Electronic Supplementary Material (ESI) for Soft Matter.

pH-regulated surface property and pH-reversible micelle transition of a tertiary amine-based gemini surfactant in aqueous solution

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Synthesis

Synthesis of compound 1

Aliphatic acid (0.2 mol) was added into a three-necked flask equipped with condenser and heated to 65 °C by oil bath. Quantitative thionyl chloride (33.8 g, 0.28 mol) was added dropwise under magnetic stirring once the aliphatic acid was melted completely. The released HCl and SO_2 were absorbed by diluted NaOH solution. Then the temperature was increased to 90 °C and 1.6 g I_2 was added as catalysis (0.5 h). The Br_2 (38.9 g, 0.24 mol) was added dropwise under magnetic stirring and reacted for 6 h. Then 30 mL of CH_3OH was gradually added under magnetic stirring at 55 °C. After the reaction products were cooled to room temperature, enough $NaHSO_3$ solution was added and a phase separation appeared. The organic layer was washed with 70 mL of water for 3 times and dried with anhydrous $MgSO_4$ overnight. Finally, the compound 1 was obtained as colorless oil.

Synthesis of compound 2

The mixture of acetone (80 mL) and K_2CO_3 (30.5 g, 0.22 mol) was heated to 60 °C under N_2 atmosphere. Quantitative hydroquinone (6.2 g, 0.05 mol) was added into the above mixture and magnetic stirring for 0.5 h. Then the compound 1 (60 g) was gradually added under magnetic stirring and the mixture was reacted for 48 h at 60 °C. The reaction products were separated by filtration and the filter cake was washed with 30 mL acetone for 3 times. The acetone in the filtrate was removed by rotary evaporation. The remaining solid was dissolved in 30 mL of CH_2Cl_2, and washed with NaOH solution (2 wt%) and water successively. Then crude product was gained by eliminating CH_2Cl_2 through rotary evaporation. Finally, the compound 2 as yellow powder was obtained by recrystallization from petroleum ether for 3 times.

Synthesis of C_m-A-C_m

The mixture of compound 2 (0.022 mol) and N,N'-dimethyl-1,3-propanediamine (8.9 g, 0.087 mol) was refluxed under nitrogen atmosphere and magnetic stirring for 24 h. The residual N,N'-dimethyl-1,3-propanediamine was removed by vacuum distillation. Then the remaining solid was recrystallized from n-heptane for 3 times, and the crude product was gained. The crude product was dissolved in CCl_4 and the insoluble impurity was removed by filtration. The filtrate was extracted by dilute HCl aqueous solution. The white precipitate was generated when NaOH solution was gradually added into above aqueous solution. The finally surfactants, C_m-A-C_m, were obtained as white powder by washing the precipitate with water for several times and removing the water in a vacuum oven successively. The final yield was 46% according to the quality of hydroquinone.

