Supporting Information

Self-assembly of Pyrene-appended Glucono Gelators: Spacer Regulated Morphological Change and Inversion of Circularly Polarized Luminescence

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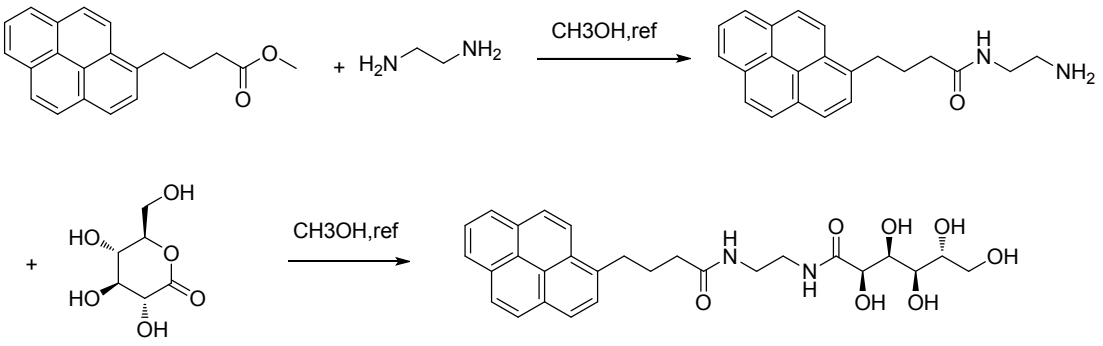
S1. Characterization and synthetic measures

Characterization: The ^{1}H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer. UV-vis spectra were recorded in quartz cuvettes with 1 cm light path on a SHIMADZU UV-2600 spectrophotometer from 250 nm to 400 nm. CD spectra were obtained using a JASCO J-815 CD spectrophotometer in quartz cuvettes with a 1 mm path length in the range of 250-500 nm. Fluorescence spectra were recorded in quartz cuvettes with 1 mm light path on a Hitachi F-4600 spectrometer. All gels were measured with excitation at 320 nm. The images of SEM were recorded using a Hitachi S-4800 FE-SEM under an accelerating voltage of 10 kV. The crystal structure (XRD) of xerogels was recorded on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu Kα radiation. The scan speed was 4° min^{-1} and scan range from 1 to 30°. Circularly Polarized Luminescence (CPL) measurements were recorded on a JASCO-200 CPL spectrometer.

Preparation of hydrogels and organogels: Adding 5 mg sample into 1 ml pure water, and heat to accelerate dissolving. In order to form hydrogel, cooling it to room temperature after getting a clearly solution. Orgnogels were prepared by dissolving 5mg sample into 1ml ethanol-water solution (ethanol : water=1:2).

Materials: 1-Pyrenebutyric acid, ethylenediamine, 1,4-Diaminbutane and delta-Gluconolactone were purchased from Innochem. All chemical solvents were provided by Beijing Chemicals.

