Support Information

Self-assembly of a strong POSS core based aspartate derivative dendrimer supramolecular gelator in different polarity solvents

Huiwen He,[a‡] Si Chen [a‡*], Xiaoqian Tong[a], Zhihang An[a], Meng Ma[a], Xiaosong Wang [b], Xu Wang[a*]

a College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China. Phone: 86-0571-88320855, Fax: 86-0571-88320855.

b xiaosong.wang@uwaterloo.ca

*Email:wangxu@zjut.edu.cn, chensi@zjut.edu.cn.

Synthesis and characterization of the POSS based dendrimers

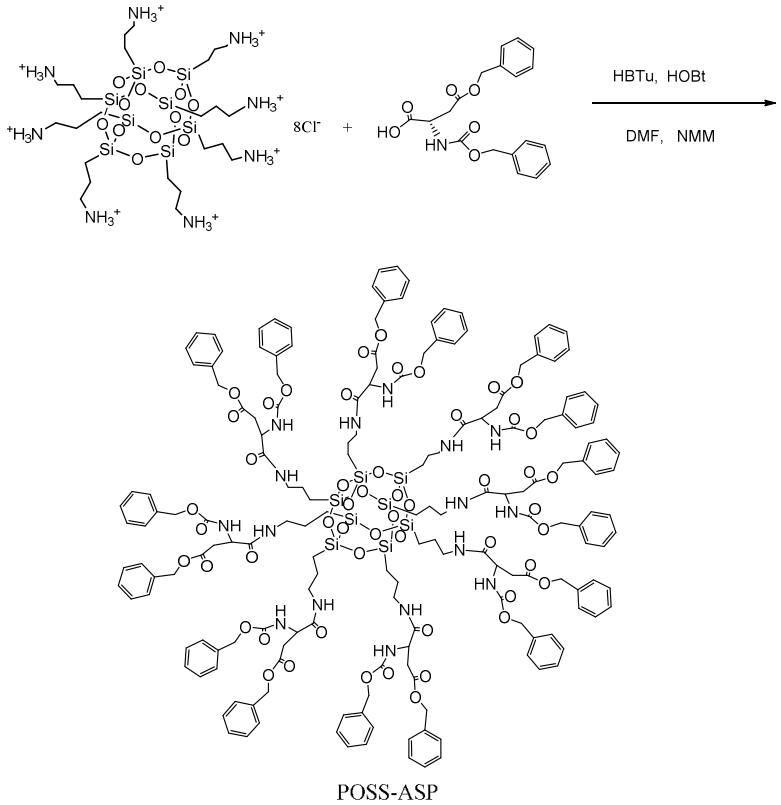
Materials

All materials employed in the paper were commercial available. Octa (3-aminopropyl) silsesquioxanes hydrochloride (Octa-Ammonium 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), Z-Asp(OBzl)-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 and characterization of POSS-ASP

The structure and synthetic route of POSS-ASP were presented on **Scheme S1**, the synthesis process was similar to the literature[1]. 3.57 g (10 mmol) Z-Asp(OBzl)-OH, 3.80 g (10 mmol) HBTU and 1.49 g (11 mmol) HOBt were dissolved in 20 mL DMF. After 5 min, 1.17g（1mmol）OctaAmmonium POSS-HCl and 1.82g（18mmol） NMM were added. The reaction mixture was stirred at room temperature for 24 h, and then 150 mL distilled water was added to get a white solid. The crude product was purified by column chromatography (silica, CH_2Cl_2: MeOH= 15:1 R_f=0.60) to get a white solid with the yield of 62.5 %. The structure of the POSS-ASP was determined by NMR (Bruker Avance III, 500 MHz), ESI-TOF MS (Agilent 6210). **^{1}H NMR (DMSO-d6, 500 MHz, ppm)** as shown in **Figure S1, δ** 7.98 (8H, s, CON*H*CH_2), 7.53 (8H, d, CHN*H*CO), 7.16-7.31 (80H, m, Ar-H), 4.99 (32H, dd, COOCH_2-Ar), 4.42 (8H, dd, COC*H*CH_2(NH)), 3.0 (16H, s, CH_2CH_2NH), 2.59-2.77 (16H, m, COC$H_2$$CH_3$), 1.43 (16H, s, Si$CH_2$$CH_2$), 0.55 (16H, s, Si$CH_2$); **FTIR (KBr) *ν*** = 3310, 3070, 2940, 1740, 1660, 1280, 1120, 685, 553, 480 cm^{-1}; **MALDI-TOF MS:** The calculated $[M+Na]^+$ of POSS-ASP was 3619.0 and the test result was 3618.9, results fit with the calculation, as shown in **Figure S2a.** **ESI-TOF MS**: The calculated $[M+2Na]2^+/2$ of

