Support Information

for

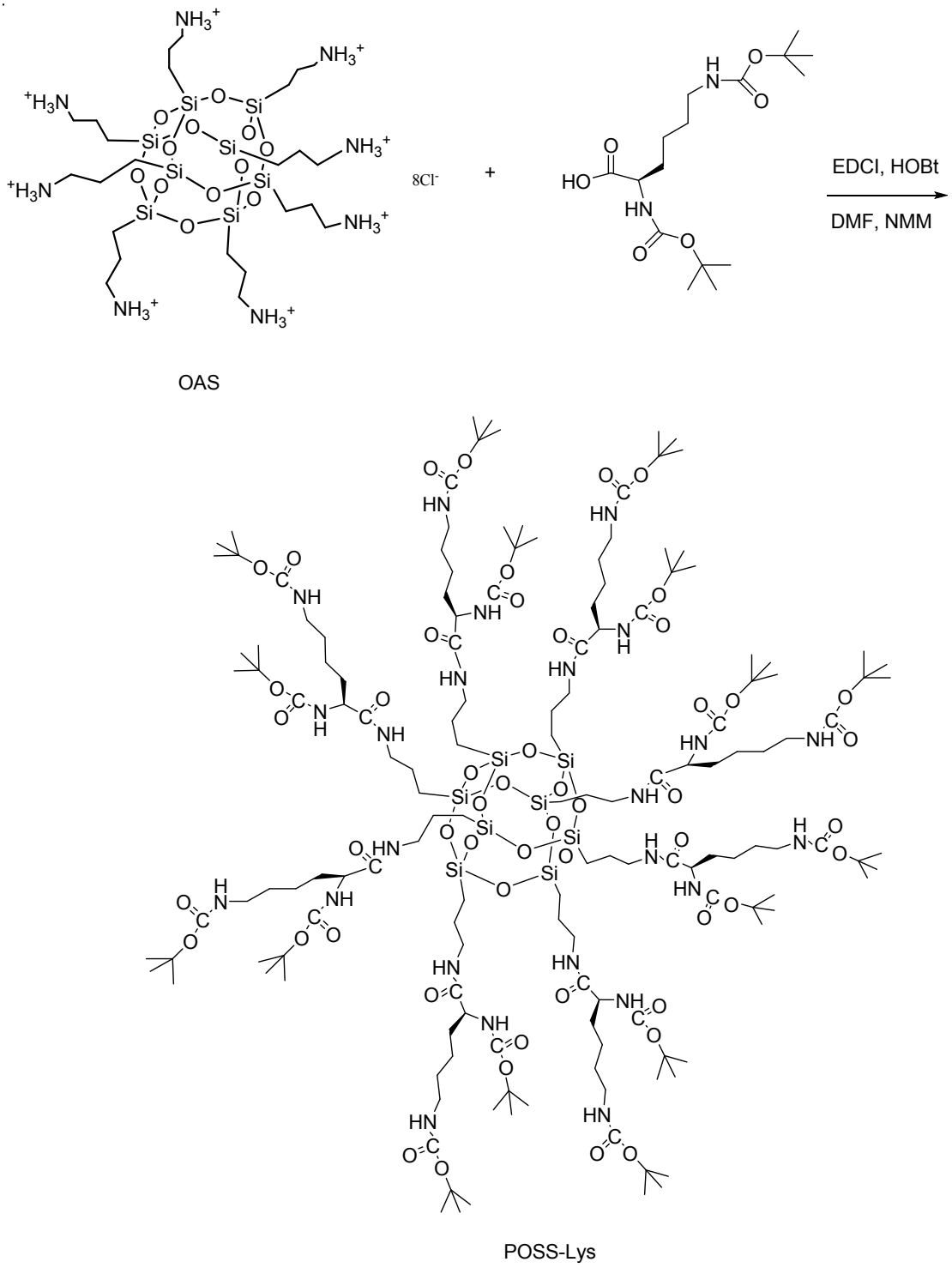
Topological structure influences on gel formation process and mechanical properties of L-lysine based Supramolecular gels

