Photoinduced morphism of gemini surfactant aggregates

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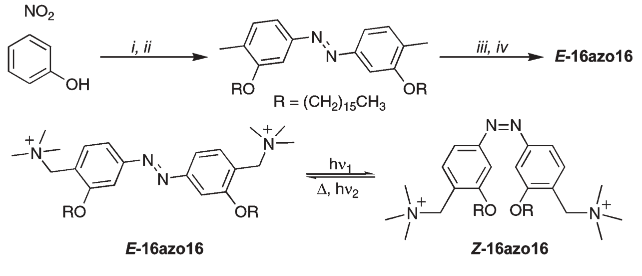
The photochemical behaviour of an azobenzene chromophore inserted in a gemini surfactant imparts photocontrol to the resulting amphiphile assemblies, including the collapse, upon irradiation, of the multi lamellar vesicles formed in aqueous solution.

Amphiphilic molecules containing photochromic elements can undergo conformational and electronic changes upon irradiation, offering an attractive alternative for morphology modulation of amphiphile assemblies using an external stimulus. Compared to the use of temperature, pH variation, or the addition of salt or co-surfactants, the use of photo-isomerisable groups in principle allows switching between morphologies associated to each of the two isomers.[1] However, the ensuing structural change is generally insufficient to provoke the collapse of vesicular aggregates. This can be brought about through the use of photo-cleavable groups, where irradiation leads to the irreversible destruction of the assemblies.[2] Gemini surfactants containing a photo-isomerisable stilbene spacer have been reported to undergo a micelle to vesicle transition,[3,4] but stilbene photoisomerisation exhibits significant fatigue because of competitive photocyclisation from the *Z* isomer to afford dihydrophenanthrene. This is not the case for the azobenzene-derived surfactant reported herein, which was designed to undergo a large structural variation upon *E*, *Z* isomerisation.

The structure of 16azo16 (Scheme 1) is based on the use of a photoactive azobenzene chromophore as a rigid scaffold to connect two cationic alkylammonium amphiphiles. Molecular modelling of the *E* and *Z* conformers suggests that isomerisation of the N=N double bond will significantly alter the relative area occupied by the polar head groups with respect to the non-polar alkyl chains. Additionally, whereas conformer *E* is expected to be near-planar, the *Z* isomer is significantly distorted because of non-bonded repulsion between the alkoxy substituents. It is therefore anticipated that upon photo or thermal *E*, *Z* isomerisation, the ensuing structural variation will induce an important reorganisation of the surfactant aggregates. In particular, in the case of vesicular aggregates, a sudden increase in the surface curvature of the surfactant aggregates can induce a transition to a micellar structure.[1] Although such vesicle to micelle transitions are not uncommon upon thermal activation, the use of light as an external stimulus generally requires a drastic change in the molecular structure (*e.g.* bond-breaking).

The synthesis of the desired symmetrical gemini surfactant was achieved by reductive coupling of the corresponding 3-alkoxy-4-methylnitrobenzene, followed by bromination and subsequent amination with trimethylamine to afford *E*-16azo16.† Its absorption spectrum (Fig. 1) is typical of azobenzene derivatives, comprised of a strongly allowed ππ* transition centred at 350 nm (λ_{max} = 325 nm) and a weakly-allowed nπ* transition at *ca.* 460 nm. Upon irradiation with UV light (365 nm), a photostationary state enriched in the *Z* isomer (80 : 20 *Z* : *E* in $CDCl_3$, as determined by ^1H NMR) is quickly reached. Thermal reversion to the *E* isomer in solution is readily followed by UV-vis spectroscopy, and is characterized by a rate constant of $k_\Delta = 7.32 \times 10^{-5}\ s^{-1}$ ($t_{1/2}$ = 160 min.). The high photosensitivity of 16azo16 is in agreement with efficient photoinduced *E*, *Z* isomerisation ($\Phi_{E,Z} = 0.25$ and $\Phi_{Z,E} = 0.43$).

The aggregation behaviour of 16azo16 and its response to UV irradiation was studied at the air–water interface by π-A isotherms which confirmed that the light-induced changes in the molecular structure have an important effect on the 2-D packing behaviour



Scheme 1 Synthesis and photoisomerisation of 16azo16. *i*, RI, K_2CO_3 18-crown-6, THF, 80 °C (95%); *ii*, $LiAlH_4$, THF, 80 °C (30%); *iii*, NBS, CCl_4, reflux (50%); *iv*, Me_3N, CH_3CN, 20 °C (90%).

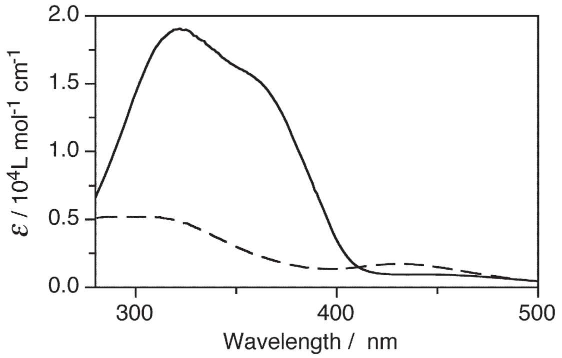


Fig. 1 Absorption spectra of *E*-16azo16 in chloroform (solid line). The spectrum of *Z*-16azo16 (dashed line) was deduced by subtracting the contribution of the *E* isomer at the photostationary state.

