Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Mechanically-sensitive hydrogels formed from β-cyclodextrin and an anionic surfactant containing a biphenyl group

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1. Synthesis of compounds

1.1 Synthesis

1.1.1 Synthesis of sodium 2-(4-phenylphenoxy)dodecanoate (C_{12}biphNa)

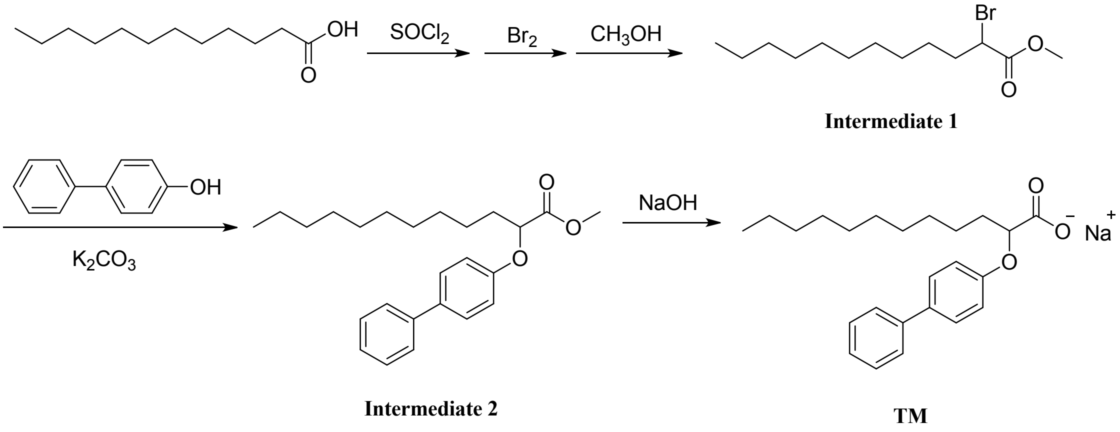

Fig.S1 The synthetic scheme of sodium 2-(4-phenylphenoxy)dodecanoate (C_{12}biphNa)

The dodecanoic acid (150.0g, 0.750mol) was added into a 500mL three-necked flask equipped with a reflux condenser. The temperature was raised to 60 °C until all the solid dissolved. Thionyl chloride (126.6g, 0.975mol) was slowly added. The produced acidic gas was absorbed with NaOH solution. After the addition was completed, the reaction was continued for another 3 hours at 75 °C. The temperature was then adjusted to 90 °C and a catalytic amount of iodine was added. Bromine (149.7g, 0.937mol) was slowly dropped in. This process shall take quite a long time to avoid the excessive loss of bromine. After all the bromine was added in, the reaction was continued for another 2 hours. The temperature was decreased to 55 °C and methanol (73.2g, 2.25mol) was added. The reaction was continued for 1 hours and the reaction mixture was cooled

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to room temperature. The deep-colored liquid was first washed with sodium sulfite solution and then with distilled water. After dried with anhydrous magnesium sulfate, the **Intermediate 1** was obtained by vacuum distillation as colorless liquid. 154-158 ^{o}C /5mmHg. 151.1g. Yield: 68.8%.

The potassium carbonate (45.3g, 0.328mol) and 200mL DMF was added into a 500mL three-necked flask equipped with a reflux condenser. After stirring 0.5 hours, 4-phenylphenol (18.6g, 0.109mol) which was dissolved in DMF was added to the three-necked flask. The temperature was then raised to 60 ^{o}C. After stirring 1 hour, the DMF solution of **Intermediate 1** (40.0g, 0.137mol) was added. The reaction was carried out at 80 ^{o}C for 24 hours. And all of this process was under N_2 protection. 100mL dichloromethane was added after the reaction mixture was cooled to room temperature. The mixture was filtered and the solvent in the filtrate was removed under reduced pressure. The residue was added 200mL cold water and extracted three times with petroleum ether. The combined organic layer was washed three times with deionized water and then dried with anhydrous magnesium sulfate. After the solvent was removed, the crude product was purified by recrystallization with methanol twice. After drying, the obtained **Intermediate 2** is 31.8g, yield: 63.32%.

