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Polycation-induced secondary assembly of amphiphilc calixarene and its multi-stimuli responsive gelation behavior

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Materials and Instruments

NMR data were recorded on Bruker AV400 M spectrometer. Poly(vinylalcohol) (PVA, average Mw~205,000 g/mol, 98% hydrolyzed) was purchased from Aldrich, dissolved in water at 5 wt%. Further purification can be achieved by dialysis against deionized water (2 days). p-Sulfonatocalix[4]arene (SC4A) was synthesized and purified according to the procedures reported previously and identified using ^{1}H NMR spectroscopy in D_2O.[1] FTIR spectra were recorded on a Bio-Rad FTS6000 spectrometer. Mass spectra were recorded on a Bruker Daltonics AutoflexIII LRF200-CID MS (MALDI) spectrometer. Elemental analyses were measured by using an elementar vario EL CUBE element analyzer.

Synthesis of PVA-MV. PVA-MV was synthesized according to the procedures reported previously.[2] Typically, to a solution of 1-(2-hydroxyethyl)-1’-methyl-[4,4’-bipyridine]-1,1’-diium di(hexafluorophosphate) (0.5 g, 1.0 mmol) dissolved in 200 mL of anhydrous acetonitrile, an excess amount of 1,6-hexamethylene diisocyanate (2 mL) and a drop of dibutyltin dilaurate (TDL) was added. The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure to approximately 10 mL, and then 200 mL of anhydrous diethyl ether was added. A sticky, yellowish precipitate was formed. The solid was collected and dried under reduced pressure to yield MV-NCO. PVA (1g) was dissolved in N-methylpyrrolidone (NMP, 60 mL), and MV-NCO (0.21 g, 0.3 mmol) was added along with TDL (3 drops). The reaction mixture was stirred overnight at room temperature. The functional polymer was then purified by precipitation from ethyl acetate, collected by filtration, and dried overnight under vacuum. Counterion exchange and further purification can be achieved by dialysis against 0.5 wt % aqueous sodium chloride solution (2 wt%, 12 h) followed by dialysis against deionized water (2 days). Lyophilization yields the title compound as a fluffy, yellowish solid. ^{1}H NMR (D_2O, 400 MHz, ppm) δ 9.10-8.99 (4H, Ar-*H*), 8.51-8.45 (4H, Ar-*H*), 4.92 (2H, MV-CH_2-CH_2-OCN-), 4.56 (2H, br, MV-CH_2-CH_2-OCN-), 4.43 (3H, MV-CH_3), 4.03-3.68 (-NCO-*CH* and HO-*CH* from the backbone), 3.05-2.88 (4H, -CH_2-NCO-), 2.09-1.11 (polymer backbone and hexamethylene linker).

