pH and Light Reconfigured Complex Emulsions by Stimuli-Responsive Surfactants

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1 Synthesis of C_{10}AZOC_{2}N_{3}

The synthetic route of 1-[2-(4-decylphenylazo-phenoxy)-ethyl]-1-diethylenetriamine (C_{10}AZOC_{2}N_{3}) was shown in Scheme S1. \textsuperscript{1}H NMR and \textsuperscript{13}CNMR spectra were recorded on Bruker Digital NMR Spectrometer AscendTM400 at room temperature and ESI-MS spectra were recorded using LCQ Fleet ion trap mass spectrometer.

\[ \text{Scheme S1 Synthetic route of C}_{10}\text{AZOC}_{2}\text{N}_{3}. \]

1.1 Synthesis of 4-decyl-(4'-hydroxy)azobenzene (C_{10}AZOH)

4-Decylaniline (5 g, 21 mmol) was dissolved in the mixture of water (17 mL), hydrochloric acid (6 mL) and acetone (17 mL) under 0°C. Then, sodium nitrite (15 mL, 1.4 mol·L\textsuperscript{-1}) was added slowly into the solution. After 30 min stirring under 0°C, the aqueous solution (30 mL) of phenol (2 g, 0.021 mol), sodium hydroxide (0.84 g, 0.021 mol) and sodium carbonate (2.3 g, 0.021 mol) was added slowly into this solution, lasting for about 1 h. The mixture was reacted under 0°C for additional 2 h, and then stirred overnight at room temperature. The reaction mixture was filtered. The crude product was purified by silica gel column chromatography with petroleum ether and dichloromethane (v/v, 1/1) to yield a yellow solid C_{10}AZOH (5.8 g, 80%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 0.88 (t, 3H, CH\textsubscript{3}), 1.26 (m, 16H, CH\textsubscript{2}), 2.67 (t, 2H, CH\textsubscript{2}), 3.69 (t, 2H, CH\textsubscript{2}), 6.94 (d, 2H, H-Ar), 7.31 (d, 2H, H-Ar), 7.80 (d, 2H, H-Ar), 7.86 (d, 2H, H-Ar).

1.2 Synthesis of 4-decyl-(4'-(2-bromoethyl)phenyl)azobenzene (C_{10}AZOC_{2}Br)

1,2-dibromoethane (56 g, 0.30mol) and potassium carbonate (5 g, 0.0375mol) was added into ethanol (40 mL) in a 100 mL flask, and heated to 70°C. Then, the acetone solution (100 mL) of C_{10}AZOH (5 g, 0.015 mol) was added dropwise under stirring. The solution was refluxed for 12 h. Finally, the solvent was removed and the residual was purified on silica gel using petroleum ether and dichloromethane (v/v, 1/1) as the eluent. 5.55 g bright yellow chemical was obtained, yield 84%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 0.88 (t, 3H, CH\textsubscript{3}), 1.26 (m, 16H, CH\textsubscript{2}), 2.67 (t, 2H, CH\textsubscript{2}), 3.69 (t, 2H, CH\textsubscript{2}), 4.38 (t, 2H, CH\textsubscript{2}), 7.01 (d, 2H, H-Ar), 7.31 (d, 2H, H-Ar), 7.79 (d, 2H, H-Ar), 7.89 (d, 2H, H-Ar).

1.3 Synthesis of 1-[2-(4-decylphenylazo-phenoxy)-ethyl]-1-diethylenetriamine (C_{10}AZOC_{2}N\textsubscript{2})

C_{10}AZOC_{2}Br (5 g, 0.011 mol) was dissolved in tetrahydrofuran (100 mL), and added dropwise into the mixture of diethylenetriamine (20 mL) and tetrahydrofuran (20 mL) under stirring at 0°C. Then, the mixture reacted for 12 h at room temperature. The solution was evaporated under vacuum-rotary, and the residue was dissolved in dichloromethane and then extracted with 1 mol·L\textsuperscript{-1} NaOH and water for 8–10 times to remove generated hydrogen bromide and excess diethylenetriamine approximately. The oil phase was dried with magnesium sulfate and filtered, and the filtrate was evaporated under vacuum-rotary to obtain the crude product, which was purified by column chromatography with dichloromethane and methyl alcohol (v/v, 1/1) to yield a yellow product C_{10}AZOC_{2}N\textsubscript{2} (4.72 g, 90%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 0.88 (t, \( J = 6.8 \) Hz, 3H), 1.26–1.32 (m, 16H), 2.18 (s, 4H), 2.65–2.71 (m, 6H), 2.77–2.85 (m, 4H), 3.06 (t, \( J = 5.2 \) Hz, 2H), 4.16 (t, \( J = 5.2 \) Hz, 2H), 7.02 (d, \( J = 9.2 \) Hz, 2H), 7.31 (d, \( J = 8.4 \) Hz, 2H), 7.79 (d, \( J = 8.4 \) Hz, 2H), 7.89 (d, \( J = 9.2 \) Hz, 2H). \textsuperscript{13}CNMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 14.14, 22.69, 29.59, 31.35, 35.86, 41.71, 48.68, 49.23, 50.70, 52.39, 53.45, 67.67, 114.67, 122.52, 124.56, 129.06, 145.94, 147.13, 150.95, 161.05. ESI-MS: [M+H]+ C_{32}H_{45}N_{10}O\textsuperscript{+}, Calcld 468.3, Found 468.3.
$^{1}$H NMR, $^{13}$C NMR and ESI-MS spectra of C$_{10}$AZOC$_{2}N_3$
2 The stability of the H/F/W complex emulsion

Fig. S1  (a) Photograph and micrograph of the complex emulsion droplets in aqueous solutions of 0.1% Zonyl FS-300, scale bar, 200 µm.
(b) Number distribution of diameters of the complex emulsion droplets.

3 Effect of the concentration of C$_{10}$AZOC$_2$N$_3$ on the complex emulsion

Fig. S2  Photographs of complex emulsions fabricated in the presence of 0.1% Zonyl FS-300 and different concentration of C$_{10}$AZOC$_2$N$_3$.

4 pH titration curve of C$_{10}$AZOC$_2$N$_3$

Fig. S3  pH titration curve of 4mmol·L$^{-1}$ C$_{10}$AZOC$_2$N$_3$ aqueous solution at 25 °C.
5 Effect of pH on the complex emulsion

![Figure S4](image_url) Photographs of complex emulsions fabricated at different pH in the presence of 0.1% Zonyl FS-300 and 0.07% C_{10}AZOC_{2}N_{3}.

6 The droplet topology change by pH variation at low C_{10}AZOC_{2}N_{3} concentration

![Figure S5](image_url) Micrographs of the complex emulsion droplets in aqueous solutions of 0.1% Zonyl FS-300 and 0.03% C_{10}AZOC_{2}N_{3} at different pH:
(a) 4.34, (b) 6.11, (c) 8.16, (d) 9.87, and (e) 11.29. Scale bar, 100 µm.

7 Effect of UV light irradiation on the complex emulsion

![Figure S6](image_url) Photographs of complex emulsions fabricated in the presence of 0.1% Zonyl FS-300 and 0.05% C_{10}AZOC_{2}N_{3} at pH 7.92 before and after UV light irradiation.