Electronic Supplementary Information for

Chaperone Gelator for Chiral Self-assembly of All Proteinogenic Amino Acids and Their Enantiomers

Jie Chen,[a] Tianyu Wang[a] and Minghua Liu*[ab]

[a] Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

[b] Collaborative Innovation Centre of Chemical Science and Engineering, Tianjin, P. R. China.

1: Experimental Section

Materials: All starting materials and solvents were purchased from Aldrich, TCI or Beijing Chemicals and used as received unless otherwise stated. Solvents were purified and dried according to standard methods. Milli-Q water (18.2 MΩ cm^{-1}) was used in all cases.

Synthesis of amphiphilic L-histidine (LH): L-histidine methyl ester dihydrochloride (3 g) was dissolved in dichloromethane (250 mL), and added with triethylamine (2.6 g). The mixture was stirred at room temperature for 2 h. Then octadecyl isocyanate (3.5 g) was dropwisely added into the mixture under ice water bath within 2 h. The solvent was removed under reduced pressure, and the remaining

substance was dissolved in ethanol (100 mL). The ethanol solution was poured into 0.5 % Na_2CO_3 aqueous solution (1000 mL). The obtained white solid was filtered and dried under vacuum to give 5.6 g of crude product (98 %). The pure LH can be obtained from recrystallization in ethanol.

^{1}H NMR (400 MHz, **DMSO-d6**, 25 °C, TMS): δ=0.87 (m , 3H; CH_3), 1.23 (s, 32 H; CH_2), 2.82–2.84 (d, 2 H, CH_2), 2.91–2.95 (m, 2 H; CH_2), 3.57 (s, 3 H; CH_3), 4.34–4.41 (m, 1 H; CH), 6.08-6.10 (m, 1H; NH), 6.15-6.19 (m, 1H; NH), 6.78 (s, 1 H; imi-C(4)H), 7.53 (s,1 H; imi-C(2)H), 11.88 (s, 1 H; imi-NH). MALDI-TOF-MS: m/z (%): 465.4 $[M+H]^+$, 487.4 $[M+Na]^+$, 503.4 $[M+K]^+$; elemental analysis calcd (%) for $C_{26}H_{48}N_4O_3$: C 67.18, H 10.34, N 12.06; found: C 67.13, H 10.41, N 11.92.

Instruments and methods: ^{1}H NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer. Mass spectral data were measured by using a BIFLEIII matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) instrument. Elemental analysis was performed on a Carlo–Erba-1106 Thermo-Quest. Scanning electron microscopy (SEM) was carried out on a Hitachi S-4800 FE-SEM microscope. Xerogel on silica plate were prepared for the measurement of Fourier transform infrared (FT-IR) spectra on a JASCO FT/IR-660 plus spectrophotometer with a wave number resolution of 4 cm^{-1} at room temperature. X-ray diffraction (XRD) was carried out on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with CuKα radiation (λ=1.5406 Å), which was operated at 45 kV, 100 mA.

Procedures: For the SEM measurements, a small amount of gels was placed onto a single-crystal silicon plate (Pt-coated) after being vacuum dried for 12 h. In the case of preparing samples for XRD measurements, gels were cast onto glass plates and dried under vacuum. Pellets made from the mixture of vacuum-dried supramolecular polymers and KBr powders were used for FT-IR spectral measurements.

Gelation studies: All the supramolecular gels were prepared in septum-capped test tubes. The amphiphilic L-histidine (LHC18) and different amino acids with equal molar ratio were dispersed in Milli-Q water and DMF and then heated until transparent. The obtained clear solution was let cool to room temperature and the gels formation was confirmed by the tube-inversion method.

2: Supplementary table and figures

Table S1. The DMF/water gelation volume ratios for forming LH/amino acids two-component supramolecular gels.

