Supplementary Information

Loofah-like gel network formed by the self-assembly of 3D radial symmetric organic/inorganic hybrid gelator

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1. Synthesis and characterization of the hybrid gelator

1.1 Materials and methods

All the materials required in this reaction were commercial available. Octa(3aminopropyl)silsesquioxanes hydrochloride (OctaAmmonium POSS-HCl) was purchased from hybrid plastic (Hattiesburg, MS). 1-hydroxy benzotriazole (HOBt), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI), N α ,N ϵ -dit-BOC-L-lysine [(di-t-BOC)-L-lys-OH] and N-Methylmorpholine (NMM) 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.

1.2 Synthesis and characterization

The synthesis process was similar to the literature¹, with slightly modification.

(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 NaHCO₃ aqueous saturated solution giving a white solid. The crude product was purified by column chromatography (silica, CH₂Cl₂: MeOH, 94: 6) to give a white solid with the yield of 1.12 g (73.1%). R_f 0.53 (CH₂Cl₂: 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). ¹H NMR (CDCl₃, 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,







POSS-Lys

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



Figure S1. The ¹H NMR spectra of POSS-Lys hybrid gelator

The ¹H NMR spectra of POSS-Lys hybrid gelator was presented in Figure S1. The assignment of the protons was presented in the spectra. All the signals in the spectra were attributed to corresponding protons.

The ESI-TOF MS spectra of POSS-Lys hybrid gelator was presented in Figure S2. 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. The MALDI-TOF MS spectra of POSS-Lys hybrid gelator was presented in Figure S3. The calculated [M+Na] of POSS-Lys was 3528.88 and the tested result was 3528.8.

These results showed that the designed hybrid gelator was synthesized ..;

130522 POSS-G1-1 CDC13



Figure S2. ESI-TOF MS spectrum of POSS-Lys hybrid gelator



Figure S3. MALDI-TOF MS spectrum of POSS-Lys hybrid



Figure S4. The GPC spectrum of POSS-Lys

The polydispersity of POSS-Lys was tested by GPC and the calculated polydispersity was 1.02. This suggested that the hybrid gelator was synthesized with monodispersity.

2. Results and discussion

2.1 Investigation of the gelation behavior in various organic solvents

Solvents	α	β	π^*	state
<i>n</i> -hexane	0.00	0.00	-0.08	Р
cyclohexane	0.00	0.00	0.00	Р
toluene	0.00	0.11	0.54	TG (4)
benzene	0.00	0.10	0.59	TG (6)
chlorobenzene	0.00	0.07	0.71	TG (4)
1,2-dichlorobenzene	0.00	0.03	0.80	TG (0.5)
methyl methacrylate	0.00	N/A	N/A	TG (5)
ethyl acetate	0.00	0.45	0.55	TG (5)
butyl acetate	0.00	N/A	0.46	TG (4)
1,2-dimethoxyethane	0.00	0.41	0.53	TG (10)
acetone	0.08	0.48	0.71	VS
THF	0.00	0.55	0.58	S
chloroform	0.44	0.00	0.69	S
dichloromethane	0.30	0.00	0.73	S
ethanol	0.83	0.77	0.54	S
methanol	0.93	0.62	0.60	S

 Table S1.
 Gelation behavior of POSS-Lys in various solvents^a

^a P = precipitate, TG = transparent gel, VS = vicious solution, S = solution. α , β , π^* are the Kamlet-Taft parameters relating to the ability of the solvent to donate and accept hydrogen bonds and a generalized polarity parameter, respectively, N/A = not available. The data in brackets represents the minimal gel concentration (MGC), mg/mL.

The gelation ability of novel hybrid gelator POSS-Lys was examined in various organic solvents (Table S1). Kamlet-Taft model was used in order to better understand the effect of solvent on gelation². It is evident that gels are best supported in those solvents where the α parameter is zero, β parameter is low meanwhile π^* parameter is high — i.e., toluene, benzene, chlorobenzene, 1,2-dichlorobenzene (DCB), methyl methacrylate (MMA), ethyl acetate and 1,2-dimethoxyethane (DME). The minimal gel concentration (MGC) of these gels are all below 10 mg/mL (1% w/v), indicative of high efficiency of gelating solvents for POSS-Lys. All these gels were

highly transparent and thermally stable for a few months at room temperature.



