

## Electronic Supporting information (ESI)

# Thermal, Light and pH Triple Stimulated Changes in Self-assembly of a Novel Small Molecular Weight Amphiphile Binary System

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## 1. Material

4-(Trifluoromethyl)salicylic acid (4FS, 98%) was purchased from Acros and used as received, C<sub>10</sub>AZOC<sub>2</sub>IMB was synthesized according to Scheme S1. The samples were prepared directly by dissolving weighed amounts of C<sub>10</sub>AZOC<sub>2</sub>IMB and desired amounts of 4FS under continuous stirring at 85 °C until the solution became homogeneous, then left in a dark incubator at 25 °C at least 48 h before any measurements.

## 2. Measurements

**light irradiation.** For light-triggered *trans* to *cis* isomerization of C<sub>10</sub>AZOC<sub>2</sub>IMB: a 10 mL sample was placed in a quartz tumbler and was irradiated using a fan-cooled FC-100/FA with 100 W mercury arc lamp (wavelength 365 nm, Spectronice, USA) with stirring. For light-triggered *cis-trans* isomerization of C<sub>10</sub>AZOC<sub>2</sub>IMB: a 3 mL UV irradiated sample was placed in a quartz cuvette and was irradiated using an OPTIMAX™ 450 (wavelength 450 nm, Spectronice, USA) with stirring. Experimental temperatures were kept at 25 °C using a thermostat water bath, and the distance between the sample and light source was fixed at 15 cm.

**UV-vis spectra measurements.** UV-vis spectra measurements were carried out on a UV-vis Tu-1901 spectrophotometer (Pgeneral, China) using ultrapure deionized water (Millipore) as a blank at 25 °C.

**Rheological measurements.** Steady and dynamic rheological measurements were performed on a RS 600 stress-controlled rheometer (TA Instruments) using a couette geometry DG 41 or a plate PP 35 according to the fluid viscosities. A Peltier-based temperature controller maintained the sample at different temperatures. The samples were equilibrated for at least 30 min before measurements. A solvent trap was used to minimize sample evaporation.

**Cryo-transmission electron microscopy.** For cryo-TEM, a small amount (3-5 μl) of sample

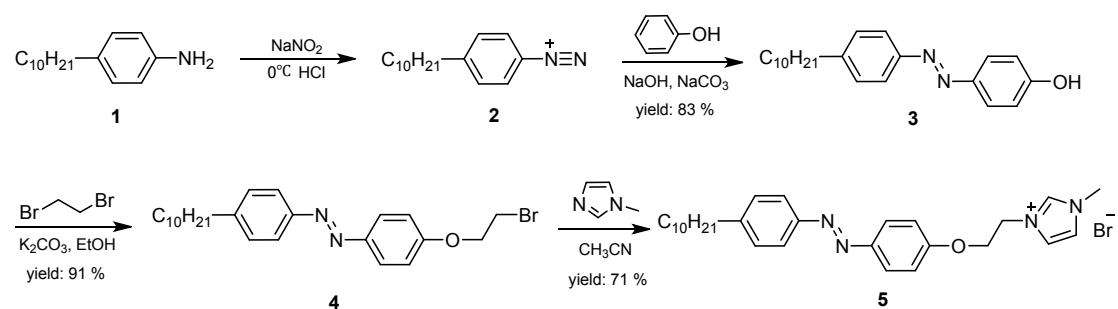
solution was deposited on the surface of a TEM copper grid covered by a holey carbon film. After blotting away the excess solution to form a thin liquid film, the grid was immediately plunged into liquid ethane cooled by liquid nitrogen (-175 °C). The specimens were maintained at approximately -173 °C and imaged in a transmission electron microscope (JEOL 2010) at an accelerating voltage of 200 KV under low dose conditions.

**Turbidity measurements.** Turbidity readings at 600 nm were obtained on a UV-vis Tu-1901 spectrophotometer (Pgeneral, China) using water as blank. The absorbance of surfactant solution at the different concentrations was recorded.