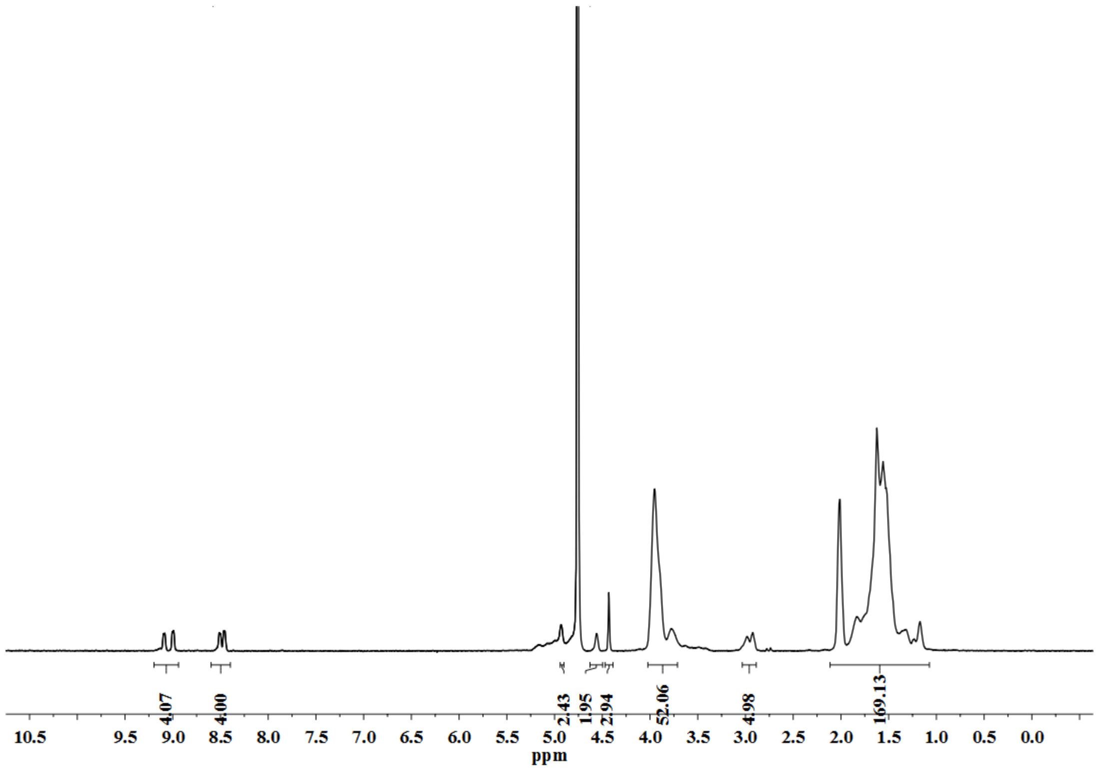
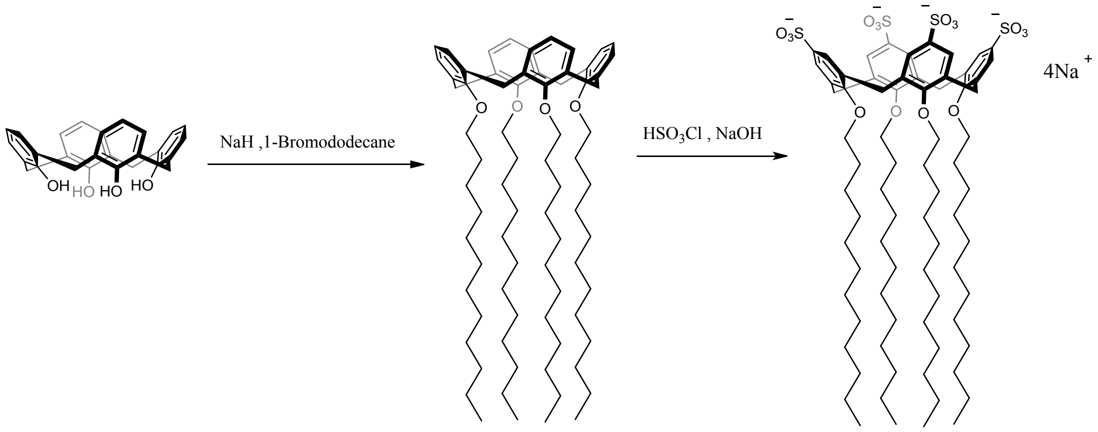


Figure S1. Partial ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of PVA-MV

Synthesis of SC4AD



Calix[4]arene tetradodecyl ether (C4AD) was synthesized and purified according to the procedures reported previously.[3]

