Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Light-Responsive Self-Assembly of a Cationic Azobenzene Surfactant at High Concentration

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1. Materials

The synthesis and characterisation of **C_8AzoOC_2TAB** has been previously reported by the authors.[1]

Millipore™ water was obtained by passing distilled water through a Mill-Q purifier (resistivity = 18.2 MΩ cm^{-1} at 25 °C).

2. Methods

UV-Vis Absorption Spectroscopy: UV-Vis absorption spectra were recorded using a Shimadzu UV2401 PC UV-Vis scanning spectrometer with a scanning slit width of 2 nm and in a quartz cell with a 10 mm path length, at room temperature. The kinetics experiments were carried out using an ILT 950 spectroradiometer over a wavelength range of 250-1050 nm with a resolution of 1.4 nm and 25 μm slits. Optical data were recorded with a SpectraLight III software. A DH-2000 deuterium tungsten halogen light source was used to produce light over a 215-2000 nm range.

Irradiation of Samples for Photoisomerisation: Photoconversion of *trans*-surfactants to the *cis*-form was obtained by exposure of aqueous surfactant solutions to a UV light-emitting diode (LED) (LedEngin®) with an illumination wavelength of 365 nm and a power output of 5 mW cm^{-2}, when placed at 6 cm from the sample. Reverse *cis*- to *trans*-isomerisation was performed using a blue LED (Prolight®) with an illumination wavelength of 465 nm and a power output of 5 mW cm^{-2}, when placed at 3 cm from the sample. Solutions were placed in 10 mm path length quartz cuvettes to allow light transmission. The progress of photoisomerisation was followed by UV-Vis absorption spectroscopy. The photostationary state was determined to be reached when the absorbance at 315 nm (λ_{max} *cis*-isomer) or 350 nm (λ_{max} *trans*-isomer) did not increase further upon continued irradiation. The photostationary states are typically obtained after 3 minutes of irradiation for dilute solutions (< 20 mM).

Photoisomerisation Kinetics: Solutions of **C_8AzoOC_2TAB** (5.0×10^{-5} M) were freshly prepared in Millipore™ water. The *trans-cis* photoisomerisation was followed by UV-Vis absorption spectroscopy by recording an absorption spectra every 3 seconds for 1.5 minutes while being irradiated at λ = 365 nm. The *cis-trans* photoisomerisation was followed by UV-Vis absorption spectroscopy by recording a absorption spectra every 3 seconds for 3 minutes while being irradiated at λ = 465 nm. The experiments were conducted at room temperature (T = 20 °C).

Polarised Optical Microscopy (POM): POM experiments were carried out on a Nikon Eclipse E400 microscope with a 50 W halogen reflector lamp, equipped with an Olympus DP71 camera. Pictures were taken using a microscope magnification of 4×, 10×, 40× and a 530 nm polariser. Sample mixtures were prepared using Millipore water and drop-cast on a glass support before experiments. All experiments were performed in the absence of external light sources to avoid any competitive photoisomerisation of the samples. The effect of the instrument light source was also checked and showed no modification of the POM images.

Small-Angle X-Ray Scattering (SAXS): Synchrotron SAXS measurements were performed on the BioSAXS beamline B21, Diamond Light Source, Harwell, United Kingdom.[2] B21 operates in a fixed sample to detector distance (4.014 m) with X-ray beam energy E = 12.4 keV giving a *q*-range of 0.031–3.8 nm^{-1}. Data were collected using a Pilatus Dectris 2 M detector. The background was manually subtracted using ScÅtter (v3.0 developed by Dr Robert Rambo, Diamond Light Source) and consisted of both the solvent (water) and the empty cell. Heating studies were performed from 20 °C to 60 °C with a 10 °C increment and 3 min equilibration time between steps. The *cis*-isomer samples were irradiated with UV-light (λ = 365 nm) for 3 minutes prior to loading or injection. UV-Vis absorption

spectra were recorded before and after experiments to investigate potential sample damage or reverse isomerisation. In case of X-ray degradation of the *cis* samples, the first 5 frames of the run (30 frames total) were averaged, as this was the point before which any obvious deviation from the initial frame was observed.

