Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Materials

All materials employed in the paper were commercially available. PSS-[3-(2-Aminoethyl) amino] propyl-Heptaisobutyl substituted (PSS-NH_2) was purchased from SIGMA-ALDRICH (Shanghai, China). Octa(3-aminopropyl)silsesquioxanes hydrochloride (POSS-HCl) was purchased from hybrid plastic (Hattiesburg, MS). N, N, N, N'-Tetram-ethyl-O-(1H-benzotriazol-1-yl) uroniumhexafluorophosphate (HBTU), 1-hydroxybenzotriazole (HOBt), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI), (S)-2,6-Bis-tert-butoxycarbonylaminohexanoic acid (Boc-Lys(Boc)-OH), N-Methylmorpholine (NMM), were supplied by Aladdin (Shanghai, China), and used as received. All 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) provided by Qingdao Haiyang Chemical (Qingdao, China). Thin layer chromatography was performed on commercially available glass backed silica plates.

Synthesis of PSS-Lys

The synthetic route of PSS-Lys was shown in Scheme S1 and specific steps of synthesis were as followed. The double Boc protected lysine Boc-Lys(Boc)-OH (0.52 g, 1.50 mmol) was dissolved in 40 mL trichloromethane, then the solution was added to a 100 mL round bottom flask with a magnetic stirrer. HBTU (0.57 g, 1.50 mmol) and HOBt (0.22 g, 1.65 mmol) were added to the round bottom flask. The mixture was stirred in the ice-bath for 5 min. Then PSS-NH_2 (0.92 g, 1.00 mmol) was added to the round bottom flask andNMM was added dropwise. After 24 h, the mixture was further extracted with saturated sodium bicarbonate and sodium bisulfate. The organic layers were washed with water. The crude product was purified by column chromatography and dried in vacuo for 8 h. The stationary phase is 200-300 mesh silica gel, and the mobile phase is mixed solvent of dichloromethane/methanol = 6/1. The appearance of the product is transparent crystal. Yield=60.00 %.

Synthesis of POSS-Lys

The synthesis route was same as the literature 1, as shown in Scheme S2, and specific steps of synthesis were as followed. 2.36 g (6.8 mmol) Boc-Lys(Boc)-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 an ice bath. After 5 min, 0.50 g (0.43 mmol) POSS-HCl was added. The reaction mixture was warmed to room temperature and stirred at room temperature for 24 h, and then added 150 mL (0.5 M) citric acid aqueous solution was added to obtain a white viscous precipitate. The precipitate was then treated with acetonitrile and $NaHCO_3$ aqueous saturated solution to obtain a white solid. The crude product was purified by column chromatography and dried in vacuo for 8 h. The stationary phase is 200-300 mesh silica gel, and the mobile phase is dichloromethane/methanol = 15/1 mixed solvent. The appearance of the product was the white solid. Yield=73.00 %.

Experimental Section

Gelation ability tests The properties of gels formed by gelators were determined through tube inversion method., The gelators that were accurately weighed were added into a 3mL glass vial containing 1mL of a specific solvent, which was test tube. And the vial was sonicated at room temperature for 10 minutes. Then the test tube was heated in oil bath at 120 ^{o}C until the compound was completely dissolved in the solvent. Next, it was cooled down to room temperature in the air. Finally, we could clearly observe whether the gel is formed. The standard for gel formation is when the tube is inverted, and the solvent does not flow along the tube wall.

Scanning electron microscopy (SEM) A FEI Nova Nano SEM 450 operating at 15 kV was used to obtain the SEM images. The solution of PSS-Lys and PSS-Lys: POSS-Lys=1:1, 4:1, 8:1 (mol: mol) in MMA, were carefully dropped to the silicon wafer. Then the silicon wafer was fixed to the platform through conducting resin and dried overnight in air. Then, 10 nm-thick platinum films were deposited on the sample before direct observation.

