Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Azobenzene Moiety Variation Directing Self-assembly and Photoresponsive Behavior of Azo-surfactants

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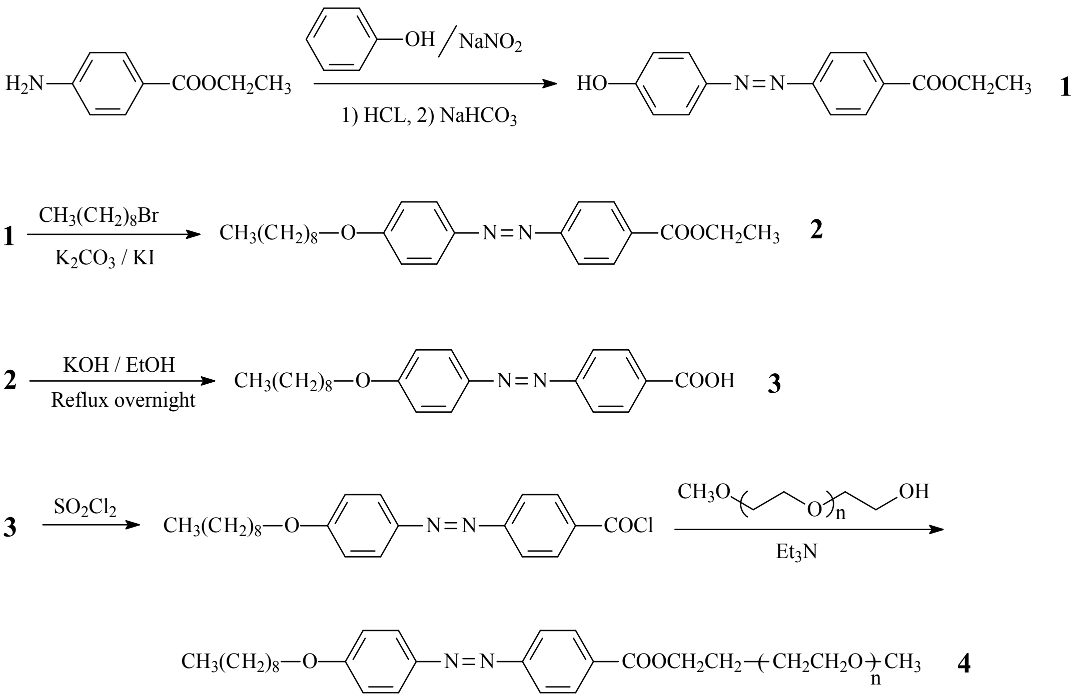
1. Synthesis of azosurfactant B.

The synthesis of azo-surfactant B is illustrated in Scheme 1 and the detailed preparation method was given as follows. Compounds (1), (2), and (3) were prepared according to the previously reported synthetic route and experimental data is in accordance with that reported.[1] Azo-surfactant (4) was prepared in the following procedure: PEG (5.0 g, 14 mmol) was dissolved in THF (50 mL) then combined with triethylamine (1.51 g, 15 mmol) and stirred in a nitrogen atmosphere. Compound (3) (10 g, 27 mmol) was refluxed for three hours in thionyl chloride (30 mL). Unreacted thionyl chloride was removed under reduced pressure. The resulting acid chloride (7.74 g, 20 mmol) was dissolved in THF (20 mL) and added dropwise to the PEG and triethylamine mixture prepared above. The reaction mixture was stirred at room temperature overnight under a nitrogen blanket. After filtration to remove salt, the filtrate was concentrated and the residue was purified by elution with ethyl acetate through a neutral alumina column. Fractions were collected and the solvent was removed under reduced pressure to afford (4) (9.52 g, 69 %) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.54Hz, 2H), 7.93 (d, *J* = 8.95Hz, 2H), 7.90 (d, *J* = 8.54Hz, 2H), 7.01 (d, *J* = 8.99Hz, 2H), 4.50 (t, *J* = 9.62 Hz, 2H), 4.05 (t, *J* = 13.13 Hz, 2H), 3.87 ~ 3.54 (m, 48H), 3.37 (s, 3H), 1.82 (m, 2H), 1.67 (m, 2H), 1.48 (m, 2H), 1.29 (m, 8H), 0.89 (t, *J* = 13.60 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.8, 161.6, 151.3, 147.2, 146.0, 129.3, 124.8, 122.8, 114.9, 77.6, 77.3, 72.2, 70.9, 70.8, 69.5, 68.2, 63.7, 59.3, 35.8, 34.3, 33.8, 29.2, 25.9, 24.9, 22.6, 14.2 ppm. MS analysis further confirmed the structure of azo-surfactant B (calculated for $C_{37}H_{58}N_2O_{10}$ $[M]^+$: 690.4091; found: 690.4058).