Differential Scanning Calorimetry (DSC): DSC was performed using a Perkin Elmer Pyris Diamond Differential Scanning Calorimeter at a heating rate of 5 °C min^{-1}. All samples were prepared in sealed aluminium crucibles and measurements were performed in a nitrogen atmosphere.

3. Determination of the Photostationary State (PSS)

The *trans*- to *cis*-ratio of the PSS at λ = 365 nm can be quantified by calculating the isomerisation degree ($ID_{trans\text{-}cis}$) for conversion to the cis-isomer using the following equation:

$$ID_{trans-cis} = \frac{A(0)_{365} - A(PSS)_{365}}{A(0)_{365}} \times 100\% \quad \text{(Eq. 1)}$$

where $A(0)_{365}$ and $A(PSS)_{365}$ are the absorbance at 365 nm before and after UV light illumination (365 nm), respectively, when the PSS is reached. Before irradiation, $A(0)_{365} = A(PSS)_{365}$, so the $ID_{trans\text{-}cis}$ equals zero, which corresponds to the photosurfactant in its pure *trans*-configuration. It is important to note that $ID_{trans\text{-}cis}$ depends on the intensity of light, the exposure time and the irradiation wavelength. Consequently, careful control of these parameters is necessary to ensure the conversion to the PSS.

The reverse *cis*- to *trans*- photoisomerisation is obtained upon visible light exposure at λ = 465 nm for 3 minutes. The t*rans*-isomer absorbs light at this wavelength, which leads to a second photostationary state, where the *trans*-isomer is the majority. The *ID* of the reverse *cis-trans* photoisomerisation ($ID_{cis\text{-}trans}$) can be calculated using:

$$ID_{cis-trans} = \frac{A(PSS)_{365}}{A(0)_{365}} \times 100\% \quad \text{(Eq. 2)}$$

where $A(0)_{365}$ and $A(PSS)_{365}$ are the absorbance at 365 nm before and after blue light illumination (465 nm), respectively. Complete conversion back to the pure *trans*-isomer from the *cis*-PSS was obtained by thermal relaxation in the dark (2 days at 20 °C for 1 hour at 60 °C).

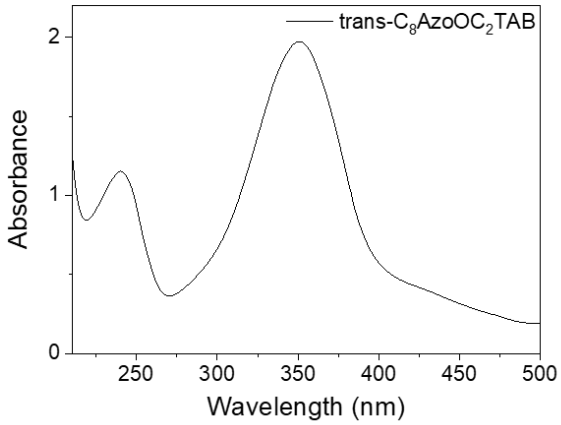

Figure S1. UV-Vis absorption spectrum of an assembly of *trans*-C_8AzoOC_2TAB (90 mM in water) recovered from the *cis*-PSS by heating at 60 °C for one hour.

4. Kinetics of Photoisomerisation

The photosurfactants in their *trans*-form were illuminated at λ = 365 nm and absorption spectra were recorded every 3 seconds for a total duration of 1.5 minutes. Rapid *trans-cis* photoisomerisation is observed within the first 30 seconds (Figure S1). Continued illumination increases the concentration of the *cis*-isomer until the photostationary state is reached after 1.5 minutes. The photosurfactants were subsequently illuminated at λ = 465 nm with a blue LED and absorption spectra were simultaneously recorded every 3 seconds for a total duration of 3 minutes (Figure S1).