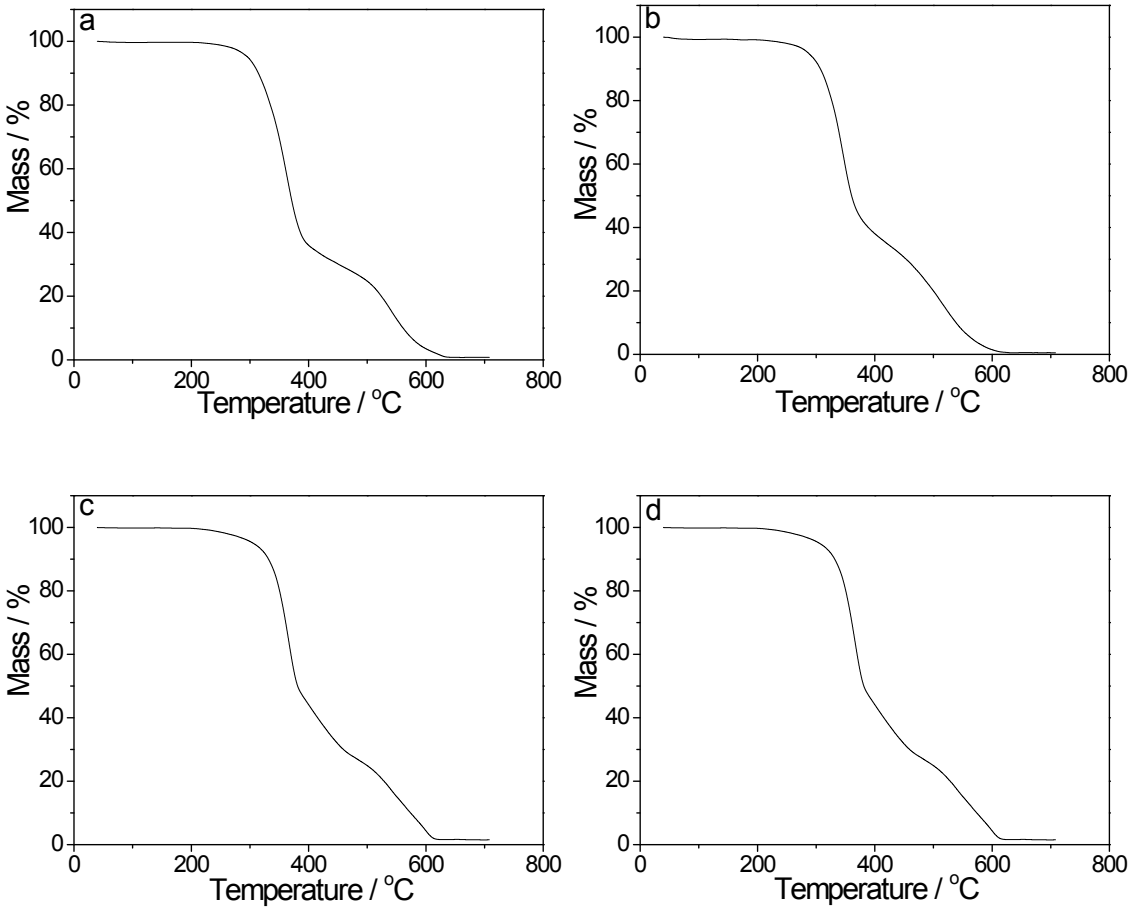

Fig. S1 TGA curves of (a) C_8-A-C_8, (b) C_{10}-A-C_{10}, (c) C_{12}-A-C_{12}, and (d) C_{14}-A-C_{14}.

Table S1 The melting points (mp), decomposition temperature (dt), and element analyses of C_m-A-C_m

Surfactant	mp (°C)	dt (°C)		C (%)	H (%)	N (%)	O (%)
C_8-A-C_8	100.0	293	Calc.	68.9	10.5	8.9	10.2
			Found	68.8	10.4	8.8	10.3
C_{10}-A-C_{10}	102.4	298	Calc.	71.1	11.0	8.3	9.5
			Found	71.2	10.8	8.2	9.2
C_{12}-A-C_{12}	103.8	308	Calc.	72.2	11.2	7.7	8.8
			Found	72.1	11.6	7.5	8.7
C_{14}-A-C_{14}	105.9	323	Calc.	73.2	11.4	7.1	8.1
			Found	72.9	11.4	7.1	8.6