Amino acids	DMF(μL)	H_2O(μL)
Gly	800	600
L-Ala	500	400
D-Ala	500	400
L-Val	600	200
D-Val	500	300
L-Leu	750	645
D-Leu	500	400
L-Ile	900	645
D-Ile	500	400
L-Phe	500	200
D-Phe	500	300
L-Tyr	700	500

D-Tyr	500	400
L-Trp	700	400
D-Trp	500	200
L-Cys	600	400
D-Cys	0	400
L-Met	400	200
D-Met	600	400
L-Ser	600	400
D-Ser	600	400
L-Asn	300	200
D-Asn	400	200
L-Gln	600	300
D-Gln	600	300
L-Thr	600	600
D-Thr	600	400
L-Pro	600	400
D-Pro	500	400
L-Lys	400	200
D-Lys	400	300
L-Arg	300	200
D-Arg	300	200
L-His	700	500
D-His	650	550
L-Asp	500	600
D-Asp	200	500
L-Glu	200	500
D-Glu	200	500

Table S2. The concentrations of amino acids in all the two-component supramolecular gels and the corresponding gel–sol transition temperature "T_{gel}" as well as the critical gelation concentrations.

Amino acids	C(mg/mL)	T_{gel}(°C)	CGC(mg/mL)
Gly	0.58	53.6	0.48
L-Ala	1.07	71.0	0.81
D-Ala	1.07	65.4	0.88
L-Val	1.58	66.0	1.33
D-Val	1.58	51.6	1.21
L-Leu	1.01	54.3	0.78
D-Leu	1.57	51.2	1.21

L-Ile	0.91	43.7	0.80
D-Ile	1.57	46.4	1.44
L-Phe	2.54	63.7	1.74
D-Phe	2.22	65.1	1.60
L-Tyr	1.63	64.3	1.29
D-Tyr	2.17	61.2	1.65
L-Trp	2.00	50.3	1.37
D-Trp	3.14	59.8	2.17
L-Cys	1.30	52.7	1.12
D-Cys	3.26	68.4	2.17
L-Met	2.68	53.8	2.07
D-Met	1.61	67.4	1.07
L-Ser	1.13	54.1	0.96
D-Ser	1.13	52.2	0.93
L-Asn	2.84	59.3	2.29
D-Asn	2.37	63.7	1.79
L-Gln	1.75	69.8	1.45
D-Gln	1.75	56.2	1.45
L-Thr	1.07	63.1	0.82
D-Thr	1.28	40.2	0.98
L-Pro	1.24	68.0	1.00
D-Pro	1.38	55.6	1.04
L-Lys	2.62	50.4	2.23
D-Lys	2.25	47.6	1.87
L-Arg	3.75	56.2	3.43
D-Arg	3.75	55.0	3.37
L-His	1.39	57.2	1.25
D-His	1.39	56.8	1.22
L-Asp	1.30	78.2	0.85
D-Asp	2.05	67.8	1.59
L-Glu	2.26	82.4	1.71
D-Glu	2.26	66.4	1.74