**Dynamic light scattering measurements (DLS).** Dynamic light scattering (DLS) measurements were performed on the Zetasizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He-Ne laser ( $\lambda = 633$  nm). Solutions of investigated surfactants were filtered with a 0.2- $\mu\text{m}$  filter of mixed cellulose acetate to remove any interfering dust particles. To obtain the diameter, the intensity autocorrelation functions were analyzed using CONTIN.

**pH titration.** pH titration was performed on a Rex model PHSJ-5 digital pH meter (Leici, China) with a temperature sensor using an E-201D combination pH electrode. 1 mol L<sup>-1</sup> sodium hydroxide aqueous solution was initially added to 10 mL 5 mM 4FS aqueous dispersions until pH ~ 12, and was then subsequently titrated with 0.1 mol L<sup>-1</sup> hydrochloric acid aqueous solution. Each titration point was recorded until the potential drift was stable.

### 3. Synthesis of C<sub>10</sub>AZOC<sub>2</sub>IMB



**Scheme S1.** Synthesis pathway for C<sub>10</sub>AZOC<sub>2</sub>IMB

Scheme S1 shows the procedure for the synthesis of cationic surfactant 1-[2-(4-decylphenylazo-phenoxy)-ethyl]-3-methylimidazolium bromide (C<sub>10</sub>AZOC<sub>2</sub>IMB), details are described below.

**4-decyl-(4'-hydroxy)azobenzene (3):** 4-decylaniline (5 g, 21 mmol) were dissolved and thoroughly stirred in 17 mL of H<sub>2</sub>O, 6 mL of concentrated HCl and 17 mL acetone at 0 °C. Then 15 mL of sodium nitrite (1.4 mol.L<sup>-1</sup> in water) was added slowly. The reaction mixture was left to react for 30 min at 0 °C. Then a mixture of phenol (2 g, 0.021 mol), sodium hydroxide (0.84 g, 0.021 mol) and sodium carbonate (2.3 g, 0.021 mol) in water (30 mL) was added slowly at 0 °C. After stirred for 2 h at 0 °C, a yellow solid precipitated. The reaction mixture was filtered. A khaki solid obtained was purified by silica gel column chromatography (petroleum ether: dichloromethane = 1:1) to give a yellow solid **3** (6 g, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.91 (t, 3H, CH<sub>3</sub>), 1.29 (m, 14H, CH<sub>2</sub>), 1.69 (m, 2H, CH<sub>2</sub>), 2.70 (t, 2H, CH<sub>2</sub>), 6.95 (d, 2H, H-Ar), 7.32 (d, 2H, H-Ar), 7.81 (d, 2H, H-Ar), 7.88 (d, 2H, H-Ar).

**4-decyl-(4'-(2-bromoethyl)phenyl)azobenzene (4):** 1, 2-dibromoethane (28 g, 0.15 mol) and K<sub>2</sub>CO<sub>3</sub> (4 g, 0.03 mol) was added into 40 mL ethanol in a 100 mL flask, and heated to 80 °C. Then, **3** (5 g, 0.015 mol) in 20 mL ethanol was added dropwise under stirring. The solution was refluxed for 12 h. Finally, the solvent was removed and the residual was purified over silica gel using the petroleum ether/dichloromethane mixture as the eluent. 7 g bright yellow chemical was obtained, yield 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.91 (t, 3H, CH<sub>3</sub>), 1.29 (m, 14H, CH<sub>2</sub>), 1.68 (m, 2H, CH<sub>2</sub>), 2.70 (t, 2H, CH<sub>2</sub>), 3.71(t, 2H, CH<sub>2</sub>), 4.40 (t, 2H, CH<sub>2</sub>), 7.04 (d, 2H, H-Ar), 7.32 (d, 2H, H-Ar), 7.82 (d, 2H, H-Ar), 7.92 (d, 2H, H-Ar).

