

Bio-based Hydrogels Induced by Salts

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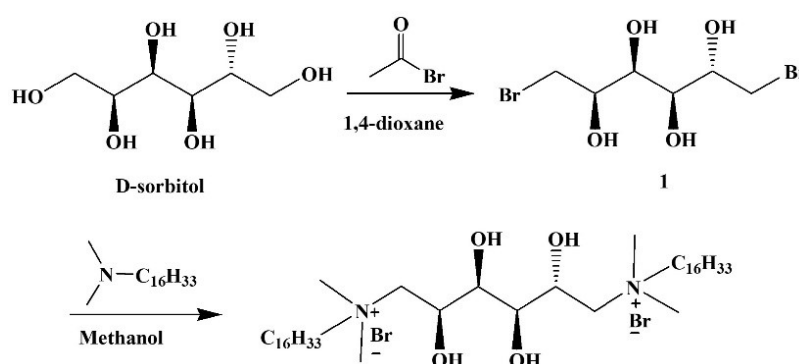
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Materials and methods

Materials

D-Sorbitol (purity $\geq 99\%$), N,N-Dimethylhexadecylamine (95%), D₂O (99.9%), CDCl₃ (99.8%) were purchased from Acros and used without any further purification. Acetyl bromide (purity $> 98\%$), ethanol (A. R. grade), 1,4-dioxane (A. R. grade), dichloromethane (A. R. grade), acetone (A. R. grade) were obtained from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of SGCTB



Scheme 1. The synthesis procedures of surfactant SGCTB

The synthesis of intermediate 1, 6-dibromosorbitol was carried out following a previously reported method. To begin, 1.11 g of d-sorbitol was dissolved in 16 mL of dioxane. Then, 1.1 mL of acetyl bromide was added to the solution while maintaining in an ice bath. The mixture was stirred at 18 °C for 48 hours. Afterwards, dichloromethane was used to extract the desired intermediate. The obtained intermediate was dried with anhydrous magnesium sulfate and the solvent was subsequently removed.

The intermediate (3.08 g) was added to a methanol solution containing 0.022 mol of N,N-dimethylcetylamine and stirred at 35°C for 48 hours. Upon completion, ethanol and acetone were utilized for triple recrystallization, resulting in white powder. The target

surfactant was obtained by subsequent drying.

^1H NMR spectra for variations in chemical shifts were obtained on a proton frequency of 600.13 MHz spectrometer in D_2O at 25 °C. MS spectra were determined with BEFLEX III for MALDI-TOF mass spectrometer.

^1H -NMR (400 MHz, DMSO): δ = 0.79-0.88 (t, 6H, $-\text{CH}_3$), 1.13-1.37 (m, 24H), 2.64-2.86 (s, 12H), 2.89-3.07 (m, 4H), 3.28-3.36 (m, 4H); MALDI-TOF-MS ($\text{M}+\text{Na}$) $^+$: Calcd. For $\text{C}_{42}\text{H}_{90}\text{Br}_2\text{N}_2\text{O}_4$: 846.9. Found: 847 ($\text{M}+\text{H}$), 869 ($\text{M}+\text{Na}$).

Measurements

Equilibrium surface tension. The equilibrium surface tension was examined by the Wilhemy plate method (Data physics DCAT21, Germany) using a platinum plate of \sim 5 cm perimeter. The solutions were immersed into a constant-temperature bath at the desired temperature 30.0 ± 0.05 °C. Sets of measurement were taken at certain intervals until the surface tension was constant for 30 min.

NMR experiments. All 400 MHz NMR studies were carried out on a Bruker DPX 400 MHz spectrometer at 300 K

FT-IR Spectroscopy. All reported FT-IR spectra were taken using a Shimadzu (Japan) model FT-IR spectrophotometer. A Nicolet FT-IR instrument [Magna IR-750] spectrometer (series II) was used to obtain solid state and dried gel state FT-IR spectra.

Scanning electron microscopy (SEM). Samples were prepared and dried under the ambient conditions for 24 hours. 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.