1. Synthesis and characterization of the gelators

1.1 Materials and methods

All the materials required in this reaction were commercial available. Octa(3-aminopropyl)silsesquioxanes hydrochloride (OctaAmmonium POSS-HCl) was purchased from hybrid plastic (Hattiesburg, MS). 1-hydroxy benzotriazole (HOBt), N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDCI), Nα,Nε-di-t-BOC-L-lysine [(di-t-BOC)-L-lys-OH], N-Methylmorpholine (NMM), N,N,N,N'-Tetram-ethyl-O-(1H-benzotriazol-1-yl)uroniumhexafluorophosphate (HBTU), HATU, 4-Dimethylaminopyridine (DMAP), 1,12-Diaminododecane, Trifluoroacetic acid (TFA), Boc-6-Ahx-OH, anhydrous magnesium sulfate and Pentaerythritol were supplied by Aladdin. Co., Ltd (Shanghai, China), and used as received. All the solvents used in the synthesis were analytical pure and used without further purification. Silica column chromatography was carried out using silica gel (200-300 mesh) provide by Qingdao Haiyang Chemical. Co., Ltd (Qingdao, China). Thin layer chromatography was performed on commercially available glass backed silica plates.

The structure of the product was determined by NMR (Bruker Avance III, 500 MHz), ESI-TOF MS (Agilent 6210) and MALIDI-TOF MS (Bruker Autoflex III TOF/TOF) in linear mode with α-cyano-4-hydroxycinnamic acid as a matrix. GPC (Waters 1525) was carried out to characterize the polydispersity of the product, using THF as eluent and linear polystyrene as calibration.



Scheme S1. The synthetic route of POSS-Lys hybrid gelator

1.2 Synthesis and characterization of POSS-Lys.

The synthesis process was similar to the literature[1], (Synthetic route see Scheme S1). 2.36 g (6.8 mmol) (di-t-BOC)-$_L$-lys-OH was dissolved in 20 mL DMF. 1.39 g (13.6 mmol) NMM was added, followed by the mixture of EDCI (1.44 g 6.8 mmol) and HOBt (1.01 g 7.5 mmol) in ice bath. After 5 min, 0.50 g (0.43 mmol) OctaAmmonium POSS-HCl was added. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 24 h, and then added 150 mL (0.5 M) citric acid aqueous solution giving a white, sticky precipitate. The precipitate was then treated with acetonitrile and $NaHCO_3$ aqueous saturated solution giving a white solid. The crude product was purified by column chromatography (silica, CH_2Cl_2: MeOH, 94: 6) to give a white solid with the yield of 1.12 g (73.1%). R_f 0.53 (CH_2Cl_2: MeOH, 15:1). ESI-TOF: The calculated [M+3Na]/3 of POSS-Lys was 1191.96 and the tested result was 1192.3; calculated [M+2Na]/2 was 1776.44 and the tested result was 1776.9.MALDI-TOF (m/z, $[M+Na]^+$): 3528.87 (calculated for C152H288N24O52Si8Na), 3528.80 (measured). PDI 1.02 (GPC, polystryrene). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ 7.58 (8H, br, CONH), 5.88 (8H, br, NHBoc), 4.85 (8H, br, NHBoc), 4.22 (8H, br, COCH(R)NH), 3.30 (16H, br, CH2NHCOCH(R)), 3.08 (16H, br, CH2NHBoc), 1.71-1.35 (208H, m, CH2, CH3), 0.63 (16H, m, SiCH2CH2(R)).