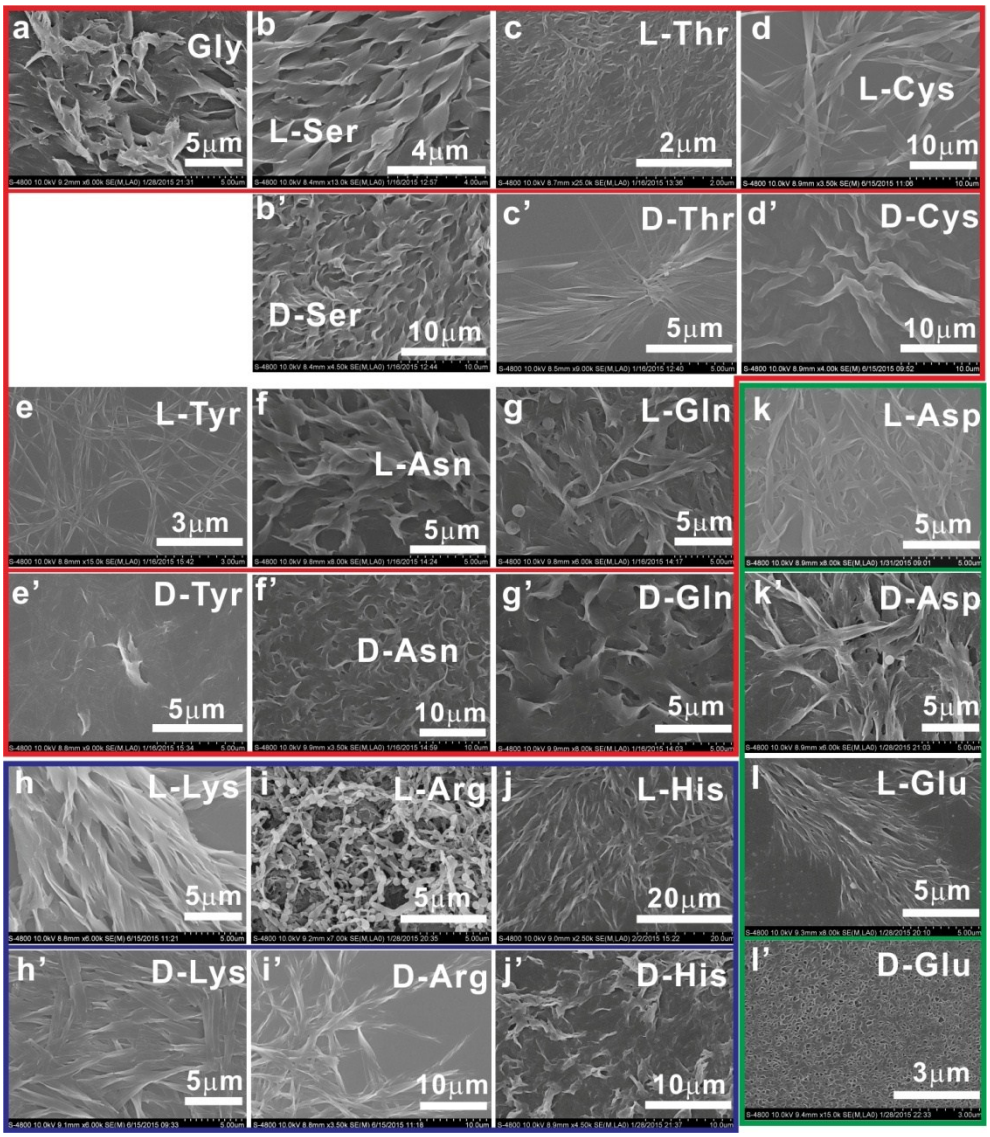

Figure **S1**. SEM images of the supramolecular gels formed by the co-assembly of LHC18 and polar amino acids. (a) Gly/LH assemblies; (b) L-Serine/LH assemblies; (b') D-Serine/LH assemblies; (c) L-threonine/LH assemblies; (c') D-threonine/LH assemblies; (d) L-Cysteine/LH assemblies; (d') D-Cysteine/LH assemblies; (e) L-Tyrosine/LH assemblies; (e') D- Tyrosine/LH assemblies; (f) L-Asparagine/LH assemblies; (f') D-Asparagine/LH assemblies; (g) L-Glutamine/LH assemblies; (g') D-Glutamine/LH assemblies; (i) L-Asparagine/LH assemblies; (i') D-Asparagine/LH assemblies; (j) L-Histidine/LH assemblies; (j') D-Histidine/LH assemblies; (k) L-Aspartic acid/LH assemblies; (k') D-Aspartic acid/LH assemblies; (l) L-Glutamine/LH assemblies; (l') D-Glutamine/LH assemblies.