Rheological behavior of the solution. Steady shear viscosities of the emulsions and with different salts were characterized using a TA ARES-G₂ Rheometer (TA Instruments, United States) with parallel plates ($d = 20$ mm), and a gap between plates

of 1000 μm . The temperature was regulated by a circulating water bath using a Peltier system. Apparent viscosity was determined with the shear rate range of 0.1-100 s^{-1} and a time waiting process of 30 s was applied before each test. Oscillatory measurement of storage modulus G' was performed from 0.01 to 100 Hz and all measurements were performed within the identified linear viscoelastic region and made at 1% strain. All the experiments were carried out at 25 $^{\circ}\text{C}$.

SAXS. SAXS was conducted at 1W2B station in BSRF. The obtained 2D SAXS images were obtained from the detector and then transformed into the profiles of intensity (I) vs. wavevector (q) using the software SAXS Data Preprocess V2.0.0. The fractal dimension D of MOF materials was calculated and analysed using the method reported.¹

Gelation test: These tests were performed by adding the weighed amount of SGCTB into the measured volume of solvent in the 10 mL tube and then heating the tube until the gelators were dissolved or could not be dissolved ever. A “stable to inversion test tube method” was adopted. Each experiment was done in duplicate.

Circular dichroism spectroscopy (CD): All circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. Samples were scanned from 600 to 200 nm at a rate of 500 nm min^{-1} . The CD spectra of SGCTB in desired concentration with different salts were recorded.

Supplementary Figures

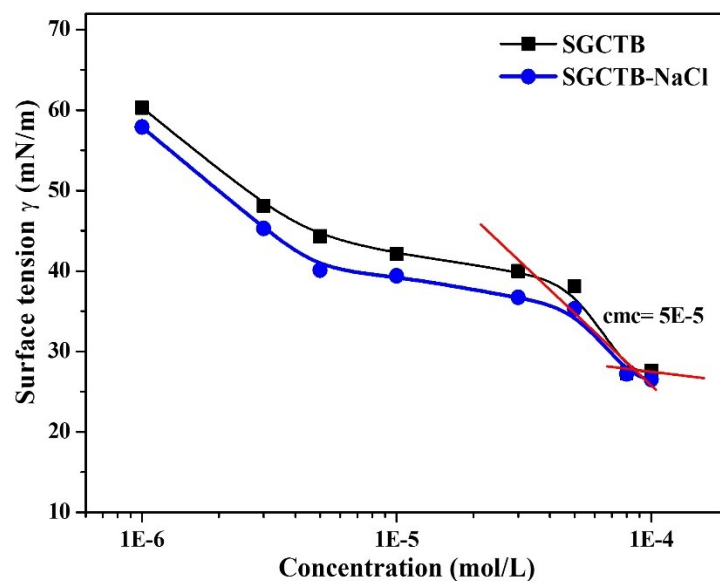


Fig. S1 (a) Equilibrium surface tension isotherms of the obtained surfactant as function of surfactant concentrations at 30 °C and the effect of salt addition on surface tension curve (0.3 wt% NaCl).

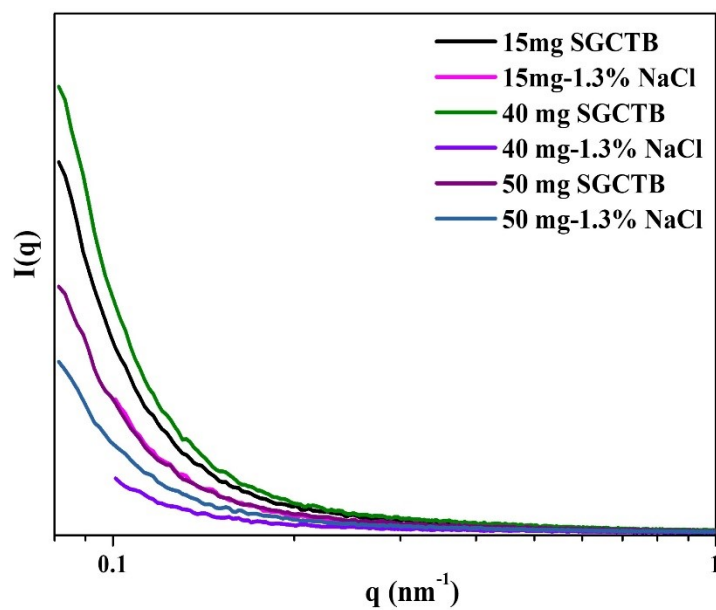


Fig. S2 SAXS curves of SGCTB solution with and without NaCl.

