Electronic Supplementary Information

for

Isomeric effect in the self-assembly of pyridine-containing L-glutamic lipid: substituent position controlled morphology and supramolecular chirality

Pengfei Duan, Xuefeng Zhu and Minghua Liu*

Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese

Academy of Sciences, P. R. China, 100190. E-mail: liumh@iccas.ac.cn

Experimental section

Materials: All starting materials were obtained from commercial suppliers and used as received. Solvents were purified and dried according to standard methods. MS spectra were determined with BEFLEX III for MALDI-TOF mass spectrometer. Elemental analyses were performed on a Carlo-Erba-1106 instrument.

Synthesis of the target compound: In previous reports, we have demonstrated the synthesis of an organogelator containing a Boc group: N, N'-bisoctadecyl-L-Boc-glutamic-diamide (LBG).[1] In this paper, we changed the Boc group to pyridyl groups. The Boc group of LBG was made to free amino by mixing with trifluoroacetic acid in dichloromethane. 1.50 g LBG was dispersed in dichloromethane under icy bath. Then 5 mL trifluoroacetic acid was added to the above mixture and stirred at 0 °C for 3 h. After that, the solvent was removed by rotary evaporation and oily product was obtained. The oily compound was dissolved in 10 mL THF and poured into 300 mL aqueous solution saturated of $NaHCO_3$. After filtration, the product was purified by reprecipitation in THF to give a white solid LGA (1.28 g, 98%).

LGA (0.65 g, 1 mmol) was dispersed in dichloromethane (60 mL) and stirred for 30 min. Then, 2-picolinic acid/nicotinic acid/isonicotinic acid (2PLG/3PLG/4PLG) (0.12 g, 1 mmol) was added into the above mixture and stirred at 0 °C for 30 min. After that, 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride

(EDC·HCl) (0.23 g, 1.2 mmol) and 1-hydroxybenzotrizole (HOBt, 0.16 g, 1.2 mmol) were added to the mixture. The obtained mixture was stirred for 5 days at room temperature. After that, the solvent was removed by rotary evaporation and orange solid was obtained. The crude product was dissolved in 10 mL THF, and poured into 300 mL aqueous solution saturated of $NaHCO_3$. After filtration, the product was purified by reprecipitation in ethanol to give white solid:

2PLG: (0.45 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.85-8.87 (d, J = 8 Hz, 1H), 8.58-8.60 (d, J = 8, 1H), 8.12-8.14 (d, J = 8, 1H), 7.82-7.86 (t, J = 8, 1H), 7.42-7.45 (t, J = 8, 1H), 6.76-6.79 (t, J = 8, 1H), 6.14 (m, 1H), 4.56-4.61 (m, 1H), 3.23-3.28 (m, 4H), 2.15-2.61 (m, 4H), 1.46-1.50 (m, 4H), 1.24 (br, 64H), 0.86-0.89 (m, 6H). MALDI-TOF-MS Calcd for $C_{47}H_{86}N_4O_3$: 755.2. Found: 778.2 (M^+ + Na), 794.2 (M^+ + K). Anal. Calcd for $C_{47}H_{86}N_4O_3$: C 74.75, H 11.84, N 7.42; Found: C 74.52, H 11.66, N 7.31.

3PLG: (0.60 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.15 (s, 1H), 8.73-8.74 (m, 1H), 8.47-8.49 (d, J = 8, 1H), 8.20-8.22 (d, J = 8, 1H), 7.38-7.41 (m, 1H), 7.03-7.06 (m, 1H), 5.96-6.02 (m, 1H), 4.56-4.58 (m, 1H), 3.23-3.28 (m, 4H), 2.15-2.61 (m, 4H), 1.46-1.50 (m, 4H), 1.24 (br, 64H) 0.86-0.89 (m, 6H). MALDI-TOF-MS Calcd for $C_{47}H_{86}N_4O_3$: 755.2. Found: 778.2 (M^+ + Na), 794.2 (M^+ + K). Anal. Calcd for $C_{47}H_{86}N_4O_3$: C 74.75, H 11.84, N 7.42; Found: C 74.49, H 11.90, N 7.47.