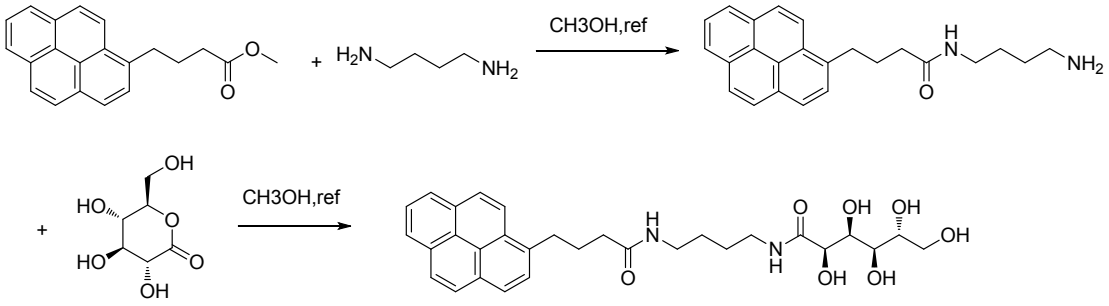


Scheme S1. Synthesis of gelator 1

Synthesis of gelator 1: Firstly, 1-Pyrenebutyric acid and thionyl chloride were dissolved in methanol and reacted for 30 minutes at 0℃，increased the temperature to 70℃ and continued to react for 6 h to yield 4-(1-pyrenyl)butyric acid methyl ester. Then, 4-(1-pyrenyl)butyric acid methyl ester (3.0 g, 10 mmol) was dissolved in methanol (300 ml), ethylenediamine (1.2 g, 20 mmol) was added and the mixture was stirred for 24h at 80℃. The solvent was removed under reduced pressure to obtain 2,3,4,5,6-pentahydroxy-N-(2-(4-(pyren-1-yl)butanamido)ethyl)hexanamide. Finally, The gelator 1 was prepared by 4-(pyren-1-yl) butanamido)ethyl)hexanamide with delta-Gluconolactone (3.56 g, 20 mmol) in methanol and stirred at 80℃ for 12 hours. The solvent was removed under reduced pressure and washed three times with water, then dried under vocuum to give 3.2 g white solid.

^{1}H NMR (400 MHz, DMSO): δ 8.39 (d, *J* = 9.3 Hz, 1H), 8.30 – 8.17 (m, 4H), 8.16 – 8.08 (m, 2H), 8.05 (t, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.87 (s, 1H), 7.81 (s, 1H), 5.39 (d, *J* = 4.4 Hz, 1H), 4.55 (dd, *J* = 18.0, 3.3 Hz, 2H), 4.46 (d, *J* = 6.9 Hz, 1H), 4.36 (t, *J* = 5.4 Hz, 1H), 4.01 (d, *J* = 3.8 Hz, 1H), 3.95 (d, *J* = 6.4 Hz, 1H),3.66 – 3.27 (m, 6H), 3.19 (s, 4H), 2.24 (t, *J* = 7.1 Hz, 2H), 2.09 – 1.94 (m, 2H).

MALDI-TOF: m/z (%): calcd. for C28H32N2O7 M^+: m/z=508.22; found M^+: m/z=507.9 and $[M+Na]^+$: m/z=530.8



Scheme S2. Synthesis of gelator 2

The synthesis methods of gelator 2 were the similar with gelator 1

^{1}H NMR (400 MHz, DMSO): δ 8.38 (d, *J* = 9.2 Hz, 1H), 8.30 – 8.19 (m, 4H),

8.16 – 8.09 (m, 2H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.82 (s, 1H), 7.63 (s, 1H), 5.36 (d, *J* = 4.5 Hz, 1H), 4.52 (d, *J* = 26.5 Hz, 2H), 4.40 (d, *J* = 7.1 Hz, 1H), 4.35 (s, 1H), 3.99 (s, 1H), 3.92 (s, 1H), 3.63 – 3.45 (m, 3H), 3.34 – 3.24 (m, 3H), 3.13 – 2.99 (m, 4H), 2.23 (t, *J* = 7.0 Hz, 2H), 2.08 – 1.93 (m, 2H), 1.41 (s, 4H).

MALDI-TOF: m/z (%): calcd. for C30H36N2O7 M^+: m/z=536.25; found M^+: m/z=537.0 and $[M+Na]^+$: m/z=559.0

S2. Supplementary Figures

Table S1. Solvent selection of gelators 1-2

Entry	Solvent	state 1	state 2	CGC **1** (mg/mL)	CGC **2** (mg/mL)
1	petroleum ether	I	I	-	-
2	dichloromethane	I	I	-	-
3	n-hexane	I	I	-	-
4	cyclohexane	I	I	-	-
5	acetone	I	I	-	-
6	ethyl acetate	I	I	-	-
7	THF	I	I	-	-
8	acetonitrile	I	I	-	-
9	methanol	I	I	-	-
10	ethanol	I	I	-	-
11	DMF	S	S	-	-
12	DMSO	S	S	-	-
13	ethanol-H_2O 1-1	S	S	-	-
14	ethanol-H_2O 1-2	G	G	3	5
15	ethanol-H_2O 1-4	G	G	4	5
16	ethanol-H_2O 1-6	G	G	4	6
17	H_2O	G	G	5	5
18	THF-H_2O 1-1	S	S	-	-
19	THF-H_2O 1-2	S	S	-	-
20	THF-H_2O 1-5	G	G	5	5
21	DMSO-H_2O 1-1	G	S	5	-
22	DMSO-H_2O 1-2	G	G	4	6