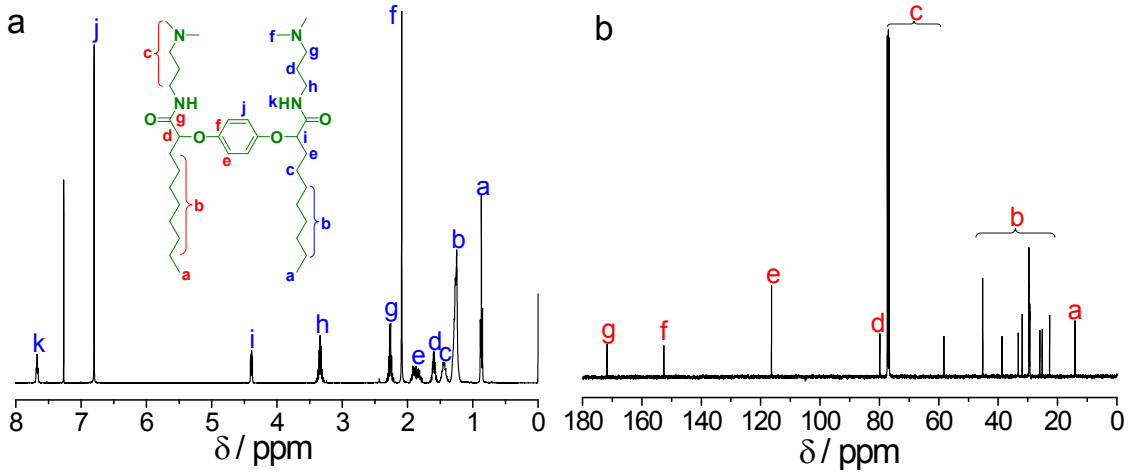

Fig. S2 (a) ^{1}H NMR (400 MHz, $CDCl_3$) and (b) ^{13}C NMR (100 MHz, $CDCl_3$) of C_8-A-C_8.

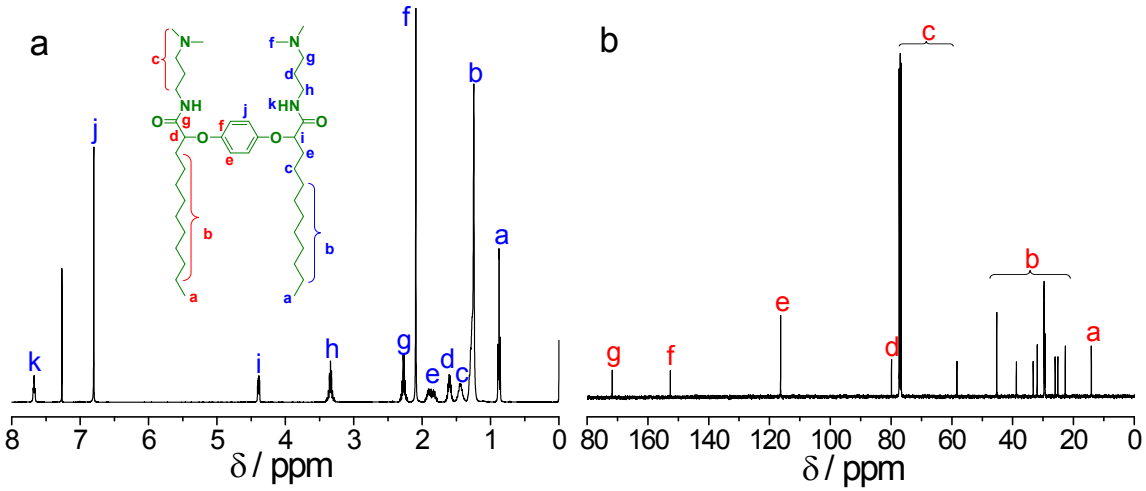

Fig. S3 (a) ^{1}H NMR (400 MHz, $CDCl_3$) and (b) ^{13}C NMR (100 MHz, $CDCl_3$) of C_{10}-A-C_{10}.

