Tailor-made design of lipidic bicontinuous cubic matrices by using amino acid ionic liquids as self-assembly media

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Characterization of AAILs

[Ch][Asp]: ^{1}H NMR (400 MHz, D_2O) δ =4.06-4.04 (m, 2H), 3.90-3.86 (m, 1H), 3.51 (t, J = 5.0 Hz, 2H), 3.19 (s, 9H), 3.69-2.62 (m, 2H). ^{13}C NMR (100 MHz): δ = 180.25, 177.00, 70.11, 58.30, 56.56, 54.93, 39.30. Elemental analysis: Calculated for $C_9H_{20}N_2O_5$ + 0.80 H_2O: C, 43.12; H, 8.69; N, 11.18; C/N ratio, 3.86. Found: C, 43.16; H, 8.69; N, 11.38; C/N ratio, 3.79.

[Ch][Glu]: ^{1}H NMR (400 MHz, D_2O) δ =4.07-4.03 (m, 2H), 3.75-3.72 (m, 1H), 3.51 (t, J = 5.0 Hz, 2H), 3.19 (s, 9H), 2.36-2.32 (m, 2H), 2.16-2.00 (m, 2H). ^{13}C NMR (100 MHz): δ = 184.06, 177.41, 70.18, 58.37, 57.42, 56.63, 36.27, 29.81. Elemental analysis: $C_{10}H_{22}N_2O_5$ + 0.50 H_2O: C, 46.32; H, 8.94; N, 10.80; C/N ratio, 4.29. Found: C, 46.53; H, 9.09; N, 10.86; C/N ratio, 4.28.

[Im][Asp]: ^{1}H NMR (400 MHz, D_2O) δ =7.49 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 2.4 Hz, 1H), 4.38 (t, J = 5.0 Hz, 2H), 3.90 (s, 3H), 3.87 (t, J = 3.6 Hz, 1H), 3.82 (t, J = 4.8 Hz, 2H), 3.37 (s, 3H), 2.83-2.62 (m, 2H). ^{13}C NMR (100 MHz): δ = 180.26, 176.98, 139.07, 126.24, 125.19, 72.51, 60.89, 54.95, 51.59, 39.29, 38.40. Elemental analysis: $C_{11}H_{19}N_3O_5$ + 1.20 H_2O: C, 44.80; H, 7.31; N, 14.25; C/N ratio, 3.14. Found: C, 44.73; H, 7.54; N, 14.43; C/N ratio, 3.10.

[Im][Glu]: ^{1}H NMR (400 MHz, D_2O) δ =7.50 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 2.4 Hz, 1H), 4.39 (t, J = 4.8 Hz, 2H), 3.89 (s, 3H), 3.83 (t, J = 5.2 Hz, 2H), 3.74 (t, J = 6.0 Hz, 1H), 3.38 (s, 3H), 2.37-2.32 (m, 2H), 2.17-2.01 (m, 2H). ^{13}C NMR (100 MHz): δ = 183.96, 177.23, 139.07, 126.24, 125.19, 72.51, 60.90, 57.36, 51.59, 38.41, 36.20, 29.67. Elemental analysis: $C_{12}H_{21}N_3O_5$ + 0.65 H_2O: C, 48.20; H, 7.52; N, 14.05; C/N ratio, 3.43. Found: C, 47.98; H, 7.33; N, 14.32; C/N ratio, 3.35.