Transmission electron microscopy (TEM) JEM-1230 transmission electron microscope was used to obtain the TEM images at an accelerating voltage of 80 kV. The dilute solution of PSS-Lys, PSS-Lys: POSS-Lys=1:1, 4:1, 8:1 (mol: mol) was carefully dropped onto the amorphous carbon-coated Cu grids by suspension and dried at room temperature for 24 hours before direct observation

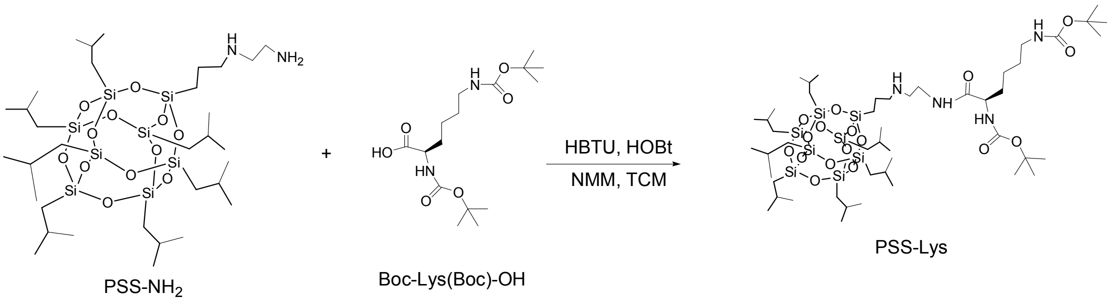
Fourier-Transform Infrared Spectroscopy (FT-IR) Fourier transform infrared spectra of PSS-Lys, POSS-Lys and PSS-Lys: POSS-Lys=1:1, 4:1, 8:1 (mol: mol) were collected on a Nicolet 6700

FT-IR spectrophotometer (Thermo Fisher Scientific Inc., USA) by loading the samples into a KBr cuvette.

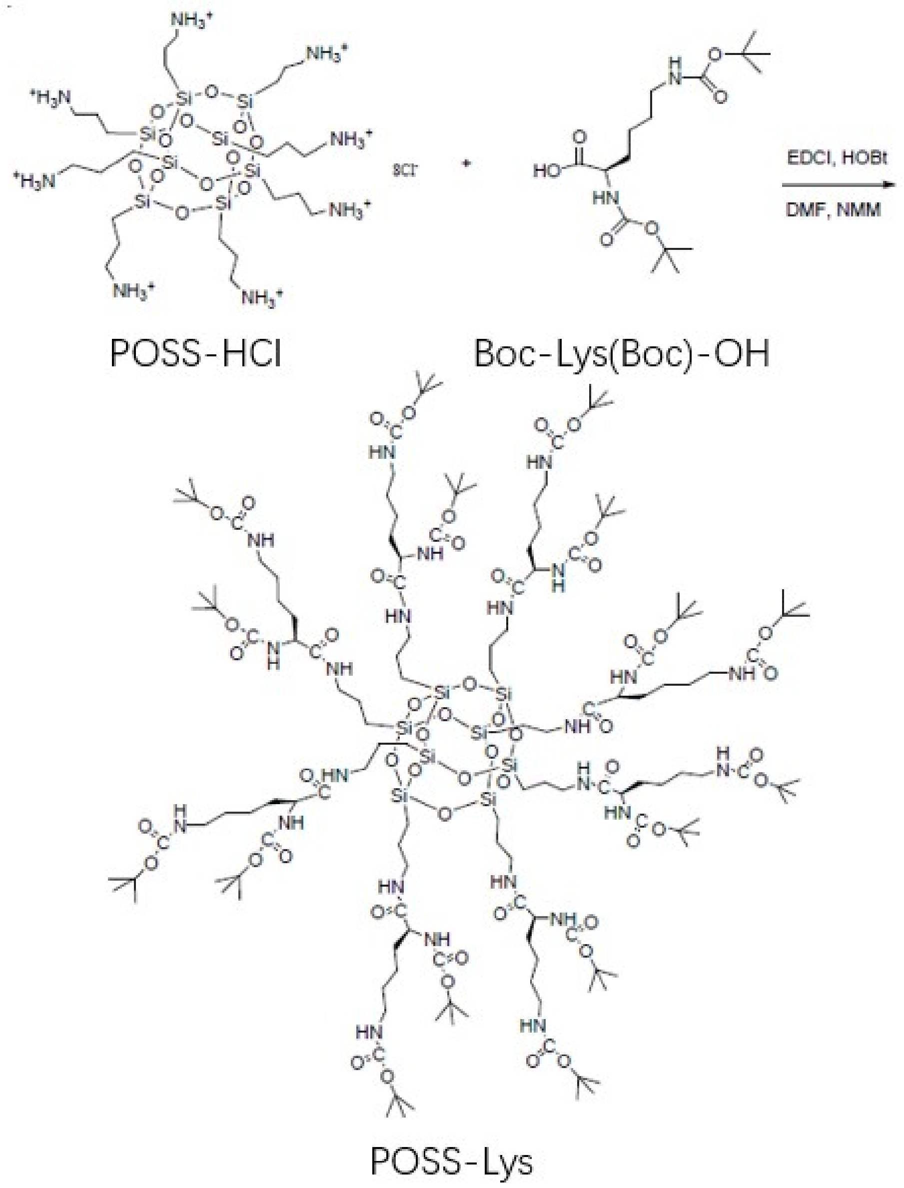
Rheology All Rheological experiments were performed an Anton Paar MCR302 Rheometer with plate geometry (PP 25). The gap distance between plates was fixed at 0.5 mm. Rheological measurements were carried out on prepared gels and were placed on the rheometer plate.

