

Electronic Supplementary Information for

Copper (II)-response Gel-Sol Phase Transition in Supramolecular Gel Systems of Salen-appended Sorbitol

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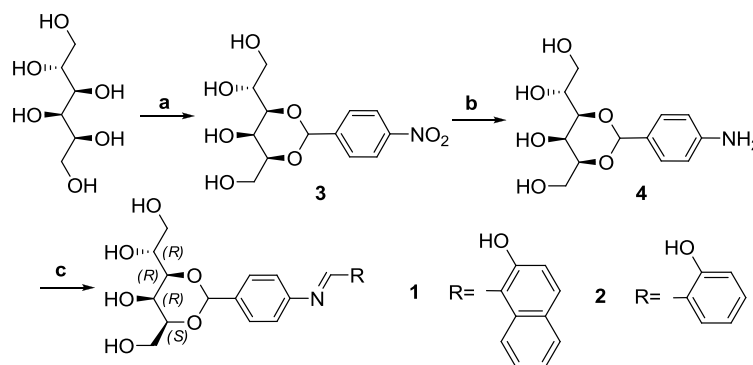
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1. General information

The reagents used in the study were purchased from Tianjin Chemical Reagent Factory. All solvents were purified and dried by standard procedures and distilled prior to use. ^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. ^1H NMR of a solution and a gel was measured in $[\text{D}_6]\text{DMSO}/\text{D}_2\text{O}$ (V/V=1/1). ^1H NMR titration of **1** with Cu^{2+} was performed in $[\text{D}_6]\text{DMSO}$. UV spectroscopy was performed on a Jasco V-570 UV/vis/NIR spectrophotometer. The path length of the quartz cell was 1 mm. Fluorescence emission spectra were recorded on a Hitachi F-2500 fluorimeter. The excitation slit and emission slit were set to a 10 nm bandpass. The scanning electron microscope (SEM) was performed on a Hitachi S-4800 (Hitachi, Japan) microscope. Compounds **3** and **4** were easily synthesized by reacting the appropriate D-sorbitol with p-nitrobenzaldehyde using the method previously reported in the literature.¹

2. Synthetic procedures and characterization



(a) p-NO₂C₆H₄CHO, H₂SO₄, 50%, CH₂Cl₂, CTAB, 22 h, rt; (b) NH₂NH₂ · H₂O, Ni-Raney, dioxane, 16 h, 60 °C; (c) RCHO, C₂H₅OH, 4 h, reflux.

2.1 Synthetic procedure for 2:4-(4-nitrobenzylidene)-D-sorbitol (compound 3)

A mixture of D-sorbitol (10.0 g, 55 mmol) and CTAB (0.1g) dissolved in H₂SO₄ (50%, 20 mL) and p-nitrobenzaldehyde (8.3 g, 55 mmol) dissolved in CH₂Cl₂ (30 mL) was stirred at room temperature for 22 h. The resulted suspension was filtered and the precipitate was washed several times with H₂O, CH₂Cl₂ and dried, then recrystallized with water to get white powdery product **3** (8.3 g, 47%).

Compound 3

m.p. 194-196 °C; IR (KBr) ν = 3333, 2879, 1637, 1608, 1523, 1400, 1348, 1101, 1026, 856 and 705 cm⁻¹. ^1H NMR (DMSO-d₆, 400 MHz): δ = 8.25 (d, J = 8.8 Hz, 2H, Ar-H), 7.77 (d, J = 8.7 Hz, 2H, Ar-H), 5.71 (s, 1H, benzylidene-H), 4.74 (d, J = 5.6 Hz, 1H, OH), 4.71 (d, J = 5.7 Hz, 1H, OH), 4.52 (d, J = 7.9 Hz, 1H, OH), 4.45 (t, J = 5.8 Hz, 1H, OH), 3.87 (t, J = 6.0 Hz, 1H, CH), 3.61-3.56 (m, 6H, 2CH, 2CH₂), 3.46-3.41 (m, 1H, CH). Anal. Calcd for 1 (C₂₄H₂₅NO₇): 65.59% C, 5.73% H, 3.19% N; Found: 65.67% C, 5.75% H, 3.25% N; R_f (1:4 hexanes / ethyl acetate) = 0.25.