S:solution, I:insolution, G:gel

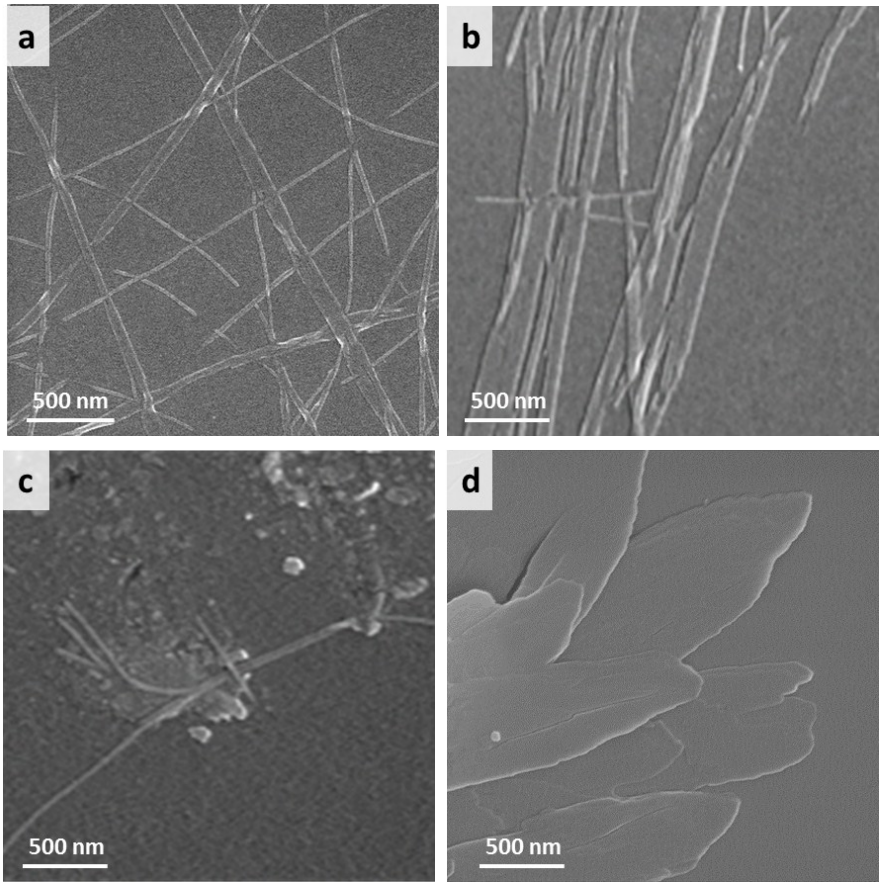


Figure S1. SEM images of **gel$_1$** in EtOH and water mixture solvent. a) **gel$_1$** in EtOH/H_2O=1:2, b) **gel$_1$** in EtOH/H_2O =1:4, c) **gel$_1$** in EtOH/ H_2O =1:6, d) **gel$_1$** in H_2O.

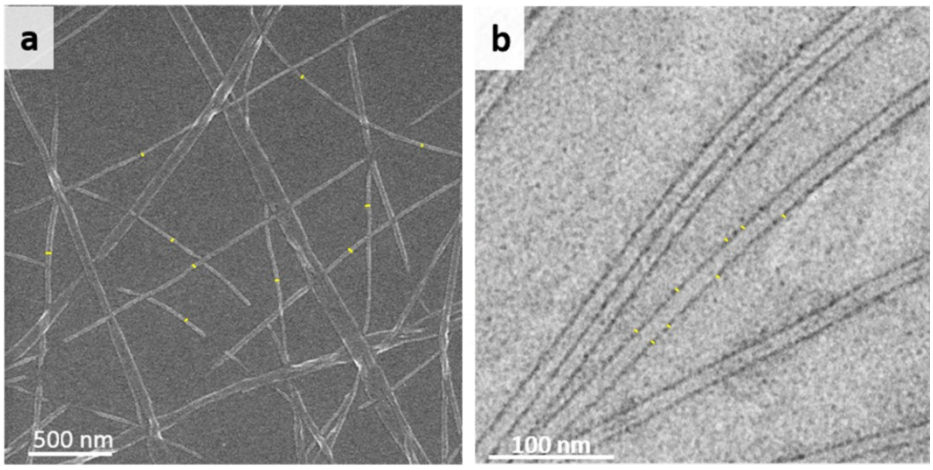


Figure S2. a) The size distribution of nanofibers in **gel$_1$**, which was about 15±1 nm; b) the size distribution of nanotubes in **gel$_2$**, which was around 2.5-2.7 nm.