POSS-ASP was 1821.0 and the test result was 1820.6, results fit with the calculation, as shown in **Figure S2b, S2c**.



Scheme S1. The synthesis scheme for POSS-ASP

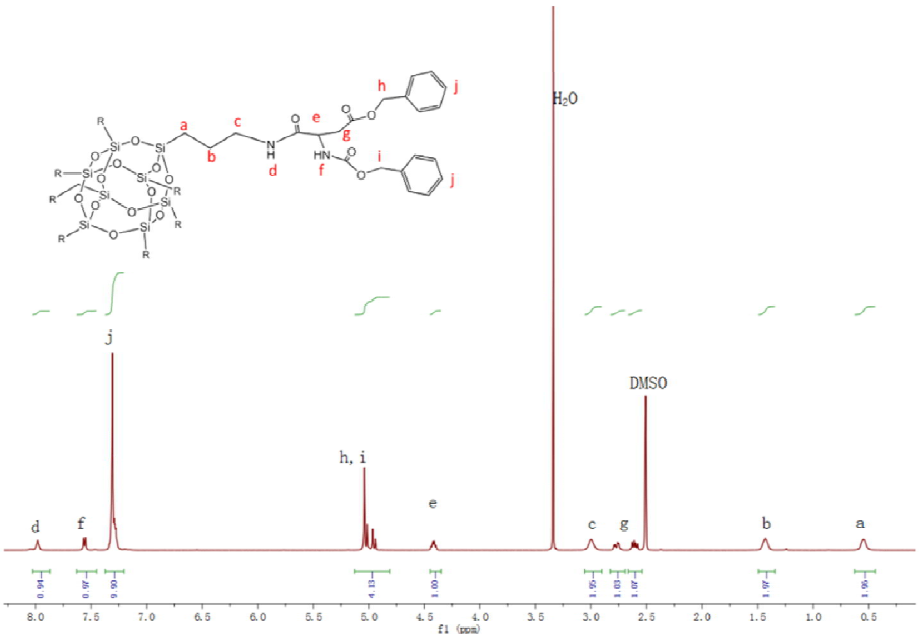


Figure S1. ^{1}H NMR spectra of POSS-ASP in DMSO-d6.