2.2 Synthetic procedure for 2:4-(4-aminobenzylidene)-D-sorbitol (compound 4)

To a stirred solution of compound **3** (1.4 g, 4.4 mmol) in 30 mL dioxane kept at 60 °C, freshly

prepared Ni-Raney (0.03 g) was added and then dropwise, $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ (3 mL) in 30 min. The reaction mixture was stirred for 16 h at 60 °C, cooled and the catalyst removed by filtration. The filtrate was concentrated under reduced pressure and the residue was taken in CHCl_3 (15 mL) and sonicated until precipitates. The solid was filtered and washed several times with CHCl_3 . Thus compound **4** (0.9 g, 72%) was obtained as white flocculent crystals.

Compound 4

m.p. 189-190 °C; IR (KBr) $\nu = 3504, 3308, 2945, 1637, 1618, 1521, 1400, 1265, 1104, 1049, 867$ and 624 cm^{-1} . $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): $\delta = 7.11$ (d, $J = 8.4$ Hz, 2H, Ar-H), 6.50 (d, $J = 8.4$ Hz, 2H, Ar-H), 5.35 (s, 1H, benzylidene-H), 5.10 (s, 2H, NH_2), 4.67 (d, $J = 5.9$ Hz, 1H, OH), 4.62 (t, $J = 5.6$ Hz, 1H, OH), 4.38 (t, $J = 5.7$ Hz, 1H, OH), 4.25 (d, $J = 8.0$ Hz, 1H, OH), 3.73 (t, $J = 6.0$ Hz, 1H, CH), 3.66 (t, $J = 7.2$ Hz, 1H, CH), 3.59-3.55 (m, 4H, CH_2), 3.53-3.48 (m, 1H, CH), 3.39 (t, $J = 6.0$ Hz, 1H, CH). Anal. Calcd for **1** ($\text{C}_{24}\text{H}_{25}\text{NO}_7$): 65.59% C, 5.73% H, 3.19% N; Found: 65.67% C, 5.75% H, 3.25% N; R_f (1:4 hexanes / ethyl acetate) = 0.21.

2.3 General procedure for the synthesis of the salen derivatives (1 and 2)

2-hydroxy-1-naphthaldehyde (or salicylaldehyde) (0.5 g, 2.9 mmol) was added to the solution of compound **4** (0.8 g, 2.9 mmol) in ethanol (30 mL). The reaction mixture was refluxed for 4 hrs. after cooling to room temperature, yellow precipitates was filtered, washed three times with absolute ethanol and recrystallized from ethanol/water (v/v=4:1) to give **1** (or **2**).

Compound 1

m.p. 214-216 °C; IR (KBr) $\nu = 3390, 2937, 1623, 1604, 1493, 1401, 1282, 1097, 1016, 831$ and 752 cm^{-1} . $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): $\delta = 15.80$ (s, 1H, OH), 9.66 (s, 1H, HC=N), 8.49 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.93 (d, $J = 9.3$ Hz, 1H, Ar-H), 7.79 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.62 (m, 4H, Ar-H), 7.36 (m, 2H, Ar-H), 7.00 (d, $J = 9.2$ Hz, 1H, Ar-H), 5.62 (s, 1H, benzylidene-H), 4.72-4.68 (m, 2H, OH), 4.44-4.42 (m, 2H, OH), 3.84 (t, $J = 5.8$ Hz, 1H, CH), 3.72-3.60 (m, 6H, 2CH, 2 CH_2), 3.58 (d, $J = 8.4$ Hz, 1H, CH). ESI-MS: $m/z = 440.3$ ($(\text{M}+\text{H})^+$, 100%); UV-Vis (DMSO): λ_{max} (ϵ) = 319 (1.01×10^4), 440 (0.85×10^4), 461 (0.82×10^4) nm ($\text{cm}^{-1}\text{M}^{-1}$); Fluorescence (DMSO): $\lambda_{\text{max}} = 512$ nm, $\lambda_{\text{exc}} = 375$ nm; Anal. Calcd for **1** ($\text{C}_{24}\text{H}_{25}\text{NO}_7$): 65.59% C, 5.73% H, 3.19% N; Found: 65.67% C, 5.75% H, 3.25% N; R_f (1:4 hexanes / ethyl acetate) = 0.15.

