Electronic Supplementary Information for

Universal Chiral Twist via Metal ion Induction in the Organogel of Terephthalic Acid Substituted Amphiphilic L-Glutamide

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Experimental section

Materials:

All the starting materials were obtained from commercial suppliers and used as received. Solvents were purified and dried according to standard methods.

The synthesis of the gelator molecules are as follows. The Boc protected L-glutamic acid was reacted with octadecylamine to form N,N'-bisoctadecyl-L-Boc-glutamic diamide (LBG2C18) according to the previous reports (Y. G. Li, T. Y. Wang, M. H. Liu, *Soft Matter*, 2007, **3**, 1312). The LBG2C18 was then subjected deprotection using TFA to give a L-glutamide with free amine group (LGA). This compound was then reacted with dicarboxybenzene to give the target gelator molecules.

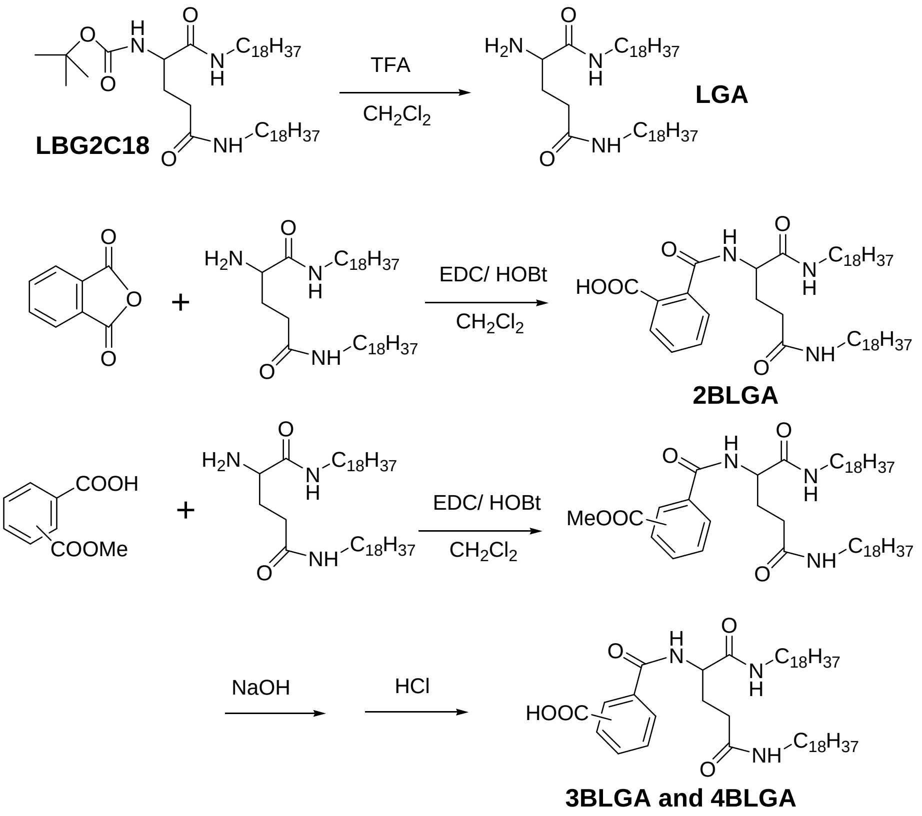


Figure S1. Synthetic route for all the gelator molecules.

In order to perform the reaction easily, 2BLGA was obtained by using phthalic anhydride, while the other two were obtained using methyl isophthalate and methyl terephthalate, respectively, followed by hydrolysis.