**1-[2-(4-decylphenylazo-phenoxy)-ethyl]-3-methylimidazolium bromide (5):** **4** (10 g, 0.022 mol) was dissolved into 100 mL acetonitrile in a 250 mL flask, and heated to 80 °C under N<sub>2</sub>. Then, N-methylimidazole (1.8 g, 0.022 mol) in 50 mL acetonitrile was added dropwise under stirring. The mixture was refluxed for 48 h at 80 °C under N<sub>2</sub>. After cooling to room temperature, the yellow solid was precipitated from the solution. This product was recrystallized three times from the mixture of ethyl acetate/ethanol and dried under vacuum. 11.8 g bright yellow product was obtained, yield 71%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.88 (t, 3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.26 (m, 14H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.62 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-Ar), 2.64 (t, 2H, -CH<sub>2</sub>-Ar), 4.07 (s, 3H, IM-CH<sub>3</sub>), 4.50 (t, 2H, -O-CH<sub>2</sub>-), 4.92 (t, 2H, -CH<sub>2</sub>-IM), 7.00 (d, 2H, H-Ar), 7.40

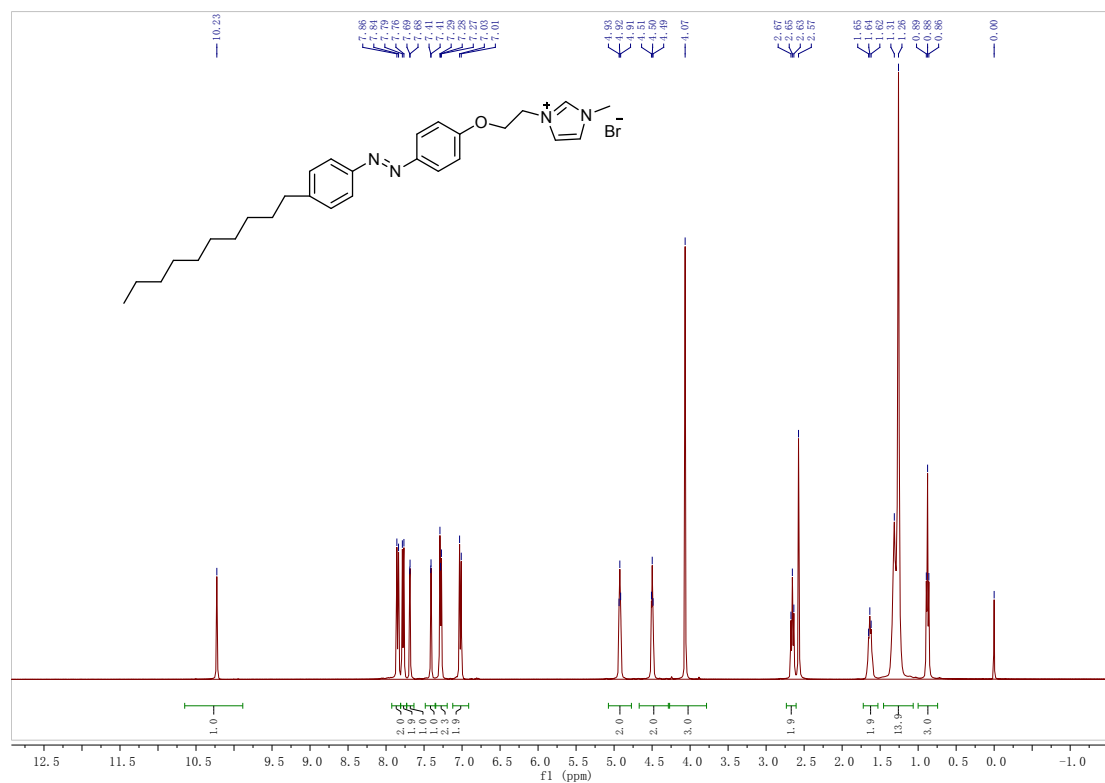
(m, 1H, H-IM), 7.67 (m, 1H, H-IM), 7.77 (d, 2H, H-Ar), 7.84 (d, 2H, H-Ar), 10.39 (m, 1H, H-IM).