2.2 Investigation of thermal stability of POSS-Lys gels

Figure S5. Phase diagram of POSS-Lys gels

The thermal stabilities of POSS-Lys gels from solvents were measured using a simple tube-inversion method. We define the temperature at which the gels begin to flow the gel-sol transition temperature (T_{gel}). Like the most traditional low molecular weight gels, as the concentration was increased, the T_{gel} values increased until a plateau region was reached. Gels from solvents which have low β parameter such as DCB and chlorobenzene are more thermal stable than those of gels from middle β parameter solvents such as MMA and ethyl acetate.

2.3 Varying temperature ¹H NMR



Figure S6. ¹H NMR spectra of POSS-Lys in Acetone-d₆ with varying temperature, the concentration of hybrid gelator was 0.5 % w/v (2.5 mg, 0.5 mL).

Figure S5 was the varying temperature ¹H NMR spectra of POSS-Lys in Acetone-d₆. It shown that the initially broad peaks of amide ^aH, carbamate ^bH and ^cH gradually transformed to sharper peaks and got upfield shifted at higher temperatures, which was attributed to the weakening of hydrogen bonding interactions. This proved that the hydrogen bonding interaction involving amides and carbamates was the driving force for the gelation of POSS-Lys hybrid gelator.

2.4 SEM and TEM images of POSS-Lys in MMA



Figure S7. SEM and TEM images of POSS-Lys in MMA with concentrations of 5 mg/mL and 0.5 mg/mL, respectively.

Loofah-like gel network was imaged by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in MMA. Particularly, in TEM, the relatively heavy Si atoms in the gelator allowed the assemblies formed by POSS-Lys to be observed even in the absence of heavy atom staining agent. Interestingly, furcate fibers were once again obtained which induced irregular closed meshes with diameter of 1-2 μ m. Importantly high-density junction points of the network were observed even at extremely low concentration, indicative of POSS-Lys being born to undergo the "loofah-like" assembly model.

2.5 additional SEM images from different solvents



Figure S8. SEM images of POSS-Lys in benzene (6 mg/mL), A; chlorobenzene (4 mg/mL), B; ethyl acetate (5 mg/mL), C.

Additional SEM images were obtained from different solvents including benzene, chlorobenzene and ethyl acetate with minimal gel concentration respectively. Interestingly, very similar morphologies were found in such solvents as observed in MMA, with solvents modifying the fiber width to a lesser extent (300-500 nm). This indicated that the unique loofah-like structure is truly induced by the self-assembly of POSS-Lys, not by chance.





Figure S9. Dynamic frequency sweep of the butyl acetate gel containing POSS-Lys with concentration of 2% w/v. A: storage modulus G' and loss modulus G'' versus angular frequency at a strain of 0.1%; B: complex viscosity versus angular frequency at a strain of 0.1%.

Dynamic frequency sweep between 0.1 and 100 rad/s shows G' > G'', which confirms that the gel has a predominantly elastic character (Fig. S 9A). The elasticity of the gel is further evident from the fact that the G' and G'' values are minimally

sensitive to frequency, with a slight increase when increasing frequency, which indicated that the gel system formed a stable elastic network³. The double logarithmic plot of the dynamic complex viscosity versus the angular frequency has a gradient close to -1 (Fig. S 9B), which is characteristic of a strong cohesive gel⁴.

2.7 Circular Dichroism (CD) spectra



Figure S10. The CD spectra of POSS-Lys hybrid gelator in DME at concentration of 0.06% w/v.

Figure S10 was the CD spectra of POSS-Lys hybrid gelator in DME in solution

state. DME was selected as the solvent because it can be gelated by POSS-Lys and importantly it was transparent at the absorption wavelength of amide gelator. The spectra had maxima at ca. 220 nm, caused by the absorbance of the amide carbonyl groups, which were placed in a nanoscale chiral environment within the self-assembled fibril⁵.

Reference:

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