Scheme 1. Synthesis of azo-surfactant B.

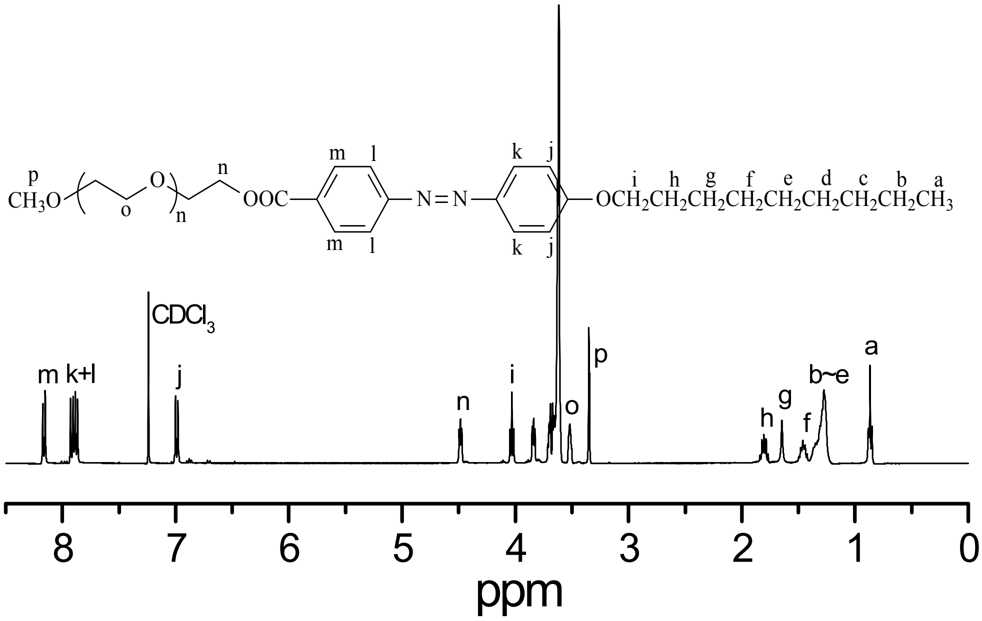


Fig. S1 ^{1}H NMR spectra of azo-surfactant B.

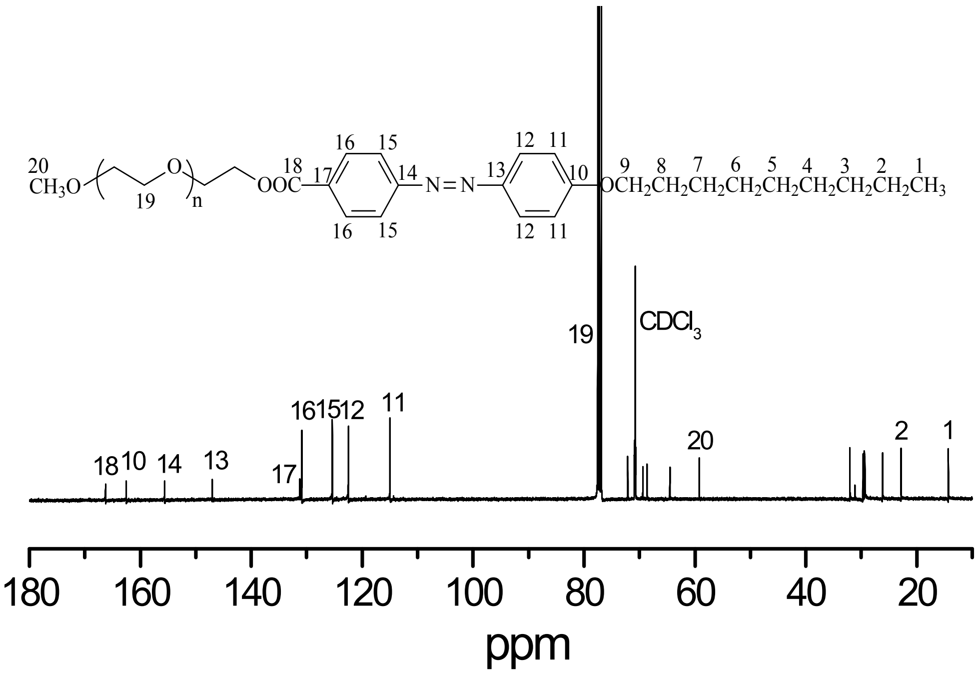


Fig. S2 ^{13}C NMR spectra of azo-surfactant B.