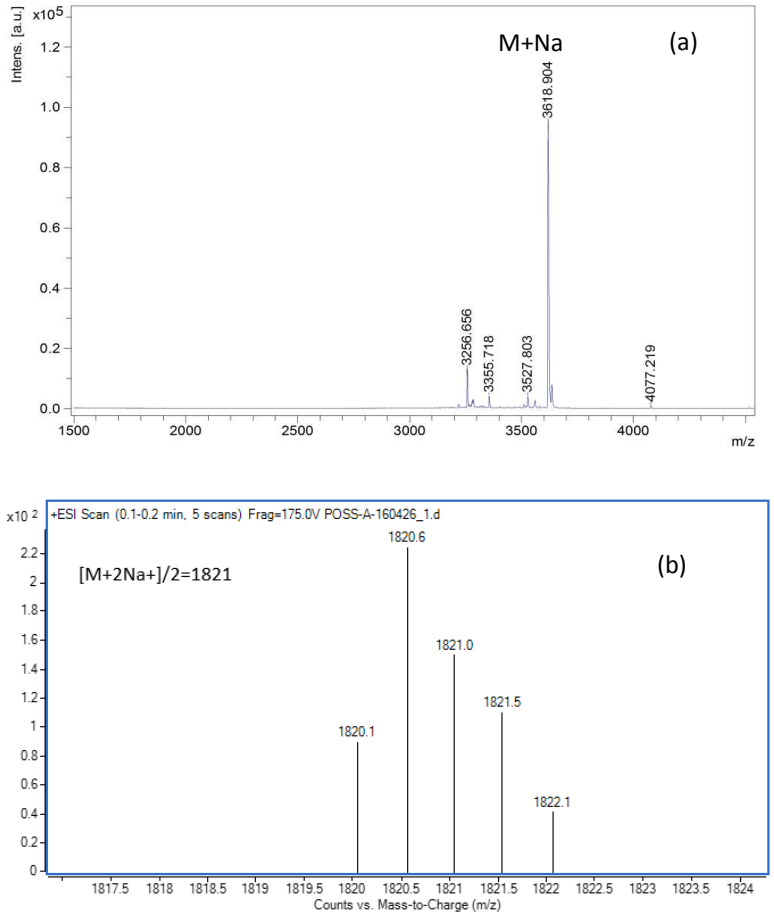


Figure S2. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) (a) and Time of Flight Mass Spectrometry (ESI-TOF MS) (b) of POSS-ASP in methanol.

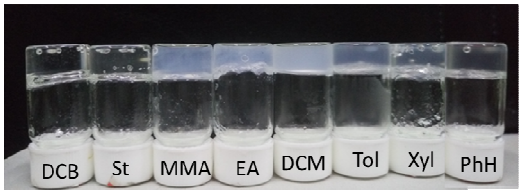


Figure S3. Photograph of POSS-ASP gels in different solvents (25°C).

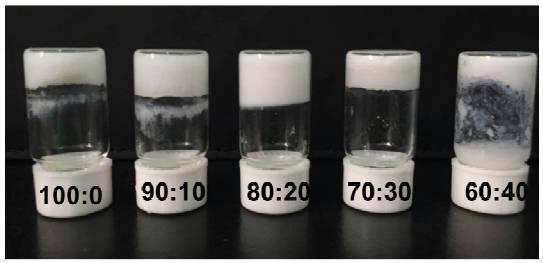


Figure S4. Digital photos of POSS-ASP gels from THF/Water mixed solvent with 0-40% water contained, the concentration of gelators are 40 mg/mL (25°C).

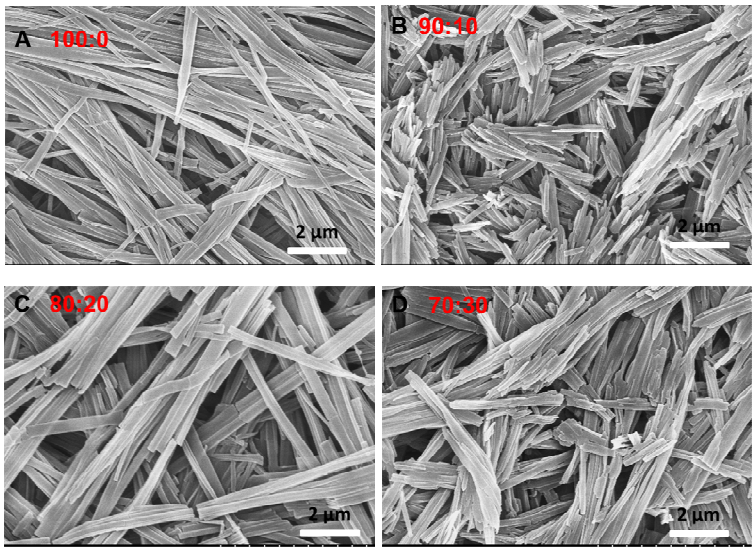


Figure S5. FE-SEM images of POSS-ASP xerogels from THF/Water mixed solvent with 0-30% water contained, the concentration of gelators are 40 mg/mL.