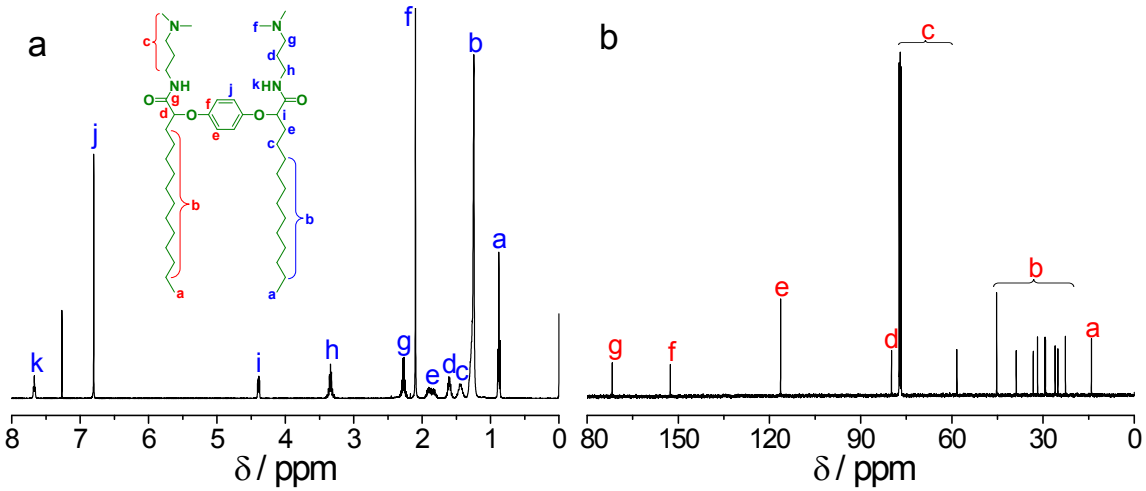

Fig. S4 (a) ^{1}H NMR (400 MHz, $CDCl_3$) and (b) ^{13}C NMR (100 MHz, $CDCl_3$) of C_{12}-A-C_{12}.

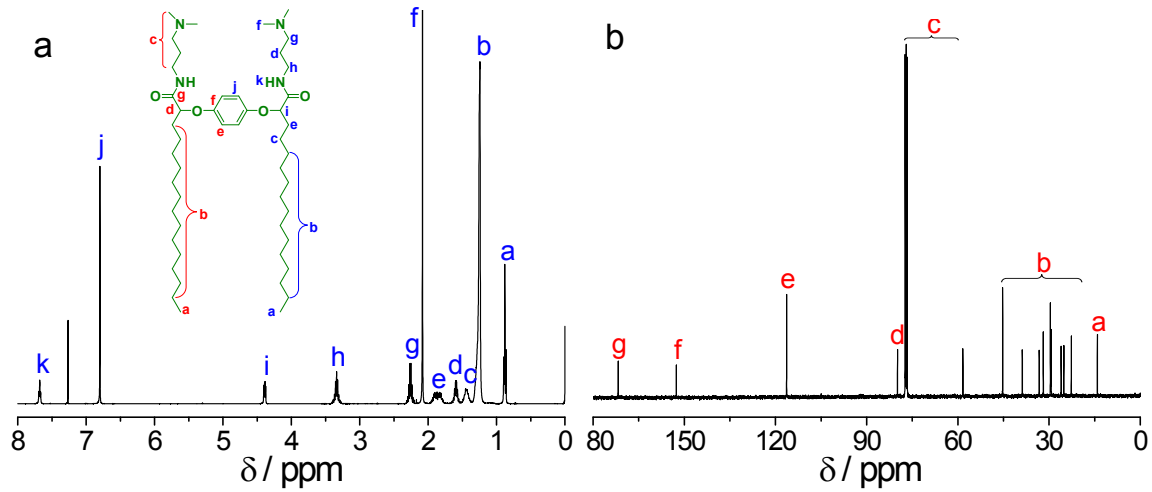

Fig. S5 (a) ^{1}H NMR (400 MHz, $CDCl_3$) and (b) ^{13}C NMR (100 MHz, $CDCl_3$) of C_{14}-A-C_{14}.

