Electronic Supplementary Material (ESI) for Soft Matter.

Support Information

Photoresponsive aqueous foams with controllable stability from nonionic azobenzene surfactants in multiple-components systems

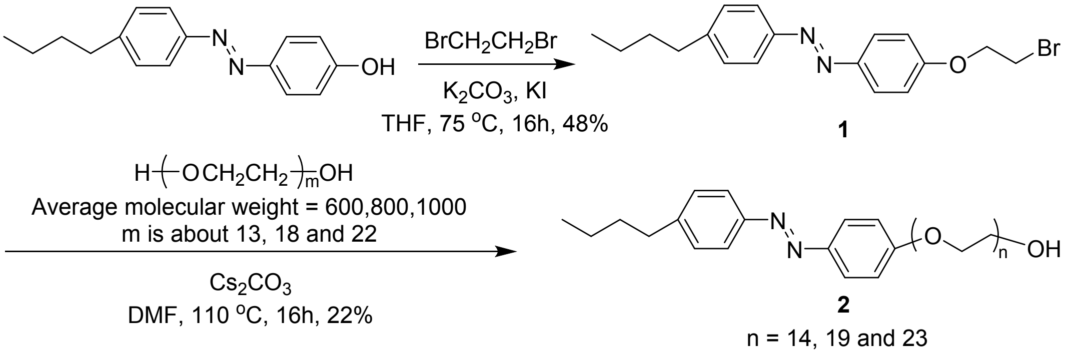
*Shaoyu Chen, Liang Fei, Fangqing Ge, Chaoxia Wang**

Key Laboratory of Eco-Textile, Ministry of Education, College of Textile & Clothing,

Jiangnan University, 1800 Lihu Road, Wuxi 214122, People's Republic of China.

Corresponding author's e-mail: wangchaoxia@sohu.com.

Synthesis of BEO-n-Azo



Scheme S1. Synthetic route of nonionic azobenzene surfactants (BEO-n-Azo, **2**).

Materials. 4-butyl-4'-hydroxyazobenzene (>98.0%) was purchased from Shanghai Dibai Biotechnology Co., Ltd. 1,2-dibromoethane (>99.0%), potassium carbonate (K_2CO_3; >99.0%), tetrahydrofuran (THF; >99.0%), N,N-Dimethylformamide (DMF; >99.5%), ethyl acetate (EtOAc; >99.5%), petroleumether (60–90 °C, 99%), dichloromethane (CH_2Cl_2; >99.5%), Methanol (MeOH, >99.5%) and silica gel (FCP) were bought from Sinopharm Chemical Reagent Co., Ltd. Potassium iodide (KI; >99.0%), Caesium carbonate (Cs_2CO_3; >99.0%), polyethylene glycol (PEG Mw. =600, 800 and 1000) were purchased from Aladdin Industrial Inc. All the chemicals were used as received. Deionized water was used in all experiments.

Compound 1:

4.5 g of 1,2-dibromoethane (3 *eq*) and KOH (3 *eq*) were placed in 40 ml THF and maintained at 75 °C for 0.5 h, accompanying with vigorous stirring in the three-necks flask. Thereafter, 4-butyl-4'-hydroxyazobenzene (1 *eq*) dissolved in THF was dropwise added to the flask and thoroughly stirred at 75 °C for 16 h in reflux condition. Then, the reaction system was cooled to ambient temperature, followed by removing THF via a rotary evaporator under reduced pressure. Furthermore, the crude was extracted by EtOAc. The EtOAc was removed by rotary evaporation and the residue was purified by column chromatography (SiO_2, petroleum ether/EtOAc 7/1) to yield **1** as a yellow solid. Yield: 48% (0.97g). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 39.2, 8.5 Hz, 4H), 7.31 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.9 Hz, 2H), 4.37 (t, J = 6.3 Hz, 2H), 3.68 (t, J = 6.3 Hz, 2H), 2.69 (t, J = 7.7 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.39 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