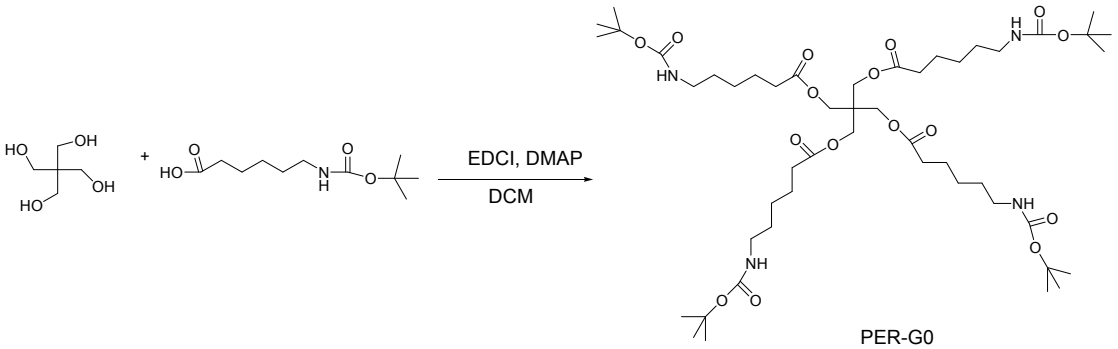
1.3 Synthesis and characterization of PER-G0, PER-Lys and PER-G2.

The synthesis process was similar to the literature[2], (Synthetic route see Scheme S2).

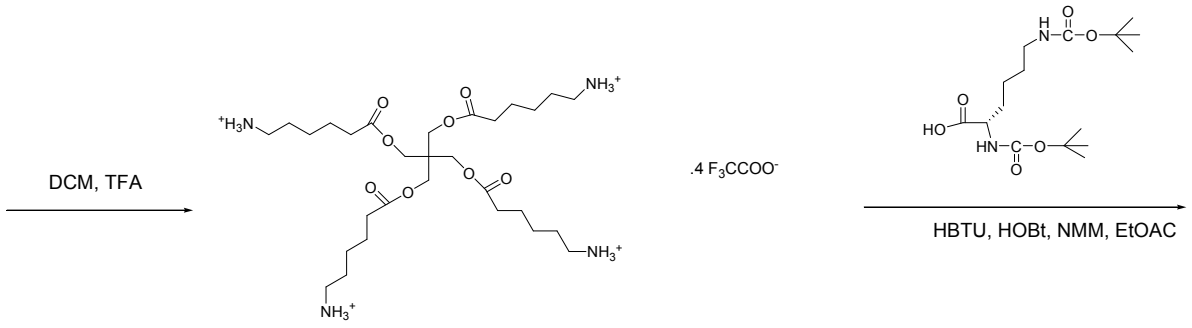
PER-G0: 0.50 g (3.67 mmol) Pentaerythritol was dissolved in 20 mL dichloromethane (DCM), 4.08 g (17.62 mmol) Boc-6-Ahx-OH was added, stirred for 5 min in ice bath followed by the mixture of DMAP 0.22 g (1.76 mmol) EDCI 3.71g (19.38 mmol) and NMM 1.96g (19.38 mmol). The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 16 h, and then washed by $NaHCO_3$ aqueous saturated solution. The organic phase was dried by rotary evaporators got a white solid with the yield of 2.86 g (79%). ^{1}H NMR (500 MHz,

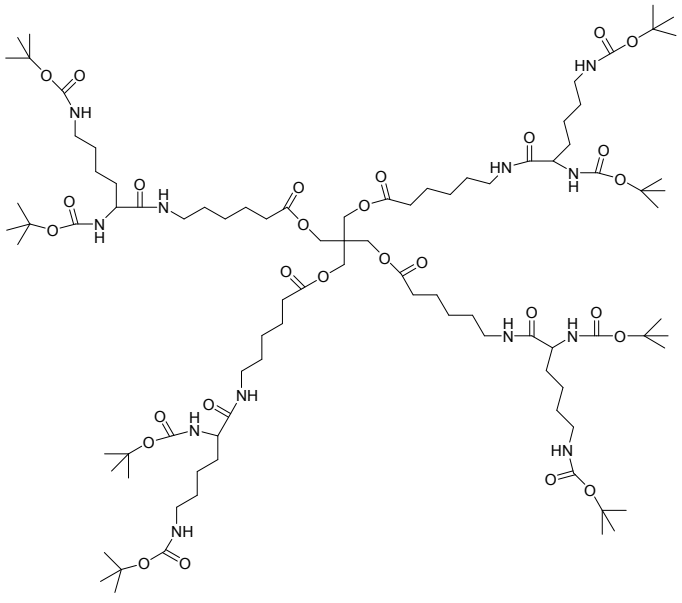
$CDCl_3$, ppm): δ 4.67 (brs, 4H; N*H*BOC), 4.11 (s, 8H; CCH_2O), 3.11 (br, 8H; CON*H*), 2.33 (t, 8H; COCH_2), 1.63 (m, 8H; $COCH_2CH_2$), 1.51-1.45 (m, 44H; CH_2CH_2NH, BOC), 1.34 (m, 8H; $CH_2CH_2CH_2NH$). ESI-TOF: The calculated of PER-G0 $[M+Na]^+$ was 1011.62, and the tested result was 1011.5, The calculated of PER-G0 $[M+K]^+$ was 1027.62, and the tested result was 1027.5, the tested result fit the calculated result.