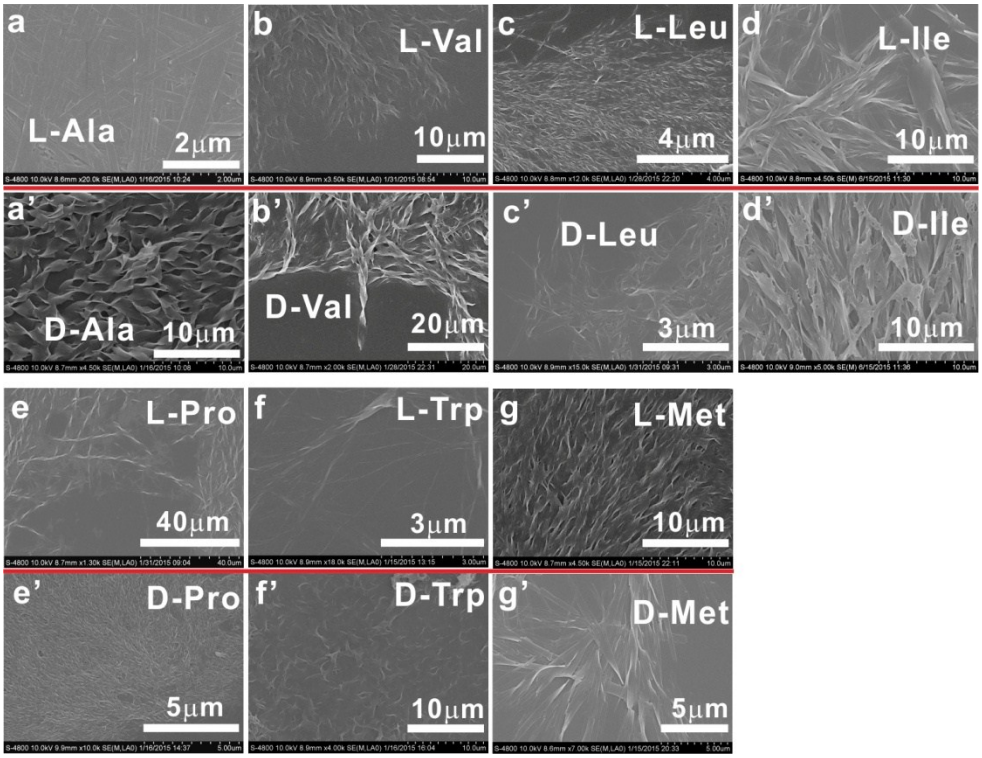

Figure **S2**. SEM images of the supramolecular gels formed by the co-assembly of LHC18 and nonpolar amino acids. (a) L-Alanine/LH assemblies; (a') D-Alanine/LH assemblies; (b) L-Valine/LH assemblies; (b') D-Valine/LH assemblies; (c) L-Leucine/LH assemblies; (c') D-Leucine /LH assemblies; (d) L-Isoleucine/LH assemblies; (d') D-Isoleucine/LH assemblies; (e) L-Proline/LH assemblies; (e') D-Proline/LH assemblies; (f) L-Tryptophan/LH assemblies; (f') D- Tryptophan/LH assemblies; (g) L- Methionine/LH assemblies; (g') D-Methionine /LH assemblies.

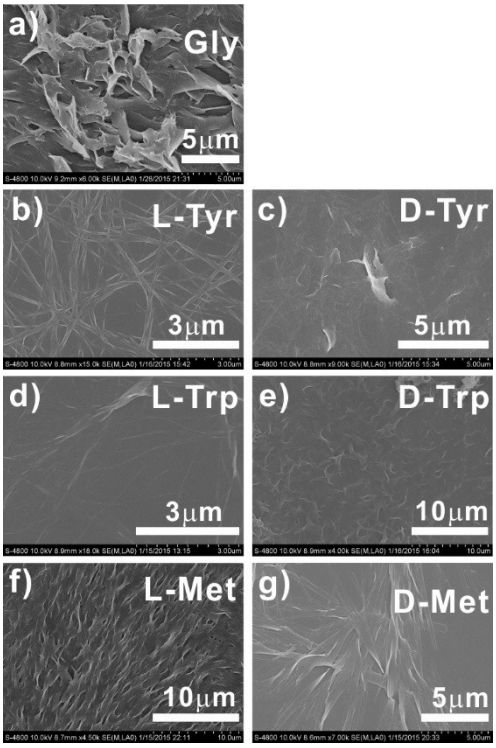

Figure **S3**: SEM images of the supramolecular gels formed by the co-assembly of LHC18 and nonpolar amino acids. (a) Gly/LH assemblies; (b) L-Tyr/LH assemblies; (c) D-Tyr/LH assemblies; (d) L-Trp/LH assemblies; (e) D-Trp/LH assemblies; (f) L-Met/LH assemblies; (g) D-Met/LH assemblies.

