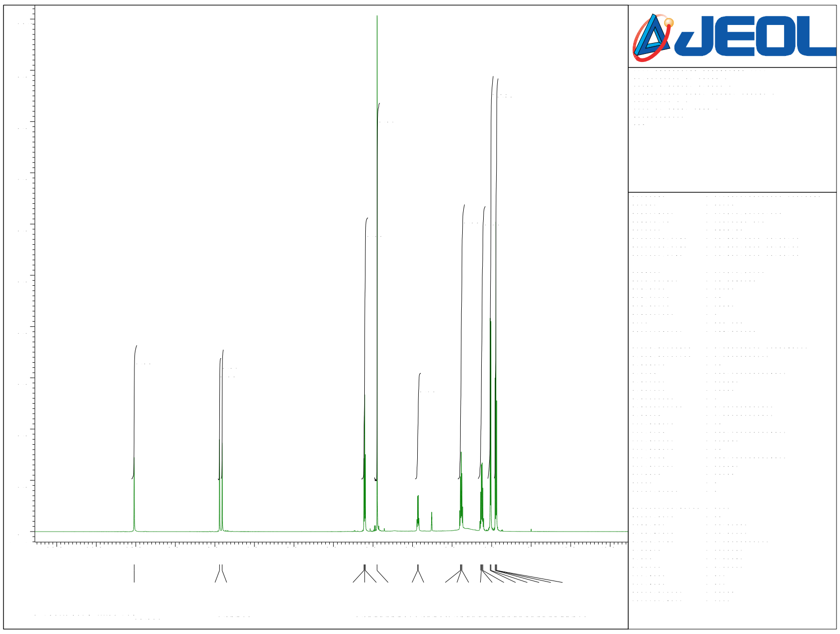




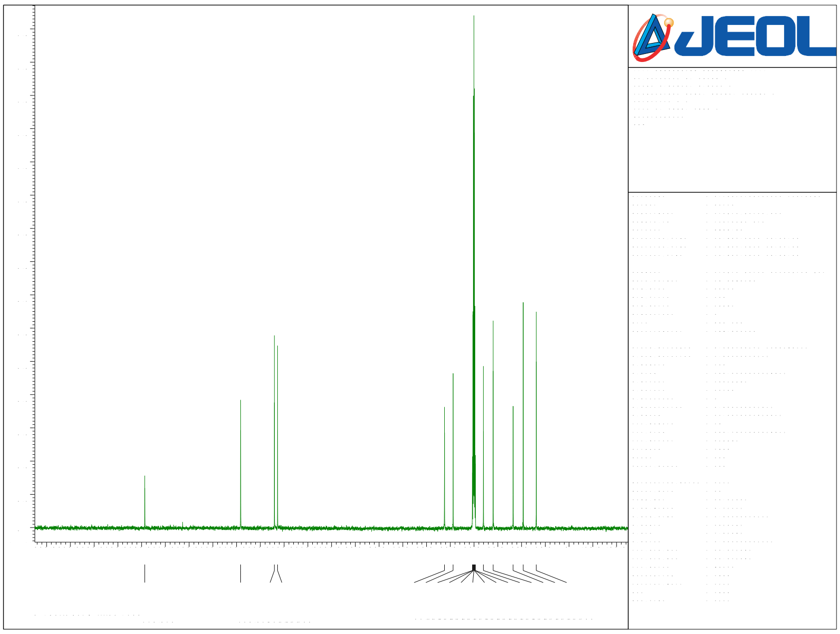
[bmim][Ala]

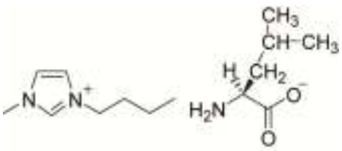
^{1}H-NMR (400MHz, DMSO, δ/ppm relative to TMS): 0.89 (3H, t, *J* = 7.4 Hz), 1.02 (3H, d, *J* = 6.8 Hz), 1.24 (2H, m), 1.77 (2H, m), 2.86 (1H, q, *J* = 6.8 Hz), 3.90 (3H, s), 4.21 (2H, t, *J* = 7.4 Hz), 7.82 (1H, s), 7.88 (1H, s), 10.04(1H, s). ^{13}C-NMR (100 MHz, DMSO): δ= 178.67, 138.32, 124.08, 122.76, 52.44, 48.82, 36.05, 31.97, 23.57, 19.31, 13.80.