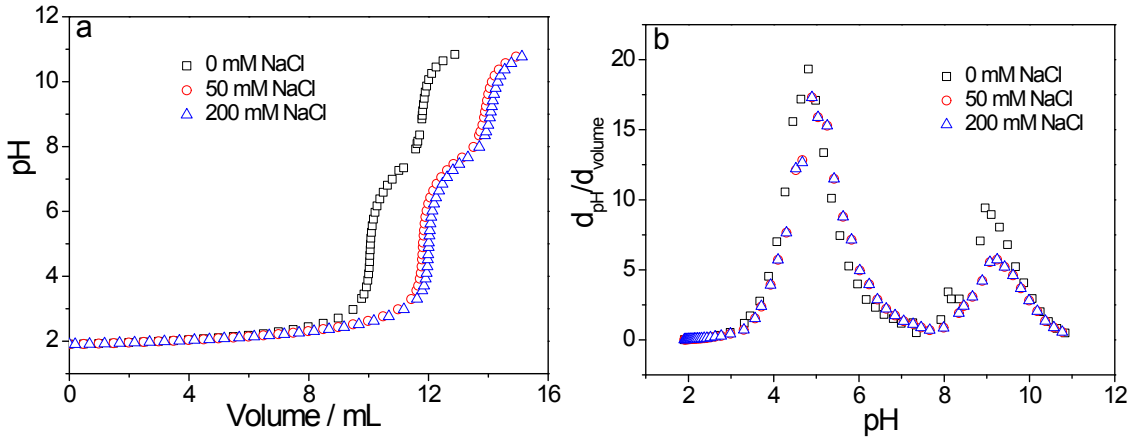

Fig. S6 (a) pH titration curves of C_{12}-A-C_{12} aqueous solutions (2 mM) in the presence of NaCl at 25 °C and (b) the corresponding differential curves calculated from the data of (a).

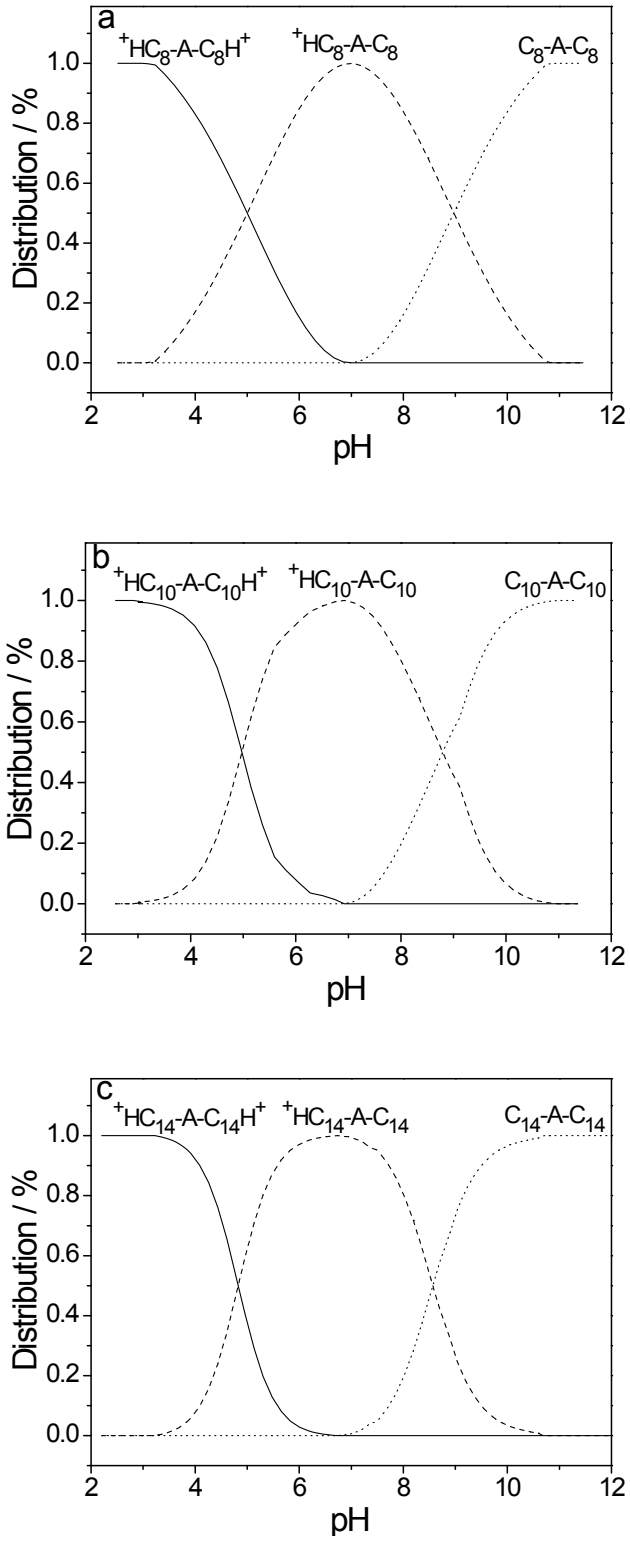

Fig. S7 Molecule state distributions of (a) C_8-A-C_8, (b) C_{10}-A-C_{10}, and (c) C_{14}-A-C_{14} in aqueous solution varying with pH value.