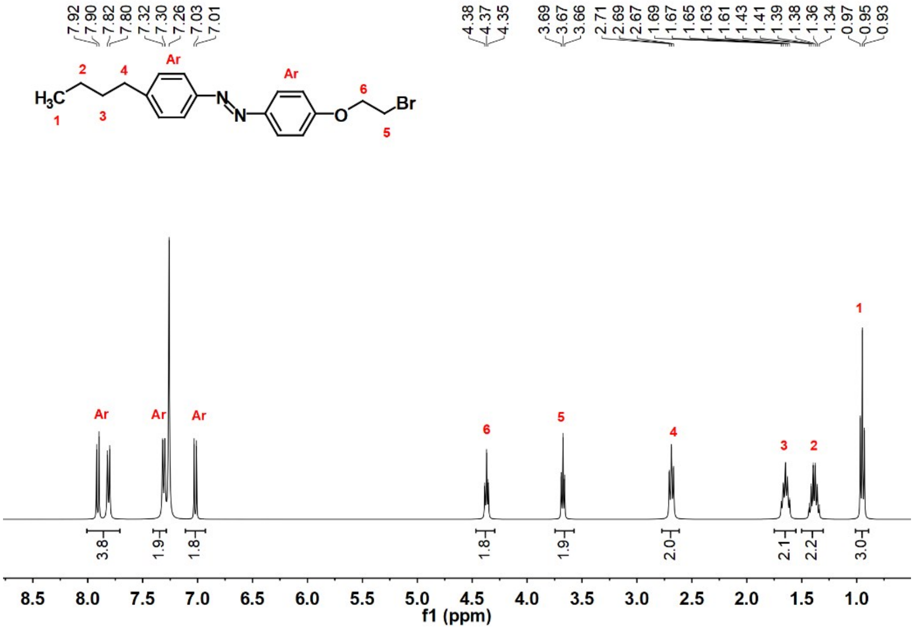


Figure S1. ^{1}H-NMR spectrum of compound 1.

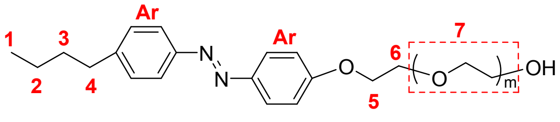
Compound 2 (BEO-n-Azo):

The mixture of polyethylene glycol (2.5 eq, the average molecular weights were 600, 800 and 1000, respectively) and Cs_2CO_3 (5eq) in DMF (15mL) were heated to 110 °C, followed by adding the solution of compound **1** (0.9 g, dissolved in 5 mL DMF) dropwise and thoroughly stirred at 110 °C for 16 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 and brine and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 10/1) to yield **2** as a yellow oil. Yield: 22%. ^{1}H nuclear magnetic resonance measurement was performed to confirm the structure of BEO-n-Azo (n=14, 19, 23), as shown in Figure S2-4.

BEO-14-Azo**:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.85 (dd, *J* = 45.5, 8.7 Hz, 4H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 4.14 (t, J = 4.6 Hz, 2H), 3.91 (t, J = 4.8 Hz, 2H), 3.82 (t, *J* = 5.7 Hz, 2H), 3.76 – 3.56 (m, 50H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

BEO-19-Azo: ^{1}H NMR (400 MHz, CD_3OD) δ 7.86 (dd, *J* = 45.6, 8.7 Hz, 4H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 4.15 (t, *J* = 4.9, 4.5 Hz, 2H), 3.91 (t, J = 4.9 Hz, 2H), 3.81 (t, J = 4.6 Hz, 2H)3.55-3.68 (m, 70H), 2.70 (t, J = 7.6 Hz, 2H), 1.65 (m, 2H), 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

BEO-23-Azo: ^{1}H NMR (400 MHz, CD_3OD) δ 7.86 (dd, *J* = 45.7, 8.7 Hz, 4H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 4.15 (t, J = 5.0, 4.4 Hz, 2H), 3.91 (t, J = 4.8 Hz, 2H), 3.82 (t, J = 4.5 Hz, 2H),, 3.75 – 3.51 (m, 86H), 2.70 (t, J = 7.7 Hz, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).