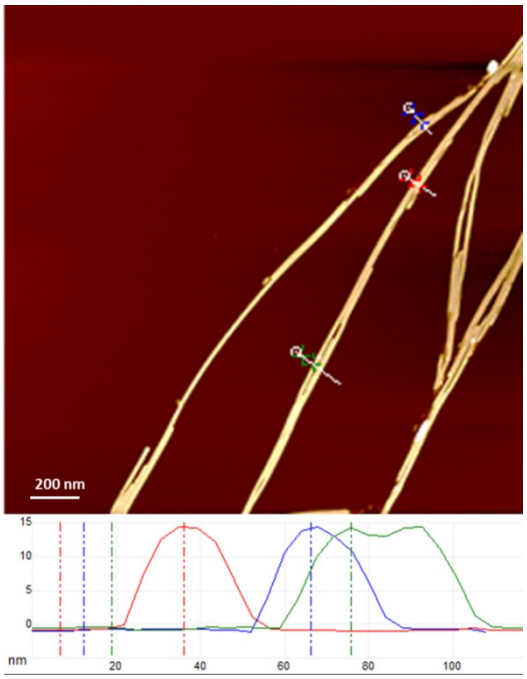


Figure S3. AFM image of gel_1 in ethanol water mixture solution (1:2), the height of nanofibers was about 15 nm.

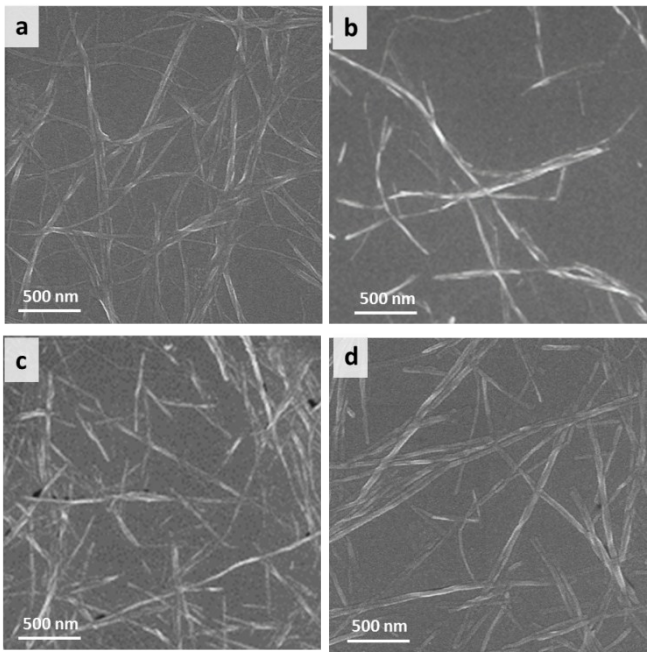


Figure S4. SEM images of **gel_2** in EtOH and water mixture solvent. a) **gel_2** in EtOH/H_2O=1:2, b) **gel_2** in EtOH/H_2O =1:4, c) **gel_2** in EtOH/ H_2O =1:6, d) **gel_2** in H_2O.2