Synthesis of 2BLGA

LGA (0.65 g, 1 mmol) was dispersed in dichloromethane (60mL) and stirred for 30min. Then, phthalic anhydride (0.15 g, 1 mmol) was added into the above mixture and stirred at 0℃ for 30 min. After that, 1-ethyl-3-(3-(dimethylamino) propyl) carbodiimide hydrochloride (EDC HCl; 0.23g, 1.2mmol) and 1-hydroxybenzotrizole (HOBt; 0.16 g, 1.2mmol) 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 yellow solid was obtained. The crude product was dissolved in 10 mL of THF and poured into a 400 mL saturated aqueous solution of $NaHCO_3$. After filtration, the product was purified by precipitation in ethanol twice to give a white solid (0.71 g, 90%). ^{1}H-NMR (d_6-DMSO, 300Hz, 341K, ppm): δ=0.86-0.88 (t, 6H, CH_3), 1.26 (m, 60H, CH_2), 1.39-1.42 (m, 4H, CH_2), 1.83-1.84 (q, 2H, CH_2), 2.06-2.19 (m, 2H, CH_2), 3.04-3.06 (m, 4H, CH_2), 4.29 (s, 1H, CH), 7.47 (s, 2H), 7.49-7.52(m, 2H), 7.79-7.81(d, 1H), 8.36(s, 1H, NH). MALDI-TOF MS: calcd. for $C_{48}H_{87}N_3O_3$ M^+: m/z = 798.2; found $[M+ Na]^+$: m/z = 820.9. Elemental Analysis: calcd. for $C_{48}H_{87}N_3O_3$: C, 73.73; H, 10.99; N, 5.26; found: C, 73.46; H, 11.22; N, 5.35.

Synthesis of 3BLGA / 4BLGA

LGA (0.65 g, 1 mmol) was dispersed in dichloromethane (60mL) and stirred for 30min. Then, methyl isophthalate / methyl terephthalate (0.18 g, 1 mmol) was added into the above mixture and stirred at 0℃ for 30 min. After that, 1-ethyl-3-(3-(dimethylamino) propyl)-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 yellow solid was obtained. The crude product was dissolved in 10 mL of THF and poured into a 400 mL aqueous saturated solution of $NaHCO_3$. After filtration and desiccation, the product was dissolved in 20 mL THF, then 10 mL aqueous solution of NaOH (0.08 g, 2 mmol) added to the mixture, electromagnetic stirred for 5 h at room temperature. Then hydrochloric acid (1 M) was added dropwise until adjusting the pH value to 3, gave a white precipitate. After filtration, the product was purified by precipitation in ethanol to give a white solid (3BLGA, 0.65g, 81% ; 4BLGA, 0.69g, 86%).

3BLGA: ^{1}H-NMR ($CDCl_3$, 300Hz, 319K, ppm): δ=0.87-0.89 (t, 6H, CH_3), 1.25 (m, 60H, CH_2), 1.48-1.50 (m, 4H, CH_2), 2.20-2.37 (m, 4H), 3.23-3.27 (m, 4H, CH_2), 4.85 (s, 1H, CH), 5.76 (t, 1H, NH), 6.96 (t, 1H, NH), 7.50-7.54 (m, 1H), 8.19-8.25 (m, 1H), 8.90-8.95 (m, 2H). MALDI-TOF MS: calcd. for $C_{48}H_{87}N_3O_3$ M: m/z = 798.2; found $[M+ Na]^+$: m/z = 821.0, $[M + K]^+$: m/z = 837.0. Elemental Analysis: calcd. for $C_{48}H_{87}N_3O_3$: C, 73.73; H, 10.99; N, 5.26; found: C, 73.93; H, 10.95; N, 5.33.

4BLGA: ^{1}H-NMR ($CDCl_3$, 300Hz, 315K, ppm): δ=0.87-0.89 (t, 6H, CH_3), 1.26 (m, 60H, CH_2), 1.51 (m, 4H, CH_2), 2.22 (m, 2H), 2.37-2.55 (m, 2H), 3.27 (m, 4H, CH_2), 4.60 (s, 1H, CH), 5.95 (t, 1H, NH), 6.98 (t, 1H, NH), 7.88-7.90 (d, 2H), 8.02-8.05 (d, 2H), 8.09 (d, 1H, NH). MALDI-TOF MS: calcd. for $C_{48}H_{87}N_3O_3$ M: m/z = 798.2; found $[M+ Na]^+$: m/z = 821.0, $[M + K]^+$: m/z = 836.9. Elemental Analysis: calcd. for $C_{48}H_{87}N_3O_3$: C, 73.73; H, 10.99; N, 5.26; found: C, 73.90; H, 10.95; N, 5.28.