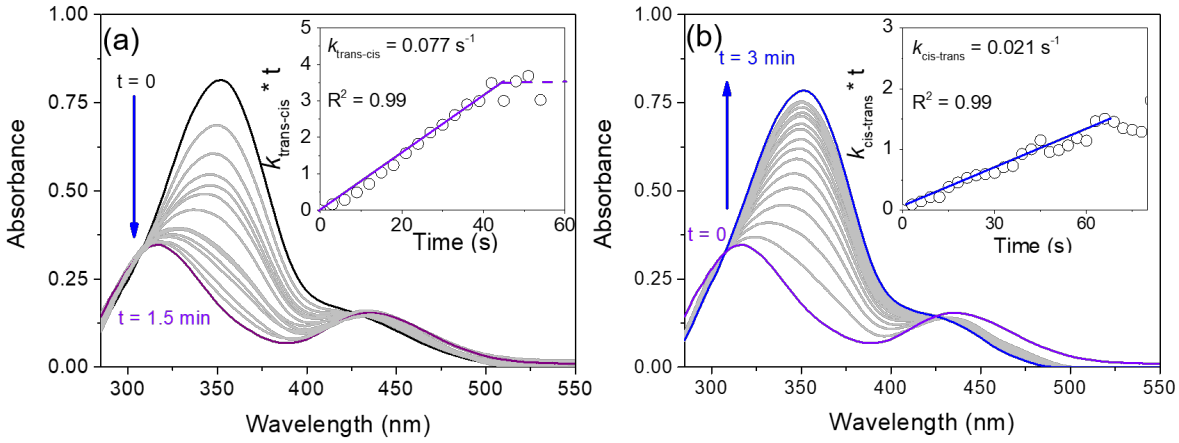

Figure S2. Kinetics of photoisomerisation of **C_8AzoOC$_2$TAB** (5.0 × 10^{-5} M in water). (a) UV-Vis absorption spectra at 3 second intervals of UV irradiation (365 nm) over 1.5 min. Inset: Determination of the first order rate constant, $k_{trans-cis}$, for the *trans-cis* isomerisation. (b) UV-Vis absorption spectra at 3 second intervals of blue light irradiation (465 nm) over 3 min. Inset: Determination of the first-order rate constant, $k_{cis-trans}$, for the *cis-trans* isomerisation.

The *trans-cis* photoisomerisation process obeys first order kinetics, whose rate equation may be given by:

$$-\ln\left(\frac{A_{t,365\,nm} - A_{PSS,365\,nm}}{A_{0,365\,nm} - A_{PSS,365\,nm}}\right) = -k_{trans-cis}t \qquad \text{(Eq. 3)}$$

where $A_{t,\,365\ nm}$ is the absorbance at λ = 365 nm at time *t*, $A_{PSS,365\ nm}$ is the absorbance of the photostationary state, $A_{0,365\ nm}$ is the initial absorbance of the *trans*-isomer before UV irradiation at λ = 365 nm and $k_{trans-cis}$ is the rate constant describing the *trans-cis* photoisomerisation. A plot of the natural logarithm of the ratio of relative absorbance at λ = 365 nm against time is linear and the slope yields the rate constant, as shown in the inset of Figure S1. Similarly, the *cis*- to *trans*-isomerisation rate constant, $k_{cis-trans}$, can be obtained, using the same approach at λ = 365 nm, by following the growth of the trans-isomer upon excitation at 465 nm.