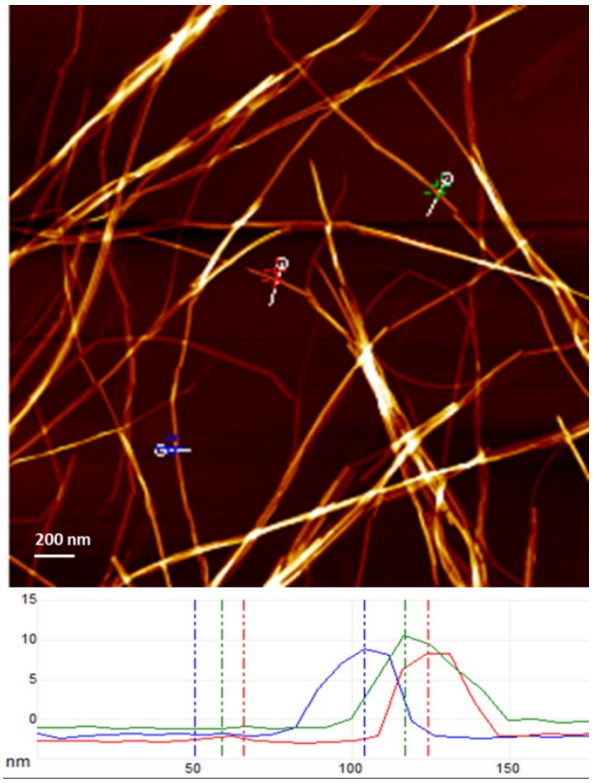


Figure S5. AFM image of **gel$_2$** in ethanol water mixture solution (1:2), the height of nanofibers was around 5-10 nm.

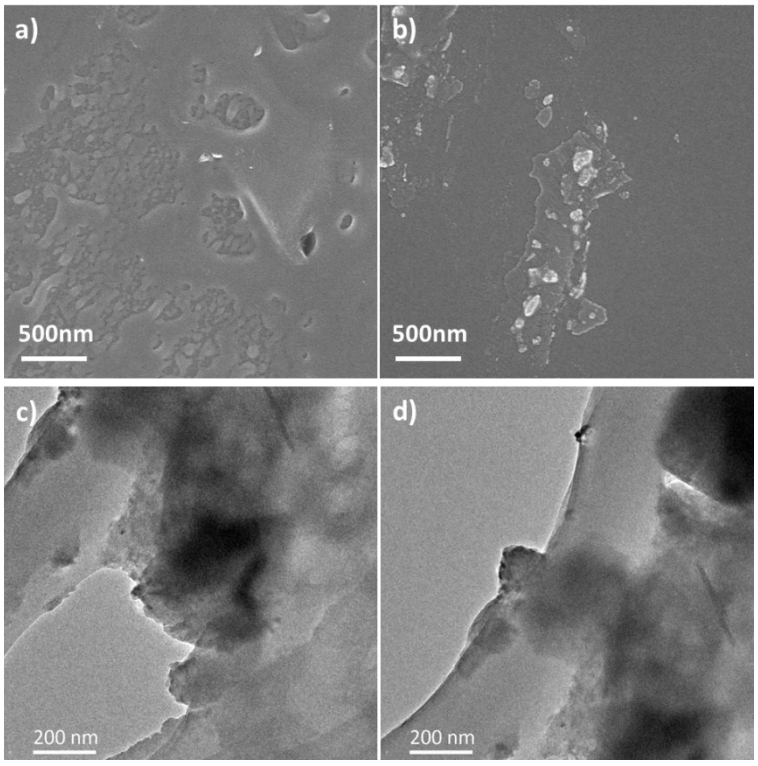


Figure S6. SEM image of a) gelator **1** and b) gelator **2** in DMSO, TEM image of a) gelator **1** and b) gelator **2** in DMSO.

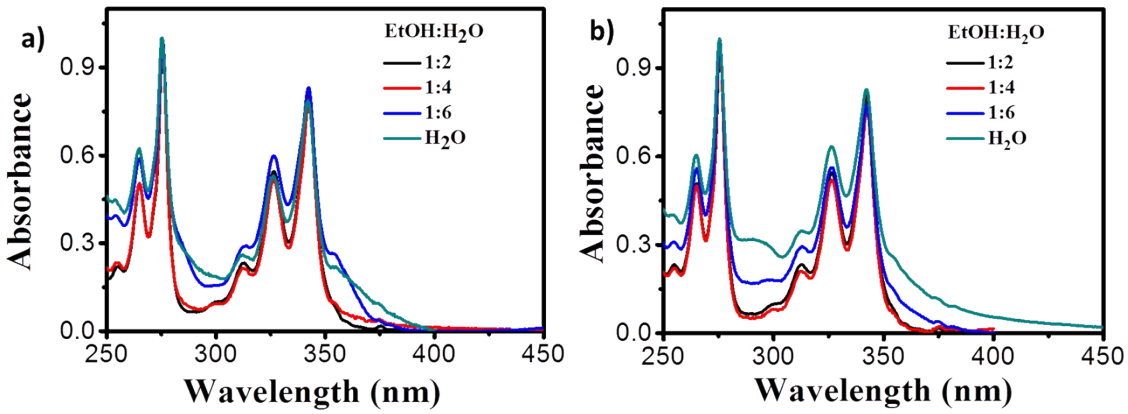


Figure S7. UV-vis spectra of a) **gel$_1$** and b) **gel$_2$** in EtOH and water mixture solvent, the absorption peaks were nearly same in the gel state.