The formation of organogels in DMSO are following: Gelator 4BLGA (4.8 mg) and solvent DMSO (1.0 mL) were mixed in a capped test tube, and the mixture was heated until the solid was dissolved completely. The solution was subsequently cooled down to room temperature under ambient conditions. After 30 min, the gel formed. The formation of gel was determined by the absence of flow of the solvent when the tube was inverted. A variety of 0.1 mmol / mL metal ions DMSO solution were prepared. Take Cu^{2+} ions for example, adding 30 μL Cu^{2+} stock solution to the 4BLGA gel, then heated the mixture until the gel was dissolved completely. The inverted test tube method confirmed the gel formation. In other solvents, the formation of organogels is similar.

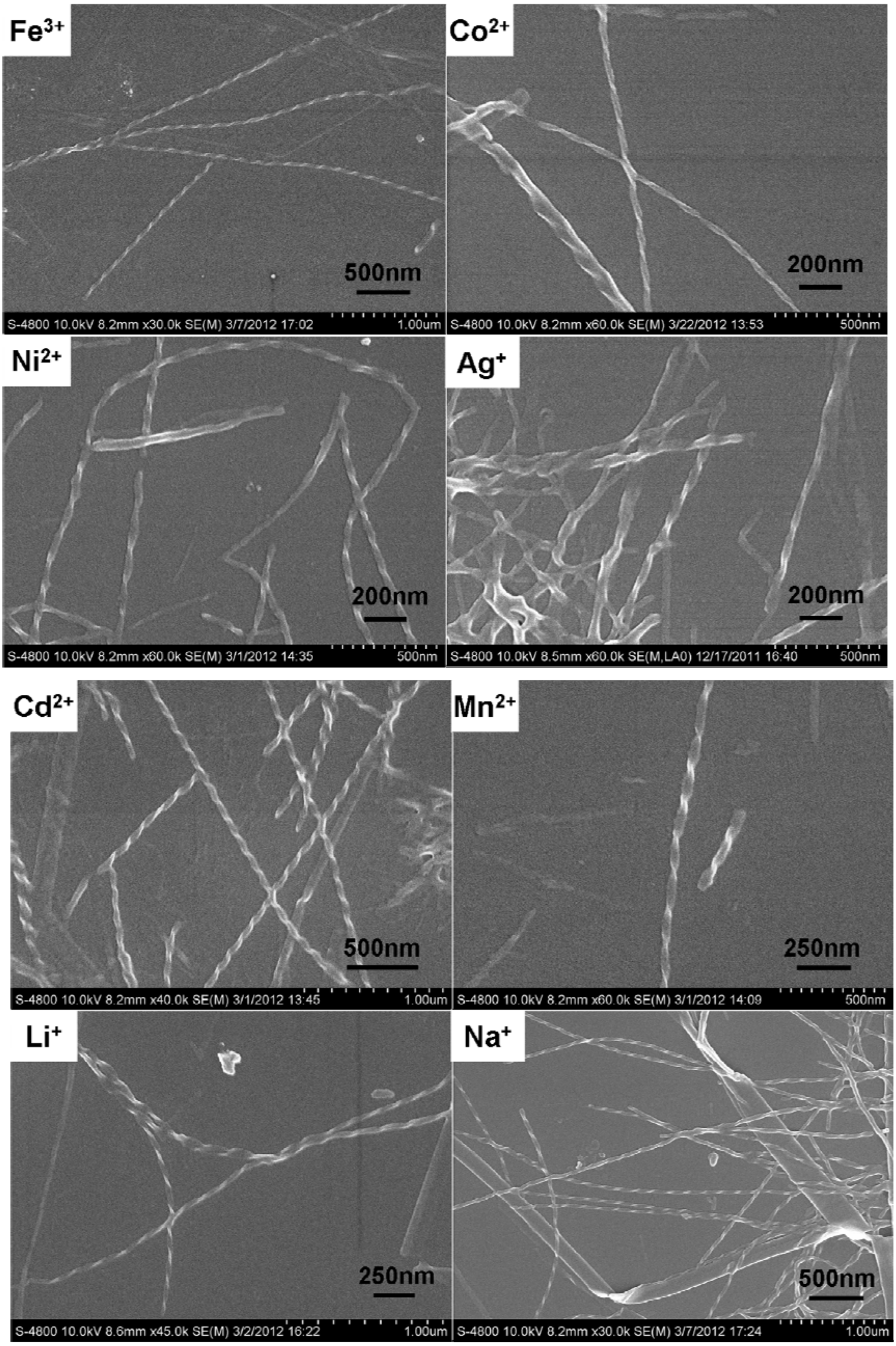
Instruments and methods :