The following tests were performed: the samples were transmitted to this parallel-plate very quickly to minimize solvent evaporation. Dynamic frequency sweep tests were increased from 0.1 to 100 rad•s^{-1} (kept a strain $\gamma = 0.1\%$) at 25 ^{o}C. Oscillatory frequency sweep experiments were carried out in the linear viscoelastic region in order to ensure that experimentally obtained parameters correspond to an intact network structure.

Optical contact angle tests The sample was dissolved in MMA, then the solution was dripped onto the slide. When the solvent evaporated, the coat of the sample was formed.



Scheme S1. The synthetic route of PSS-Lys.



Scheme S2. The synthetic route of POSS-Lys.

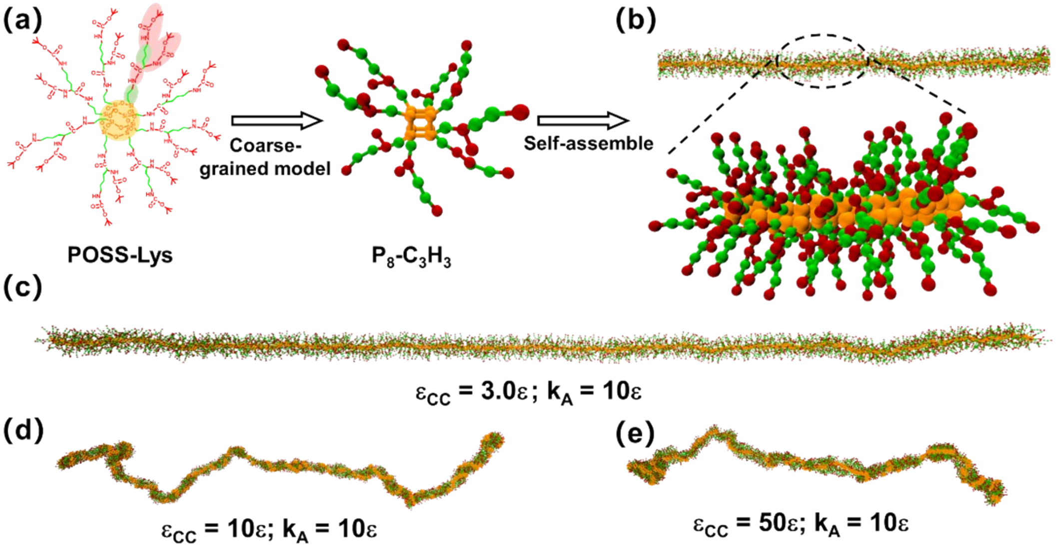


Figure S1. (a) Coarse-grained model and mapping relationship. (b) Partial enlarged detail of fibrous morphologies. (c-e) Simulation snapshots of aggregates morphologies formed at various interaction parameter: (c)□CC= 3.0□, kA= 10; (d)□CC= 10, kA= 10; (e)□CC= 3.0, kA= 10.

(Quote from 45 T. Shan, L. Gao, X. Tong, Q. Du, Z. An, H. He, J. Lin, S. Chen, X. Wang, Chem. Eur. J., 2019, 25, 12098-12104.)

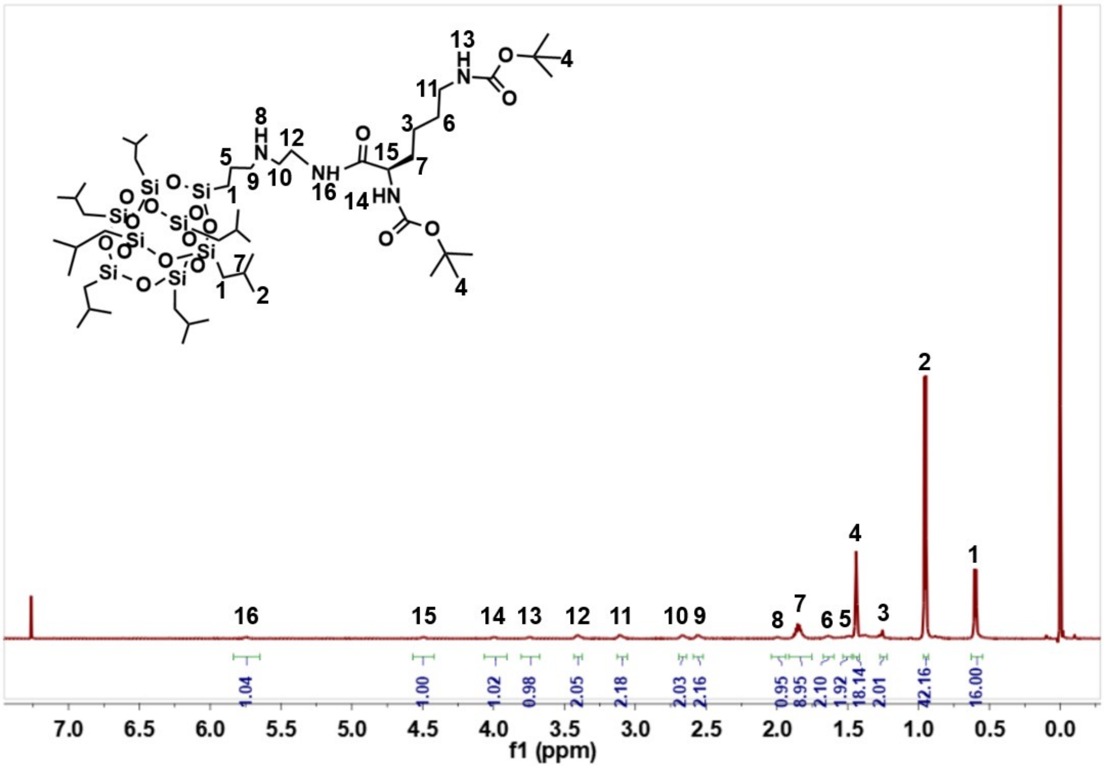


Figure S2. ^{1}H NMR spectrum of PSS-Lys.