p-Sulfonatocalix[4]arene tetradodecyl ether (SC4AD): A solution of 2.0 g (1.82 mmol) C4AD in 50.0 mL of $CHCl_3$ was stirred under argon at ice bath temperature for 30 min. Then 0.5 mL (7.50 mmol, dissolved in 60.0 mL of $CHCl_3$) of HSO_3Cl was added. The mixture was stirred at 0°C for another 3 h and then concentrated. The residue was dissolved in 100.0 mL of anhydrous EtOH. After a solution of 360 mg (9.00 mmol) of NaOH in anhydrous EtOH was then added, the mixture was stirred for 30 min. After centrifugation, the resulting white precipitate was recrystallized from water yielding 2.14 g (78%) of SC4AD. ^{1}H NMR (400 MHz, DMSO-d_6]): δ = 7.12 (s, 8H, Ar-*H*), 4.34 (d, 4H, *J* = 12.4 Hz, Ar-CH_2-Ar), 3.87 (br, 8H, Ar-O-CH_2), 3.25 (d, 4H, *J* = 12.4 Hz, Ar-CH_2-Ar), 1.92 (br, 8H, -O-CH_2-CH_2), 1.37-1.25 (br, 72H, alkyl chain), 0.75 (s, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.77 (CH_3), 22.03, 28.77, 29.16, 29.25, 29.37, 29.48, 29.58, 29.71, 31.29 (alkyl chain), 74.92 (Ar-CH_2-Ar), 125.73, 133.09, 141.56, 156.20 (Ar). Elemental Analysis: Calculated for $C_{76}H_{116}Na_4O_{16}S_4$: C = 60.61%, H = 7.76%; Found: C = 60.58%, H = 7.73%.

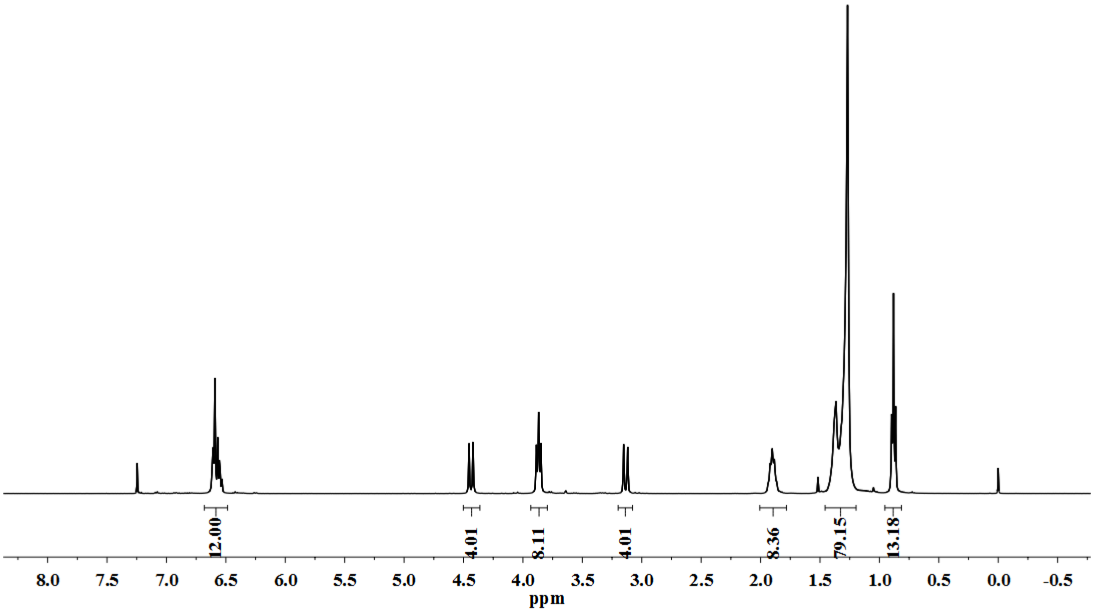


Figure S2. Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of C4AD.

