Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

Synthesis of Photo-responsive Azobenzene Molecules with Different Hydrophobic Chain Length for Controlling Foam Stability

Shaoyu Chen, Chaoxia Wang*, Yunjie Yin and Kunlin Chen

Key Laboratory of Eco-Textile, Ministry of Education, School of Textile & Clothing, Jiangnan University, 1800 Lihu Road Wuxi, 214122, People's Republic of China.

*Corresponding author: wangchaoxia@sohu.com

Structural characterization of HnAzo

The identity of HC_nAzo were further confirmed by FT-IR, LC-MS and H-NMR analysis. The FT-IR spectra of HC_nAzo were showed in Figure S1. As for the spectrum of $HC_{12}Azo$ (Figure S1(c)), the peaks at 3281 cm^{-1} and 1251 cm^{-1} were associated with the stretching vibration of O-H and C-O, respectively, which proved the existence of –OH group. The adsorption peaks corresponding to the C-H stretching vibration of CH_3 group were observed at 2955 cm^{-1} and 2872 cm^{-1}, and its C-H bending vibrations appeared at 1394 cm^{-1} and 1473 cm^{-1}. The peaks at 2917 cm^{-1} and 2848 cm^{-1} belong to the C-H stretching vibration and the peak at 1497 cm^{-1} was assigned to the C-H bending vibrations of CH_2 group. In addition, the peak at 720 cm^{-1} was due to the rocking vibration of alkyl $-CH_2-$ group. All these peaks indicated that the dodecyl chain have been successfully substituted the hydrogen of hydroxyl group. The characteristic peaks of HC_4Azo (Figure S1(a))and HC_8Azo (Figure S1(b)) were similar with $HC_{12}Azo$. The differences were that the peak intensity and wavenumber. The peak intensity increased and the peaks shifted to lower wavenumber with the increase of the hydrophobic chain length.

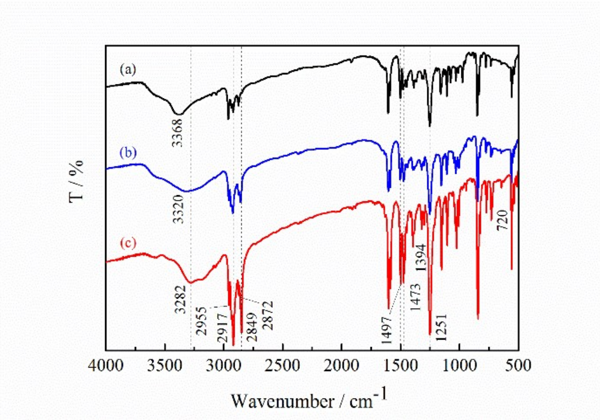


Figure S1. FT-IR spectra of (a) HC_4Azo, (b) HC_8Azo and (c) $HC_{12}Azo$.

The LC-MS spectra (Figure S2) presented the m/z value of quasi-molecular ion and fragment of the samples. For example, in Figure S2(C), the ion at m/z 381.3 was the most abundant, corresponding to the quasi-molecular ion of $HC_{12}Azo$. Furthermore, the ion at m/z 212.1 was assigned to the $HC_{12}Azo$ fragment, i.e., the $HC_{12}Azo$ lost dodecyl chain. The m/z values of 381.3 and 212.1 in LC-MS spectrum were matched with the quasi-molecular ion and fragment of $HC_{12}Azo$, which provided powerful evidence for identifying $HC_{12}Azo$.

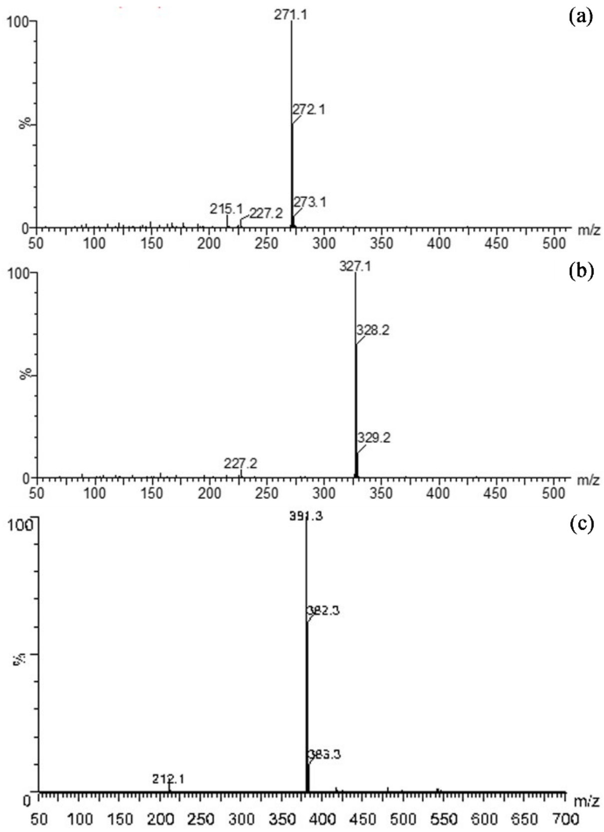


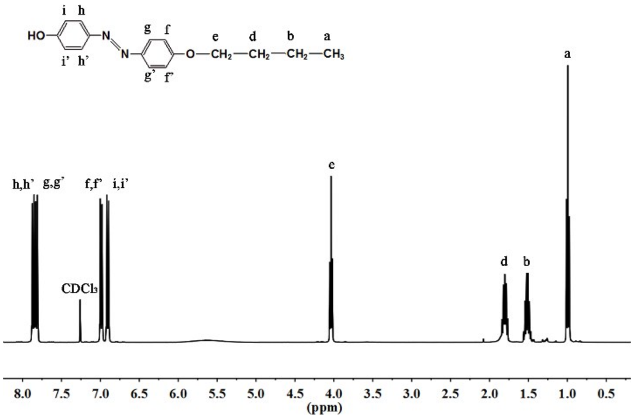
Figure S2. LC-MS spectra of (a) HC_4Azo, (b) HC_8Azo and (c) $HC_{12}Azo$.