The sodium hydroxide (2.4g, 0.060mol), **Intermediate 2** (20.0g, 0.055mol) and 200mL ethanol were added into a 500mL round-bottom flask equipped with a reflux condenser.. The reaction was carried out for 12 hours at 70 ^{o}C. After cooling, the solvent in the reaction mixture was removed under reduced pressure. The resulted solid was recrystallized three times with ethanol. After dried under vacuum at 50 °C, the final product C_{12}biphNa (**TM**) was obtained as white solid. 18.7g, yield: 87.3%.

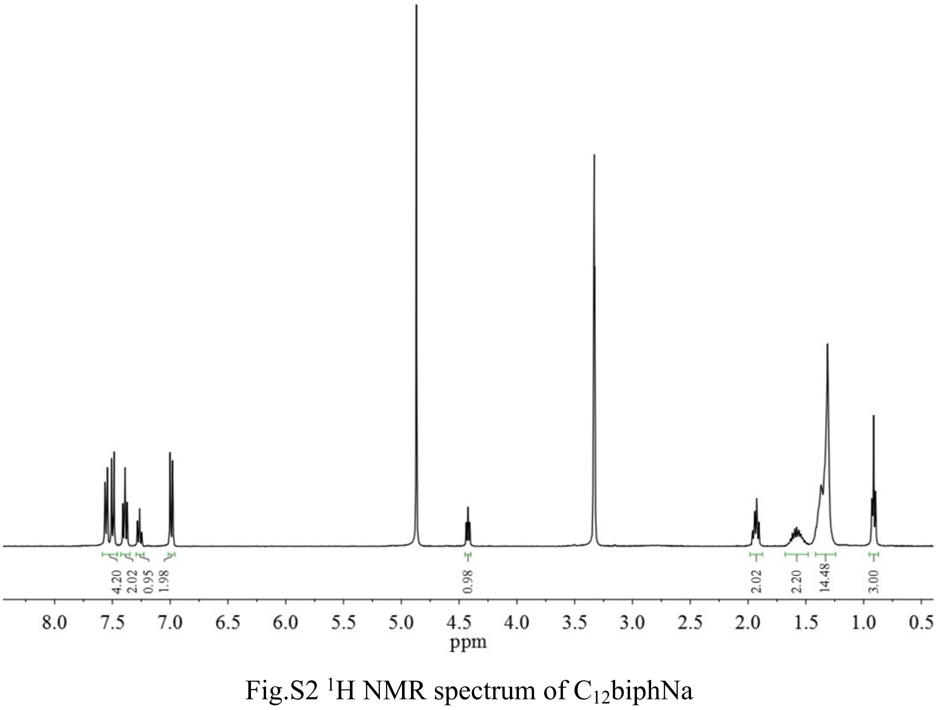
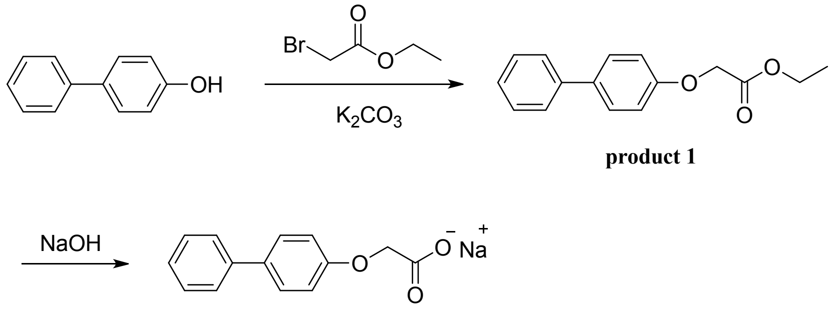


Fig.S2 ^{1}H NMR spectrum of C_{12}biphNa

^{1}H NMR (400 MHz, MeOD) δ7.53 (dd, 4H), δ7.39 (t, 2H), δ7.26 (t, 1H), δ6.99 (d, 2H), δ4.42 (t, 1H), δ1.94 (m, 2H), δ1.58 (m, 2H), δ1.34 (m, 14H), δ0.91 (t, 3H).

