Creation of Photo-Modulated Multi-State and Multi-Scale Molecular Assemblies via Binary-State Molecular Switch

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The synthesis of sodium (4-phenylazo-phenoxy)-acetate (AzoNa) was similar to a previous literature. [1] 4-hydroxyl azobenzene (1.98 g, 10 mmol), ethyl bromoacetate (2.09 g, 12.5 mmol), and sodium hydroxide (0.4 g, 10 mmol) was added to a round-bottomed flask containing 50 mL of ethanol. The mixture was refluxed for 4 h and cooled in an ice bath. The precipitate was collected and recrystallized from
heptane. The resulting yellow crystals were dissolved in 50 mL of water/methanol (10/90) and to the solution was added sodium hydroxide (1.2 g, 30 mmol). The mixture was heated to reflux for 5 h and a needle-like solid was obtained after cooling. The solid was collected and recrystallized three times in dilute NaOH solution. Yield: 40 %.

$^1$H NMR (400 MHz, D$_2$O), δ: 7.83 (d, 2 H), 7.76 (d, 2 H), 7.57 (m, 3 H), 7.07 (d, 2 H), 4.53 (s, 2 H). Ana. Cal. for C$_{14}$H$_{11}$N$_2$NaO$_3$: C, 60.43; H, 3.98; N, 10.07. Found: C, 59.60; H, 4.06; N, 9.89.

![Figure S1. NMR spectra of AzoNa in D$_2$O.](image)

2. DLS of mixed surfactant solution at state three and state four.

![Figure S2. Representative plot of intensity correlation function for CTAB/AzoNa at state three and state four at a scattering angle of 90°.](image)


The content of cis-AzoNa was calculated by the following equation:

\[
A_{346\text{nm}} = A_{\text{trans}}C_{\text{trans}} + A_{\text{cis}}C_{\text{cis}}
\]

wherein \(A_{346\text{nm}}\) is the absorbance at the wavelength of 346 nm, \(A_{\text{trans}}\) is the molar extinction coefficients of trans-AzoNa at 346 nm, \(C_{\text{trans}}\) is the concentration of trans-AzoNa, \(A_{\text{cis}}\) is the molar extinction coefficients of cis-AzoNa at 346 nm, \(C_{\text{cis}}\) is the concentration of cis-AzoNa.

To calculate the value of \(A_{\text{trans}}\) and \(A_{\text{cis}}\), the result of NMR and UV-vis (Fig. 1 and Fig. 2a) was combined. The value of \(A_{\text{trans}}\) and \(A_{\text{cis}}\) is 27 and 0.95 mM\(^{-1}\)cm\(^{-1}\) respectively. Then cis-fraction of surfactant mixtures is deduced from equation (1).