4PLG: (0.70 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.77 (s, 2H), 8.63-8.65 (d, J = 8, 1H), 8.78 (s, 1H), 6.97-6.99 (m, 1H), 5.82-5.85 (m, 1H), 4.51-4.55 (m, 1H), 3.23-3.28 (m, 4H), 2.13-2.61 (m, 4H), 1.50 (br, 4H), 1.24 (br, 64H) 0.86-0.89 (m, 6H). MALDI-TOF-MS Calcd for $C_{47}H_{86}N_4O_3$: 755.2. Found: 778.2 (M^+ + Na), 794.2 (M^+ + K). Anal. Calcd for $C_{47}H_{86}N_4O_3$: C 74.75, H 11.84, N 7.42; Found: C 74.77, H 11.38, N 7.35.

Characterization: The gel formation and their properties were characterized by a series of methods such as field emission scanning electron microscope (SEM), transmission electron microscope (TEM), UV-Vis absorption, circular dichroism (CD) and Fourier Transform Infrared Spectroscopy (FT-IR) measurements. X-ray diffraction (XRD) was achieved on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/Kα radiation (λ=1.5406Å), which was operated at 45 kV, 100 mA. SEM was performed using a Hitachi S-4300 system with an accelerating voltage of 15 kV. Samples for FESEM were prepared by spinning the gels on silicon slices and dried in vacuum for 2 days. After that, all samples were coated with gold. FT-IR spectra were obtained by a JASCO FT/IR-660 plus spectrophotometer. UV-vis and CD spectra were obtained using JASCO UV-550 and JASCO J-810 spectrophotometers, respectively.

Table 1.Organic solvents tested for gelation for three isomeric organogelators.[a]

Solvent	4PLG	3PLG	2PLG
DMF	WG (3.5)	WG (4.7)	WG (6.0)
DMSO	WG (1.5)	WG (5.5)	WG (8.7)
CH_3CN	WG (5.2)	P	WG (9.4)
Acetone	WG (3.8)	P	PG
Ethyl acetate	WG (3.5)	P	S
Ethanol	WG (4.2)	S	S
THF	S	S	S
o-Xylene	TG (2.7)	P	S
Toluene	TG (1.8)	P	S
Benzene	P	P	S
Cyclohexane	P	TG (5.5)	S
Hexane	WG (3.9)	WG (6.2)	PG
CCl_4	TG (3.2)	TG (4.2)	S
$CHCl_3$	S	S	S

[a] WG = white gel, TG = transparent gel, PG = partial gel, P = precipitation, S = solution. The values in parentheses are the critical gelation concentration (CGC) wt/vol%.