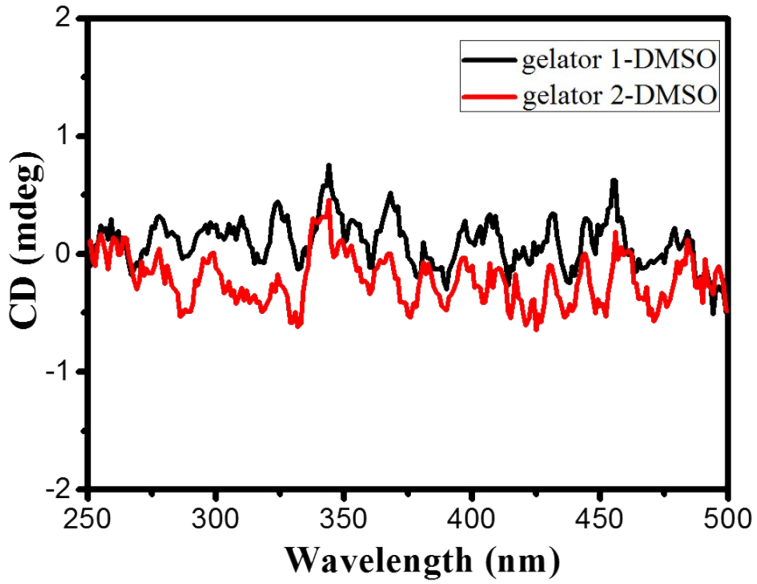


Figure S8. CD spectra of gelator **1** and **2** dissolved in DMSO.

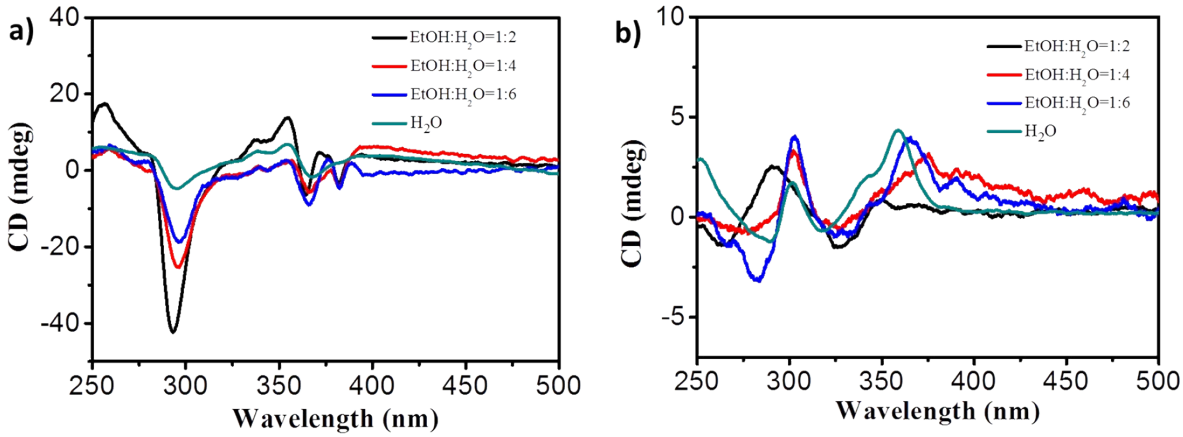


Figure S9. CD spectra of a) **gel$_1$** and b) **gel$_2$** in EtOH and water mixture solvent, all of **gel$_1$** samples under different ethanol aqueous solution present negative CD, all of **gel$_2$** samples under different ethanol aqueous solution present positive CD.