Elemental analysis: Anal. Calcd. for $C_{24}H_{21}NaO_3$: C, 73.82; H, 8.00. Found: C, 73.67; H, 8.11.

1.1.2 Synthesis of sodium 2-(4-phenylphenoxy)acetate



product 1

TM

Fig.S3 The synthetic scheme of sodium 2-(4-phenylphenoxy)acetate

The potassium carbonate (35.2g, 0.255mol) and 200mL DMF was added into a 500mL three-necked flask equipped with a reflux condenser. After stirring for 0.5 hours, 4-phenylphenol (14.5g, 0.085mol) which was dissolved in DMF was added to the three-necked flask. The temperature was raised to 60 °C. After stirring for 1 hour, the DMF solution of ethyl bromoacetate (17. 8g, 0.106mol) was added. The reaction was carried out at 80 °C for 24 hours. The whole process was under N_2 protection. The cooled reaction mixture was first filtered. Most of the solvent in the filtrate was removed under reduced pressure. The residue was added 150mL distilled water and was extracted three times petroleum ether. The combined organic layer was washed three times with deionized water and then dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica column chromatography. The effluent was petroleum ether/ethyl acetate = 5:1. The obtained **product 1** was white solid**.** 17.2g, yield: 78.82%.

The sodium hydroxide (3.0 g, 0.074mol), product 1 (17.2g, 0.067mol) and 250mL ethanol were added into a 500mL round-bottom flask. The reaction was performed for 12 hours at 70 °C. After cooling, the reaction mixture was filtered. The solid was washed with ethanol three times. After dried under vacuum at 50 °C, sodium 2-(4-phenylphenoxy)acetate (**TM**) was obtained as white solid. 14.3g, yield: 91.0%.

