Supplementary Material (ESI) for *Soft Matter*

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

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1. Synthesis of Azobenzene Derivative AzoNa.

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_2O), 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 $C_{14}H_{11}N_2NaO_3$: C, 60.43; H, 3.98; N, 10.07. Found: C, 59.60; H, 4.06; N, 9.89.

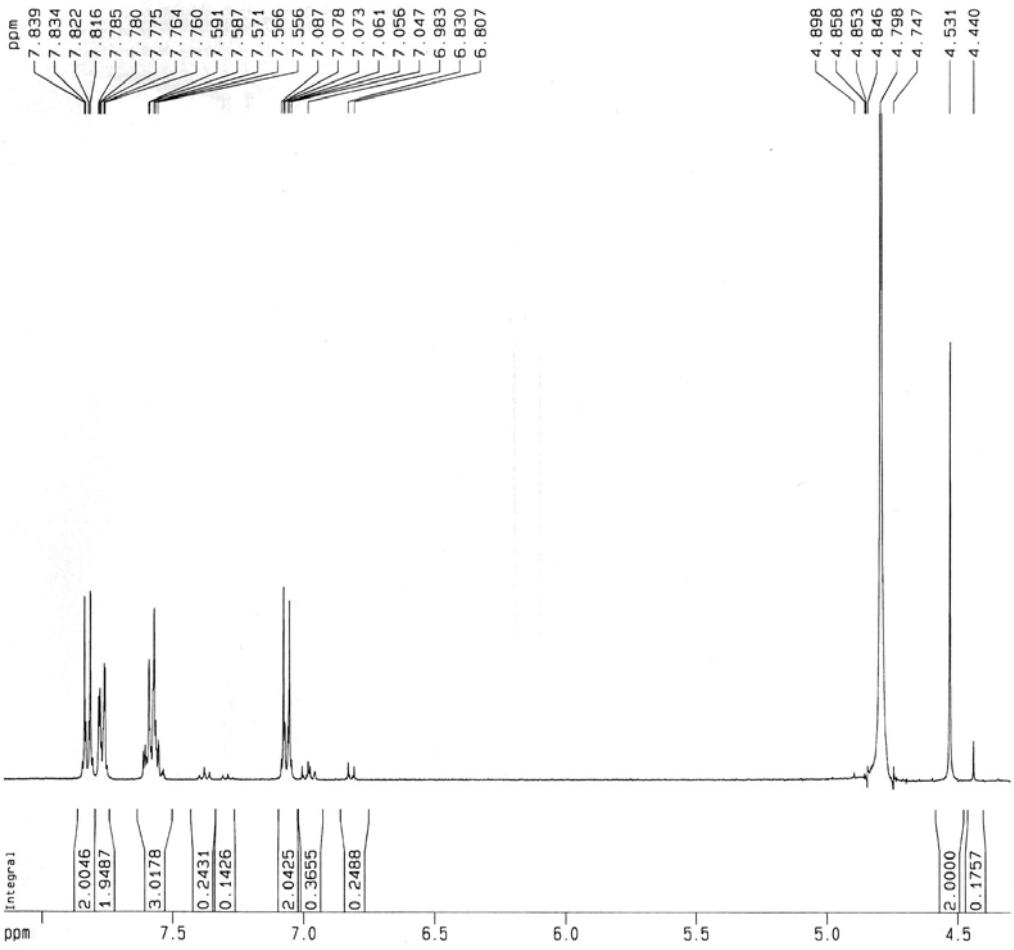

Figure S1. NMR spectra of AzoNa in D_2O.

[1] X. D. Song, J. Perlstein, D. G. Whitten, *J. Am. Chem. Soc.*, 1997, **119**, 9144.

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

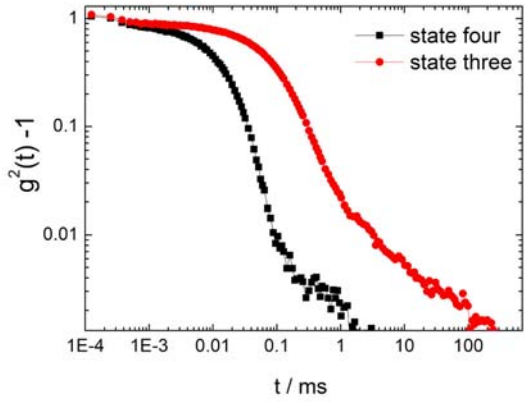

Figure S2. Representative plot of intensity correlation function for CTAB/AzoNa at *state three* and *state four* at a scattering angle of 90°.

3. Estimating the *cis*-fraction of AzoNa by UV-vis absorbance.

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

$$A_{346nm}=A_{trans}*C_{trans} + A_{cis}*C_{cis} \qquad (1)$$

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

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