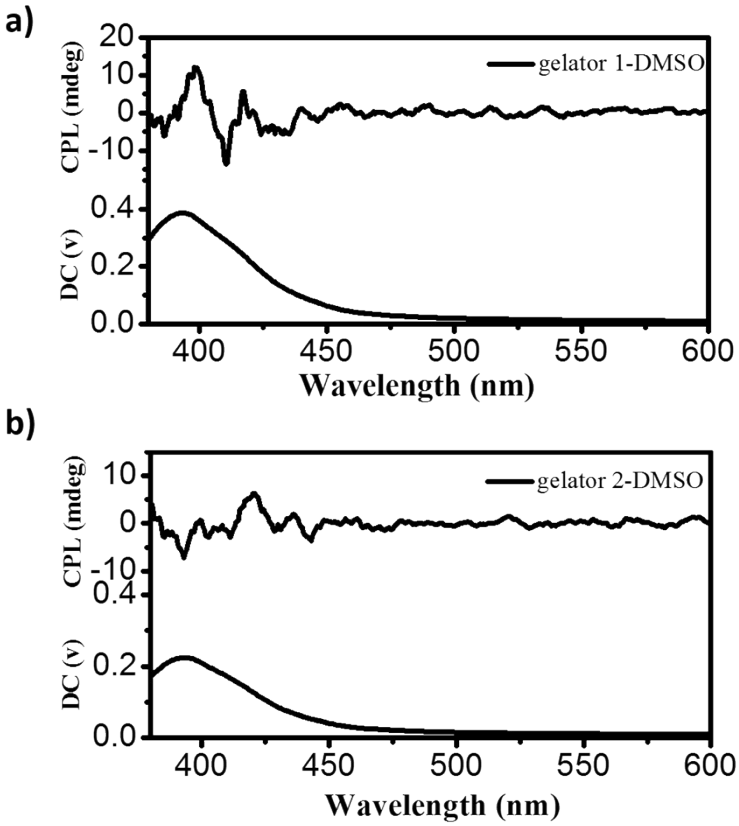


Figure S10. CPL of gelator **1** and **2** dissolved in DMSO.

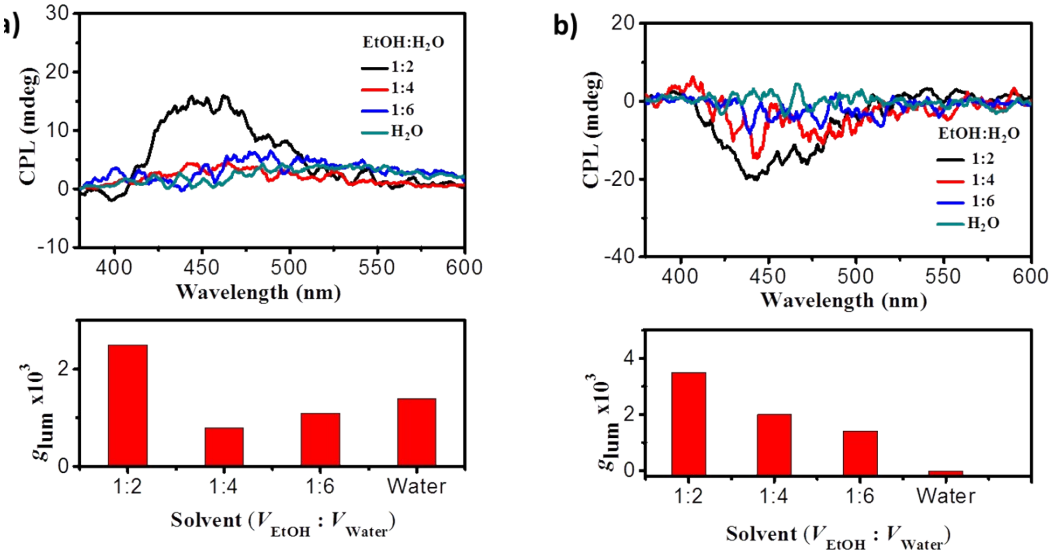


Figure S11. CPL spectra of a) **gel$_1$** and b) **gel$_2$** in EtOH and water mixture solvent, all of **gel$_1$** samples under different ethanol aqueous solution present left-handed CPL, all of **gel$_2$** samples under different ethanol aqueous solution present positive CD. The g_{lum} of **gel$_1$** and **gel$_2$** at different ethanol aqueous solvents (V_{EtOH}/V_{Water}), the highest g_{lum} was found at 1: 2 ethanol and water solvent both for **gel$_1$** and **gel$_2$**.