m = 13, 18, 22

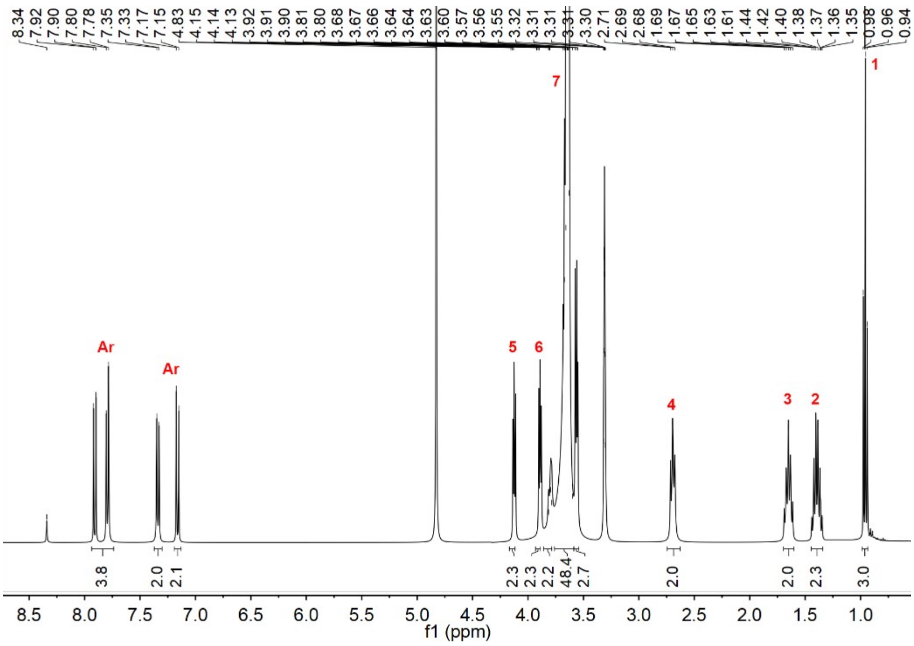


Figure S2. ^{1}H-NMR spectrum of BEO-14-Azo

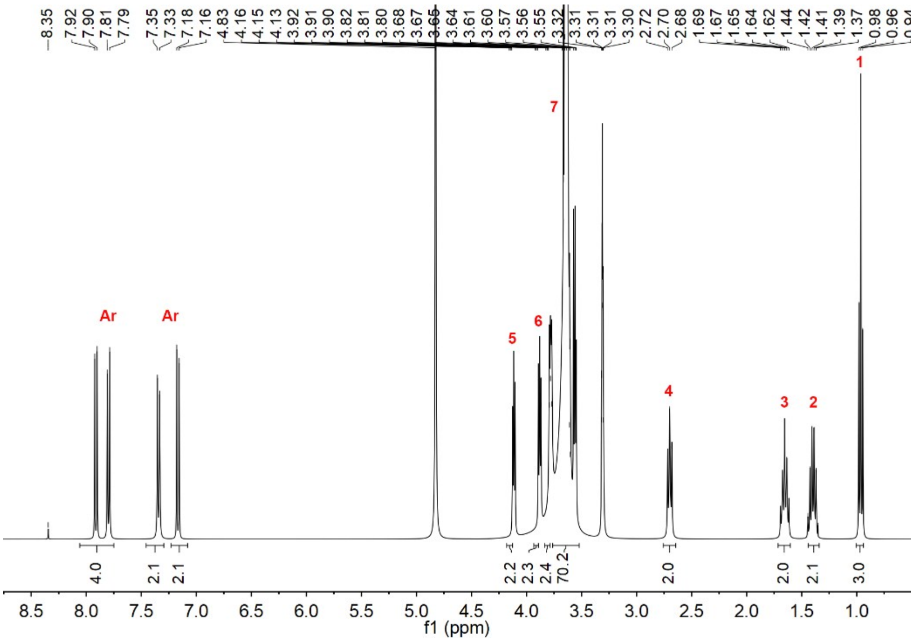


Figure S3. ^{1}H-NMR spectrum of BEO-19-Azo

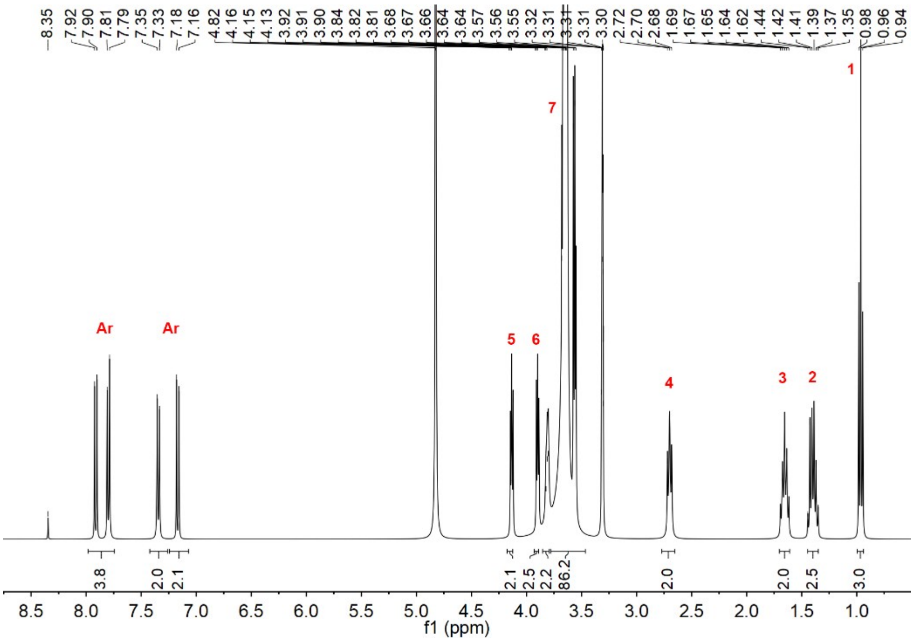


Figure S4. ^{1}H-NMR spectrum of BEO-19-Azo