

## Support Information

# Insight into a Fast-Phototuning Azobenzene Switch for Sustainably Tailoring the Foam Stability

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## Synthesis of OTAEazo

**4-hydroxy-4'-octoxy azobenzene (HOAzo).** 6.35 g of DHAzo, 6.14 g of  $K_2CO_3$  (1.5 *eq*) and 4.92 g of KI (1.0 *eq*) were placed in 30 mL EtOH and simultaneously stirred in the three-necked flask equipped with a mechanical stirrer and a reflux condenser at 80 °C for 0.5 h. Bromooctane (1 *eq*) dissolved in EtOH (40 mL) was then dropwise added to react with DHAzo at 80 °C for 8 h. Afterward, the crude was diluted with water and the product precipitated as a yellow solid. The solid was filtered, followed by further purified with column chromatography (Silica gel, petroleum ether/EtOAc 7/1). Finally, the product was dried under vacuum overnight. Yield: 61% (5.90 g).  $^1H$  NMR spectrum: (400 MHz,  $CDCl_3$ )  $\delta$  0.89(t, 3H,  $CH_3$ ), 1.29-1.37 (m, 8H,  $CH_2$ ), 1.47 (m, 2H,  $CH_2$ ), 1.81 (m, 2H,  $CH_2$ ), 4.02 (t, 2H,  $CH_2$ ), 6.91 (m, 2H,  $CH_2$ ), 6.98 (m, 2H,  $CH_2$ ), 7.81 (m, 2H,  $CH_2$ ), 7.86 (m, 2H,  $CH_2$ ).

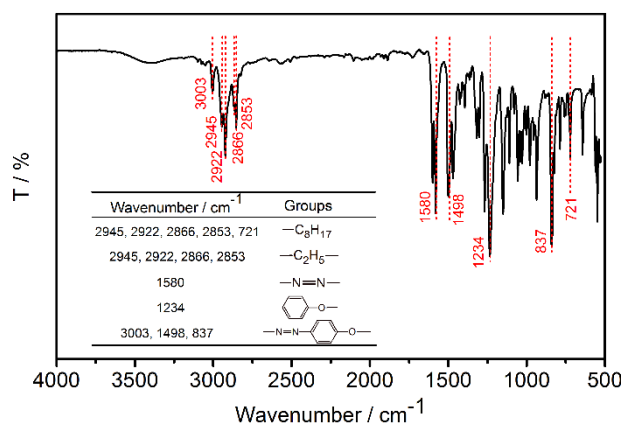
**4-bromoethyl-4'-octoxy azobenzene (BEOAzo).** 4.5 g of 1,2-dibromoethane (3 *eq*) and KOH (3 *eq*) were placed in 40 ml anisole and maintained at 75 °C for 0.5 h, accompanying with vigorous stirring in the three-necks flask. Thereafter, HOAzo (1 *eq*) dissolved in anisole was dropwise added to the 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 anisole via a rotary evaporator under reduced pressure. Furthermore, the crude was extracted by EtOAc. After removing the EtOAc, the product was further purified with column chromatography (Silica gel, petroleum ether/EtOAc 7/1) finally precipitated as a yellow solid after removing the eluent. The product was dried under vacuum overnight. Yield: 49% (1.70g).  $^1H$  NMR spectrum: (400 MHz,  $CDCl_3$ )  $\delta$  0.90(t, 3H,  $CH_3$ ), 1.29-1.38 (m, 8H,  $CH_2$ ),

1.48 (m, 2H, CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 3.87 (t, 2H, CH<sub>2</sub>), 4.03 (t, 2H, CH<sub>2</sub>), 4.36 (m, 2H, CH<sub>2</sub>), 6.91 (m, 2H, CH<sub>2</sub>), 6.98 (m, 2H, CH<sub>2</sub>), 7.81 (m, 2H, CH<sub>2</sub>), 7.86 (m, 2H, CH<sub>2</sub>) ppm.

**4-Octoxy-4'-[(trimethylamino) ethoxy] azobenzene (OTAEAzO).** 10 g of BEOAzO was dissolved in 400 mL solvent (ethanol/EtOAc (v/v)=1:2) and thoroughly stirred in the three-necked flask equipped with a reflux condenser at 65 °C for 0.5 h. A cold solution of 35% trimethylamine in ethanol (20 mL-4 *eq*) was then dropwise added in the reaction bath and kept in reflux for 48 h. After cooling to room temperature, the product (OTAEAzO) was precipitated. Finally, the yellow precipitate of OTAEAzO was filtered, followed by recrystallized in 90:10 v/v solution of EtOAc/ethanol. Yield: 65% (7.38 g).

