Electronic Supporting Information

Tuning the Helical Nanostructure and Supramolecular Chirality by Water in the Organogels

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Experimental Section

Instruments and methods:¹HNMR spectrum was obtained on a Bruker AV300 spectrometer, and tetramethylsilane was used as an internal standard substance. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was recorded on a BIFLEIII instrument. Elemental analysis was performed on a Carlo-Erba-1106 instrument. The aging gel and precipitation was cast on single-crystal silica plates, then vacuum-dried. The sample surface was coated with Pt, which were recorded on a Hitachi S-4800 FE-SEM microscope, operating at accelerating voltages of 10 kV. TEM images were performed on a JEM-1011 operating at the accelerating 200kV. The fully aging samples were cast on glass substrates and vacuum-dried for X-ray diffraction, which was performed on a Rigaku D/Max-2500 X-ray diffractometer with CuK α radiation (λ =1.5406 Å), operating at 45 kV, 100 mA. UV/Vis and circular dichroism (CD) spectra were recorded on JASCO UV-550 and JASCO J-810 CD spectrophotometers, respectively. The water contact angle was recorded by an OCA 20 (Optical Contact angle measurement) at ambient temperature. Zeta-potential measurement was carried out at 25 °C by a Zetasizer Nano ZS ZEN3600 (Nano ZS, Malvern Instruments).

Materials: All chemicals were purchased from commercial suppliers. Chloroform was distilled before

used and other reagents were used without further purification. The synthesis and characterization of the N,N'-bis-octadecyl-L-glutamicdiamide (LGAm) was reported previously by our group.¹

The synthesis of PULG: N,N'-bis-octadecyl-L-glutamicdiamide (LGAm) (2.06g, 3.0mmol)was dispersed in mixture solvents of chloroform and pyridine, and stirred at ambient temperature until the solid material dissolved completely. The 2-chloroethyl isocyanate (0.32g 3.0mmol) was dropped to the solution refluxed at 50°C for 1h, and then refluxed at 110°C for 6h. After the reaction solution was cooled to room temperature, the precipitate was yielded. The solid was isolated by filtration and washed with chloroform to remove unreacted reagents. The crude product was purified by precipitation in absolute alcohol to give a white solid. Then, the white solid was purified further by silica column chromatography (CHCl₃/methanol=1/4, R_f=0.4), the target product (46% yield) was obtained as fine white solid. ¹H NMR(300 MHz, DMSO-d₆, at 360k,): δ =8.97 (d, 2H), δ =8.55-8.57 (m,1H), δ =8.09(m, 2H), δ =7.45-7.53 (br, 2H), δ =6.45(s, 1H), δ =6.18-6.20 (d, 1H), δ =4.65 (s, 2H), δ =3.93-3.95 (m, 1H), δ =3.58-3.60 (m, 2H), δ =2.02 (m 2H), δ =1.78-1.67 (br, 2H), δ =1.64-1.24 (br, 68H) δ = 0.85-0.87 (m, 6H). MALDI-TOF MS: m/z (%) calcd for [C₄₉H₉₂N₅O₃]+ 798.7, found 798.6. Elemental analysis calcd (%) for C₄₉H₉₂Cl N₅O₃: C 70.50, H 11.11, Cl 4.25; N 8.39; found: C 70.61, H 10.94, Cl 4.34, N 8.40.

Solvent	Phase ^a	Phase ^b	Water % ^c	CGC^d	CD ^e	d-space /nm
Cyclohexane	Ι	G	1~2	12	277 positive	6.60
Chloroform	Р	G	1~2	10	276 positive	6.27
Toluene	Р	G	1	10	276 positive	6.60
Acetonitrile	Ι	G	5~30	8	273 positive	6.66
Acetone	Ι	G	10~30	8	278 positive	6.80/5.21
Ethanol	Р	G	5~20	8	287 negative	4.82
Methanol	Р	G	5~10	8	288 negative	5.08
DMSO	PG	G	5~10	8	291 negative	5.02
Water	Е					

Table S1. Gelation Behaviours of PULG in the Presence of Water in Various Organic Solvents

^aabsence of water; ^bpresence of water; ^cgelation the lowest amount of water to the maximum amount; I= insoluble; P=precipitation; E=emulsion; G=gel; PG=partial gel; ^dCGC (mg/mL) critical gelation concentration; ^eCD λ max/nmandsignal



Figure S1.SEM images of precipitates of PULG in pure organic solvents: a)CHCl₃; b)Ethanol; c)Methanol; d)DMSO

Scale bars: $2 \ \mu \ m$



Figure S2.SEM images of xerogels of PULG in different H₂O /organic solvents mixture (v%); H₂O/ Cyclohexane(1%) (a); H₂O/ Toluene (1%) (b); H₂O/CHCl₃(1%) (c); H₂O/ acetone (10%) (d); H₂O/CH₃CN (10%) (e); H₂O/CH₃CH₂OH (5%) (f); H₂O/CH₃OH (5%) (g); H₂O/ DMSO (5%) (h)



Figure S3.XRD patterns of xerogels in different ratios of H_2O /ethanol (v%) mixture solvents: 0% (a); 5% (b); 10% (c); 20% (d); 30% (e)



Figure S4.SEM images of xerogels of PULG in different ratios H₂O/CHCl₃mixture a) 0 %;b) 0.5%; c) 1%; d) 3%