PER-Lys: 2.85 g (2.88 mmol) PER-G0 was dissolved in 20 mL DCM, 5 mL TFA was added, stirred for 1 h at room temperature to wipe off the protection of BOC. The solvent was dried by rotary evaporators and further dried in vacuum for 1 h. The coarse product was dissolved in 40 mL ethyl acetate, 5.98 g (17.28 mmol) (di-t-BOC)-L-lys-OH was added, tirred for 5 min in ice bath followed by the mixture of HOBt 2.56 g (19.01 mmol) EDCI 3.31g (17.28 mmol) and NMM 1.74g (17.28 mmol). The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 24 h, and then washed by $NaHCO_3$ aqueous saturated solution, the organic phase was dehydrated by addition of anhydrous magnesium sulphate. The crude product was purified by column chromatography (silica, CH2Cl2: MeOH, 94: 6) to give a white solid with the yield of 4.84g (88%). ^{1}H NMR δH (500 MHz, $CDCl_3$) δ 6.70 (4H, br, NHCO), 5.42 (4H, br, NHBOC), 5.31 (4H, br, NHBOC), 4.75 (4H, br, COCH(R)NH), 4.11 (8H, s, CCH_2O), 3.23 (8H, m, CH_2NHCO), 3.10 (8H,br, CH_2NHBOC), 2.33 (8H, m, $COCH_2$), 1.81-1.32 (120H, m, CH_2, CH_3). ESI-TOF: The calculated of PER-Lys $[M+Na]^+$ was 1925.21, and the tested result was 1925.2, The calculated of PER-Lys $[M+H+Na]2^+/2$ was 963.1, and the tested result was 963.1, the tested result fit the calculated result.