^{1}H-NMR Spetcrum



^{13}C-NMR Spetcrum

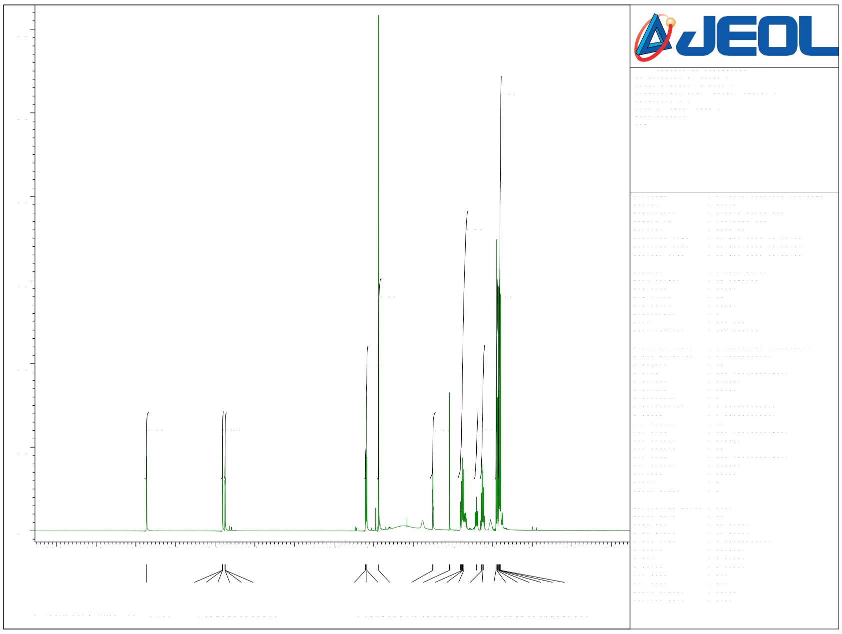




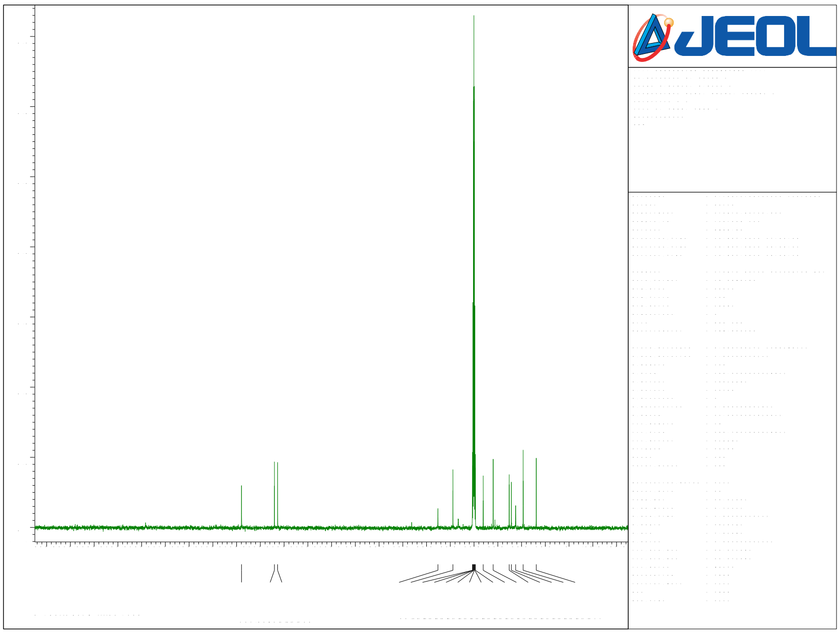
[bmim][Leu]

^{1}H-NMR (400MHz, DMSO, δ/ppm relative to TMS): 0.82 (6H, m), 0.90 (3H, t, *J* = 7.4 Hz), 1.25 (2H, m), 1.41 (1H, m), 1.75 (4H, m), 2.51 (1H, m), 3.88 (3H, s), 4.19 (2H, t, *J* = 7.4 Hz), 7.75 (1H, d, *J* = 0.8 Hz), 7.82 (1H, d, *J* = 1.0 Hz), 9.73 (1H, s). ^{13}C NMR (100 MHz, DMSO): δ= 178.33, 137.93, 124.08, 122.74, 55.22, 48.90, 36.15, 31.95, 25.21, 24.29, 22.48, 19.32, 1382.