5. Additional POM Images

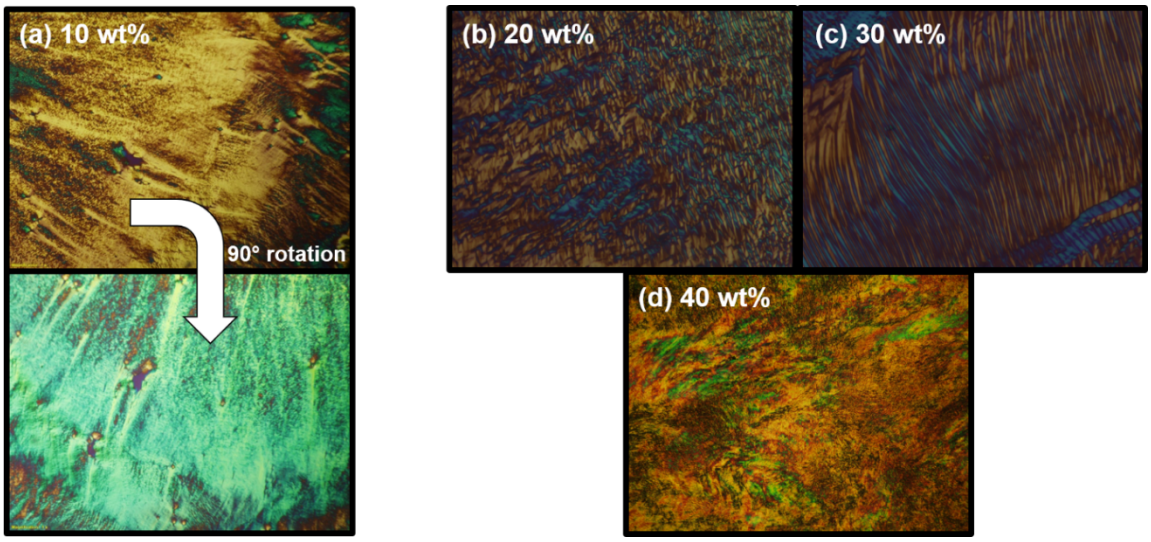

Figure S3: POM images of **C_8AzoOC_2TAB** in the native *trans*-state at (a) 10 wt% with a 90° rotation and (b) 20 wt%, (c) 30 wt% and (d) 40 wt%.

6. Temperature-Dependent Behaviour

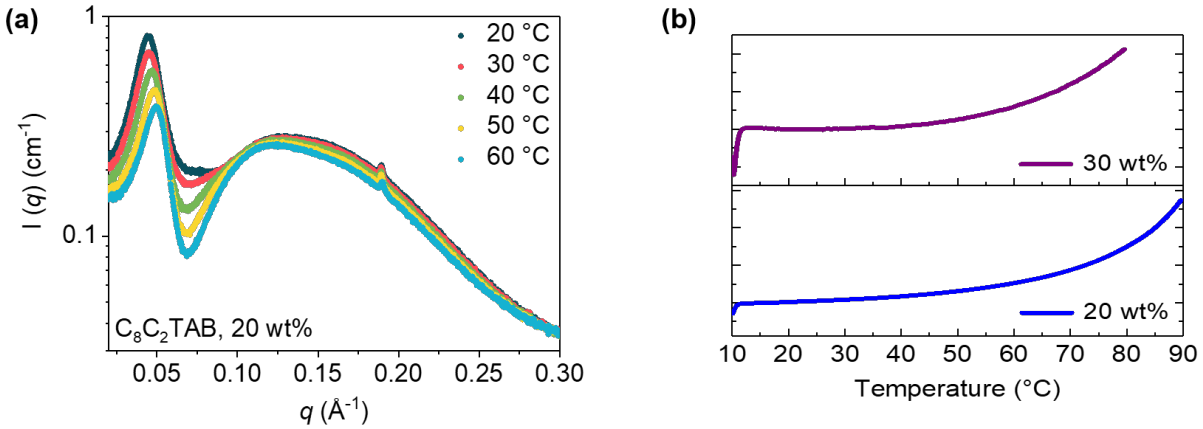

Figure S4: Behaviour of **C_8AzoOC_2TAB** in the native *trans*-state with increasing temperature. (a) SAXS profiles of 20 wt% solution as a function of increasing temperature from 20 to 60 °C and (b) DSC thermograms of 20 wt% (blue) and 30 wt% (purple) solutions show no changes with increasing temperature.

7. References

[1] C. Blayo, J. E. Houston, S. M. King and R. C. Evans, *Langmuir*, 2018, **34**, 10123–10134.

[2] N. P. Cowieson, C. J. C. Edwards-Gayle, K. Inoue, N. S. Khunti, J. Doutch, E. Williams, S. Daniels, G. Preece, N. A. Krumpa, J. P. Sutter, M. D. Tully, N. J. Terril and R. P. Rambo, *J. Synchrotron Rad.*, 2020, **27**, 1438-1446.