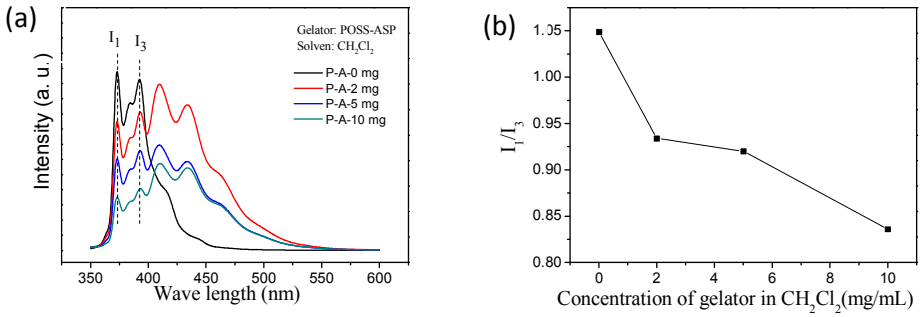


Figure S6. Fluorescence emission spectra of POSS-ASP with pyrene (5 mg/mL) incorporated in CH_2Cl_2, excitation wavelength: 335 nm, temperature 25 ^{o}C; (b) I_1/I_3 ratio of gelators in CH_2Cl_2.

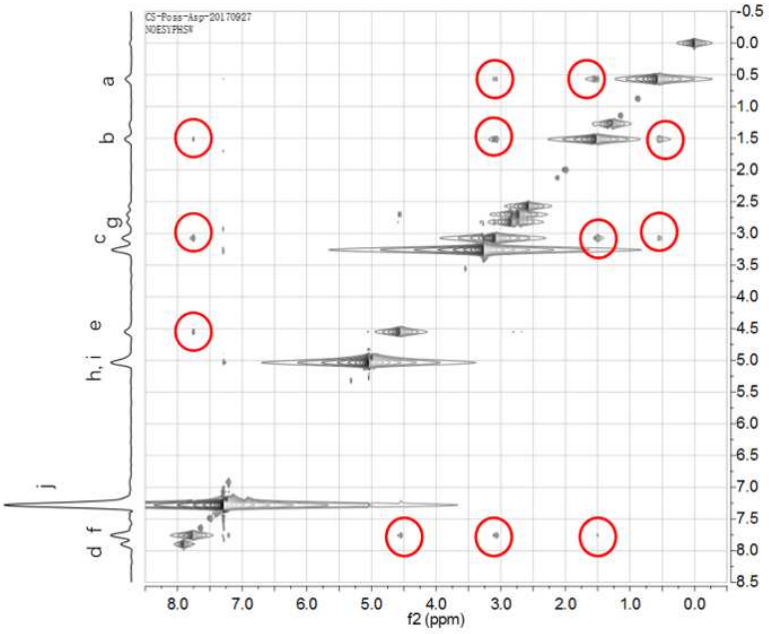


Figure S7. 2D NOESY spectra of POSS-ASP (1.5% w/v) in DMSO-d6 and with 50% $CDCl_3$.

	MMA				THF			
	2θ(°)	d (nm)	ratio	hkl	2θ(°)	d (nm)	ratio	hkl
1	3.5	2.52	1	100	3.9	2.26	1	010
2	5.6	1.58	0.62 (1/√3)	110	5.6	1.58	0.70 (1/√2)	011
3	9.7	0.91	0.36 (1/√7)	210	8.0	1.10	0.49 (1/2)	020
4	18.0	0.49			8.9	0.99	0.44 (1/√5)	021
5	19.5	0.46			12.2	0.73	0.32 (1/√10)	031
6					16.9	0.52	0.23 (1/√20)	042
7					20.6	0.43		
8					23.0	0.39		