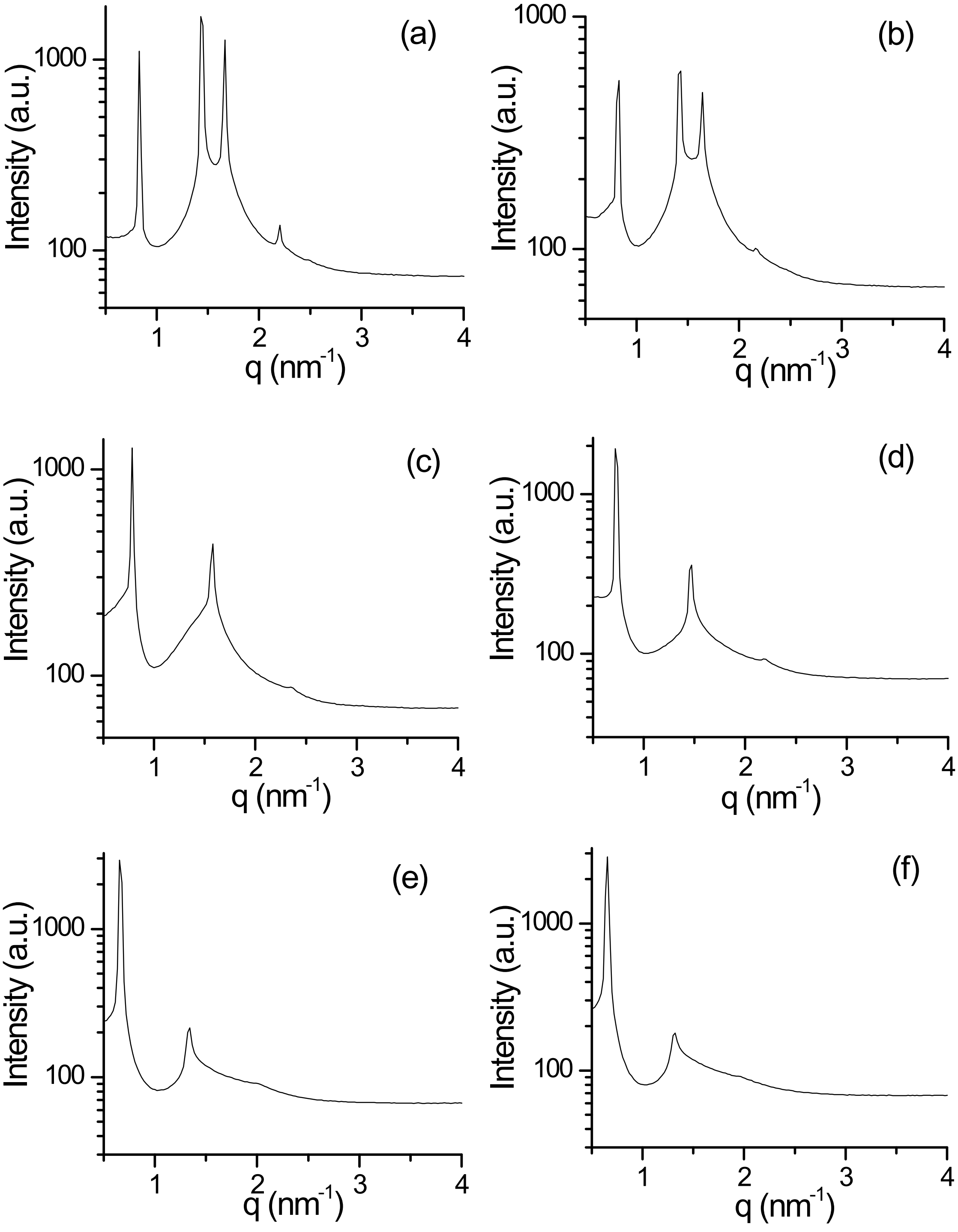


Fig. S3 SAXS patterns for the mixture of azo-surfactant A/water with 45 wt % water content at different temperatures: (a) 25; (b) 30; (c) 35; (d) 40; (e) 45; (f) 50 °C.