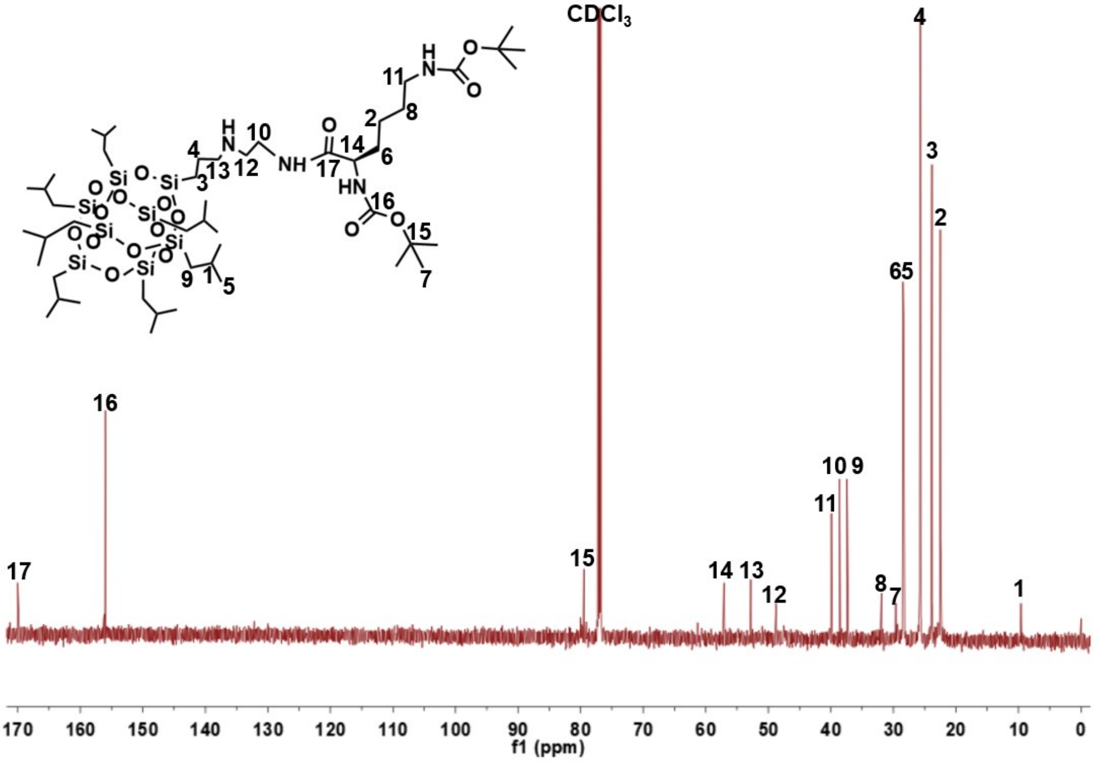


Figure S3. ^{13}C NMR spectrum of PSS-Lys.

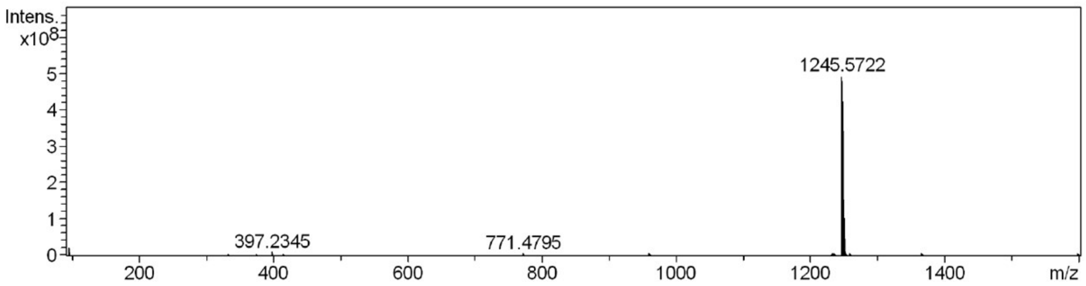


Figure S4. Mass spectrum of PSS-Lys.