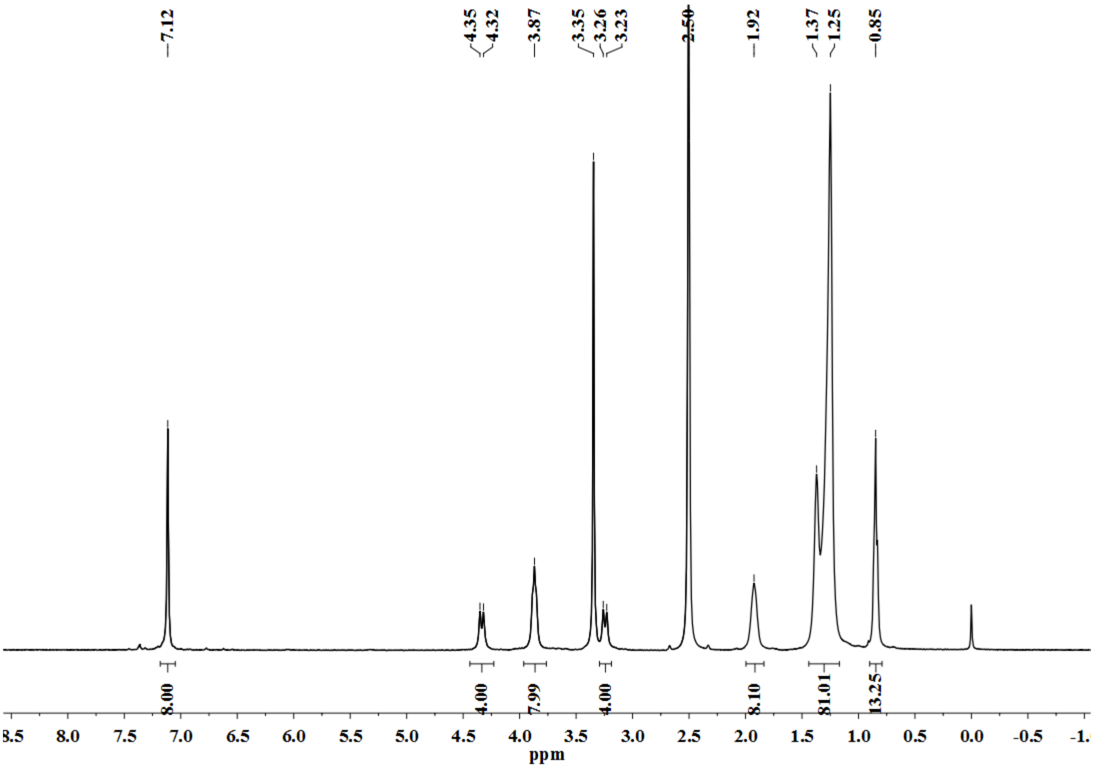


Figure S3. Partial ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of SC4AD.