Figure S5.UV spectra of PULG gel prepared in H₂O/ cyclohexane (1%) (a); H₂O/chloroform (1%) (b); H₂O/acetone (10%) (c); H₂O/DMSO (5%) (d); H₂O/ethanol (5%) (e); and hot solution in H₂O/ethanol (f dash line)

The PULG in hot water/ethanol solution (5%) exhibits an adsorption band at 260nm. Upon gel formation, the absorption band shows red shift in all solvents. While the adsorption band of the chromophore shows red shift to 264 nm in cyclohexane, chloroform and acetone gel, it exhibited as a wider band centred at 280 nm in ethanol, DMSO. We speculated that such spectral changes might be related to the π - π stacking of the pyridinium headgroups. On the other hand, the sign of the CD band is related to the absorption band. All negative Cotton effects are at around 290nm, which the positive signs appear at around 275 nm. That is so say; the negative CD signals always appeared at longer adsorption wavelength.

Zeta-potential: Zeta-potentials measurements were performed for PULG suspension in different organic solvent/H₂O mixtures. The Z-potential of PULG aggregates in polar ethanol/H₂O (10%) mixture was +47.76mv, which indicated the surface of aggregates was obviously positive charges.² We speculated the pyridinium group with positive charge packed outside and the hydrophobic chains stayed inside to form bilayer structures. In comparison, in nonpolar cyclohexane/H₂O (1%), the z-potential was -3.95mv, slightly negative, indicating the weak charges of aggregates surface. Then, in nonpolar solvents, the polar

pyridinium groups were packed inside and hydrophobic chains extended outside. The weak conductivity is possibly due to the motion of counterions through droplet fusion in inverse micelle.³



Figure S6. (A), (B) ¹H NMR spectra of PULG in ethanol- d_6 upon addition of D₂O; (C) Plot of the chemical shift of H α and HDO against D₂O amount.

The ¹HNMR was performed in ethanol-d₆with different volumes of D₂O which contains HDO as an impurity in order to investigate the intermolecular interaction of water with PULG, and tetramethylsilane was used as an internal standard substance during the process. Figure S6 shows the chemical shift of H α in pyridinium shifts upfield upon the addition of D₂O, indicating the water molecules could surround the headgroup and improve the solubility through hydration. In addition, these water molecules could also react with the urea group to form the hydrogen bonds. The change of chemical shift of HDO with its concentration is shown in FigureS6. It exhibits a faint downfield shift from 4.40 to d 4.43 ppm with the increase of water amount to 20%, maybe due to the water mainly surrounding the headgroups. With the further increasing water amount to 40%, an obvious downfield shift occurred and gel dispersed, probably because PULG intermolecular hydrogen bonding was significantly destroyed by water molecules.



Figure S7.XRD patterns of xerogels prepared in H₂O/ DMSO (5%) (a); H₂O/CH₃OH (5%) (b); H₂O/ acetone (10%) (c); H₂O/Toluene (1%) (d); H₂O/ chloroform (1%) (e); H₂O/ Cyclohexane(1%) (f)

The X-ray diffraction patterns of all PULG xerogels showed periodical diffraction peaks, indicating an ordered lamellar structure. Based on the layer distance values, these layer structures can essentially be divided into two types. The first one is the xerogels from the polar solvents/H₂O. For example, PULG xerogel obtained from DMSO/H₂O, the 001,002, 003 and 004 diffraction peak is observed, showing the layer space is 5.02nm. The length of 5.02 nm is larger than the extended molecular length of PULG molecule (3.48nm estimated by CPK molecular modeling), but smaller than the twice molecule length, which suggested an interdigitated bilayer structure. The PULG was packed in the way of the polar pyridinium groups outside and its hydrophobic chains stayed inside to form bilayer structure. In other polar solvents, such as ethanol, methanol, the same XRD pattern is presented. In the xerogels obtained from CHCl₃/ H₂O, there is well-fine diffraction peaking corresponding to the d spacing of 6.27nm, 3.15nm, 2.14nm 1.61nm until 10th (Fig. S7 showed only to 7th). The d spacing ration of 1:1/2:1/3:1/4 and so on is consistent with a lamellar structure. The length of 6.27 nm is similar to the length of the twice PULG molecule length (3.48nm), which is larger than that of in the DMSO/water (5.02nm) and ethanol/water (4.82nm), implying the different packing mode of PULG assemblies in the non-polar or less polar solvents. In the cyclohexane/water, toluene/ water, PULG xerogels show the same layer d-space as that in chloroform/water. It is worth to note that in moderate polar acetone/H₂O mixture, the XRD pattern of the xerogel shows the two kinds of lamellar structures. One is the similar with that of in

nonpolar solvents (6.80nm), the other is according with that of in polar solvents (5.21nm). It may be due to the two kinds of staking mode coexisting.

In comparison with results of CD spectra, the PULG xerogels with long d-space show positive CD signal, whereas short space present negative CD signal, further confirming that the difference in stacking mode of chromophores leads to the inversion of supramolecular chirality.

Reference

- 1.X. Zhu, Y. Li, P. Duan, and M. Liu, Chem. Eur. J. 2010, 16, 8034-8040.
- 2.Z. Iatridi and C. Tsitsilianis, Chem. Commun., 2011, 47, 5560-5562.
- 3.J. Lang, G. Mascolo, R. Zana and P. L. Luisi, J. Phys. Chem. 1990, 94, 3069-3074.