Compound 2

m.p. 202-203 °C; IR (KBr) $\nu = 3430, 2865, 1625, 1616, 1523, 1400, 1347, 1099, 854$ and 748 cm^{-1} . $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): $\delta = 13.07$ (s, 1H, OH), 8.98 (s, 1H, HC=N), 7.68 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.58 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.45-7.41 (m, 3H, Ar-H), 7.01-6.97 (m, 2H, Ar-H), 5.60 (s, 1H, benzylidene-H), 4.73-4.68 (m, 2H, OH), 4.45-4.41 (m, 2H, OH), 3.82 (t, $J = 6.1$ Hz, 1H, CH), 3.79-3.53 (m, 6H, 2CH, 2 CH_2), 3.42 (d, $J = 8.4$ Hz, 1H, CH). ESI-MS: $m/z = 390.6$ ($(\text{M}+\text{H})^+$, 100%); UV-Vis (DMSO): λ_{max} (ϵ) = 320 (1.17×10^4) nm ($\text{cm}^{-1}\text{M}^{-1}$); Fluorescence (DMSO): $\lambda_{\text{max}} = 502$ nm, $\lambda_{\text{exc}} = 338$ nm Anal. Calcd for **2** ($\text{C}_{20}\text{H}_{23}\text{NO}_7$): 61.69% C, 5.95% H, 3.60% N; Found: 61.67% C, 5.75% H, 3.49% N; R_f (1:4 hexanes/ethyl acetate) = 0.17.

3. Gelation tests

The gels were prepared by first heating solutions containing the gelators and then cooling the solutions to room temperature. The gelation properties were evaluated by dissolving test tube inversion. The minimum gelation concentration (mgc) was determined by weighing up a minimum amount of gelator needed for the formation of a stable gel through the heat/cool cycle.² When the compound did not dissolve completely, it was labeled as “insoluble”, whereas “indicates that reprecipitation occurred with cooling.

Table S1. Gelation ability of **1** and **2** in various solvents.^a

solvent	1	2
H ₂ O	P	P
methanol	S	S
methanol/H ₂ O (1:1)	G (3.0)	S
ethanol	S	S
ethanol /H ₂ O (1:1)	G (3.1)	S
DMSO	S	S
DMSO /H ₂ O (1:1)	G (2.7)	S
DMF	S	S
DMF /H ₂ O (1:1)	G (2.9)	S
o-xylene	G (6.6)	P
o-dichlorobenzene(ODCB)	G (4.3)	P
cyclohexane	I	I
n-hexane	I	I
toluene	P	P
chloroform	I	I
butyl acetate	P	P
ethyl acetate	I	I

^a G, gel; P, precipitation; S, solution; I, insoluble. Numbers in parentheses present the minimal gelation concentration (mgc) in mM.

4. General procedure for UV/vis experiments

All UV/vis spectra were carried out just after the addition of different metal salts in DMSO/H₂O (v/v=1/1) solution, while keeping the gelator **1** concentration constant. The solution of metal ions were prepared from the acetate salts of Cu²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, Ni²⁺, Cr²⁺, Fe²⁺ and Co²⁺.

5. Variable temperature ¹H NMR spectra

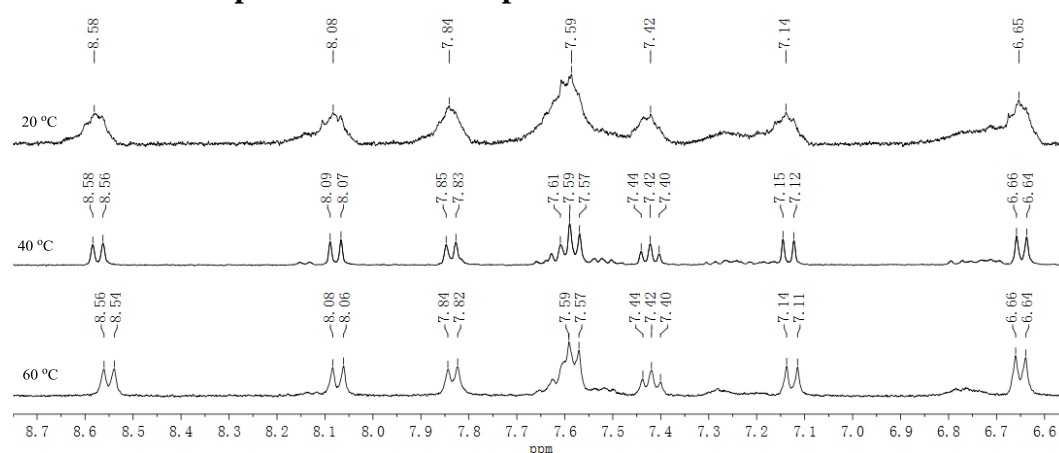


Figure S1. Variable temperature ¹H NMR spectra of **1** (3 mM) in [D₆]DMSO/D₂O (v/v=1/1).