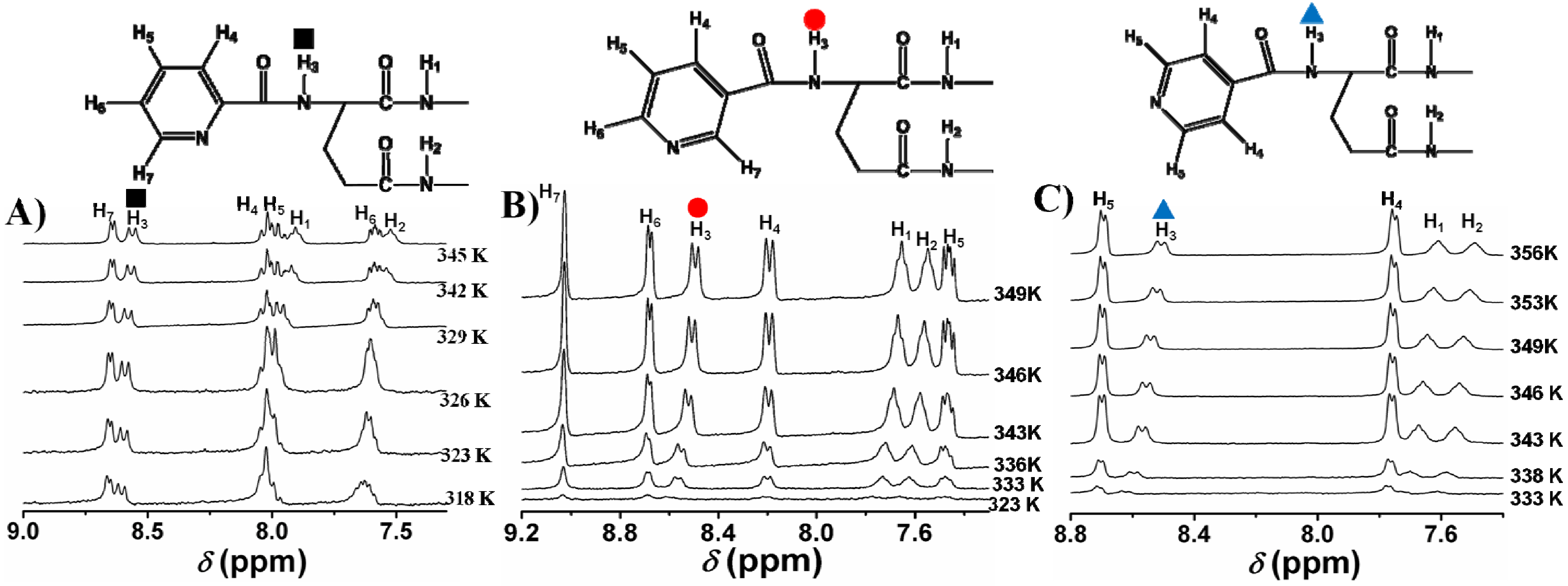

Figure S1. Temperature-dependent ^{1}H NMR spectra of 2PLG (A), 3PLG (B) and 4PLG (C) in DMSO-d_6 gels. The gel concentrations are controlled at 2PLG (0.0311 mol L^{-1}), 3PLG (0.0256 mol L^{-1}) and 4PLG (0.0118 mol L^{-1})

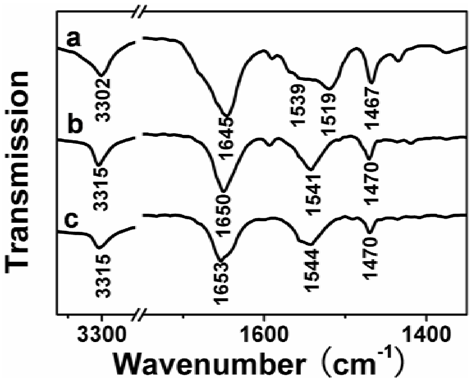

Figure S2. FT-IR spectra of the xerogels obtained from air-dried DMSO gels: (a) 2PLG, (b) 3PLG and (c) 4PLG.

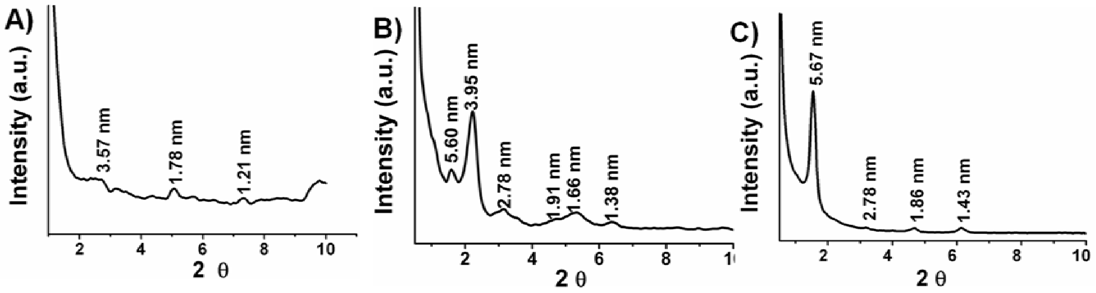

Figure S3. XRD patterns of the xerogels obtained from air-dried DMSO gels: (A) 2PLG, (B) 3PLG and (C) 4PLG.

Reference

1 Y. G. Li, T. Y. Wang and M. H. Liu, *Soft Matter*, 2007, **3**, 1312.

2 (*a*) G. S. Lim, B. M. Jung, S. J. Lee, H. H. Song, C. Kim and J. Y. Chang, *Chem. Mater.*, 2007, **19**, 460; (*b*) B. Chen, U. Baumeister, G. Pelzl, M. K. Das, X. Zeng, G. Ungar and C. Tschierske, *J. Am. Chem. Soc.,* 2005, **127**, 16578.

3 K. Borisch, S. Diele, P. Goring, H. Kresse, C. Tschierske, *J. Mater. Chem.,* 1998, **8**, 529.