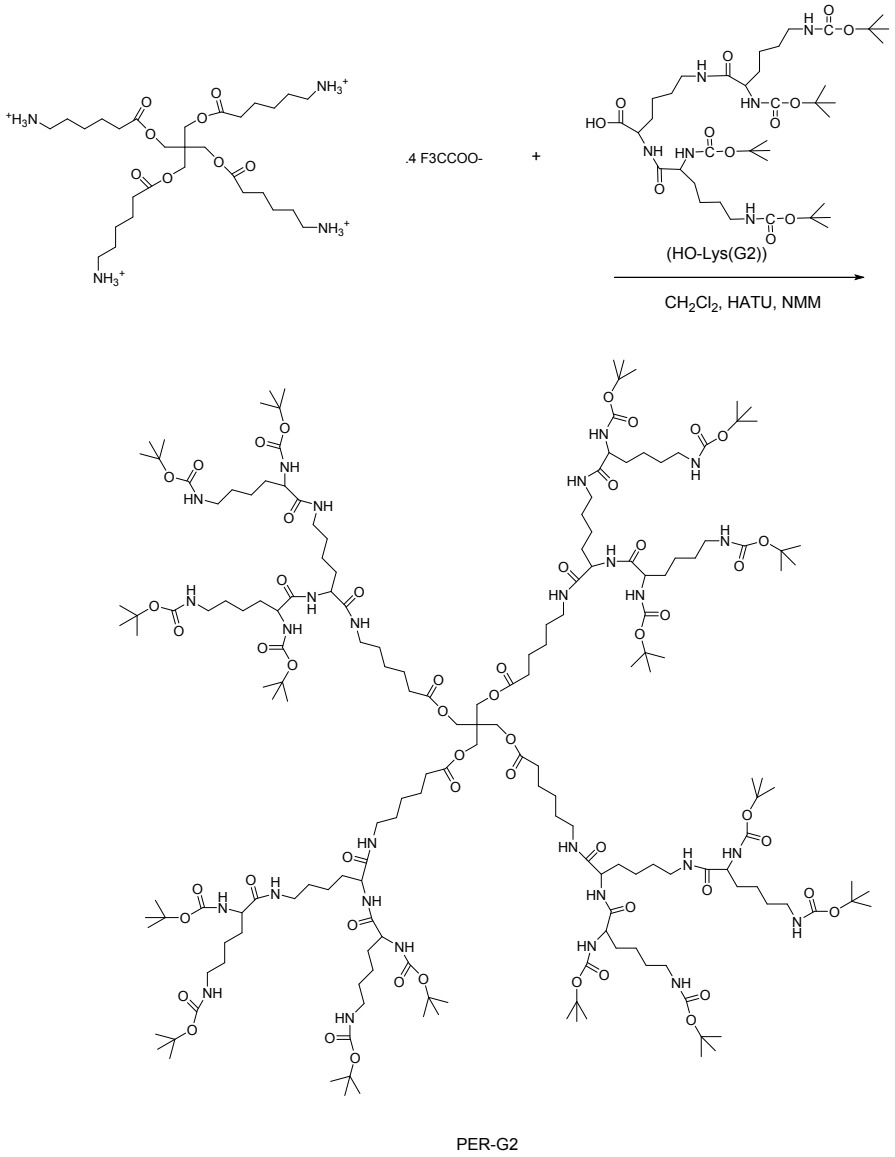
PER-G0





PER-Lys

Scheme S2. The synthetic route of PER-Lys



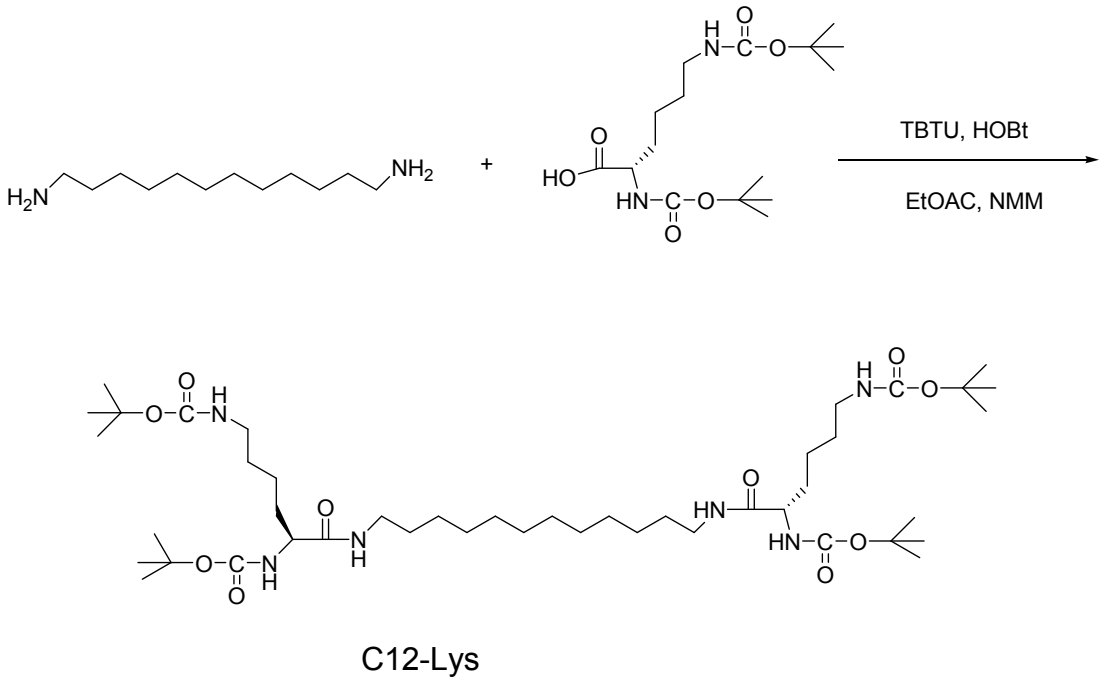
Scheme S3. The synthetic route of PER-G2

