Electronic Supplementary Information for

Tunable Self-Assembly of two-component Gels from Novel Sorbitol-appended Compounds

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1. Experimental Section

1) Materials

The reagents used in the study were purchased from Aladdin Reagent. All solvents were purified and dried by standard procedures and distilled prior to use. We have previously reported that the compounds 1 and 2 were easily synthesized by reacting the appropriate D-sorbitol with p-nitrobenzaldehyde.¹ Compounds 3 was synthesized by the follow procedures.

2) Instrumentation

NMR experiments: ¹H NMR spectroscopy was performed on a Bruker DRX 400 apparatus at 400 MHz. Chemical shifts, in ppm, are referred to TMS as internal standard.

Scanning electron microscopy (SEM): Samples were prepared and dried under the ambient conditions for 10 days. After coating the samples with the gold, the images of the samples were obtained by a Hitachi S-4800 SEM. The accelerating voltage was 5 kV, and the emission current was 10 mA.

UV spectrometer: UV spectroscopy was performed on a Jasco V-570 UV/vis/NIR spectrophotometer. The path length of the quartz cell was 1 cm.

X-Ray diffraction (XRD): Using a Rigaku D/Max 2200-PC diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm), the patterns were obtained at the ambient temperature and the samples were scanned in the 2 θ range of 3-30 ° at a scan rate of 0.2 s/ step. Data processing and analyses were performed using Materials Date JADE XRD pattern processing software. The samples were dried for 5 weeks at room conditions.

FTIR Spectroscopy. FTIR measurements were performed on a Bruker Equinox 55 spectrometer. The absorption spectra of xerogels were obtained at room temperature in the range of 400-7000 cm⁻¹ and a resolution of 2 cm⁻¹. The measured samples were dispersed in KBr pellets.

3) General information

Gelation test: These tests were performed by adding the weighed amount of gelators into the measured volume of solvent in the tube (10 mm diameter) and then heating the tube until the gelators were dissolved or could not be dissolved ever. The gelation properties were evaluated by dissolving test tube inversion.² Each experiment was done in duplicate.

Gel-sol phase transition temperature measurements (T_{gel}): These experiments were performed by solubilization of a weighed amount of gelators in a measured volume of n-octanol. T_{gel} was determined by differential scanning calorimetry (DSC). DSC measurements at heating and cooling rates of 10 °C/min were carried out on a Q20 calorimeter (TA Instruments) interfaced to a TA Thermal Analyst 3100 controller under a slow stream of nitrogen flowing. Gel samples for DSC were placed in closed aluminum pans. In none of the experiments reported was any weight loss detected after the DSC runs.

Rheological Study: Dynamic rheological measurements were done on the gels on a strain-controlled rheometer (Anton Paar Quality Control Rheometer Rheolab QC instrument) equipped with stainless coaxial cylinder rheometer (cup diameter, 16mm; bob diameter, 15mm). The hot sol (~90°C) was placed over the rheometer plate (kept at 20°C for all systems) and allowed to gel for 3min, and then the gel was stablilized for 30 min. Then the dynamic frequency sweep experiments were carried out at a constant stress of 0.2%.

2. Synthetic procedures and characterization



Scheme S1 (a) 4-Methylcarboxylbenzaldehyde, H₂SO₄, 50%, CH₂Cl₂, CTAB, 22 h, rt; (b) NH₂NH₂ H₂O, CH₃OH, 10 h, reflux.

(a) Synthetic procedure for 2:4-(4-Methylcarboxyl-benzylidene)-D-sorbitol

A mixture of D-sorbitol (10.0 g, 55 mmol) and CTAB (0.1g) dissolved in H_2SO_4 (50%, 20 mL) and 4-Methylcarboxylbenzaldehyde (9.0 g, 55 mmol) dissolved in CH_2Cl_2 (30 mL) was stirred at room temperature for 22 h. The resulted suspension was filtered and the precipitate was washed several times with H_2O , CH_2Cl_2 and dried, then recrystallized with water to get white powdery product (9.3 g, 51%).