6. UV spectra and ^1H NMR titration experiments

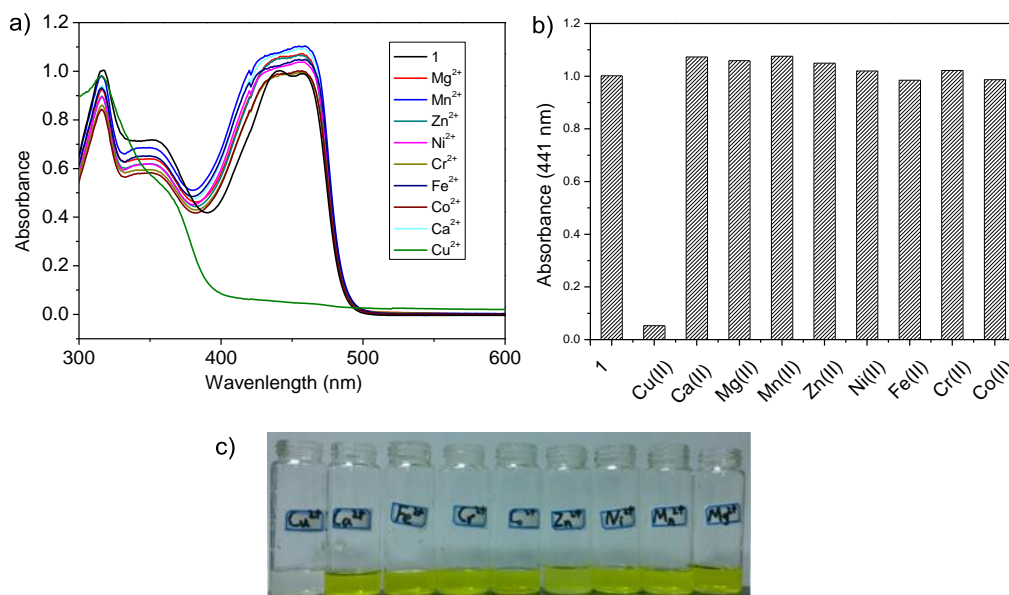


Figure S2. a) UV-Vis absorption of **1** (1×10^{-4} M) in DMSO/H₂O (v/v=1/1) upon addition of 10 equivalents of different metal cations (Cu²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, Ni²⁺, Cr²⁺, Fe²⁺ and Co²⁺). b) Absorption changes at 441 nm upon addition of 10 equivalents of different metal cations. c) Color changes observed for **1** upon the addition of 10 equivalents different metal cations in DMSO/H₂O (v/v=1/1). All solution acquired after 120 min at room temperature.

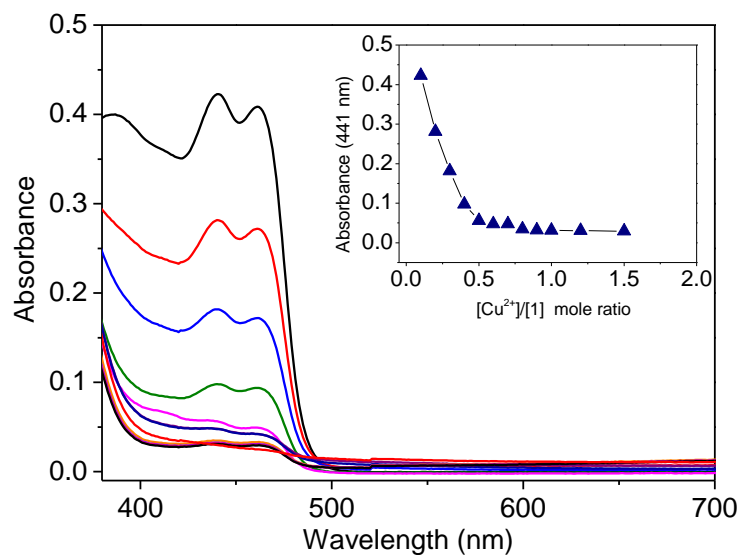


Figure S3. UV-Vis titration of gelator **1** (4×10^{-5} M) with Cu²⁺ in DMSO/H₂O (v/v=1/1), acquired after 120 min.