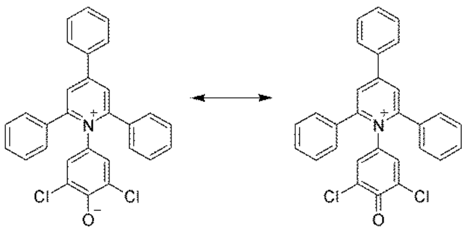
^{1}H-NMR Spetcrum



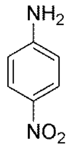
^{13}C-NMR Spetcrum



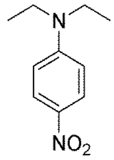
4. Measurment of Kamlet-Taft Parameters of [bmim][X]



Reichardt's dye (33)



4-nitroaniline



N,*N*-diethyl-4-nitroaniline

The Kamlet–Taft parameters of amino acid ionic liquids were examined as follows.

The solvatochromic dyes, (2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye 33) (from Fluka), 4-nitroaniline (from Tokyo Chemical Industries Co., Ltd), and *N*,*N*-diethyl-4-nitroaniline (from Kanto Chem.), were used as received.

To amino acid ionic liquid (0.2 mL), each dye was added as a concentrated dry dichloromethane solution. The dichloromethane was carefully removed by vacuum drying at 40 °C for 6 h. These dye solutions were placed into quartz cells with 1 mm light-path length. UV-vis absorption measurments were performed at 25 °C. By using the wavelength at the maximum absorption (λ_{max}), the α, β and π values were calculated by use of the following equations (1)-(4).

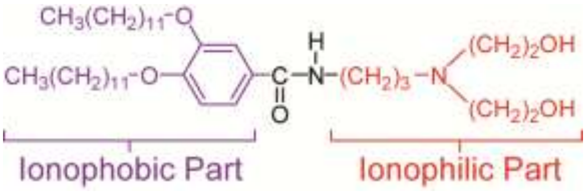
$$E_T(30) = 0.9986E_T(33) - 8.6878 \quad (1)$$

$$\pi^* = 8.649 - 0.314\,\upsilon\,(NN)_{max} \quad (2)$$

$$\beta = [1.035\upsilon\,(4N)_{max} - \upsilon\,(NN)_{max} + 2.64]/2.80 \quad (3)$$

$$\alpha = 0.0649E_T(30) - 0.72\pi^* - 2.03 \quad (4)$$

5. Thermotropic Liquid-Crystalline Property of Compound 1



1

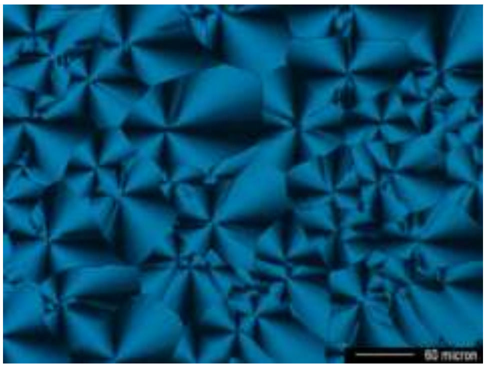


Fig. S1 Polarizing optical image of **1** in a Col$_h$ phase at 60 °C.

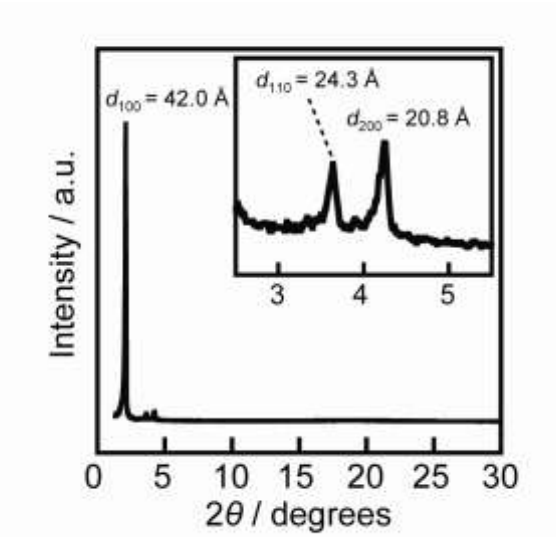


Fig. S2 Wide angle X-ray diffraction pattern of **1** in a Col$_h$ phase at 60 °C.

