Light induced structural evolution of photoswitchable carbohydrate-based surfactant micelles

Supplementary Information

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Materials and methods:

Surfactants were synthesized, purified and characterised as described previously.¹ Water was from a from a Millipore Direct-Q 5, with a minimal resistivity of 18.4 M Ω cm. Deuterium oxide was obtained from Sigma (99.98 atom% D) and used without further purification. UV-visible spectrophotometric measurements were made on a Cary 60 UV-vis instrument.

For photoswitching experiments, illumination was provided from standard 5 mm LEDs obtained from LEDSupply (Randolph, VT, USA). For trans \rightarrow cis switching, 361 nm LEDs (0.75 mW luminous intensity, 15 degree viewing angle) were used. For cis \rightarrow trans switching, 440 nm LEDs (1.5 mW, 15 degree viewing angle). The same experimental geometry was used for both SANS and spectrophotometry experiments, and is shown in Figure S1.



Figure S1: Geometry of illumination setup for SANS and UV-visible spectrophotometry experiments.

Small-angle neutron scattering (SANS) measurements were conducting using the Quokka instrument at the Bragg Institute, ANSTO, Lucas Heights NSW, Australia. For each sample, raw counts representing scattered neutrons were collected on a 128 x 128 element area detector. A single sample-detector distance of 4 m, with no detector offset. An incident neutron wavelength of 5 Å with a typical spread of 10% was used, giving an effective q-range of $0.011 - 0.19 \text{ Å}^{-1}$. Samples were prepared in Hellma quartz cells with a path-length of 2 mm, and a thermostatically-controlled automatic sample changer was used to ensure that a temperature of 25 +/– 0.05° C was maintained throughout.

Data were converted from raw counts at the detector into 1D intensity *versus* scattering vector (q) spectra by first subtracting the scattering from an empty cell and then radially averaging the resulting spectrum, concurrently normalizing for the measured sample thickness and transmission.

Model fits to experimental scattering data were made using the Guinier equation² for the form-factor P(q,a), for scattering from a spherically-capped cylindrical micelle:

$$P(q, a) = 2\Delta\rho V \sin(qL\cos a/2)/(qL\cos a/2) \frac{J_1(qr\sin a)}{qr\sin a}$$

wherein $\Delta \rho$ is the contrast (*i.e.* the difference in scattering length density between the cylinder and the D₂O continuous phase), *V* is the cylinder volume, *L* is the cylinder length, *a* is the angle between the cylinder major axis and the *q*-vector, *r* is the cylinder radius and J₁ is a first order Bessel function. Micelles were sufficiently dilute that any influence of structure factor contribution to the scattering was not detected. For all samples, a Schultz polydispersity factor was applied to the micelle radii,³ fixed at 0.15.

Parameters obtained from model fitting are given in Table S1 below. The aggregation number was calculated assuming molecular volumes as calculated previously.¹

Table S1: Parameters from model fits to SANS spectra: time of illumination at 361 nm (t_{350}), contrast between solvent and micelle ($\Delta \rho$), micelle length, radius, volume, and aggregation number (N_{agg}). Typical uncertainties in length and radius are 4% and 2.5% respectively, providing a typical effective uncertainty in aggregation number of 12%.

Surfactant -	Conc. mM	t ₃₅₀ mins	Δρ ×10 ¹⁰ cm ⁻²	Length nm	Radius nm	Volume nm ³	N _{agg} -
Glc-Azo	0.5	0 15 30 45 60 90	4.33	11.4 93.1 7.5 53.2 4.7 4.2	2.6 2.6 2.6 2.6 2.6 2.6	242 198 159 113 99 90	292 239 192 136 120 108
Glc-Tz-Azo	1.6	0 90	4.38	19.9 21.0	2.6 2.2	852 656	923 711
GIcU-Azo	2.0	0 15 30 60	4.34	1.6 1.4 1.2	2.9 2.8 1.8 -	85 70 24 -	92 76 27 (1)

Comparison of cylindrical and prolate spheroidal fits

For a given aggregate volume, the difference between a prolate spheroid and a cylinder may be geometrically very small. Thus it is pertinent to examine the quality of fit for both of these shapes when assigning geometries to micelles from SANS fitting. Whereas SANS is very sensitive to the volume of the scattering object, the specific geometry may be more difficult to ascertain with absolute certainty.



Figure S2: Comparison of quality of fit (*i.e.* the normalised error between the fitted profile and experimental data) for Glc-Azo (0.25 mM) before illumination. The dashed and solid lines show best fits assuming a cylindrical or prolate spheroidal micelle geometry respectively, and the normalised error (Err) for each case is shown in the panel below, where hollow symbols represent the cylindrical case. The two shapes are provided as an inset, where in both cases, the axis of rotation is vertical.

It is clear from Fig. S2 that for certain cases, there is no statistically significant difference in the quality of fit between a cylindrical and ellipsoidal geometry. In these cases, data from previous experiments where signal-to-noise was much higher due to longer counting times were used to assign geometries. Even in this case, for low aspect ratios, the difference is small and absolute assignments should be treated with some degree of caution.

Fitting to lower q for Glc-Tz-Azo



Figure S3. Experimental SANS data (symbols) and model fit (solid line) assuming a cylindrical geometry for Glc-Tz-Azo at a concentration of 1.6 mM. The lower pane shows the normalised error between the experimental data and fitted profile.

References:

- 1. R. F. Tabor, D. D. Tan, S. S. Han, S. A. Young, Z. L. E. Seeger, M. J. Pottage, C. J. Garvey and B. L. Wilkinson, *Chem. Eur. J.* 2014, **20**, 13881–13884.
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- 3. L. A. Feigin and D. A. Svergu, "Structure Analysis by Small-Angle X-Ray and Neutron Scattering". *Plenum Press, New York,* **1987**.