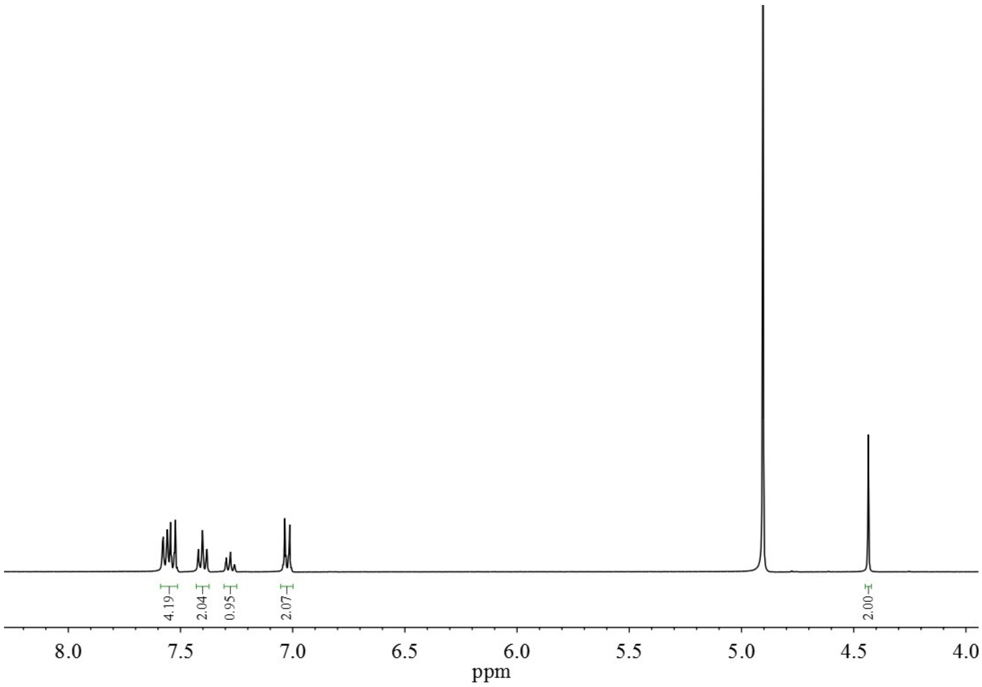


Fig.S4 ^{1}H NMR spectrum of sodium 2-(4-phenylphenoxy)acetate

^{1}H NMR (400 MHz, MeOD) δ7.55 (dd, 4H), δ7.40 (t, 2H), δ7.28 (t, 1H), δ7.05-7.00 (d, 2H), δ4.43 (s, 2H).

Elemental analysis: Anal. Calcd. for $C_{14}H_{11}NaO_3$: C, 67.20; H, 4.43. Found: C, 67.45; H, 4.61.

2. Methods

H-nuclear Magnetic Resonance(^{1}H NMR) ^{1}H NMR measurement was carried out on a Bruker Aduance Ⅲ 400 spectrometer operating at 400 MHz.

^{1}H–^{1}H 2D NOESY HNMR Measurements C_{12}biphNa, β-CD and D_2O in desired proportion was added into NMR tube. The mixture was gently heated to 70 °C until the solid was dissolved and it was then kept at 25±0.1 °C for at least 12h to make sure the formation of gel. 2D NOESY measurement was carried out on a Bruker Aduance Ⅲ 400 spectrometer operating at 400 MHz with the standard three-pulse sequence with a mixing time of 600 ms.

Polarized optical microscopy measurements The polarized optical microscopy images were observed with ZEISS Axiom Scope A1 device under cross-polarized light. The samples were placed between two glass cover slips at room temperature. Then the images were recorded.

3. Determination of the association constants of sodium laurate/β-CD and sodium 2-(4-phenylphenoxy)acetate/ β-CD inclusion complexes

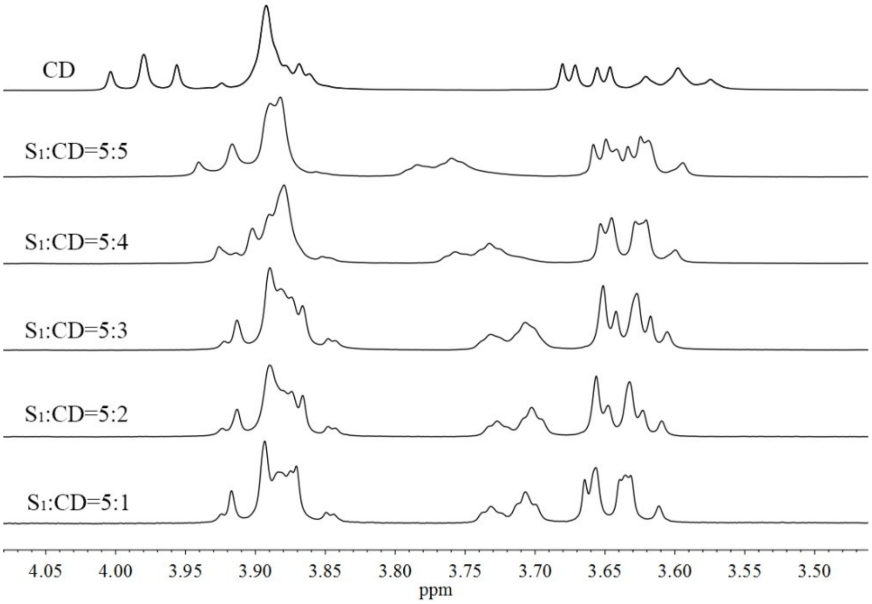


Fig.S5 ^{1}H NMR spectrum of β-CD and S_1(sodium laurate) in D_2O at different mixing ratio. The concentration of S_1 is 5mM and the ratio of S_1 and β-CD is 5:1, 5:2, 5:3, 5:4, 5:5 and 0:5, respectively, from the bottom to top.