PER-G2: 0.56 g (0.57 mmol) PER-G0 was dissolved in 3 mL DCM, 3 mL TFA was added, stirred for 1 h at room temperature to wipe off the protection of BOC. The solvent was dried by rotary evaporators and further dried in vacuum for 1 h. The coarse product was dissolved in 30 mL ethyl acetate, 2.18 g (2.7 mmol, the synthetic route of HO-Lys(G2) was shown in literature 2) HO-Lys(G2) was added, tirred for 5 min in ice bath followed by the mixture of HATU 1.03g (2.7 mmol) and NMM 1.74g (17.28 mmol). The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 16 h, and then washed by $NaHCO_3$ aqueous saturated

solution, the organic phase was dehydrated by addition of anhydrous magnesium sulphate. The crude product was purified by column chromatography (silica, CH_2Cl_2: MeOH, 10:1) to give a white solid with the yield of 1.0 g (47.2%). ^{1}H NMR δH (500 MHz, $CDCl_3$) 7.57, 7.48, 7.12 (12H, br, N*H*CO), 5.87, 5.70, 5.07, 4.84 (16H, br, N*H*BOC), 4.34 (12H, br, COC*H*(R)NH), 4.12 (8H, s, CCH_2O), 3.40-3.10 (32H, m, CH_2NH), 2.33 (8H, m, COCH_2), 1.75-1.27 (240H, m, CH_2, CH_3). ESI-TOF: The calculated of PER-G2 $[M+2Na]^{2+}$ was 1887.2, and the tested result was 1884.2, the calculated of PER-G2 $[M+3H]^{3+}/3$ was 1243.8, and the tested result was 1243.8, the calculated of PER-G2 $[M+4H]^{4+}/4$ was 933.1, and the tested result was 933.1, the tested result fit the calculated result.

1.4 Synthesis and characterization of C12-Lys.

8.73 g (25.20 mmol) (di-t-BOC)-L-lys-OH was dissolved in 50 mL ethyl acetate, 9.56 g (25.20mmol) HBTU, 3.41 g (25.20 mmol) HOBt and 5.09 g (50.04 mmol) NMM was added and stirred for 5 min, followed 1,12-Diaminododecane 1.7 g (8.50 mmol) was added. The reaction mixture was allowed to stir at room temperature for 12 h, then filtrated to remove insoluble substance. The filtrate was washed by $NaHCO_3$ aqueous saturated solution, the organic phase was dehydrated by addition of anhydrous magnesium sulphate. The crude product was purified by column chromatography (silica, ethyl acetate: petroleum ether, 60: 40) to give a white solid with the yield of 89.4%. 1H NMR δH (500 MHz,CDCl3)：6.27 (2H, br, CONH), 5.19 (2H, br, NHBOC), 4.65 (2H, br, NHBOC), 4.02 (2H, br, COCHNH(R)), 3.10-3.25 (8H, m, CH2NH), 1.25-1.82 (70H, m, CH2, CH3);ESI-TOF: The calculated $[M+H]^+$ of C12-Lys was 857.62, and the tested result was 857.6；The calculated $[M+Na]^+$ of C12-Lys was 879.62, and the tested result was879.6,the tested result fit the calculated result.



Scheme S4. The synthetic route of C12-Lys

2. Gelation behavior of PER-G2 in solvents

The gelation ability of second generation of dendritic PER-G2 were examined in various organic solvents, at last we found that PER-G2 could form stable gel in solvents as shown in Table S1. The density of hydrogen bond between PER-G2 molecules could overcome the stereo-hindrance effect of pentaerythritol molecule to form a stable network structure[3,4], thus the stable gel had been formed.

Table S1 Gelation behavior of PER-G2 in various solvents

Solvents	PER-G2[a]
toluene	G (0.5% 76 °C)
xylene	G (0.3% 85 °C)
MMA	G (1.5% 48 °C)

[a] G denote gel. Data in brackets represents minimal gelation concentration (MGC) and gel-sol transition temperature in plateau region (T_{gel}).