The molecular formula of PSS-Lys is $C_{49}H_{104}N_4O_{17}Si_8$, the calculated [M+H] of PSS-Lys was 1245.56 and the result was 1245.5722.

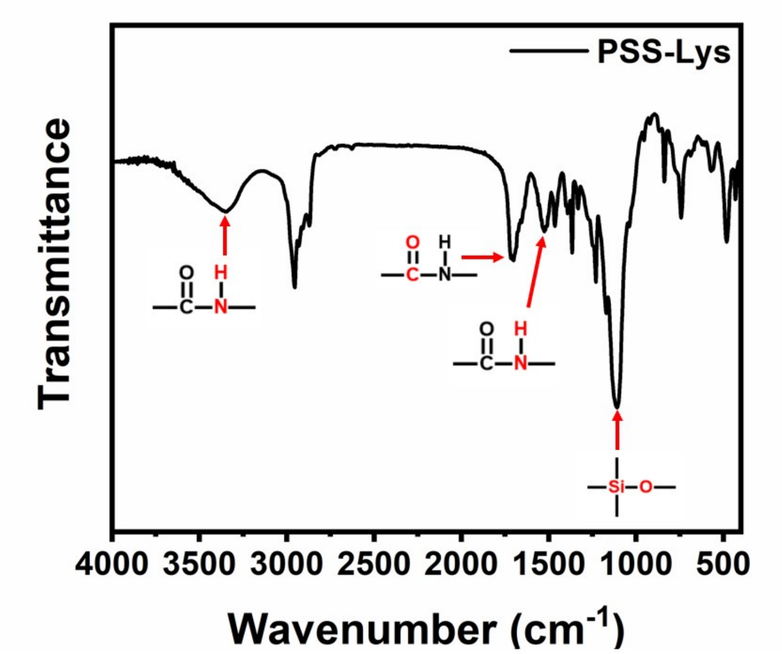


Figure S5. FT-IR spectrum of PSS-Lys.