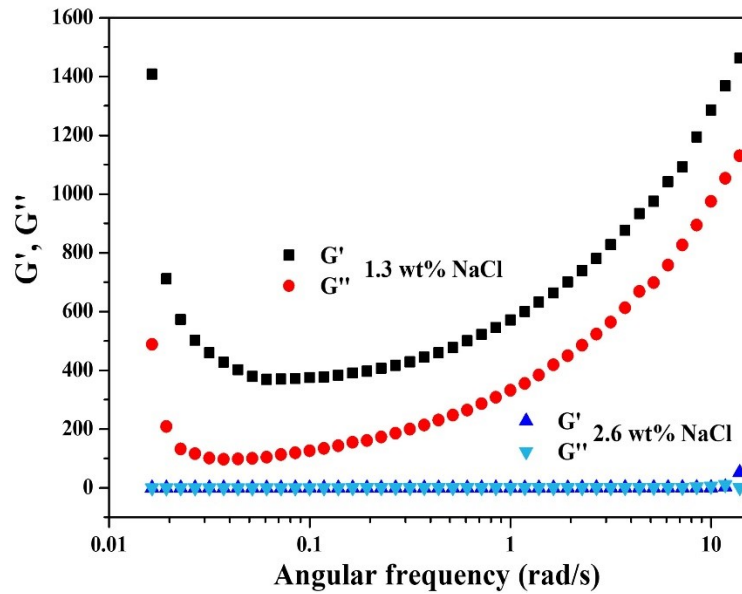


Fig. S3 Frequency sweep data comparing storage moduli (G') and loss moduli (G'') of hydrogels made with different amount of salt (2.6 wt% of SGCTB with 1.3 wt% and 2.6 wt % of NaCl).

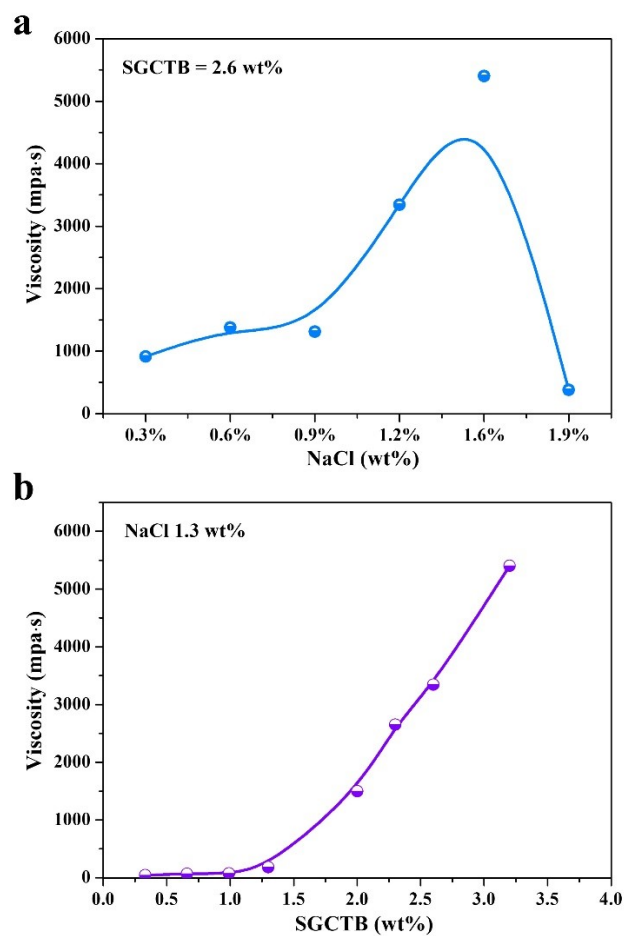


Fig. S4 (a) Viscosity of SGCTB solution (2.6 wt%) as function of NaCl concentrations; (b) Viscosity of solution with 1.3 wt% NaCl as function of SGCTB concentrations.