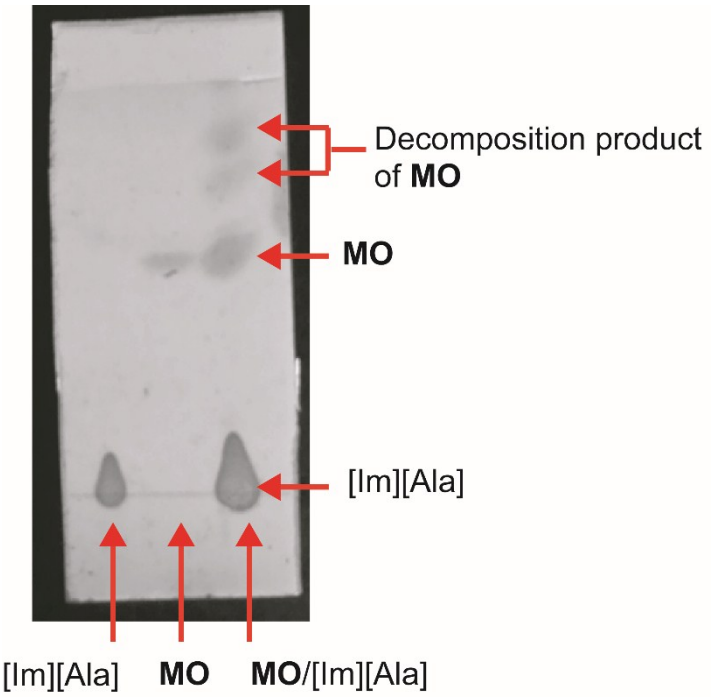

Fig. S1. Thin-layer chromatography (TLC) analysis of [Im][Ala], **MO**, and **MO**/[Im][Ala] mixture. Chloroform/methanol (90/10, v/v) was used as an eluent.

Table S1 Glass transition temperature (T_g) of AAILs.

AAIL	T_g / °C
[Ch][Asp]	–16
[Ch][Glu]	–17
[Im][Asp]	–23
[Im][Glu]	–19

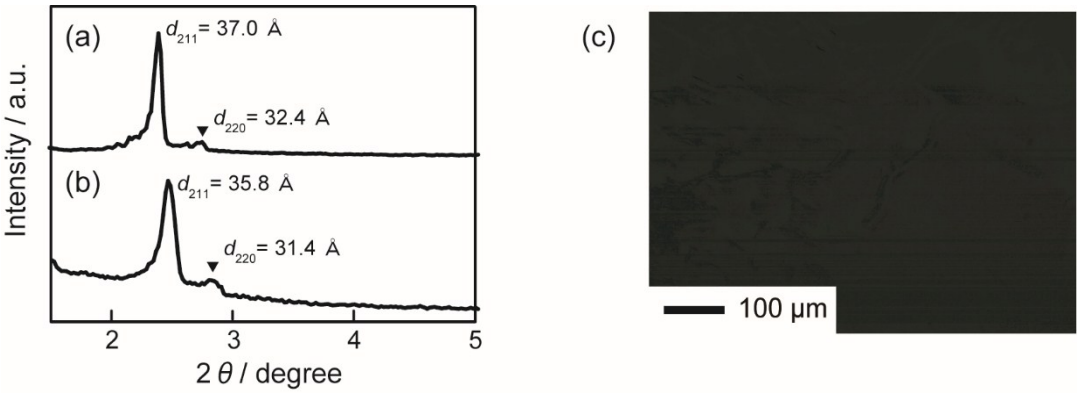

Fig. S2 (a) X-ray diffraction pattern of the **MO**/[Im][Glu] mixture (80/20 by wt%) in the Q_{II} phase at room temperature. This sample was prepared by vacuuming for 5 hours and left for 1 month without cover glass under laboratory condition. (b) X-ray diffraction pattern of the **MO**/[Im][Glu] mixture (80/20 by wt%) prepared by vacuuming for 24 hours in the Q_{II} phase at room temperature. (c) Polarizing optical image of **MO**/[Im][Glu] (80/20 by wt%) in the Q_{II} phase at room temperature. This sample was prepared by vacuuming for 5 hours and left for 1 month without cover glass under laboratory condition.

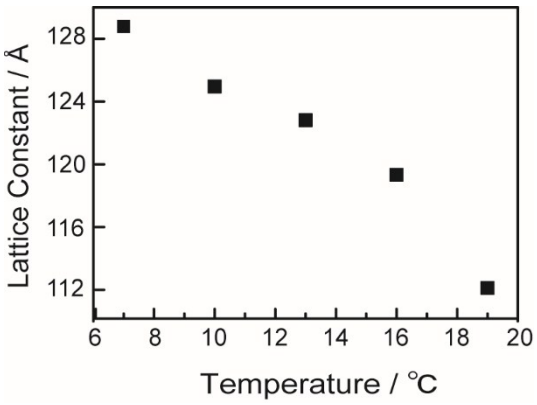

Fig. S3 Change of the cubic lattice constant of the **MO**/[Im][Glu] mixture (80/20 by wt%) in low temperature region.