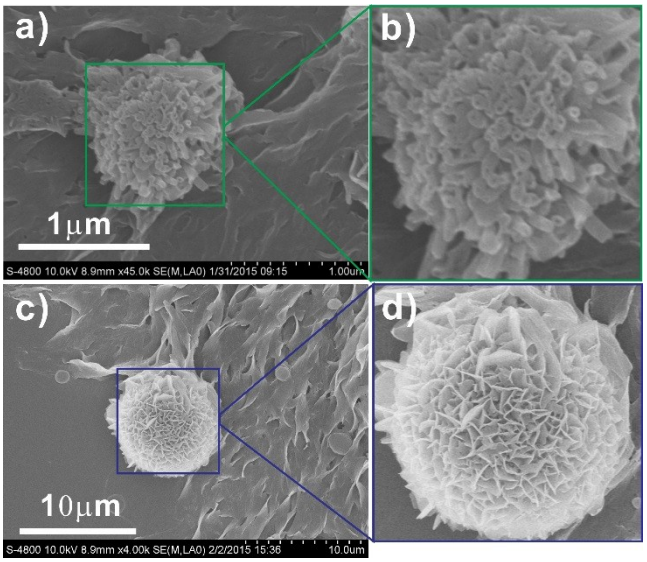

Figure **S4**. SEM images of the supramolecular gels formed by the co-assembly of LH and phenylalanine. (a, b) SEM images of L-phenylalanine/LH assemblies with supramolecular nanotubes structures; (c, d) SEM images of D-phenylalanine/LH assemblies with microcluster of lamellar structures.

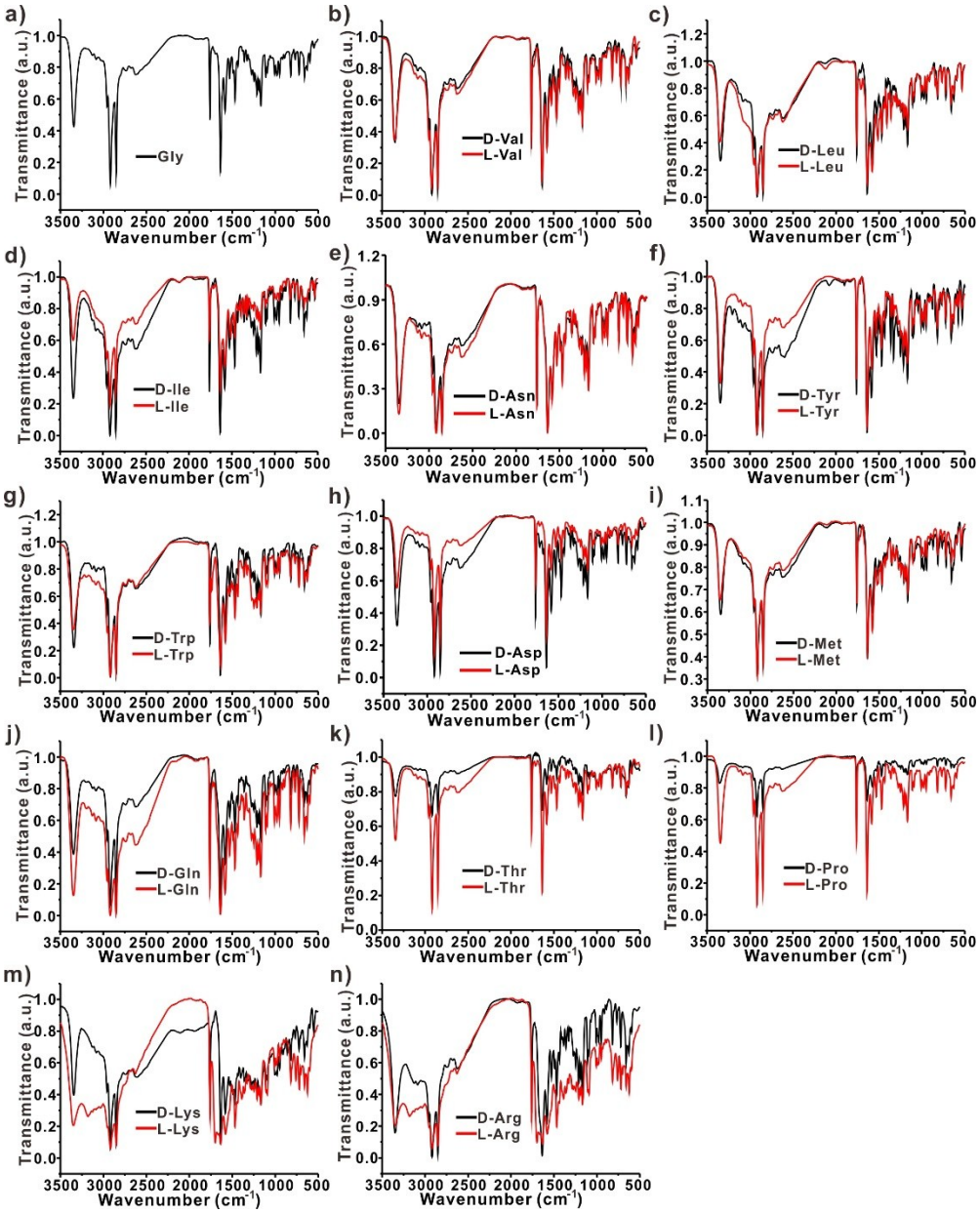

Figure **S5**: FT-IR spectra of LHC18/amino acids xerogels.