MS spectra were performed on BEFLEX III for MALDI-TOF mass spectrometer. Elemental analyses were determined with a Carlo-Erba-1106 instrument. XRD was performed on Holand PANalytical X'Pert PRO MPD, with operating at 40 kV and 40 mA, using CuKα radiation (λ = 1.5418 Å). A small amount of as-prepared gel, or suspension was cast onto single-crystal silica plates, with a thin film of Pt coated for performance on a Hitachi S-4300 FE-SEM (15 kV, 10 μA). The samples were suspended on carbon-coated Cu grids, for TEM measurement on a JEM-1011 electron microscope (100 kV). Fluorescence emission spectra were recorded on an F-4500 fluorescence spectrophotometer. FT-IR spectra were obtained by a JASCO FT/IR-660 plus spectrophotometer with the resolution of 4 cm^{-1} at ambient conditions. UV-vis and CD spectra were obtained using JASCO UV-550 and JASCO J-810 spectrophotometers, respectively. The rheological properties of 4BLGA and 4BLGA-Cu^{2+} organogel were measured at 25 ± 0.05 ℃ with a Thermo Haake RS300 rheometer (cone and plate geometry of 35 mm in diameter with the cone gap equal to 0.105 mm).

Table 1. Gelation behaviors of three isomeric amphiphilic L-glutamide in several organic solvents[a]

solvent	2BLGA	3BLGA	4BLGA
Toluene	turbid liquid	TG (0.19)	TG (0.13)
chloroform	turbid liquid	S	TG (0.13)
DMSO	G (0.24)	PG	G (0.48)
DMF	G (0.66)	PG	PG
THF	PG	S	TG (0.60)
acetonitrile	P	P	G (0.44)
ethyl acetate	turbid liquid	PG	G (0.14)
ethanol	S	S	S
hexane	PG	TG (0.12)	TG (0.26)
cyclohexane	PG	TG (0.13)	PG

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


Fe3+
500nm
S-4800 10.0kV 8.2mm x30.0k SE(M) 3/7/2012 17:02 1.00um
Co2+
200nm
S-4800 10.0kV 8.2mm x60.0k SE(M) 3/22/2012 13:53 500nm
Ni2+
200nm
S-4800 10.0kV 8.2mm x60.0k SE(M) 3/1/2012 14:35 500nm
Ag+
200nm
S-4800 10.0kV 8.5mm x60.0k SE(M,LA0) 12/17/2011 16:40 500nm
Cd2+
500nm
S-4800 10.0kV 8.2mm x40.0k SE(M) 3/1/2012 13:45 1.00um
Mn2+
250nm
S-4800 10.0kV 8.2mm x60.0k SE(M) 3/1/2012 14:09 500nm
Li+
250nm
S-4800 10.0kV 8.6mm x45.0k SE(M) 3/2/2012 16:22 1.00um
Na+
500nm
S-4800 10.0kV 8.2mm x30.0k SE(M) 3/7/2012 17:24 1.00um