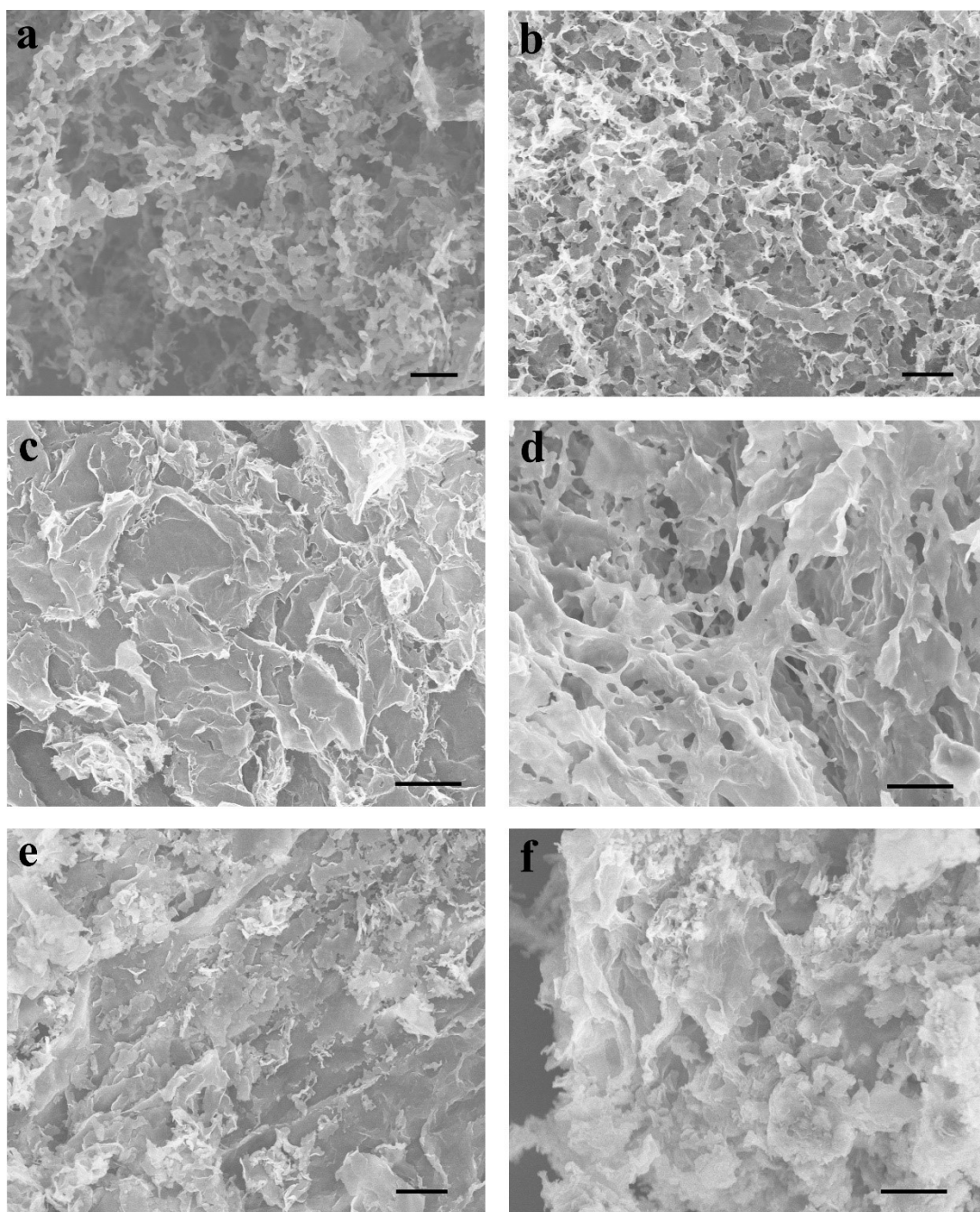


Fig. S5 Representative SEM images of hydrogels triggered by different salts. (a) SGCTB; (b) SGCTB with 1.3 wt% NaCl; (c) SGCTB with 1.3wt % Na₂SO₄; (d) SGCTB with 0.65wt % FeCl₃; (e) SGCTB with 1.3wt % NaBr; (f) SGCTB with 1.3wt % NaAc. The scale bars are 10 μ m.