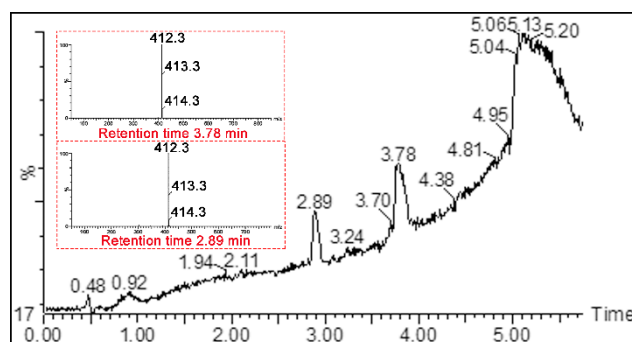
### Characterization of OTAEAzO

OTAEAzO was characterized by FT-IR, LC-MS and <sup>1</sup>H-NMR analysis. The FT-IR spectrum of OTAEAzO is presented in Figure S1. The absorption peaks at 2945 and 2866 cm<sup>-1</sup> correspond to the C-H stretching vibration of CH<sub>3</sub> group and the peaks at 2922 and 2853 cm<sup>-1</sup> belong to the C-H stretching vibration of CH<sub>2</sub> group. In addition, the peak at 721 cm<sup>-1</sup> was due to the rocking vibration of alkyl -CH<sub>2</sub>- group, confirming the presence of the alky chain. The absorption peak attributing to the C-H stretching vibration of benzene is observed at 3003 cm<sup>-1</sup>, and its bending vibration appeared at 837 cm<sup>-1</sup>. The peak at 1580 cm<sup>-1</sup> is assigned to -N=N- group, which also indicates that the -N=N- group connects to the benzene. Besides, the absorption peak of the aryl ether bond stretching vibration can be found at 1234 cm<sup>-1</sup>. All the above typical peaks support the successful synthesis of OTAEAzO.



**Figure S1** FT-IR spectrum of OTAEAzO

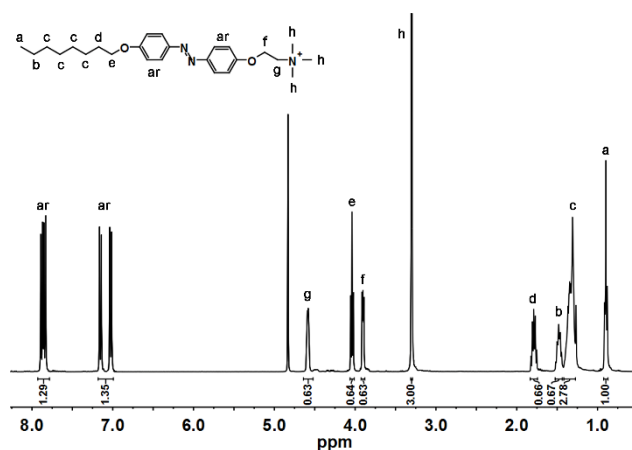
In order to identify the components and molecular mass of the product, LC-MS analysis was performed. LC spectrum (Figure S2) shows two prominent peaks at the retention time of 2.89 min and 3.78 min, indicating that the product contains two components. The ESI-MS spectra of these two retention time are presented in Figure S2 (the embedded figures), displaying the  $m/z$  value of molecular ion. All the peaks are identical in these two ESI-MS spectra, revealing that the product has two isomers. The molecular mass of OTAEAzO is calculated as 492.2. As a cationic surfactant, the mass of the molecular ion (without Br) is 412.3. Therefore, the ion at  $m/z$  412.3 in the ESI-MS spectra corresponded to the molecular ion of OTAEAzO. The ion at  $m/z$  413.3 and  $m/z$  414.3 were assigned to the isotope ions of OTAEAzO. The LC-MS spectrum confirmed that the product was OTAEAzO and there were two isomers, i.e. *trans* isomers and *cis* isomers.