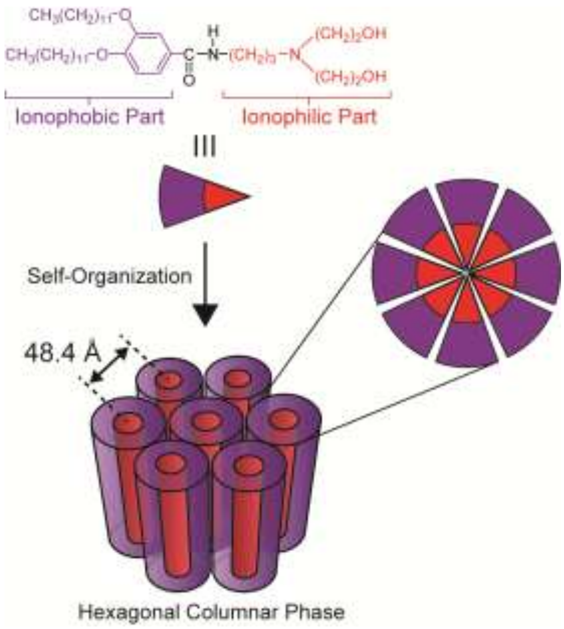
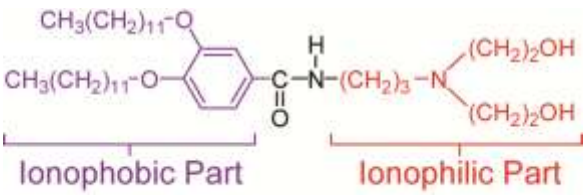


Fig. S3 Schematic illustration for the nanosegregated Col$_h$ structure formed by compound **1**.

6. Lyotropic Liquid-Crystalline Property of 1/[bmim][X] mixtures

1/[bmim][Gly] mixtures



1

[bmim][Gly]

Fig. S4 Polarizing optical images of **1**/[bmim][Gly] in an 8:2 molar ratio in a Cub_{bi} phase at 55 °C.

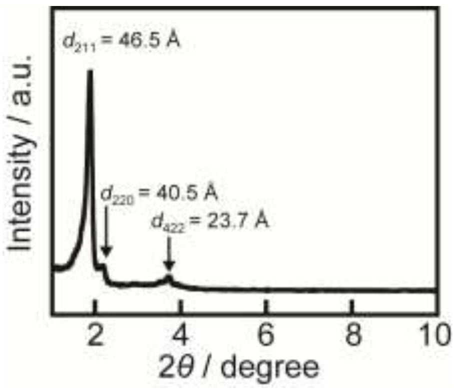


Fig. S5 Wide angle X-ray diffraction pattern of **1**/[bmim][Gly] in an 8:2 molar ratio in a Cub_{bi} phase

Fig. S6 Polarizing optical images of **1**/[bmim][Gly] in a 6:4 molar ratio in a Sm phase

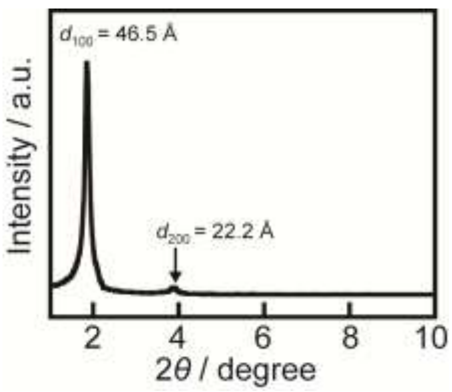
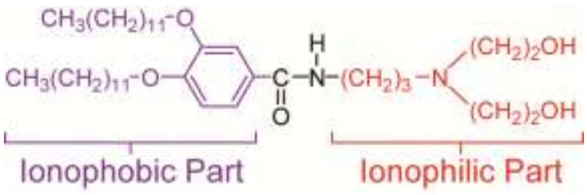


Fig. S7 Wide angle X-ray diffraction pattern of **1**/[bmim][Gly] in a 6:4 molar ratio in a Sm phase

1/[bmim][Ala] mixtures



1

[bmim][Ala]

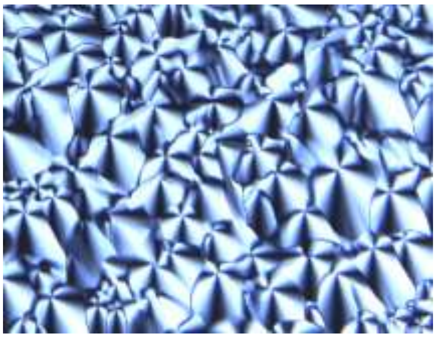


Fig. S8 Polarizing optical image of **1**/[bmim][Ala] in a 9:1 molar ratio at 65 °C in a Col_h phase.