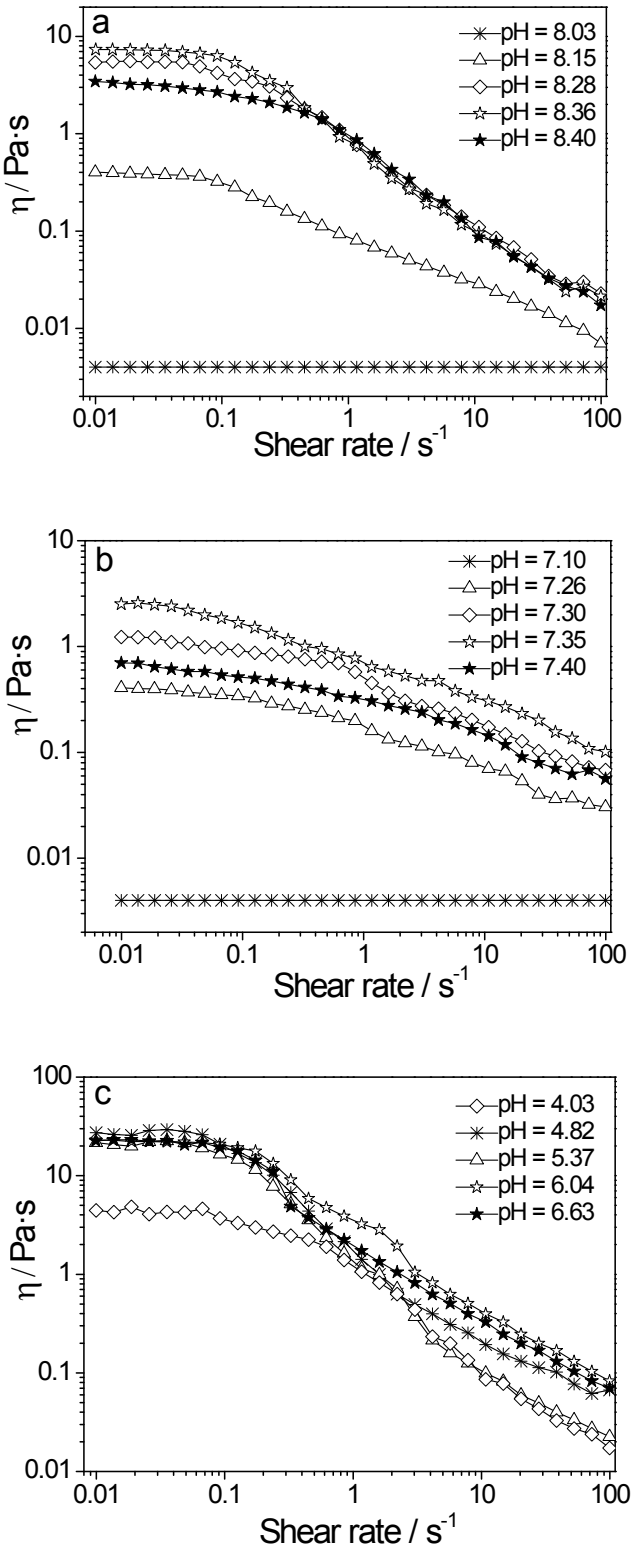

Fig. S8 The steady state shear viscosity curves of the (a) C_8-A-C_8, (b) C_{10}-A-C_{10}, and (c) C_{14}-A-C_{14} aqueous solutions (35 mM) at various pH values.