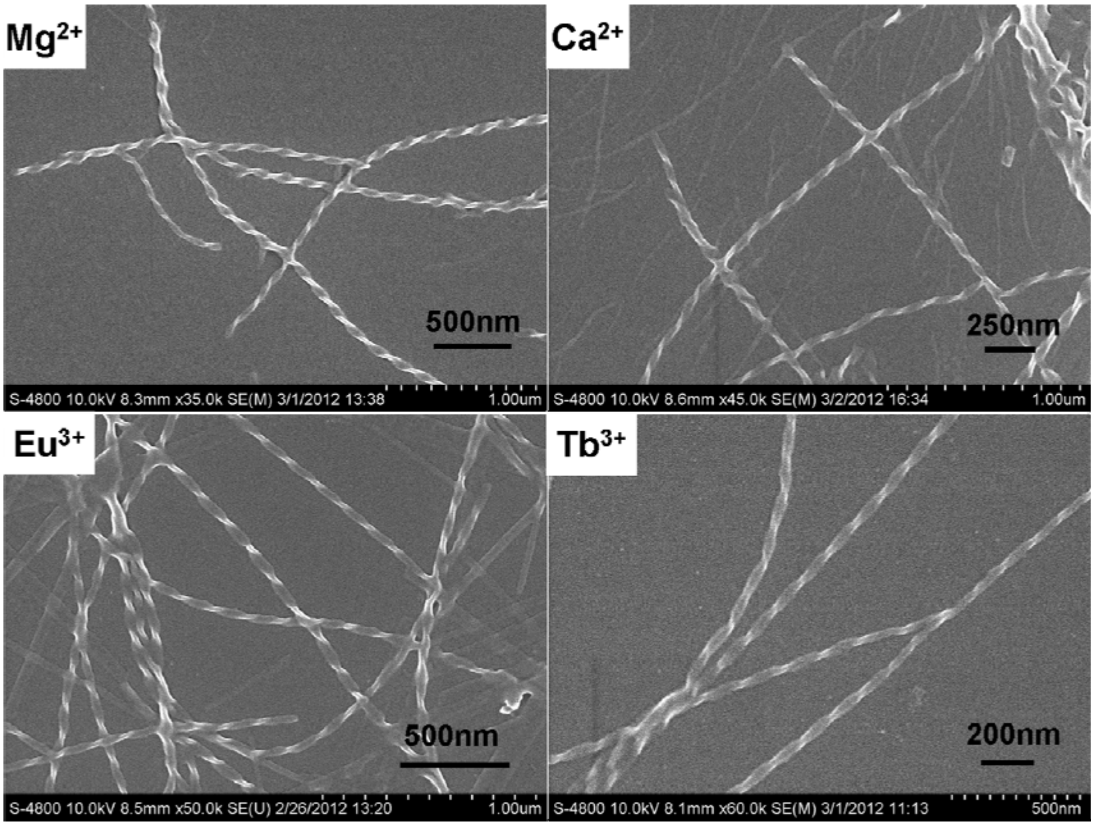
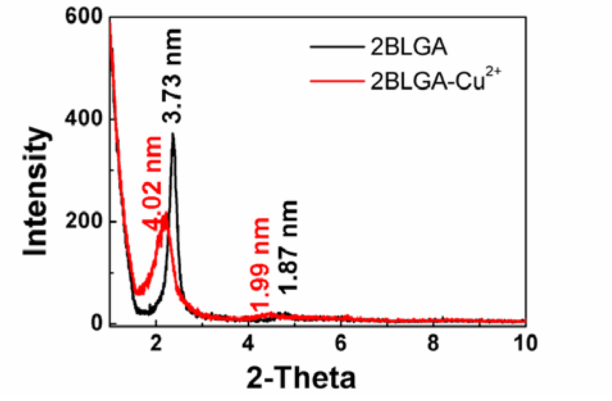
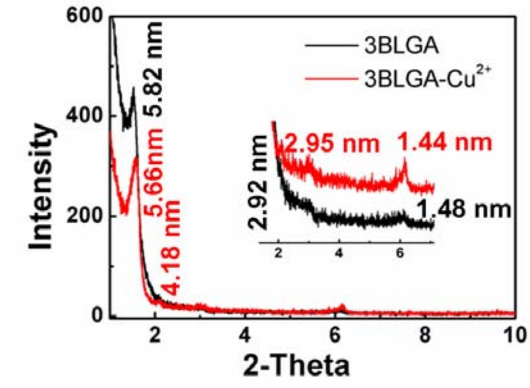


Figure S2. SEM images of the xerogel of BLGA with various metal ions.





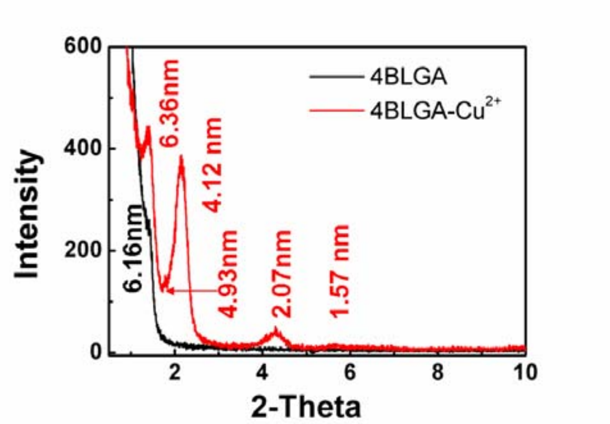


Figure S3. XRD patterns of the xerogel of BLGA in the absence and presence of Cu^{2+}.