m.p. 210-212 °C; IR (KBr) ν = 3330, 2940, 2870, 1730, 1651, 1410, 1280, 1100, 1030, 856 and 762 cm⁻¹. ¹H NMR (DMSO-d6, 400MHz): δ = 7.96 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.64 (d, *J* = 8.1 Hz, 2H, Ar-H), 5.64 (s, 1H, benzylidene-H), 4.71 (d, *J* = 5.5 Hz, 1H, OH), 4.69 (d, *J* = 5.7 Hz, 1H, OH), 4.44 (d, *J* = 7.9 Hz, 1H, OH), 4.43 (t, *J* = 5.8 Hz, 1H, OH), 3.86 (t, *J* = 6.0 Hz, 1H, CH), 3.61-3.56 (m, 6H, 2CH, 2CH₂), 3.46-3.41 (m, 1H, CH). Anal. Calced for 2:4-(4-Methylcarboxylbenzylidene)-D-sorbitol (C₁₅H₂₀O₈): 54.87% C, 6.14% H; Found: 54.67% C, 6.05% H; R_f (1:4 hexanes / ethyl acetate) = 0.34.

(b) Synthetic procedure for 2:4-(4-Hadrazincarboxyl-benzylidene)-D-sorbitol

(compound 3)

To a stirred solution of 2:4-(4-Hadrazincarboxyl-benzylidene)-D-sorbitol (1.5 g, 4.6 mmol) in 30 mL CH₃OH kept at 60 °C, and then NH₂NH₂ H₂O (1.5g, 0.026 mol) was added dropwise. The reaction mixture was stirred for 10 h at reflux, cooled and the catalyst removed by filtration. The filtrate was filtered and washed several times with CH₃OH. Thus compound **3** (0.9 g, 72%) was obtained as white powdery product (1.3 g, 83%).

Compound 3

m.p. 192-193 °C; IR (KBr) v = 3560, 3360, 2960, 2880, 1620, 1540, 1410, 1340, 1090, 1010, 840 and 660 cm⁻¹. ¹H NMR (DMSO-d6, 400MHz): δ = 9.78 (s, 1H, CONH), 7.80 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.56 (d, *J* = 8.3 Hz, 2H, Ar-H), 5.60 (s, 1H, benzylidene-H), 4.69-4.43 (m, 6H, OH+NH₂), 3.82 (t, *J* = 5.9 Hz, 1H, CH), 3.66 (t, *J* = 7.2 Hz, 1H, CH), 3.59-3.55 (m, 4H, CH₂), 3.53-3.48 (m, 1H, CH), 3.39 (t, *J* = 6.0 Hz, 1H, CH). Anal. Calced for 1 (C₁₄H₂₀N₂O₈): 48.84% C, 5.85% H, 8.14% N; Found: 48.67% C, 5.75% H, 8.25% N; R_f (1:1 hexanes / ethyl acetate) = 0.21.

3. Figures



Fig. S1 DSC thermogram of gels in n-octanol derived from 2+1 (A and B) and 3+1 (C and D) at different molar fraction of **1**. The molar fraction of **1** was 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0, respectively. Total gelator concentration = 2 wt % in each case.



Fig. S2 FTIR spectra of the xerogels of 1, 2, 3, 2+1 and 3+1 from n-octanol.



Fig. S3 Variation of storage modulus (G') and loss modulus (G") of gels in n-octanol derived from 1, 2, 3, 2+1 (1:1 molar ratio), 3+1 (1:1 molar ratio) with the applied frequency at a constant strain (0.2%) at 20°C. Total gelator concentration = 2 wt % in each case.



Fig. S4 H-H COSY spectrum of the gel from a 1:1 mixture of **1** and **2** in acetonitrile-d₃ (total gelator concentration=15 mmol).

4. Additional references

- 1) Kaiqi Fan, Jian Song, Jingjing Li, Xidong Guan, Naimin Tao, Ciqing Tong, Huahua Shen and Libo Niu. *J. Mater. Chem. C*, 2013, 1, 7479-7482.
- 2) Jingjing Li, Kaiqi Fan, Libo Niu, Yuanchao Li, and Jian Song. J. Phys. Chem. B, 2013, 117, 5989–5995.