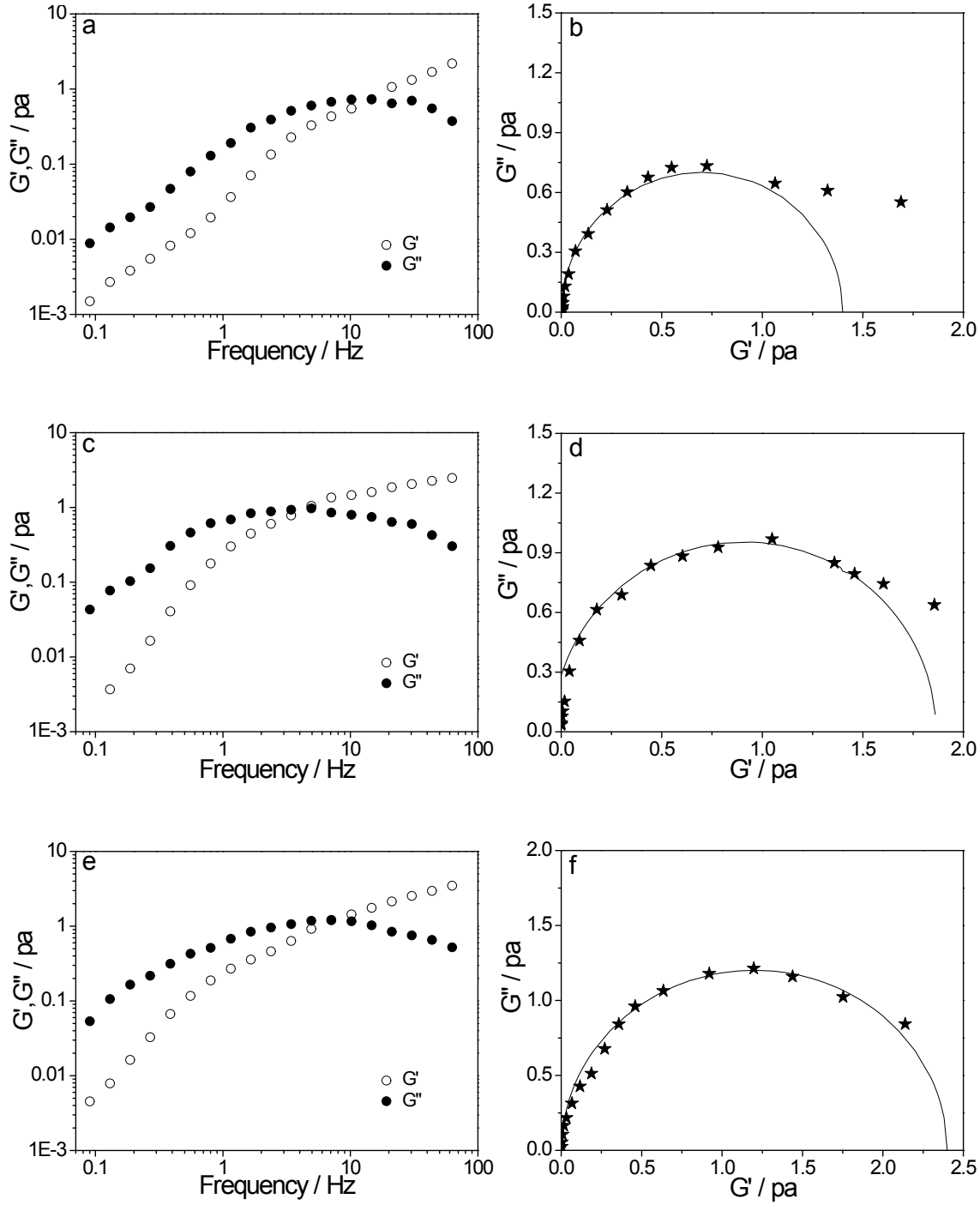

Fig. S9 (a, c and e) The dynamic oscillatory elastic (G') modulus and viscous (G") modulus varying with frequency and (b, d and f) Cole-Cole plot (solid line) of the C_8-A-C_8, C_{10}-A-C_{10}, and C_{14}-A-C_{14} aqueous solutions (35 mM) at pH = 8.36, 7.35, and 6.04, respectively.