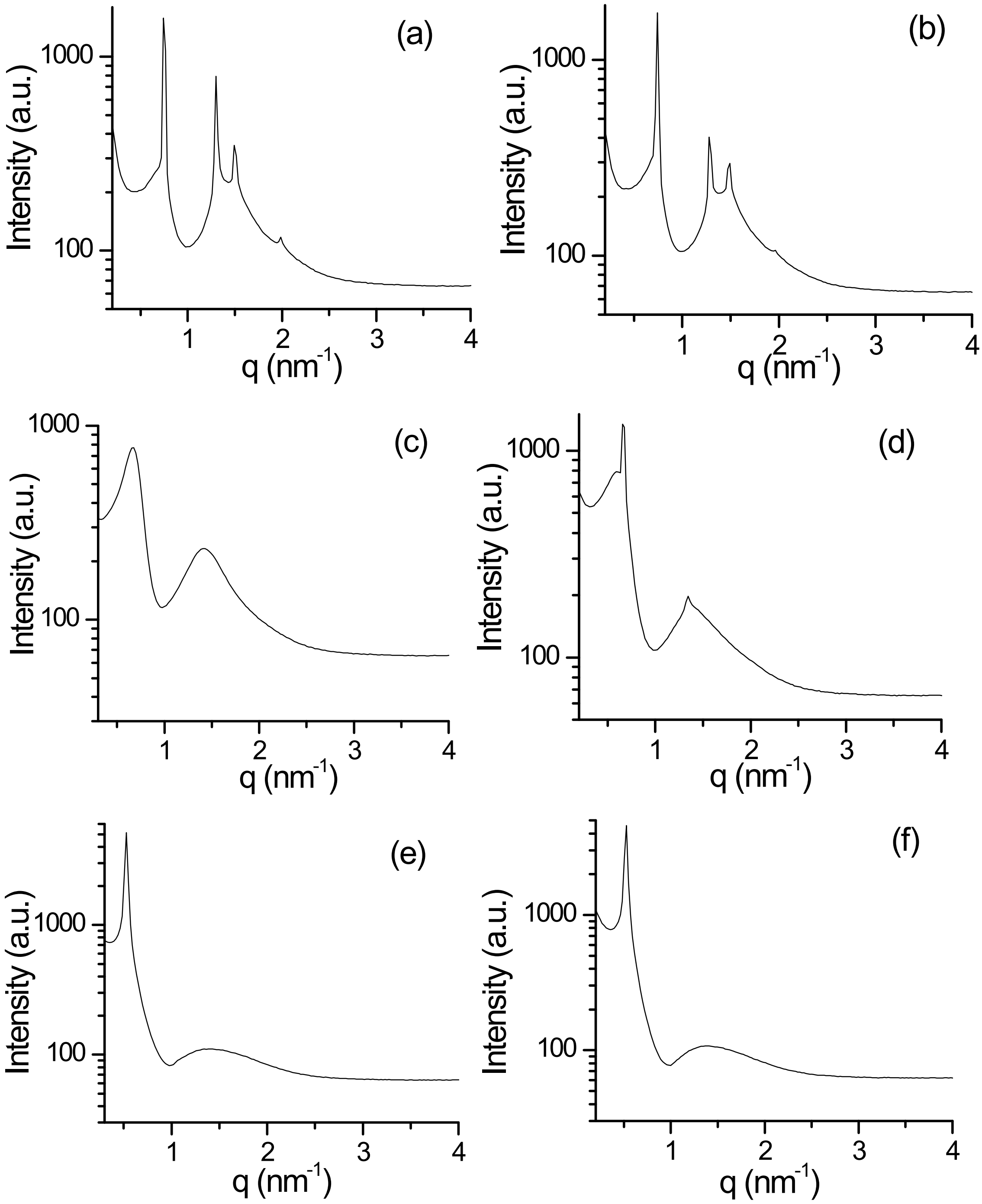


Fig. S4 SAXS patterns for the mixture of azo-surfactant A/water with 55 wt % water content at different temperatures: (a) 25; (b) 30; (c) 35; (d) 40; (e) 45; (f) 50 °C.

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[1] Vera, F.; Barbera, J.; Romero, P.; Luis Serrano, J.; Blanca Ros, M.; Sierra, T. *Angew. Chem. Int. Ed.,* **2010**, *49*, 4910.