**Figure S2** LC-MS spectra of OTAEAzO.

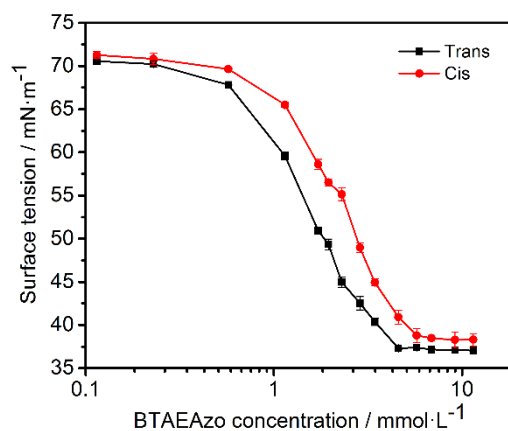
$^1\text{H}$  nuclear magnetic resonance measurement was performed to further investigate the structure of the product, as shown in Figure S3. The specific information is listed as follows.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.86 (dd,  $J = 15.5, 9.0$  Hz, 4H), 7.09 (dd,  $J = 51.0, 9.0$  Hz, 4H), 4.64 – 4.52 (m, 2H), 4.04 (t,  $J = 6.4$  Hz, 2H), 3.93 – 3.88 (m, 2H), 3.30 (s, 9H), 1.83 – 1.74 (m, 2H), 1.52 – 1.44 (m, 2H), 1.35 (m, 8H), 0.90 (t,  $J = 6.8$  Hz, 3H). These specific information of the protons matched with the structure of OTAEAzO, providing powerful evidence for identifying the structure of OTAEAzO.



**Figure S3**  $^1\text{H}$ -NMR spectrum of OTAEAzO

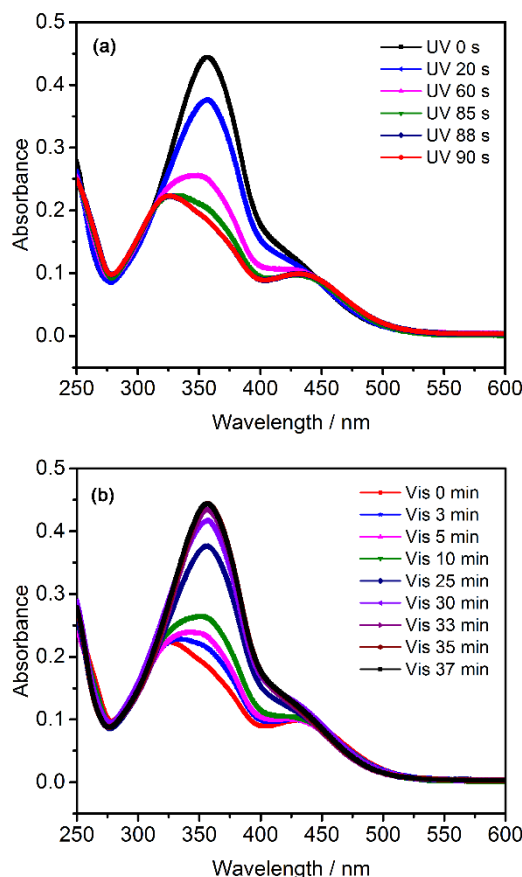
## Surface activity analysis



**Figure S4** Equilibrium surface tension of BTAEAzO.

The synthesis of BTAEAzO has been reported previously.<sup>1</sup> The surface tensions depended on BTAEAzO concentrations were investigated to determine the *CMC* of BTAEAzO (shown in Figure S4). From Figure S4, the surface tension of the *trans* isomers solution progressively decreased until the concentration of  $42.2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ , revealing that the *CMC* of *trans*-BTAEAzO is  $42.2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ . Similarly, the *CMC* of *cis*-BTAEAzO is  $59.7 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ . The *CMC* of *trans*-BTAEAzO and *cis*-BTAEAzO are more than 10 times higher than the *CMC* of OTAEAzO.

## Isomerization analysis of BTAEAzO



**Figure S5** Photo-isomerization of BTAEAzO at a concentration of  $2.0 \text{ g}\cdot\text{L}^{-1}$  (After UV or visible light irradiation, the measured samples were diluted to  $0.02 \text{ g}\cdot\text{L}^{-1}$ , followed by recording the absorption spectrum). (a) Absorption spectra in UV light. (b) Absorption spectra in visible light.

As illustrated in Figure S5(a), a prominent decrease in the absorbance at around 350-400 nm and a weak emergence at 450 nm are found after UV light irradiation. These absorbance values were changing until prolonging UV light radiation to 88 s, indicating that a *cis*-rich photo-stationary state reached after UV light irradiation for 88 s. While Figure S5(b) shows an opposite phenomenon, and absorbance values maintain unchanged when the visible light

irradiation time is longer than 35 min, revealing that the reversible photo-isomerization (*cis*-to-*trans*) occurs within 35 min visible light irradiation.

## REFERENCES

- (1) Chen, S.; Zhang, W.; Wang, C.; Sun, S. A Recycled Foam Coloring Approach Based on the Reversible Photo-isomerization of Azobenzene Cationic Surfactant. *Green Chem.* **2016**, *18*, 3972-3980.