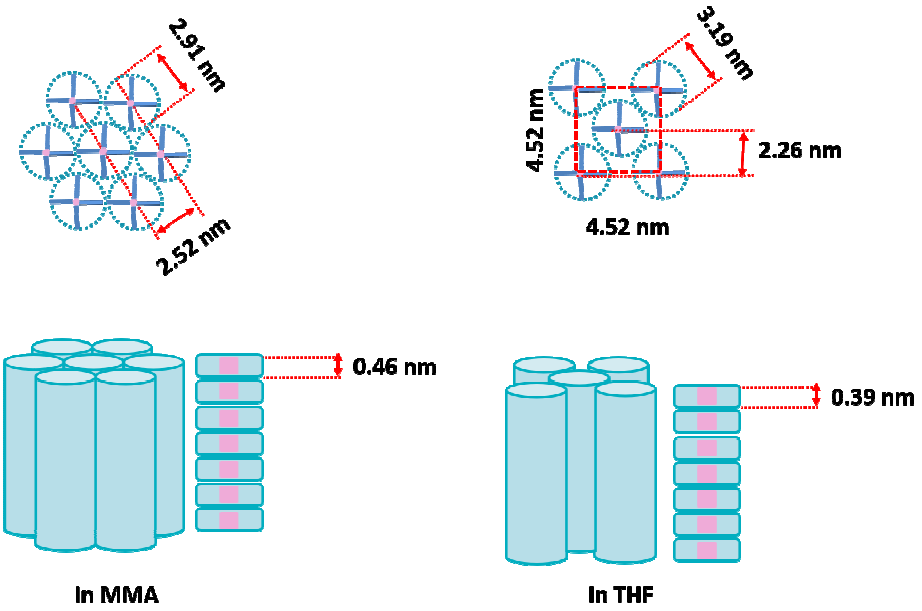


Figure S8. Value statistics of the XRD and packing models of POSS-ASP MMA xerogel and THF xreogel. Concentration of MMA gel is 30 mg/mL and THF gel is 40 mg/mL, the molecular dimension of POSS-ASP in fully extended length is 3.05 nm.

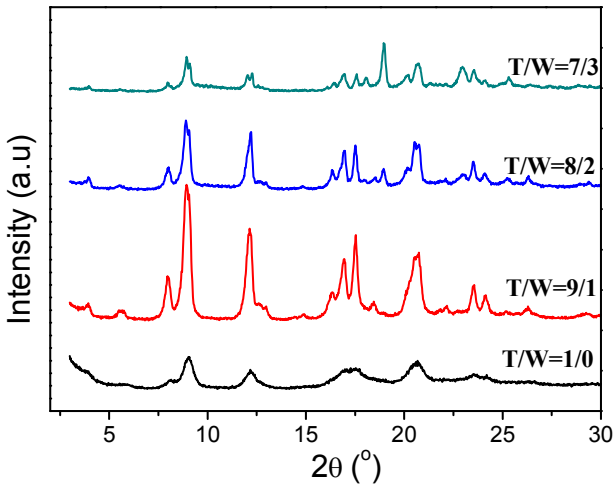


Figure S9. XRD pattern of the POSS-ASP xerogel from THF/Water mixed solvent with 0-30% water contained, the concentration of gelators are 40 mg/mL.

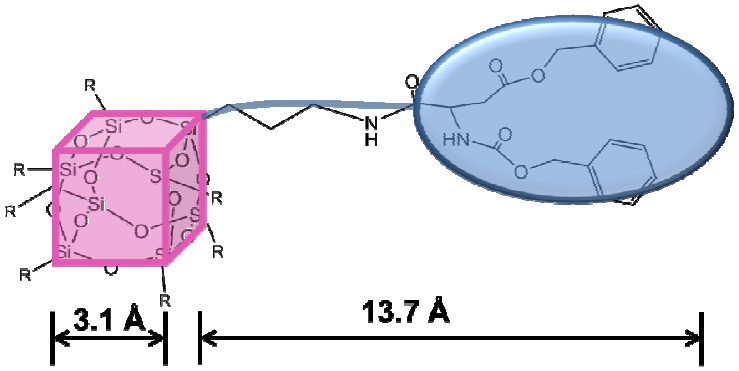


Figure S10. Molecular model of POSS-ASP, color pink represents the cubic POSS core and the color blue representing the aspartate derivative arm.