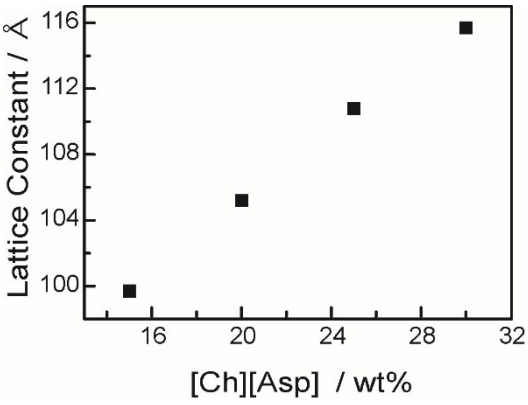

Fig. S4 Cubic lattice constant of the **MO**/[Ch][Asp] mixture (80/20 by wt%) against the component ratio of [Ch][Asp].

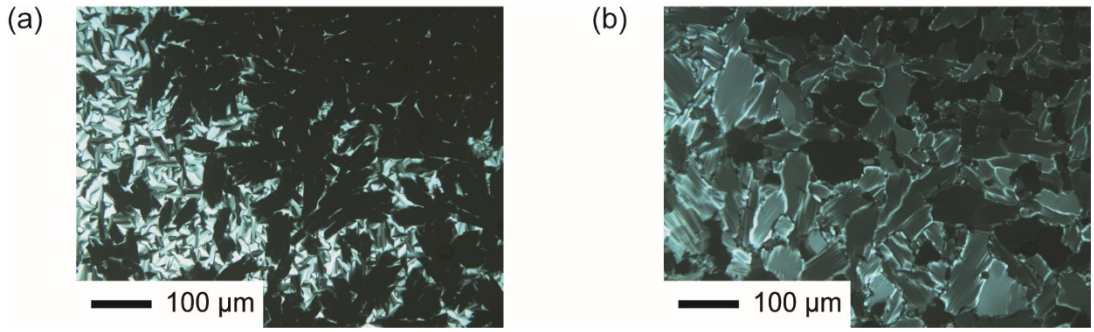

Fig. S5 (a) Polarizing optical image of the **MO**/[Ch][Asp] mixture (80/20 by wt%) from the H_{II} to Q_{II} phases at 36 °C on cooling. (b) Polarizing optical image of the **MO**/[Ch][Asp] mixture (80/20 by wt%) from the Q_{II} to H_{II} phases at 41 °C on heating.

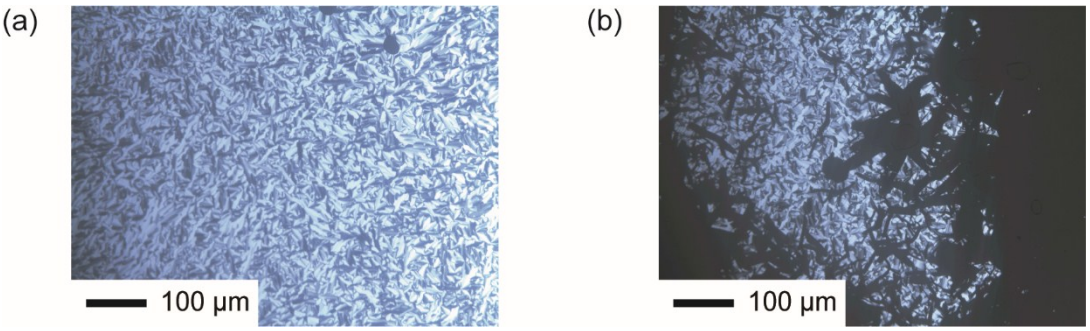

Fig. S6 (a) Polarizing optical image of the **MO**/[Ch][Glu] mixture (90/10 by wt%) in the H_{II} at 44 °C on cooling. (b) Polarizing optical image of the **MO**/[Ch][Glu] mixture (90/10 by wt%) from the H_{II} to Q_{II} phases at 12 °C on cooling.