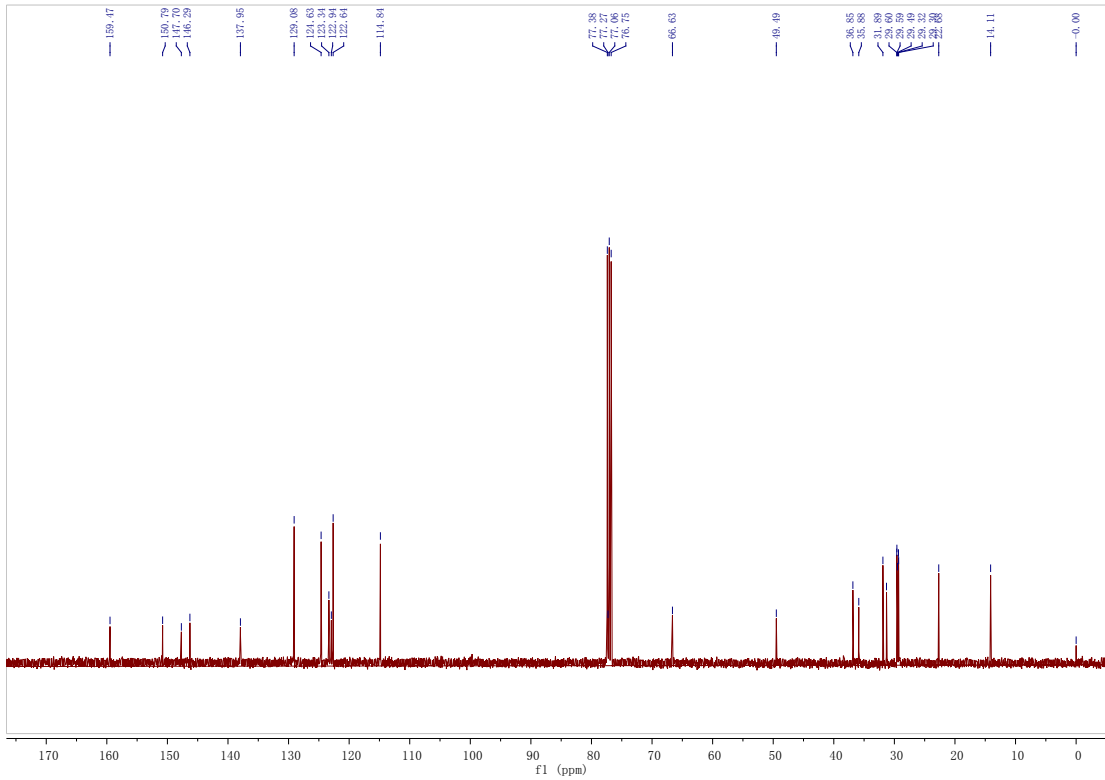
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 14.09, 22.66, 29.29, 29.48, 29.57, 31.28, 31.88, 35.86,

36.85, 49.26, 66.64, 114.87, 122.63, 123.29, 124.59, 129.07, 146.27, 150.83. ESI-MS;  $[\text{M}+\text{H}-\text{Br}]$