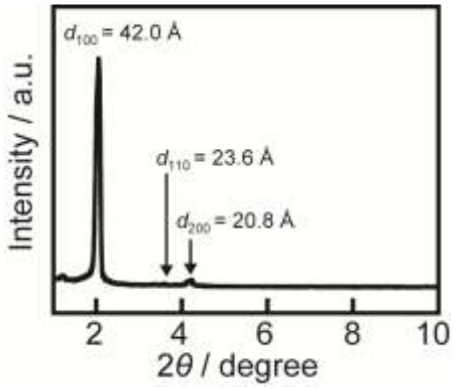


Fig. S9 Wide angle X-ray diffraction pattern of **1**/[bmim][Ala] in a 9:1 molar ratio at 65 °C in a Col_h phase

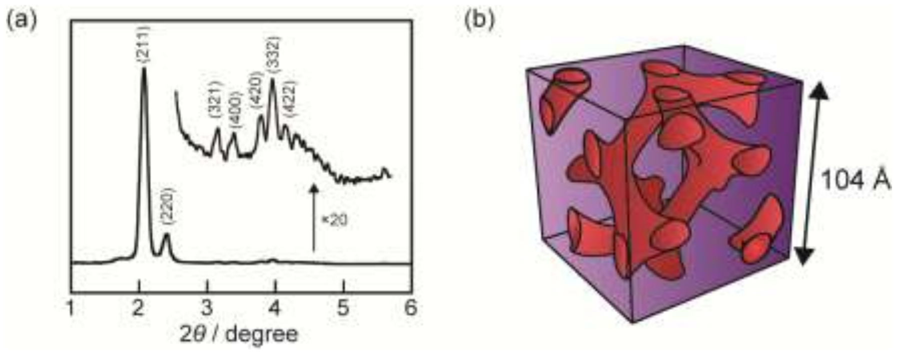


Fig. S10 (a) Small-angle X-ray scattering pattern of **1**/[bmim][Ala] in an 8:2 molar ratio at 55 °C in a Cub_{bu} phase. (b) Schematic illustration of the Cub_{bu} phase having *Ia*3*d* symmetry.

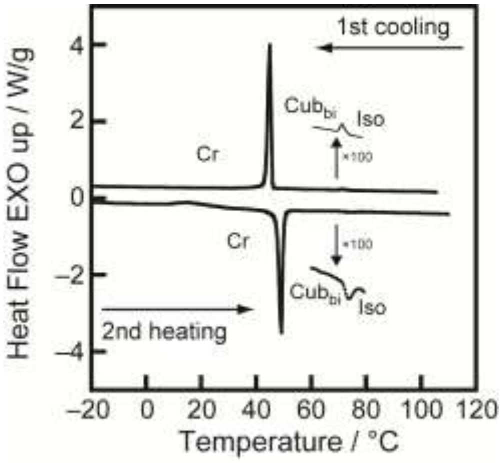


Fig. S11 DSC thermograms of **1**/[bmim][Ala] in an 8:2 molar ratio.

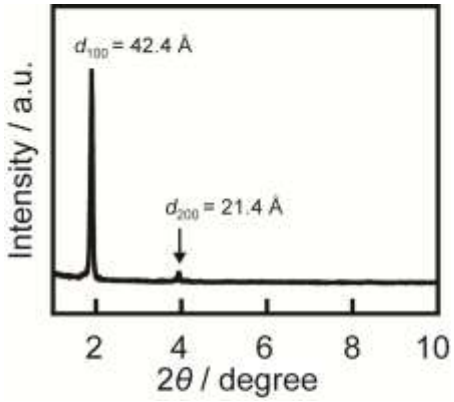
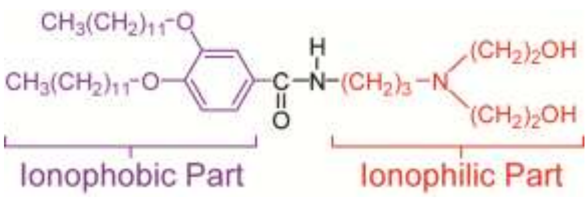
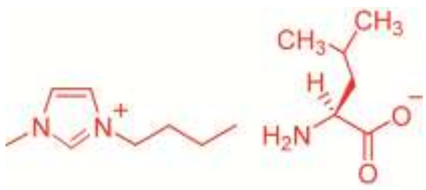


Fig. S12 Wide angle X-ray diffraction pattern of **1**/[bmim][Ala] in a 6:4 molar ratio at 60 °C in a Sm phase.