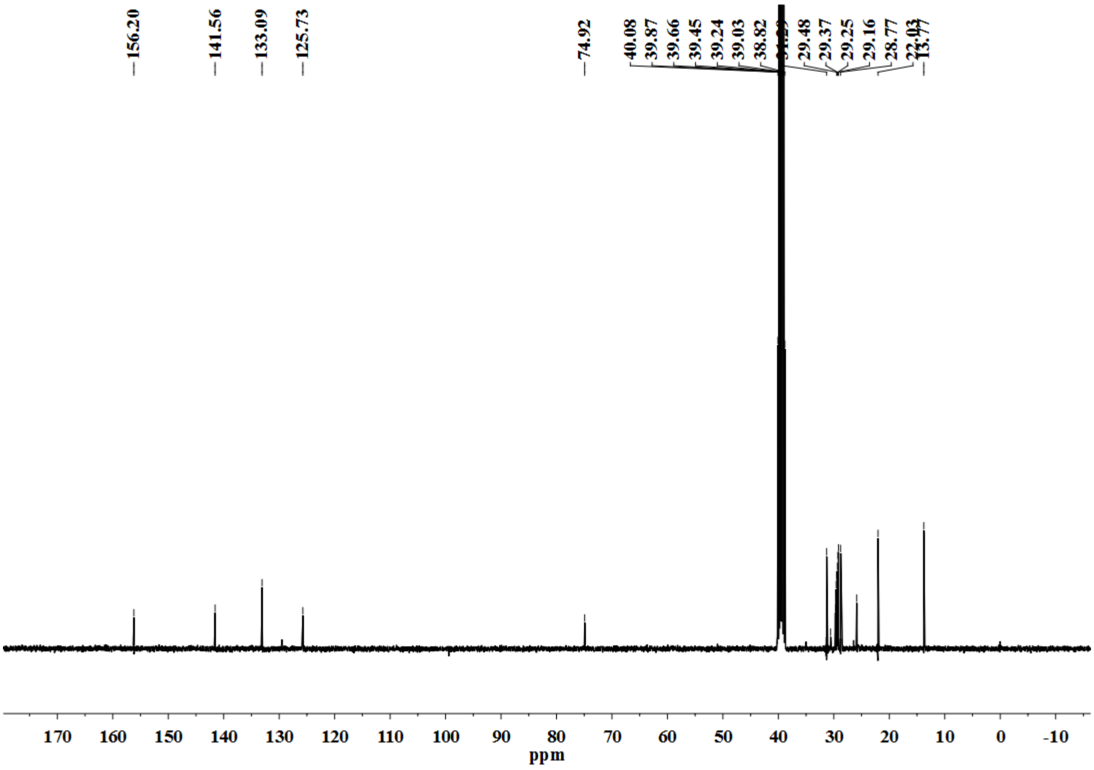


Figure S4. Partial ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298 K) of SC4AD.

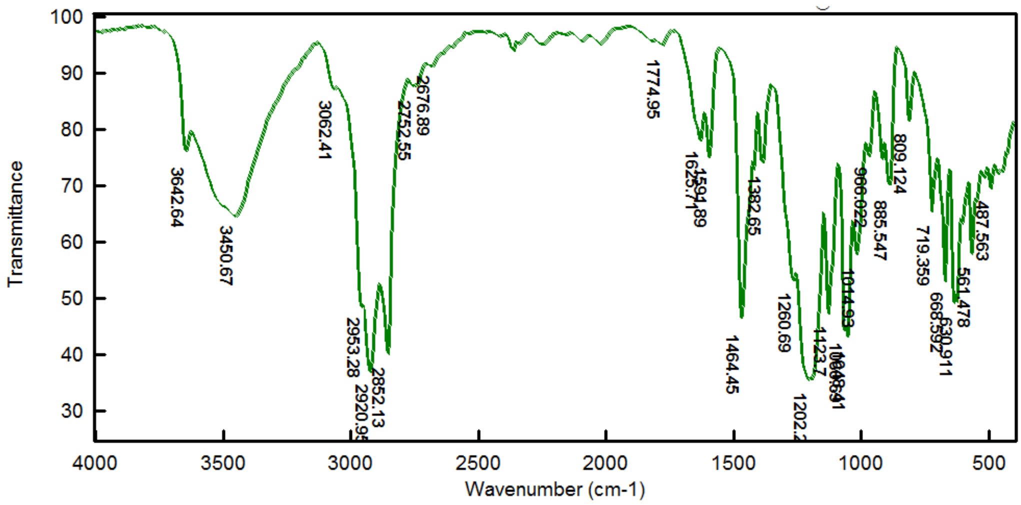


Figure S5. FT-IR spectrum of SC4AD.