All the xerogels in the absence of the Cu^{2+} showed the patterns obeying the (00l) diffraction, indicating the lamella structure. In the case of 4BLGA/Cu^{2+}, the diffraction showed the d values with the ratios of 1 : 1/1.55 : 1/3 : 1/4. In addition, a small peak was observed as 1/1.29. These data indicated that the xerogel formed a bicontinuous cubic gyroid structures (T. S. Bailey, H. D. Pham, F. S. Bates, *Macromolecules*, 2001, **34**, 6994), which is in accordance with the observation of the helical structure.

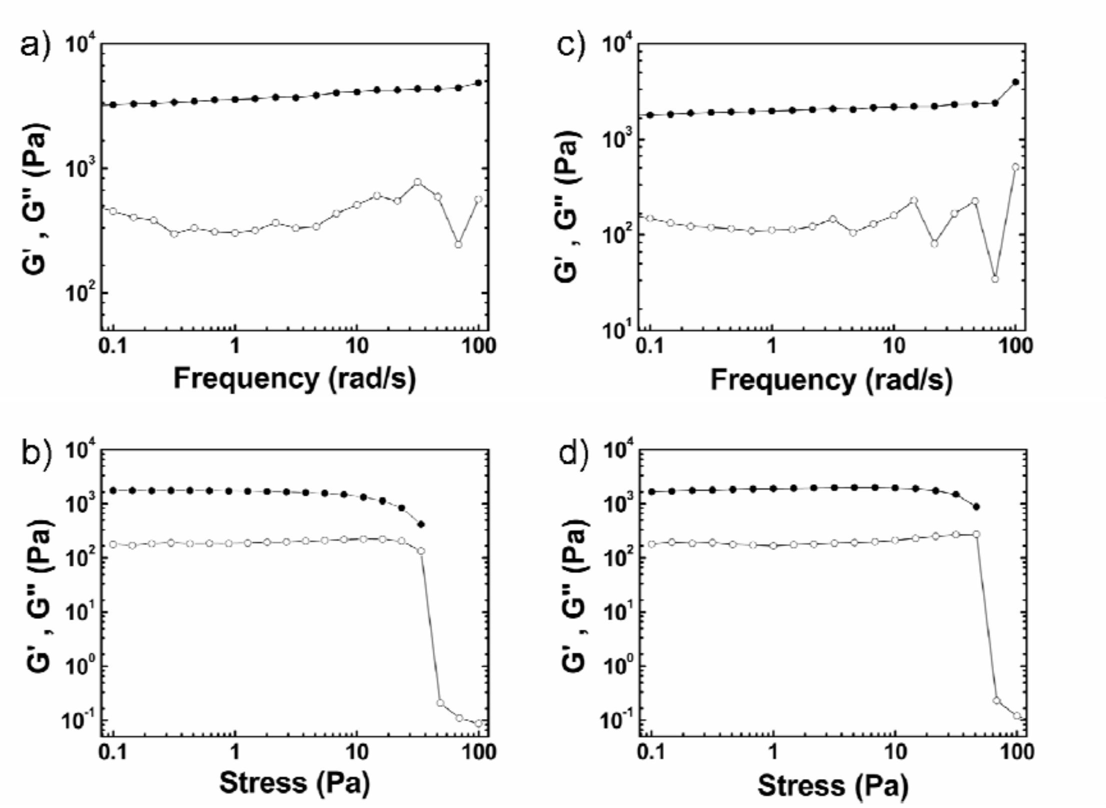


Figure S4. Dynamic rheology, frequency sweep (stress =1 Pa) of 4BLGA (a) and

4BLGA-Cu^{2+} (c) organogel; Dynamic stress sweep (f =1 Hz) of 4BLGA (b) and 4BLGA-Cu^{2+} (d). The solid symbols are donated to storage modulus G’, and the open symbols to loss modulus G”.