Table S1 The chemical shift displacements of the internal protons(H_5) of β-CD upon complex formation at different S_1 concentrations ($\Delta\delta$: the observed chemical shift displacement, $[C]_T$: the total concentration of β-CD, $[S]_T$: the total concentration of S_1(sodium laurate)).

$\Delta\delta$(ppm)	$[C]_T$(M)	$[S_1]_T$(M)
0	0.005	0
0.155	0.001	0.005
0.16	0.002	0.005
0.155	0.003	0.005
0.129	0.004	0.005
0.102	0.005	0.005

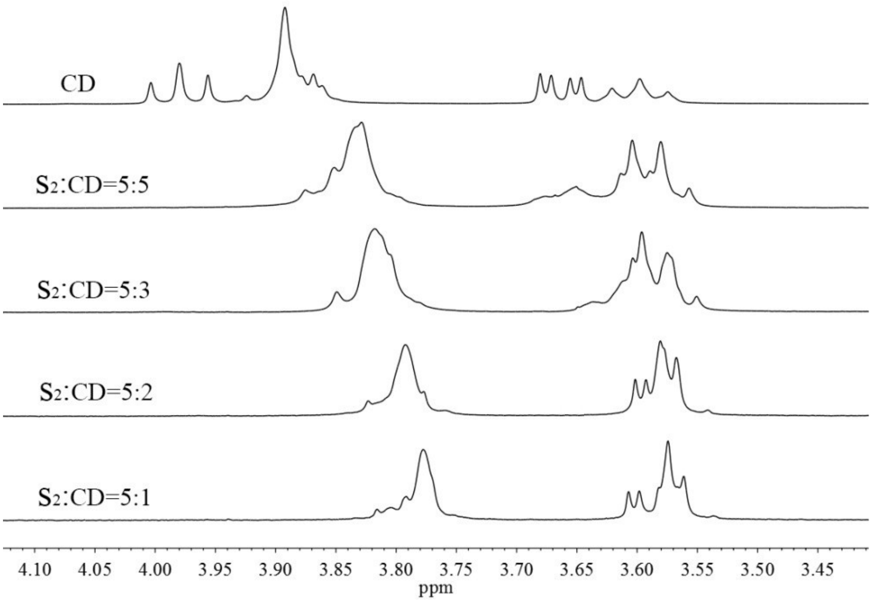


Fig.S6 ^{1}H NMR spectrum of β-CD and S_2 (sodium 2-(4-phenylphenoxy)acetate) in D_2O at different mixing ratio. The concentration of S_2 is 5mM and the ratio of S_2 and β-CD is 5:1, 5:2, 5:3, 5:5 and 0:5, respectively, from the bottom to top.

Table S2 The chemical shift displacements of the internal protons(H_5) of β-CD upon complex formation at different S_2 concentrations (Δδ: the observed chemical shift displacement, $[C]_T$: the total concentration of β-CD, $[S]_T$: the total concentration of S_2(sodium 2-(4-phenylphenoxy)acetate)).

Δδ(ppm)	$[C]_T$(M)	$[S_2]_T$(M)
0	0.005	0
0.264	0.001	0.005
0.269	0.002	0.005
0.251	0.003	0.005
0.211	0.005	0.005

The association constants of inclusion complexes in the two systems were obtained by fitting with the above data in table S1 and S2 according to equation (1) [1,2]:

$$\Delta\delta = \frac{A}{2[C]_T}\left\{[S]_T + [C]_T + \frac{1}{K} - \left(\left([S]_T + [C]_T + \frac{1}{K}\right)^2 - 4([S]_T \cdot [C]_T)\right)^{1/2}\right\} \qquad (1)$$

（Δδ: the observed chemical shift displacement of one proton; A: the chemical shift displacement of one proton in inclusion complexes; $[C]_T$: the total concentration of β-CD; $[S]_T$: the total concentration of surfactant; K: the association constant)