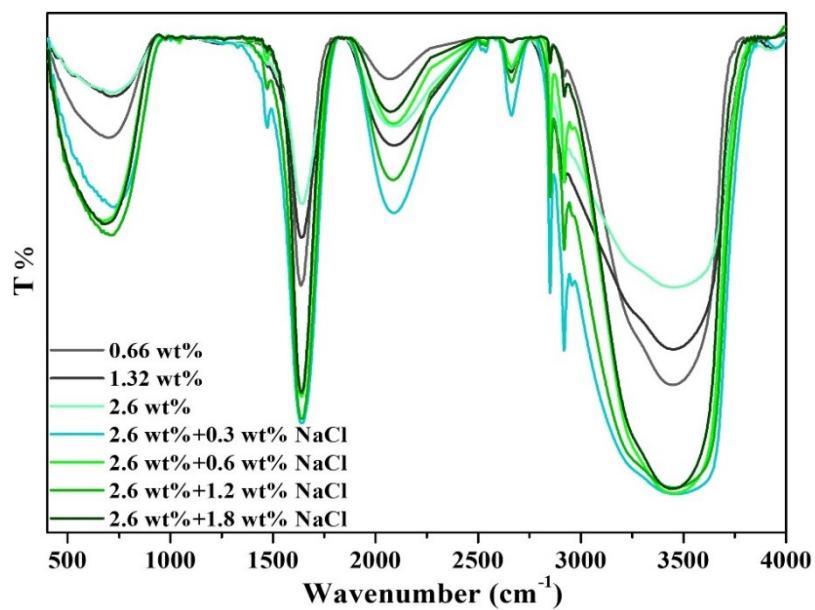


Fig. S6 FT-IR spectra of SGCTB solutions and hydrogels.

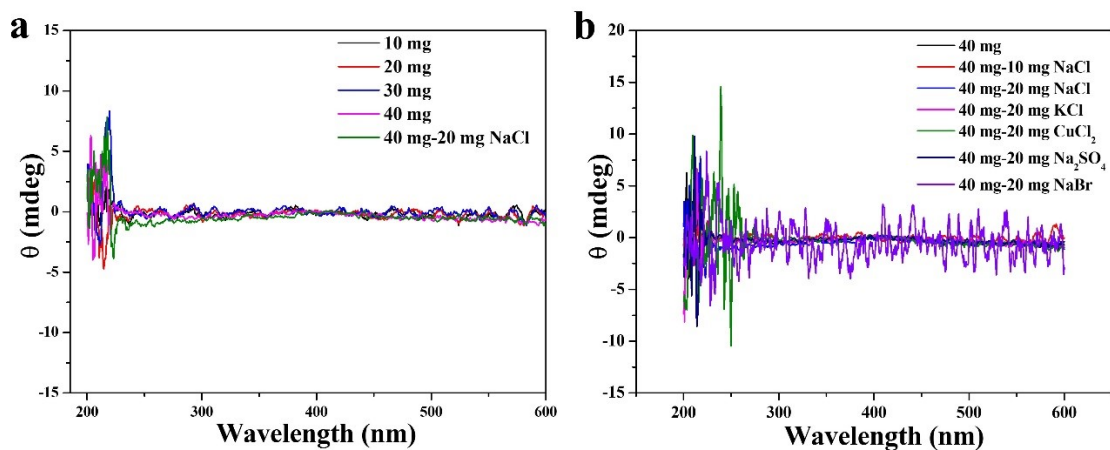


Fig. S7 CD spectra of SGCTB of the hierarchical assemblies without and with various salts at 25 °C.

Table S1 Gelation experiments of SGCTB in the presence of various salts^[a]

Sample	Additive (wt%)	State
1	KCl 0.65	Sol
2	KCl 1.3	Gel
3	NaAc 1.3	Sol
4	NaBr 0.65	Sol
5	NaBr 1.3	Sol
6	NaI 0.65	Sol
7	NaI 1.3	Sol
8	Na ₂ SO ₄ 0.65	Gel
9	Na ₂ SO ₄ 1.4	Gel
10	CuCl ₂ 0.65	Sol
11	CuCl ₂ 1.3	Gel
12	ZnCl ₂ 0.65	Sol
13	ZnCl ₂ 1.3	Sol
14	FeCl ₃ 0.65	Gel
15	FeCl ₃ 1.3	Gel

[a] Gelator concentration: 2.6 % w/v.

Reference

1. Kang, X. et al. *Chem. Sci.* 2015, **6**, 1668-1675.