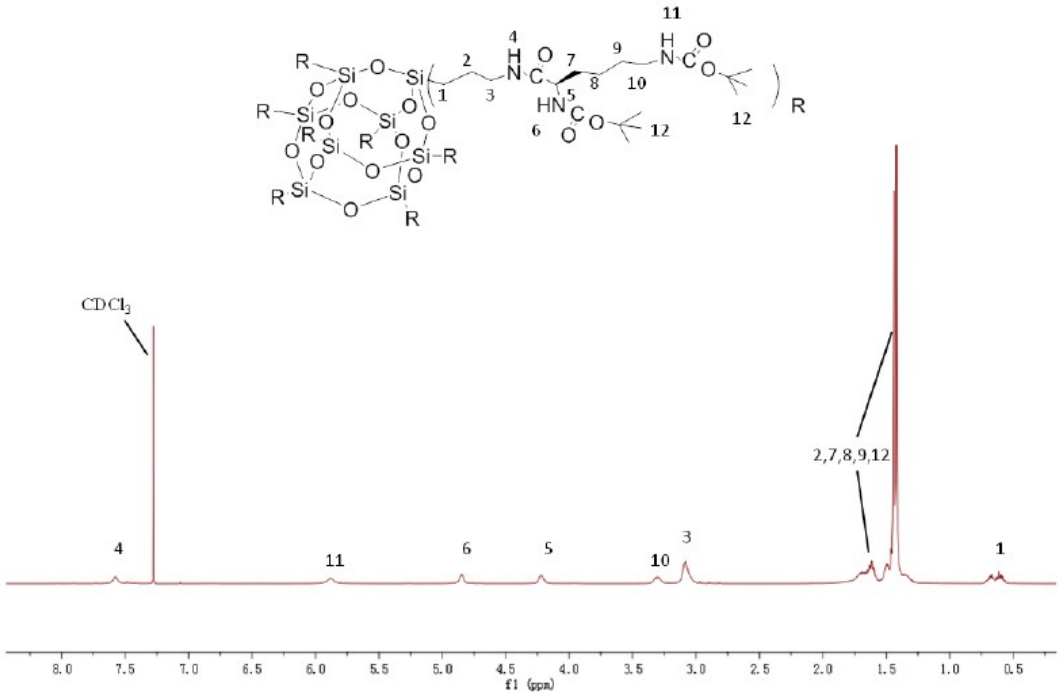


Figure S6. ^{1}H NMR spectrum of POSS-Lys.

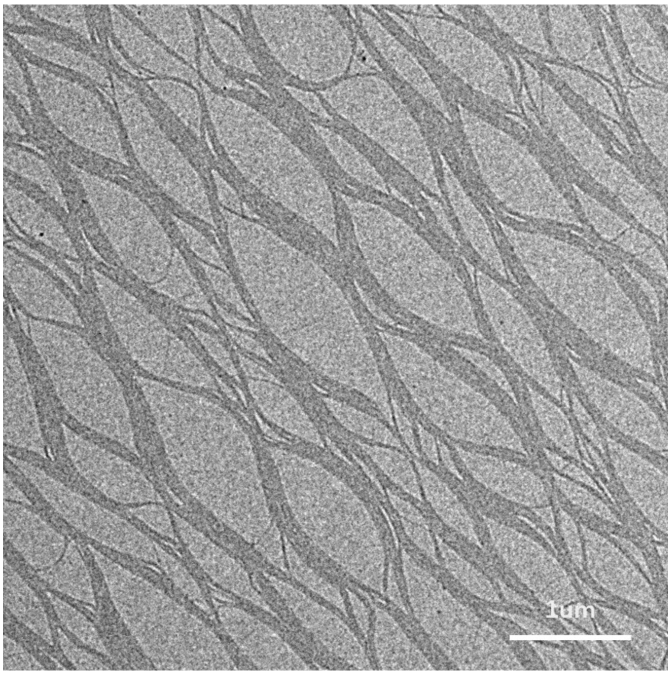


Figure S7. TEM images of loofah-like fiber networks of POSS-Lys.

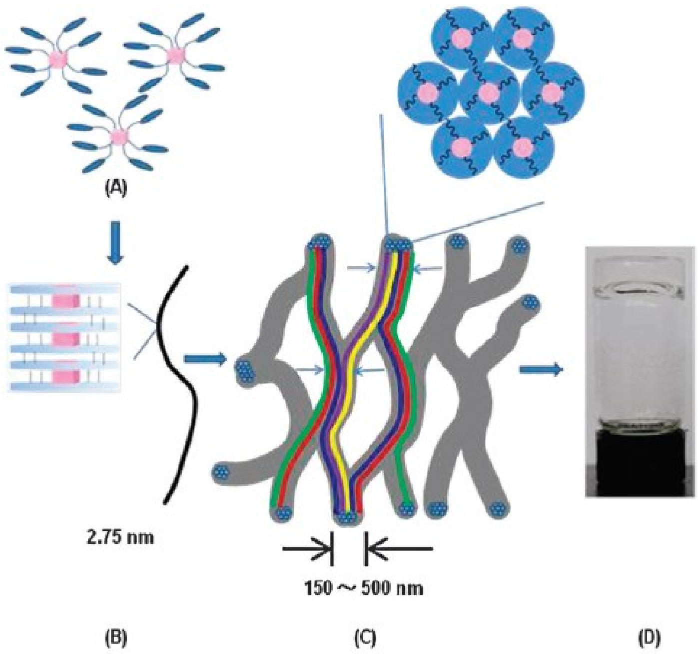


Figure S8. Proposed mechanism for the formation of the loofah-like structure self-assembled by the 3D radially symmetrical organic–inorganic hybrid gelator POSS–Lys. (A) Free molecules in solution at high temperatures; (B) a single column is formed via the plane-to-plane stacking of POSS–Lys; (C) the loofah-like hexagonal columnar network and (D) an optical image of the transparent gel.