<u>**1**/[bmim][Leu] mixtures</u>



1



[bmim][Leu]

Fig. S13 Polarizing optical images of **1**/[bmim][Leu] in a 7:3 molar ratio at 50 °C in a Sm phase.

7. Comparison with Conventional Lyotropic Liquid-Crystalline Systems

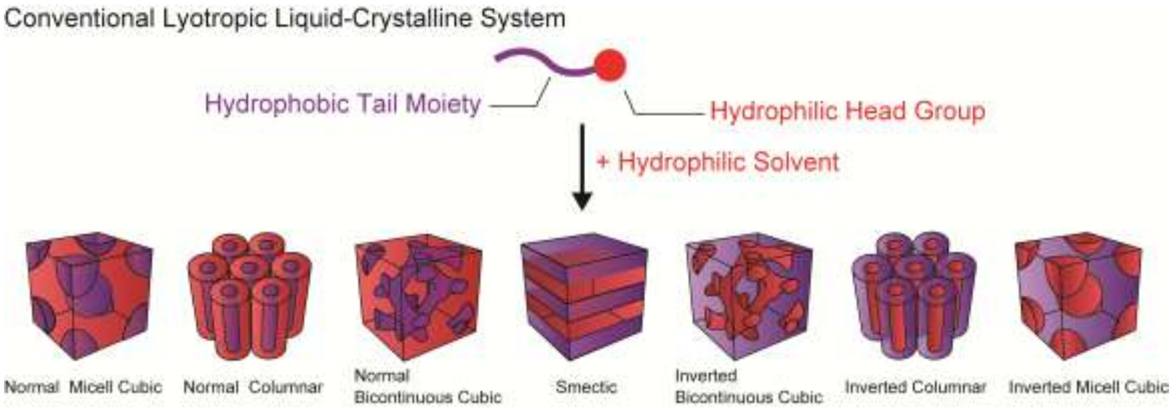


Fig. S14 Phase sequence for conventional lyotropic liquid-crystalline systems containing hydrophilic liquid, such as water, as solvent.

8. Comparison of Steric Structures of Amino Acid Anions

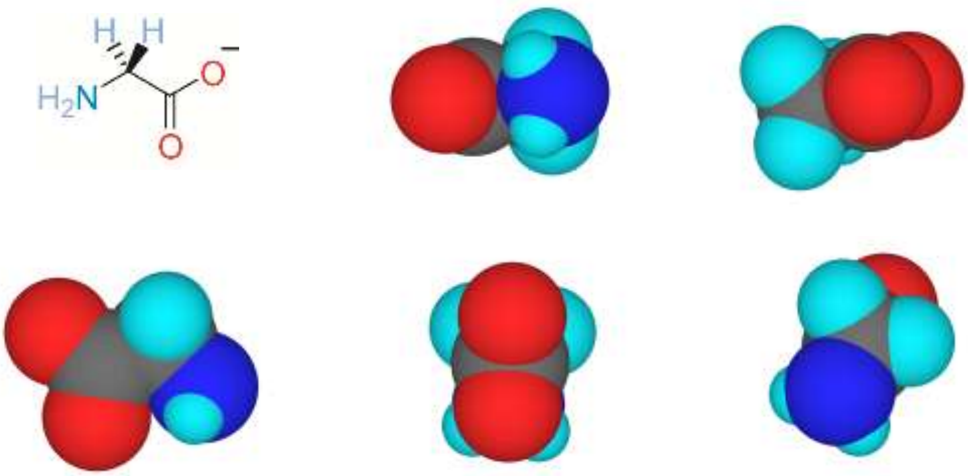


Fig. S15 Steric structure of glycine anion viewed from a variety of angles.
The hydrogen atoms are highlighted in watery blue, oxygen in red, nitrogen in blue, and carbon in gray.