Figure S1 is the SEM image of the xerogel of PER-G2 at low concentration of gelator in xylene. SEM observation shows that the gel network is composed of nanofibers with a diameter of about 100 nm and a length of about 1-2 μm, which further demonstrated that the ability of PER-G2 could form a stable gel in solvent by overcome the stereo-hindrance effect of pentaerythritol molecule to form a pyknotic network.

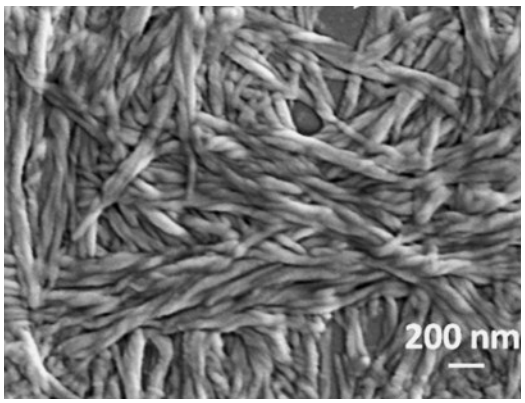


Figure S1. SEM image of PEG-G2/xylene xerogel, 5 mg/mL.

3. Gel network morphology

Figure S2 shows several major diffraction peaks which demonstrates the microcrystalline and orientation order of the gels, confirming the high orientation order observed in Fig. 3(b).

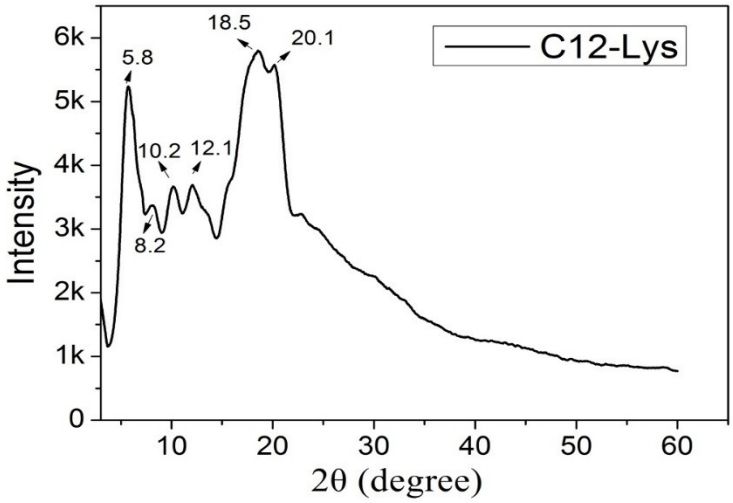


Figure S2. Powder XRD patterns of C12-Lys/DCB xerogel, 30 mg/mL. The 2 theta range spanning 3^{o} to 60^{o}, which demonstrates the microcrystalline and orientation

ordered of the gels.

Furthermore, the dry sample of C12-Lys at lower concentration (0.5%) in DCB without gelation is also observed through SEM, as shown in Figure S3, which shows no clear ordered self-assembly microstructure, indicating the ordered self-assembled structure is quite necessary to form gel networks.

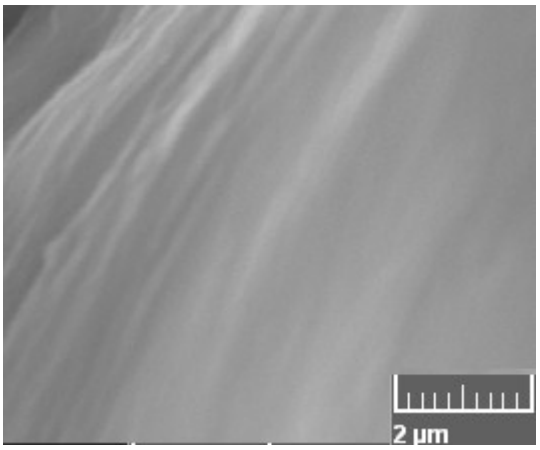


Figure S3. SEM image of C12-Lys/DCB xerogel (0.5%)

References

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