(Quote from G. Tang, S. Chen, F. Ye, X. Xu, J. Fang, X. Wang, Chem. Commun., 2014, 50, 7180-7183.)

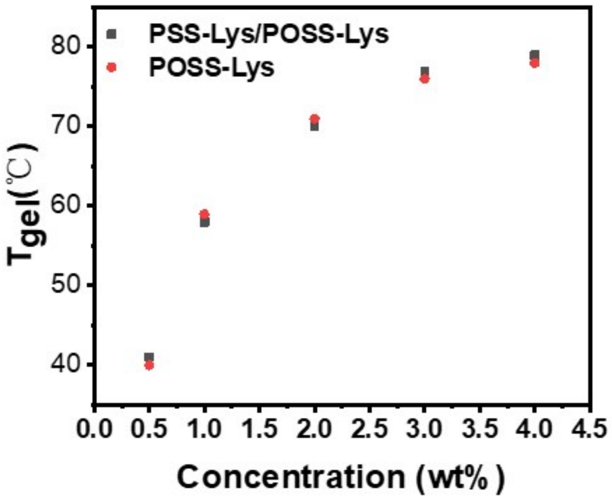


Figure S9. Gel-sol transition temperatures (T_{gel}) of POSS-Lys gel and PSS-Lys/POSS-Lys mixed gel (molar ratio=1:1).

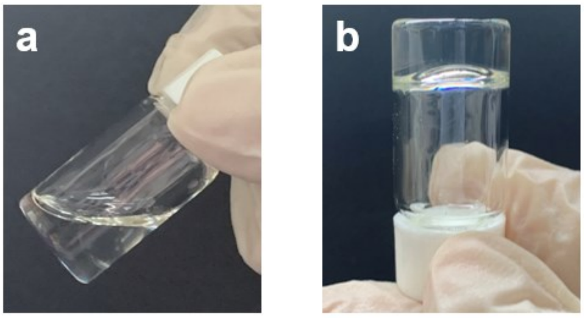


Figure S10. Digital photo of gel-sol transition of PSS-Lys/POSS-Lys mixed gel.

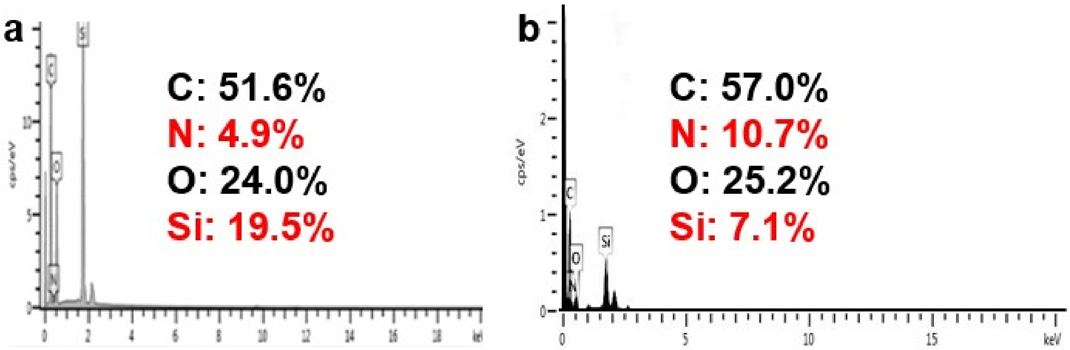


Figure S11. Energy Dispersive X-Ray Spectroscopy of (a) white lumpy aggregates and (b) loofah-like fiber networks in Figure 4a.