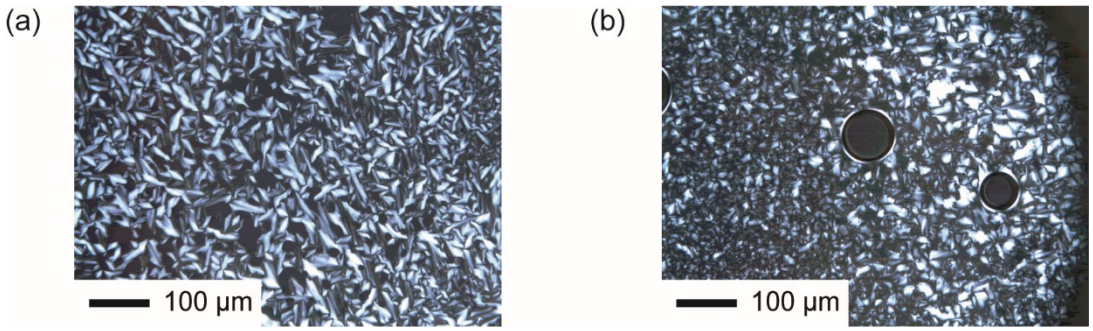

Fig. S7 (a) Polarizing optical image of the **MO**/[Im][Asp] mixture (70/30 by wt%) in the L_α phase at 104 °C on cooling. (b) Polarizing optical image of the **MO**/[Im][Asp] mixture (50/50 by wt%) in the L_α phase at 128 °C on cooling.

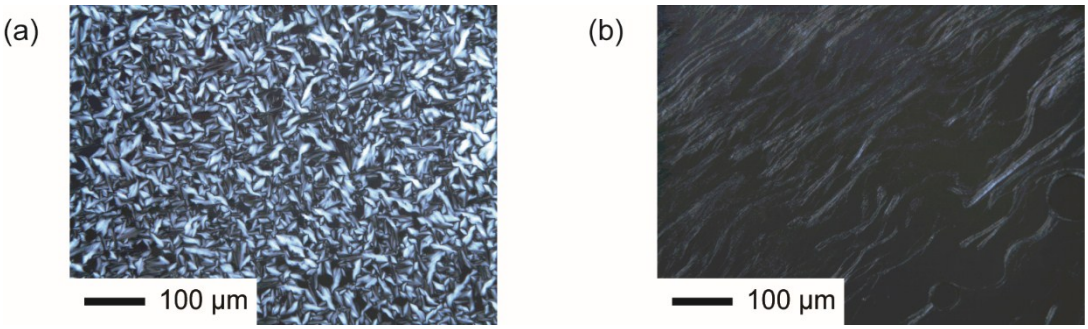

Fig. S8 (a) Polarizing optical image of the **MO**/[Im][Glu] mixture (70/30 by wt%) in the L_α phase at 93 °C on cooling. (b) Polarizing optical image of the **MO**/[Im][Asp] mixture (60/40 by wt%) in the L_α phase at 101 °C after shearing. An oil streak texture, indicative of the formation of a L_α phase, was observed.

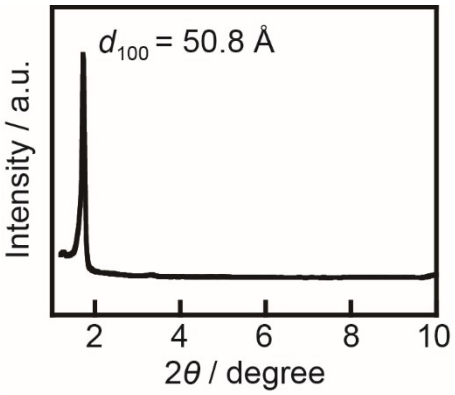

Fig. S9 X-ray diffraction pattern of the **MO**/[Ch][Glu] mixture (50/50 by wt%) in the L_α phase at 60 °C.

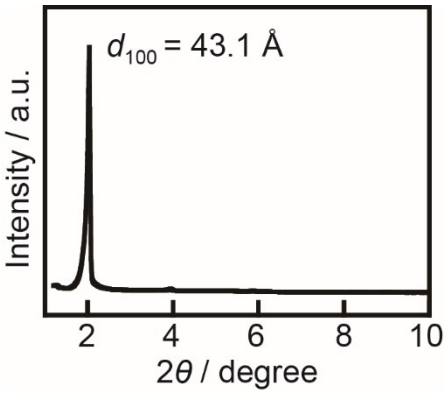

Fig. S10 X-ray diffraction pattern of the **MO**/[Im][Glu] mixture (50/50 by wt%) in the L_α phase at room temperature.