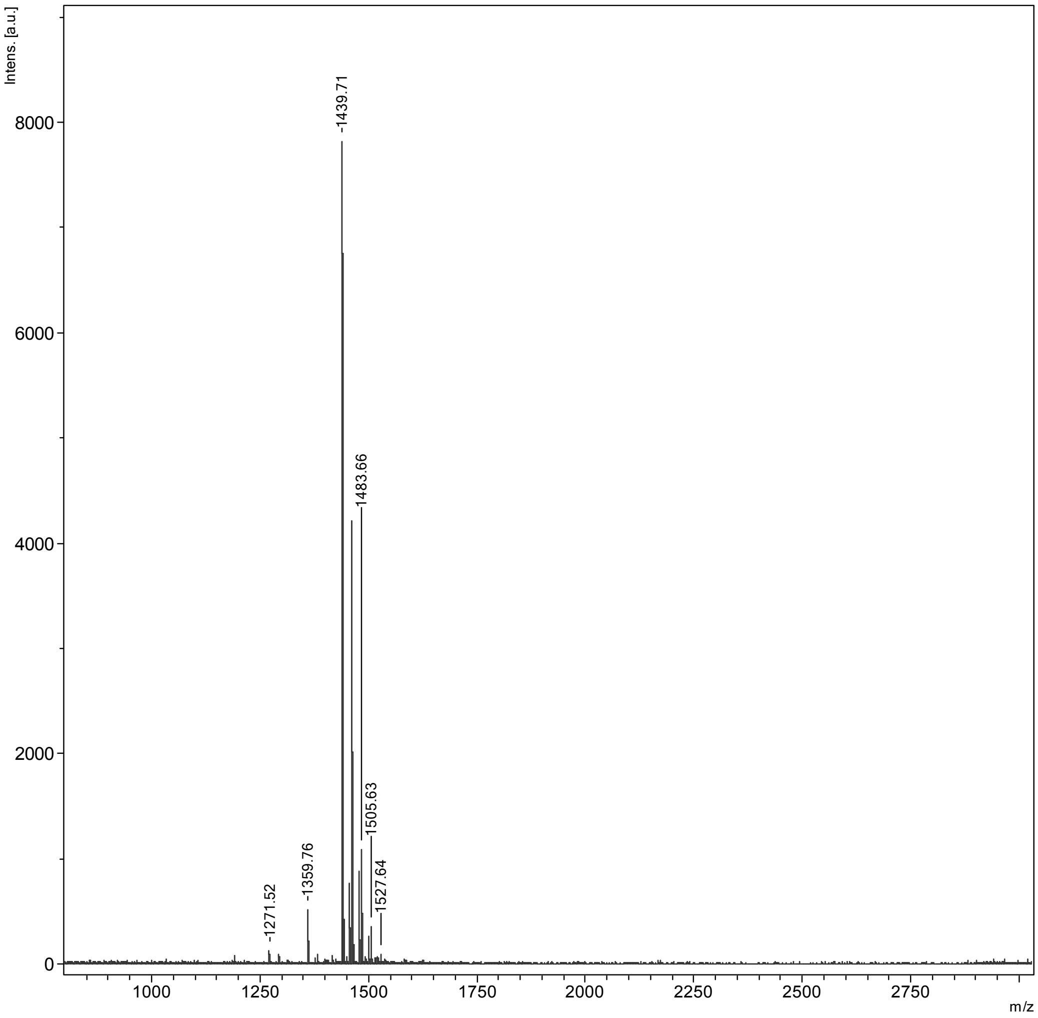


Figure S6. MALDI-MS spectrum of SC4AD.

DLS measurements

The sample solution for DLS measurements was prepared by filtering the solution through a 450 nm Millipore filter into a clean scintillation vial. The samples were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (TurboCorr) at 636 nm at a scattering angle of 90°.

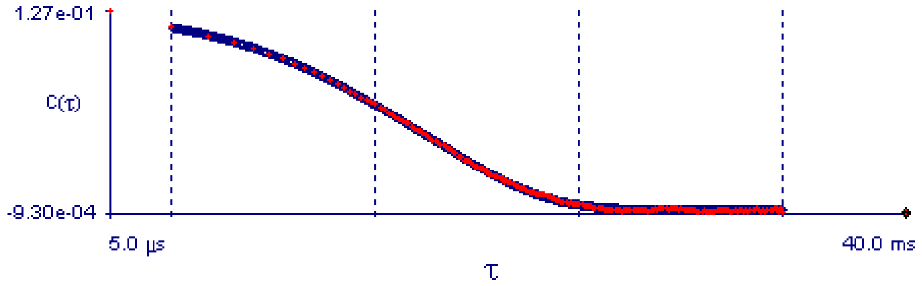


Figure S7. Representative dynamic light scattering data for 5.0 mM aqueous solution of SC4AD.

Fluorescence Spectroscopy

Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell peltier accessory to control temperature. λ_{ex} = 550 nm; bandwidth (ex), 10 nm; bandwidth (em), 5 nm.