4. ^1H–^1H 2D NOESY spectrum

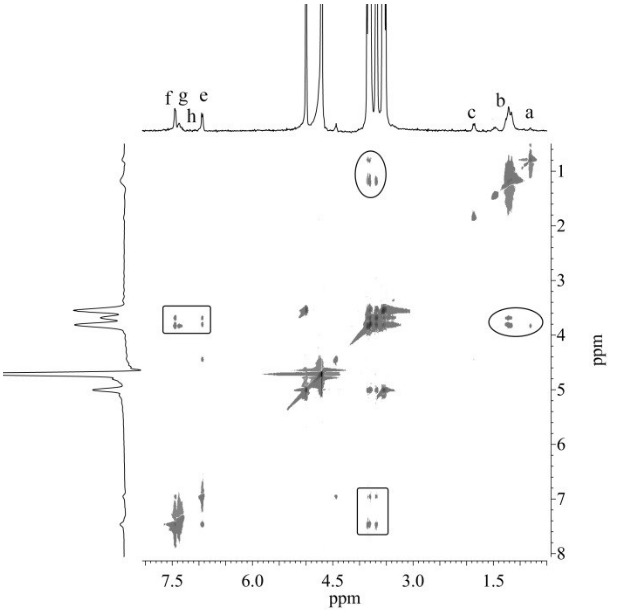


Fig.S7 ^1H–^1H 2D NOESY spectrum of a 1:3 system of C_{12}biphNa (5 mM) and β-CD in D_2O at 25 °C

5. Polarized optical microscopy

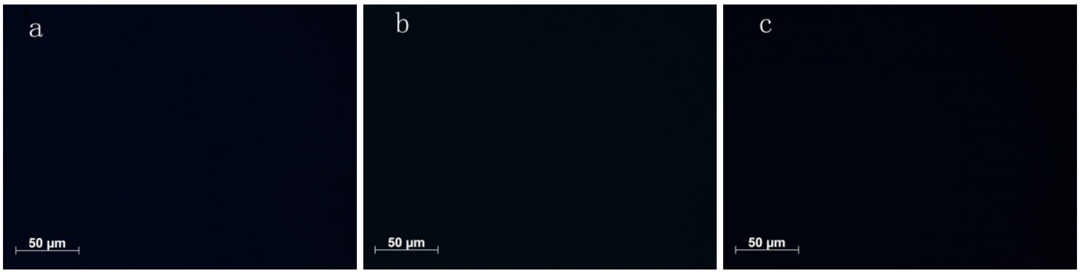


Fig.S8 Polarized optical microscopy images of (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD and (c) a 1:3 system of C_{12}biphNa (5 mM) and β-CD at 25 °C

6. Cryogenic-transmission electron microscopy (Cryo-TEM)

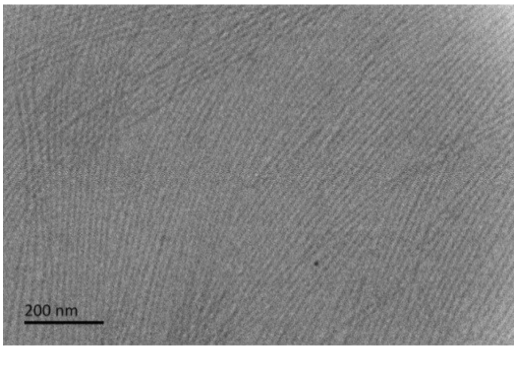


Fig.S9 Cryo-TEM images of an opaque gel formed from 1:3 system of C_{12}biphNa (13 mM) and β-CD