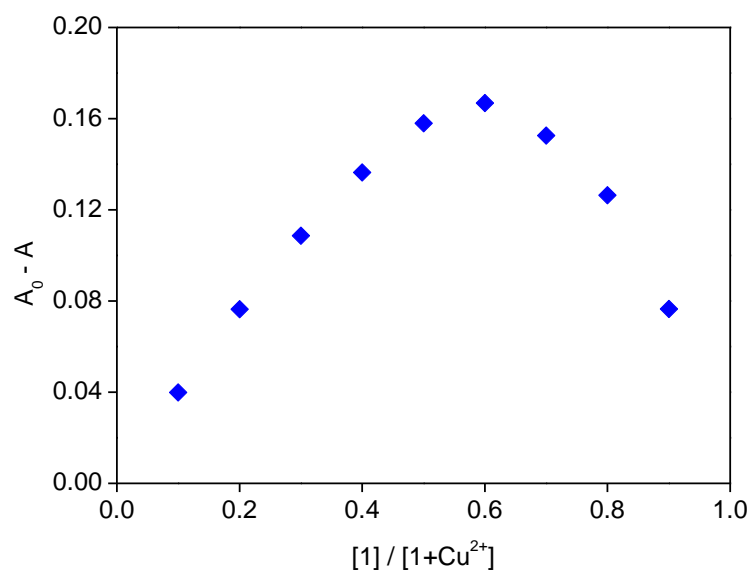


Figure S4. A Job plot of **1** and Cu^{2+} , indicating the 2:1 stoichiometry for **1**- Cu^{2+} complex.

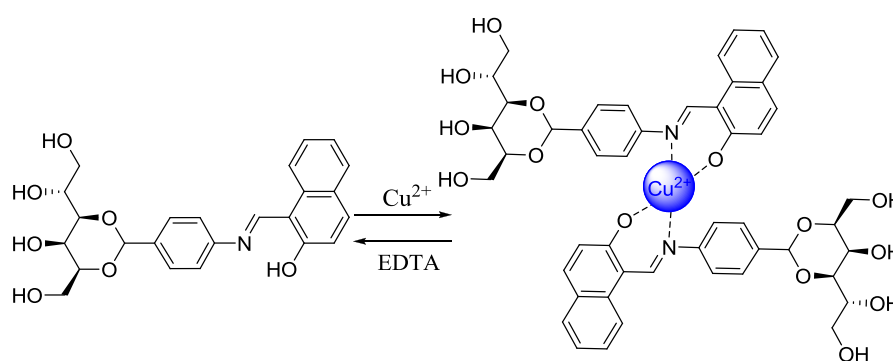


Figure S5. Possible binding mode of **1** with Cu^{2+} .

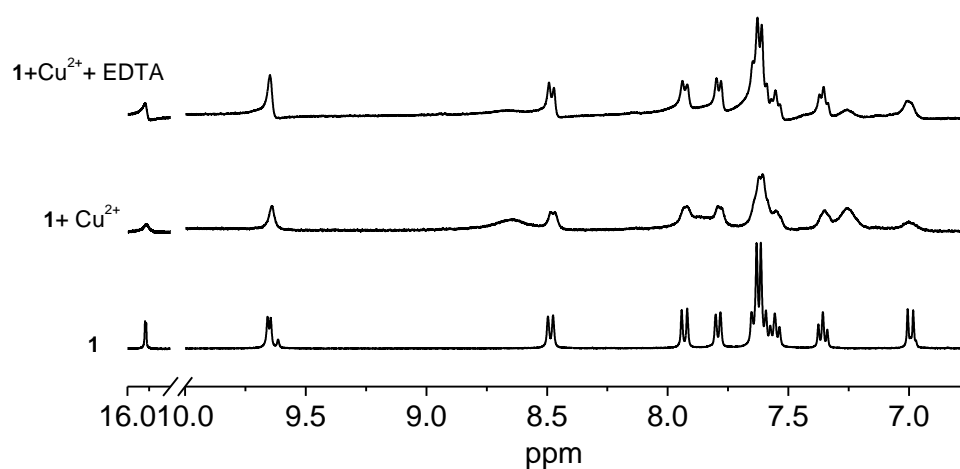


Figure S6. ^1H NMR spectra of **1** (3 mM) in the presence of Cu^{2+} (0.5 equiv) or EDTA (0.5 equiv) in $[\text{D}_6]\text{DMSO}$.

7. Additional references

1. Kobayashi, T.; Ando, K.; Nomoto, H. New sugar compounds, e.g., 4-O-(3,4-dimethylbenzylidene)-D-sorbitol, useful as gelling agents. WO9823604-A; EP945452-A; WO9823604-A1; NO9902549-A; EP945452-A1; CN1238769-A; JP10524508-X; BR9713417-A; TW396160-A; MX9905002-A1; US6187842-B1; KR2000057275-A; MX207140-B; EP945452-B1; DE69726309-E; CN1101389-C; IN9703391-I1; IN233147-B.
2. Jingjing Li, Kaiqi Fan, Libo Niu, Yuanchao Li, and Jian Song. Effects of Salt on the Gelation Mechanism of a D-Sorbitol-Based Hydrogelator. *J. Phys. Chem. B*, 2013, 117, 5989–5995.