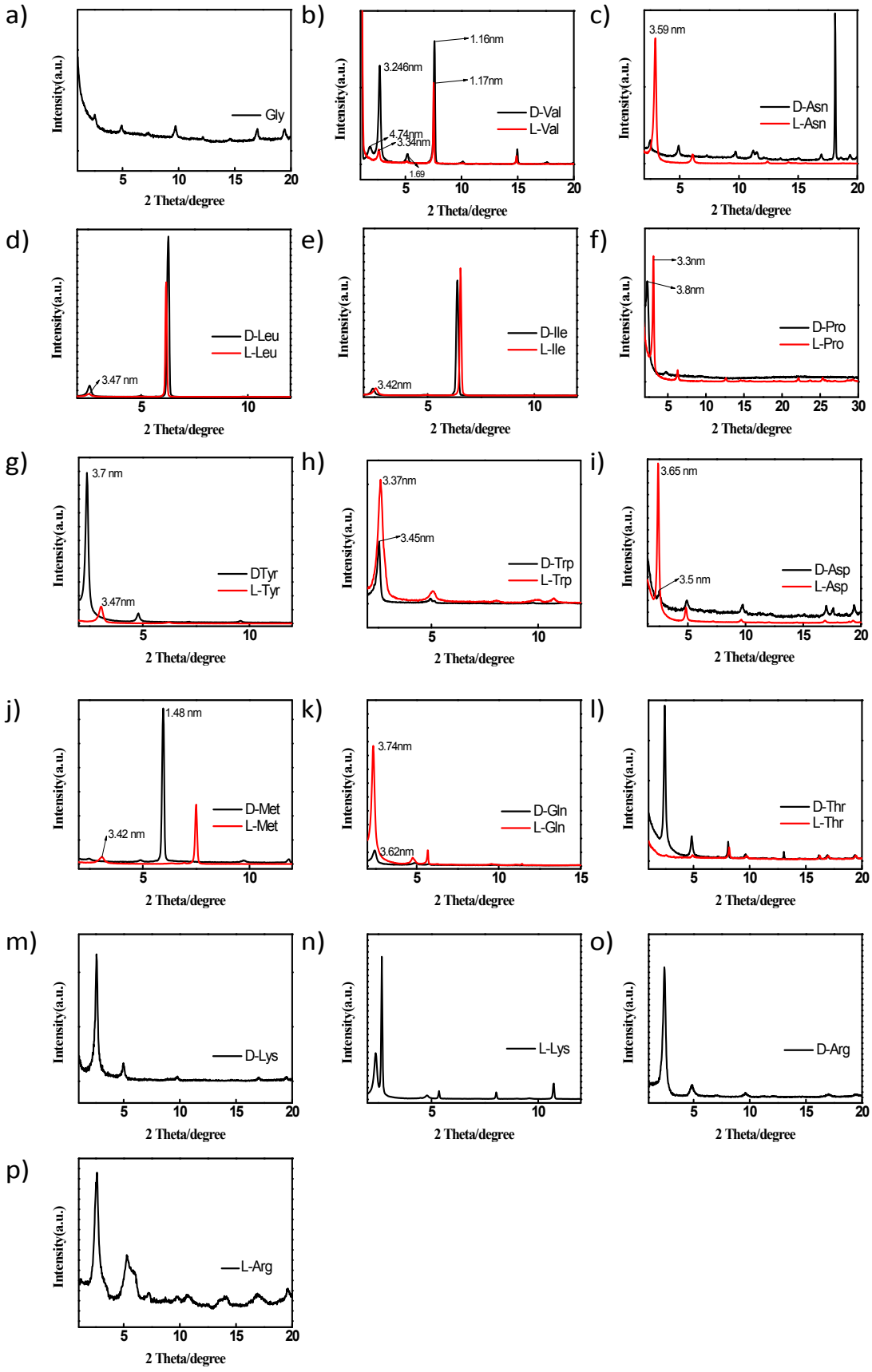

Figure **S6**: XRD pattern of LHC18/amino acids xerogels.