7. Rheology measurements

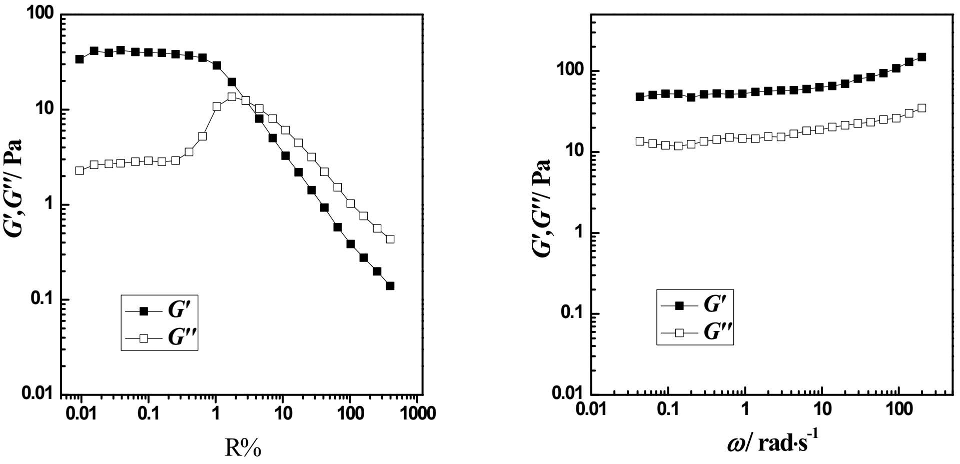


Fig.S10 Variation of G′ (storage symbols) and G″ (loss symbols) with (a) the percentage strain, and (b) shear frequency, ω, for the 1:1 system of C_{12}biphNa (10 mM) and β-CD at 25 °C.

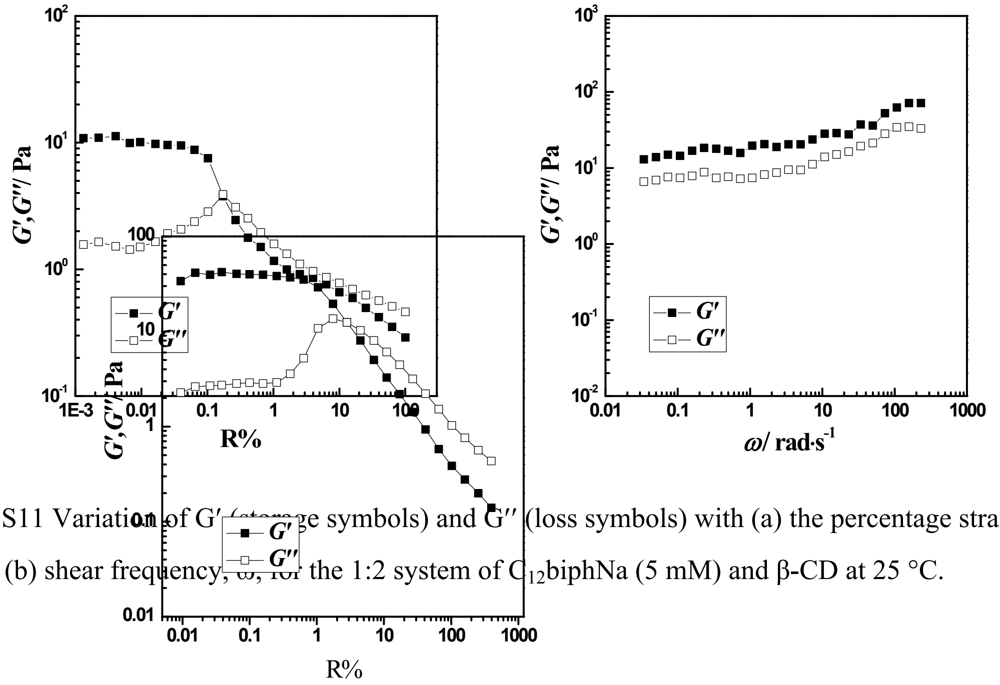


Fig.S11 Variation of G′ (storage symbols) and G″ (loss symbols) with (a) the percentage strain, and (b) shear frequency, ω, for the 1:2 system of C_{12}biphNa (5 mM) and β-CD at 25 °C.

References

1. M. Bogdan, M. R. Caira and S. I. Farcas, *Supramol. Chem.*, 2002, **14**, 427-435.
2. B. Medronho, A. J. M. Valente, P. Costa and A. Romano, *Colloid. Polym. Sci.*, 2014, **292**, 885-894.