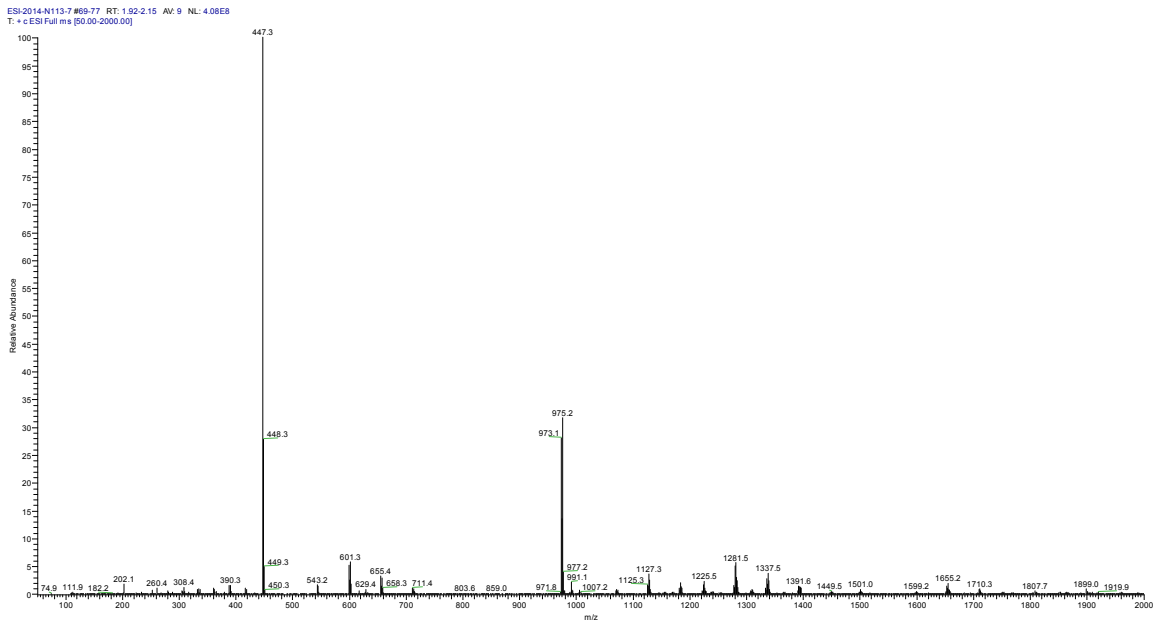
$\text{C}_{28}\text{H}_{29}\text{N}_4\text{O}^+$ : Calcd: 447.3, Found: 447.2.

#### 4. $^1\text{H}$ , $^{13}\text{C}$ NMR and ESI-MS spectra of $\text{C}_{10}\text{AZOC}_2\text{IMB}$



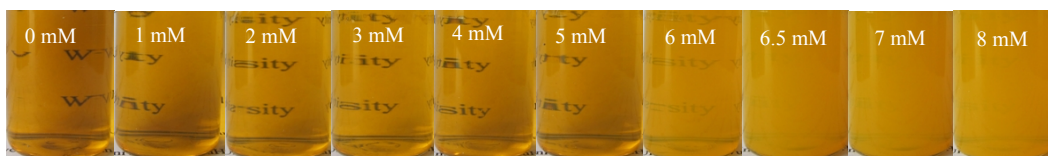


**C<sub>10</sub>AZOC<sub>2</sub>IMB: <sup>13</sup>C NMR**



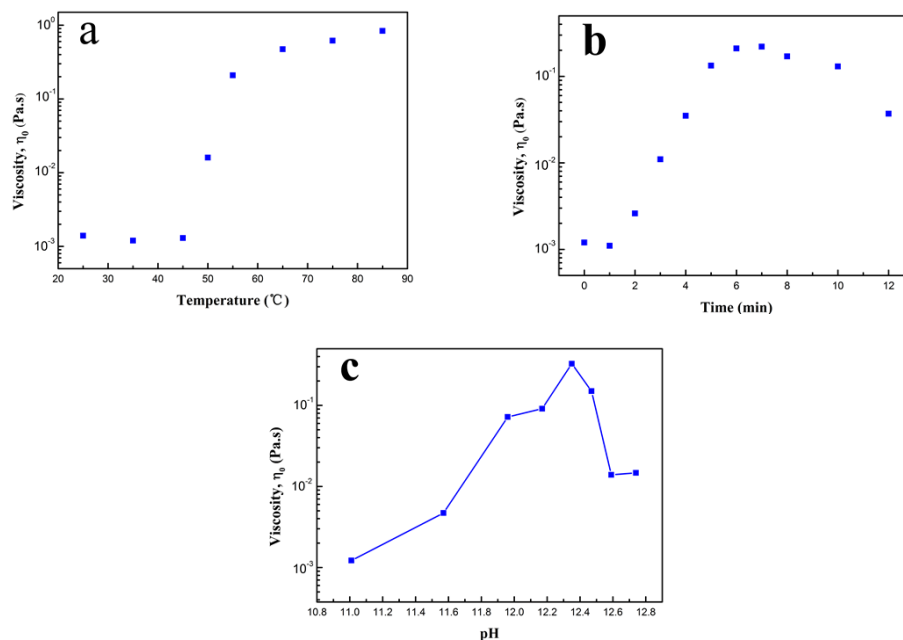
**C<sub>10</sub>AZOC<sub>2</sub>IMB: ESI-MS**