In Figure S3, the signals of the protons were correspond with the structure of HC_nAzo.

HC_4Azo. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 17.5, 8.9 Hz, 4H), 6.95 (dd, J = 33.3, 8.9 Hz, 4H), 4.04 (t, J = 6.5 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.57 – 1.45 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

HC_8Azo. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 17.5, 8.9 Hz, 4H), 6.95 (dd, J = 33.3, 8.9 Hz, 4H), 4.04 (t, J = 6.5 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.57 – 1.45 (m, 10H), 0.99 (t, J = 7.4 Hz, 3H).

$HC_{12}Azo$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 12.7, 8.9 Hz, 4H), 6.95 (dd, J = 25.0, 8.9 Hz, 4H), 4.03 (t, J = 6.6 Hz, 2H), 1.89 – 1.74 (m, 2H), 1.52 – 1.41 (m, 2H), 1.41 – 1.20 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H).



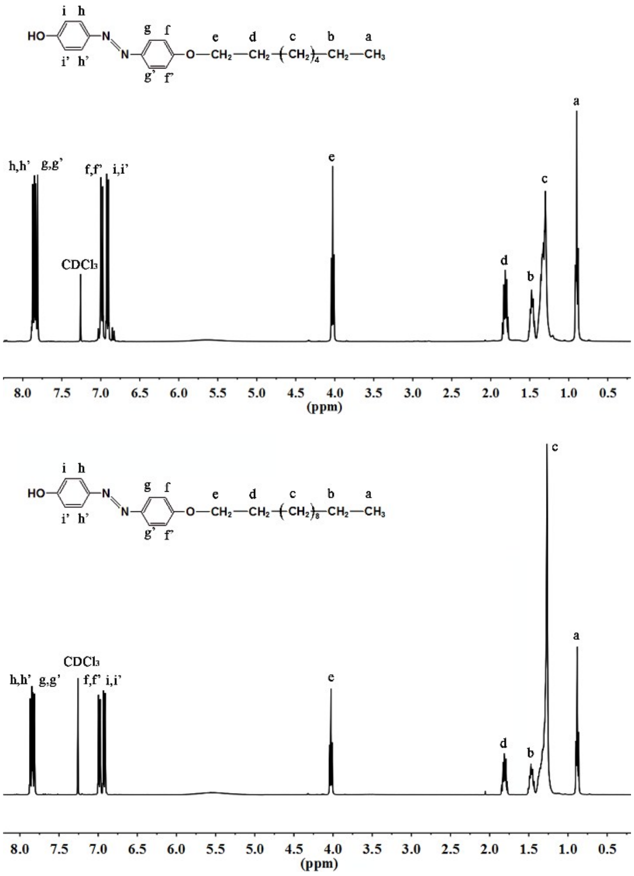


Figure S3. H-NMR spectra of the photo-responsive azobenzene molecules

Optimization of Synthetic Process Parameters

In order to obtain high yield, effects of raw materials molar ratio and reacting time were investigated. Since HC_4Azo, HC_8Azo and $HC_{12}Azo$ were synthesized in the same process and the synthesis mechanisms are the same, $HC_{12}Azo$ was taken as an example to optimize the parameters of synthesis process. Figure. S4(A) showed that the yield was increasing when the molar ratio (bromododecane/DHAzo) was less than 1.8, whereas that the yield slightly decreased when the molar ratio was higher than 1.8, suggesting that the appropriate molar ratio of bromododecane/DHAzo for high yield is 1.8. The highest yield was 82.0% at the reaction time of 7 h. However, if the reacting time was more than 7 h, the side reaction became serious, leading to low yield (Figure. S4(B)). Further, as the catalyst of the reaction, KI effectively promote the nucleophilic substitution of bromododecane and DHAzo. Bromine ion of bromododecane was replaced by iodine ion which possessed higher reactivity in nucleophilic substitution.

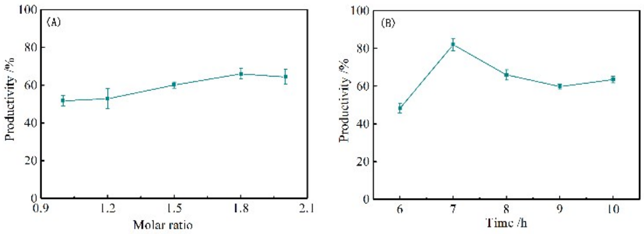


Figure S4. Synthesis Optimization. (A) Effects of molar ratio (bromododecane/DHAzo) on yield with the reacting time of 8 h. (B) Effects of reacting time on yield with the bromododecane/DHAzo molar ratio of 1.8.