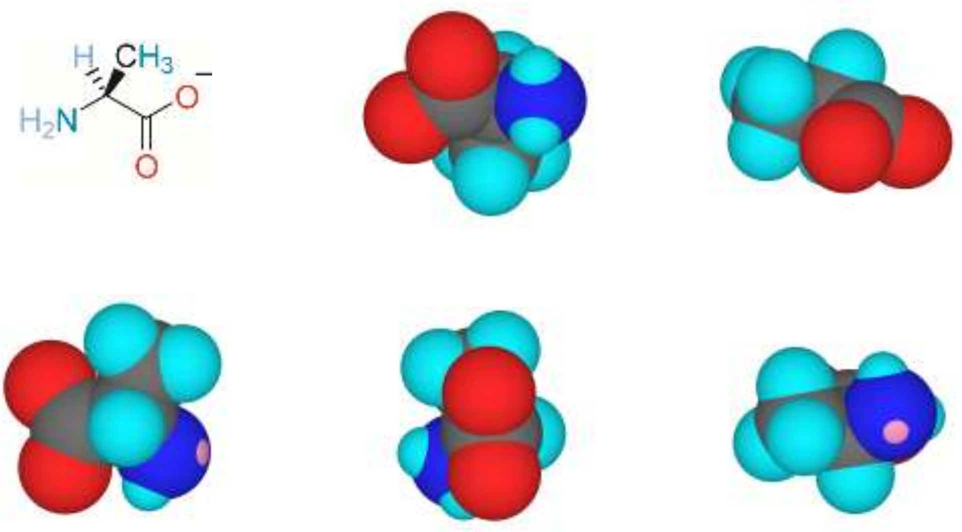


Fig. S16 Steric structure of L-alanine anion viewed from a variety of angles.
The hydrogen atoms are highlighted in watery blue, oxygen in red, nitrogen in blue, and carbon in gray.

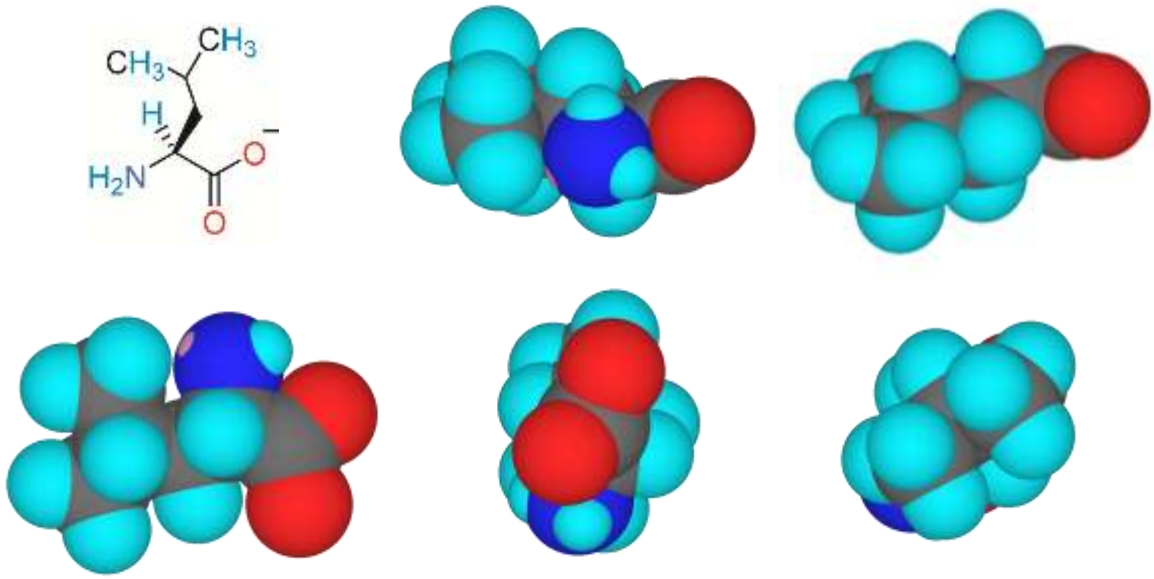


Fig. S17 Steric structure of L-leucine anion viewed from a variety of angles.
The hydrogen atoms are highlighted in watery blue, oxygen in red, nitrogen in blue, and carbon in gray.

8. Reference

1) K. Fukumoto, M. Yoshizawa and H. Ohno, *J. Am. Chem. Soc.*, 2005, **127**, 2398.
2) T. Ichikawa, M. Yoshio, S. Taguchi, J. Kagimoto, H. Ohno and T. Kato, *Chem. Sci*., 2012, **3**, 2001.