AFM measurements

Sample solutions were dropped onto newly clipped mica and then dried in air. The samples were performed by using a multi-mode IIIa AFM (Veeco Metrology, USA) in tapping mode in air at room temperature.

SEM measurements

Scanning electron microscopy (SEM) images were obtained using a Hitachi S-3500N scanning electron microscope. SEM samples were prepared by direct freezing of the supramolecular hydrogels in liquid nitrogen followed by lyophilization. The resulting cryo-dried materials were imaged after sputtering.

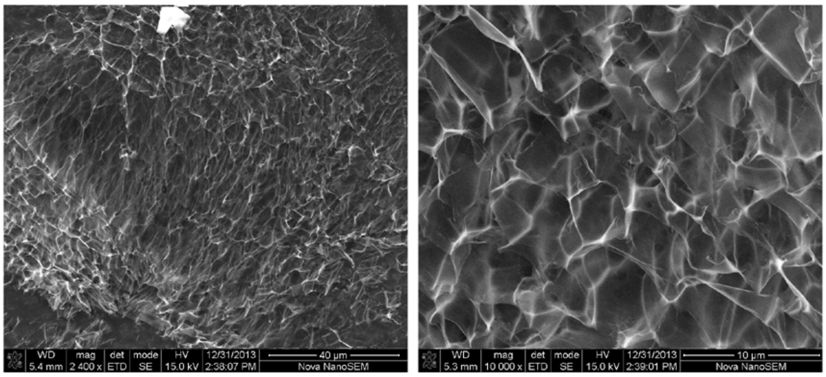


Figure S8. SEM images of cryo-dried and lyophilized samples

Rheological characterization

The rheology test was done on an AR 2000ex (TA Instrument) system, 40 mm parallel plates was used during the experiment at the gap of 500 μm. The gel was characterized by the mode of a dynamic frequency sweep in the region of 0.1–10 Hz at the strain of 1%.

The control experiments

A mixture of *p*-sulfonatocalix[4]arene and PVA-MV did not form a gel and turned to be a viscous yellow-green precipitate. A mixture of the unfunctionalized PVA polymer and SC4AD micelles did not form a gel.

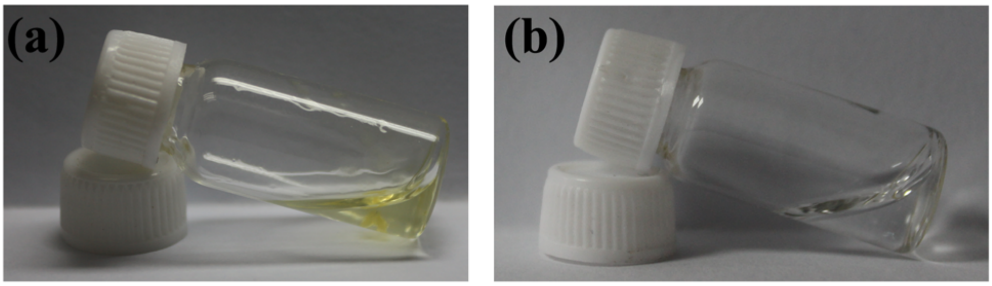


Figure S9. The photos of (a) the mixture of 10 mM *p*-sulfonatocalix[4]arene and 25 mg/mL PVA-MV (viscous yellow-green precipitate); (b) the mixture of the 25 mg/mL unfunctionalized PVA polymer and 10 mM SC4AD micelles

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1 I. Hyejae, K. Hyunjun and P. Kyungsoo, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1997–2004.

2 E. A. Appel, X. J. Loh, S. T. Jones, F. Biedermann, C. A. Dreiss and O. A. Scherman, *J. Am. Chem. Soc.*, 2012, **134**, 11767−11773.

3 Z. Qin, D.-S. Guo, X.-N. Gao and Y. Liu, *Soft Matter*, 2014, **10**, 2253−2263.