### 5. Phase behavior of C<sub>10</sub>AZOC<sub>2</sub>IMB and 4FS



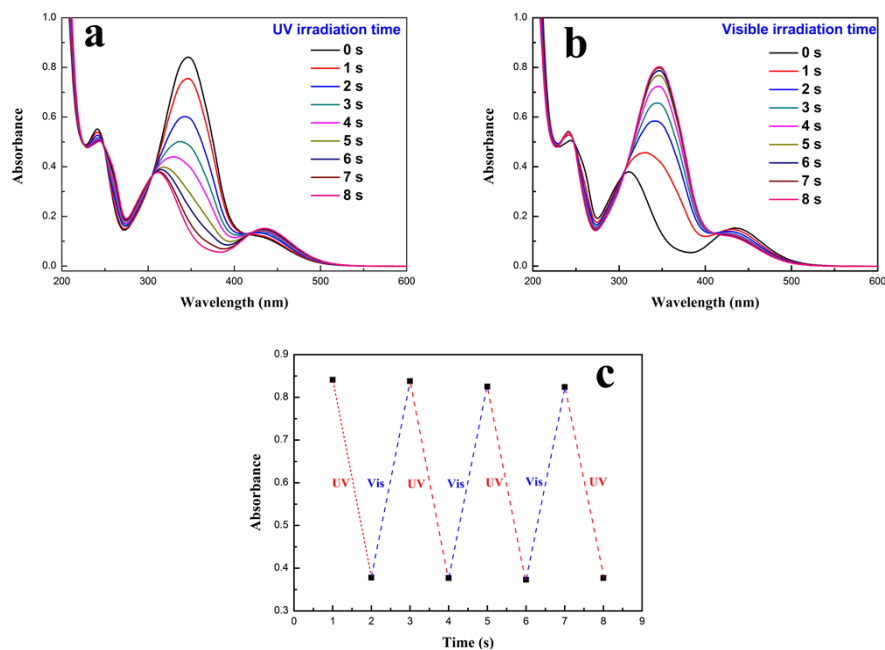
**Figure S1.** Effect of [4FS] on the appearance of  $12.5 \text{ mmol}\cdot\text{L}^{-1}$   $\text{C}_{10}\text{AZOC}_2\text{IMB}$  at  $25 \text{ }^\circ\text{C}$ . [4FS] is from 0 to  $8 \text{ mmol}\cdot\text{L}^{-1}$ , respectively.

### 6. Zero-shear viscosity of $\text{C}_{10}\text{AZOC}_2\text{IMB}$ and 4FS



**Figure S2.** the zero-shear viscosity of a sample containing  $12.5 \text{ mM}$   $\text{C}_{10}\text{AZOC}_2\text{IMB}$  and  $8 \text{ mM}$  (a) with different temperature, (b) UV irradiation time, (c) different pH values.

### 7. UV-vis spectra of $\text{C}_{10}\text{AZOC}_2\text{IMB}$ and 4FS mixtures irradiated by UV and visible light



**Figure S3.**  $\text{C}_{10}\text{AZOC}_2\text{IMB}$  solution ( $0.05 \text{ mM}$ ) (a) change in absorption of UV-vis spectra over time under UV light; (b) change in absorption of UV-vis spectra over time under visible light; (c) change in absorption of UV-vis spectra over time by alternate irradiation at UV and visible light, respectively.

## 8. Species distribution of 4FS

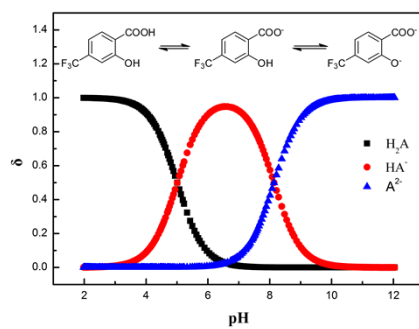


Figure S4. Species distribution resulting from an aqueous solution of 4FS at 25 °C.