Supporting Information

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SI Text

Gibbs Adsorption Isotherm. The equilibrium surface tension was measured by the Wilhelmy plate method at different bulk surfactant concentrations to establish the surface concentration, Γ, as obtained from the Gibbs adsorption isotherm for ionic surfactant systems (1), Eq. **S1**:

$$\Gamma = -\frac{1}{2RT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_{T,P}, \qquad \textbf{[S1]}$$

where R is the gas constant, T is the absolute temperature, γ is the surface tension, and C is the bulk surfactant concentration. The surface concentration Γ is easily converted to the equilibrium area per molecule at the air/water interface. The area per molecule at the interface is important for establishing the molecular geometry, which greatly affects bulk self-assembly properties, such as the onset of micellization and the shapes of resulting self-assembled structures. In visible light, for *trans* azobenzene trimethylammonium bromide (azoTAB) the area per molecule was about 40 $Å^2$, which increased to 102 $Å^2$ in UV light for *cis* azoTAB.

UV-Visible Measurements. UV-visible absorbance spectra were recorded on a Shimadzu UV-3600 UV-visible-near infrared spectrophotometer to determine approximate isomer populations of the *trans* and *cis* azoTAB solutions under different light illumination conditions. The spectra after approximately 1 h of irradiation (Fig. S1) for 0.2 mM azoTAB agree well with previous work (2, 3) and indicate that each photostationary state contains small amounts of the other isomer. Unless otherwise stated, a reference to *trans* or *cis* azoTAB refers to the photostationary mixtures that are predominantly the stated isomer.

Cis azoTAB was formed during force measurements by directing 365 nm UV light through the front window of the surface forces apparatus (SFA) 2000. To ensure that minimal reconversion from *cis* back to *trans* azoTAB was induced by the white light passing normally through the mica surfaces during the SFA measurements, a cuvette of 0.2 mM azoTAB was allowed to equilibrate for approximately 1 h in the apparatus. The spectrum for this photostationary state is shown as the SFA curve in Fig. S1 and reflects only small (<10%) reconversion of the *cis* form to the *trans* isomer over this long equilibration time. Thus, over the timescale of an SFA experiment (5–15 min), there is expected to be little if any reconversion back to *trans* azoTAB, allowing for proper examination of the *cis* azoTAB photostationary isomers.

1. Rehfeld SJ (1967) Adsorption of sodium dodecyl sulfate at various hydrocarbon-water interfaces. *J Phys Chem* 71:738–745.
2. Lee CT, Smith KA, Hatton TA (2005) Photocontrol of protein folding: The interaction of photosensitive surfactants with bovine serum albumin. *Biochemistry* 44:524–536.
3. Ny A-LML, Lee CT (2006) Photoreversible DNA condensation using light-responsive surfactants. *J Am Chem Soc* 128:6400–6408.

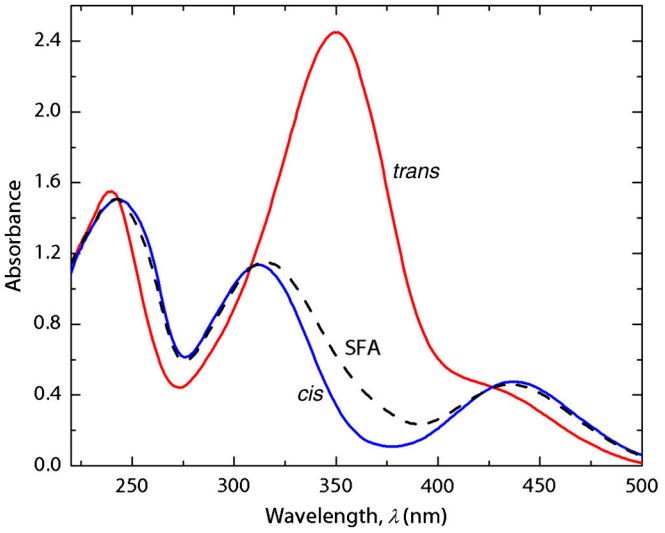

Fig. S1. UV-visible spectrum for 0.2 mM *trans* and *cis* azoTAB (red and blue solid curves, respectively), and for 0.2 mM azoTAB equilibrated in the SFA (white light) illumination with UV light shining through the front window of the SFA chamber (black dashed curve). This result confirms that during force measurements of *cis* azoTAB monolayers and layers, the amount of *trans* azoTAB present in the layers was negligible.