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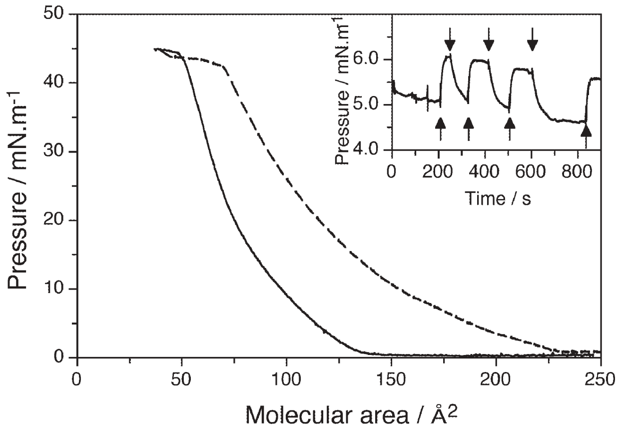

Fig. 2 Effect of 365 nm irradiation on π-A isotherms of 16azo16 at the air–water interface. Solid line: *E*-16azo16. Dashed line: 1 : 1 mixture of *E*- and *Z*-16azo16 obtained by pre-irradiation of the sample prior to deposition. Inset shows the pressure response of the balance held at constant area (*ca.* 110 Å^2/molecule) upon irradiation with a multiband UV-254/365 nm lamp (8W, up arrows: 365 nm, down arrows: 254 nm).

(Fig. 2). In the case of the *E* isomer, the detectable increase of the surface pressure from a quasi-zero value is observed at 135 Å^2/molecule, which is followed by the collapse of the film at 50 Å^2/molecule. The solution of 16azo16 was then pre-irradiated at 365 nm before deposition at the water surface ([*Z*] : [*E*] = 1 : 1), yielding a monolayer with a compression isotherm that is substantially displaced: the first detectable increase is observed at around 230 Å^2/molecule (a 70% increase), and the collapse at 70 Å^2/molecule (a 40% increase). This behaviour contrasts with what has been previously observed with a related anionic gemini surfactant containing a stilbene chromophore, in which *E*, *Z* isomerisation induced a *decrease* in molecular area.[3] In the latter case, however, the *E* isomer is expected to be less planar than the *Z* isomer due to repulsion between the polar head groups located in the *ortho* positions relative to the exocyclic double bond. Together, these results suggest that the propensity of aromatic gemini surfactants to successfully pack into a dense monolayer is directed by the overall shape (globular *vs.* planar) of the molecules rather than the relative areas occupied by the polar head groups and the non-polar alkyl chains.

The change in molecular area at the air–water interface upon irradiation can be used to construct a light-to-mechanical force transducer. By simply irradiating a monolayer of 16azo16 using a hand-held UV lamp, it is possible to provoke changes in the pressure monitored at constant surface area. The result is shown in Fig. 2 (inset) where 365 nm light induces an increase in the surface pressure as a result of the *E* → *Z* isomerisation. The process is thermally reversible and 254 nm light (or visible light) can be used to accelerate the return to the initial state. This sequence can be repeated several times without loss in performance, except for a drift in baseline resulting from slow evaporation of the aqueous subphase.

In aqueous solution, 16azo16 spontaneously forms vesicles upon sonication and gentle heating, as evidenced by optical microscopy with differential interferential contrast (DIC) technique and by freeze fracture transmission electron microscopy (FFTEM) (Cryo-electron Microscope FEI EM120 (120 kV)). The vesicles are polydisperse with a size distribution ranging from a few hundred nm to ~10 μm. Irradiation of the solution was performed using the medium pressure Hg lamp associated to the epifluorescence microscope (330–380 nm bandpass filter), which presents the advantage of allowing *in situ* monitoring of the sample during irradiation. The vesicles remained unchanged under and after irradiation of the sample, and their integrity was further confirmed by FFTEM.

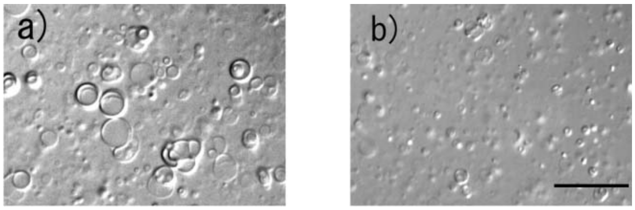

Fig. 3 DIC optical microscope images of vesicles formed from a 10 : 1 mixture of 16azo16 and CTAB before (a) and after (b) irradiation. Scale bar 100 μm.

These results indicate that *E*, *Z* isomerisation is insufficient to inducing a morphology change of the 16azo16 vesicles. One way to approach the phase transition is to "destabilise" the bilayers through the addition of molecules capable of interacting with the surfactant aggregate surface. This was achieved by the addition of a small amount of micelle-forming surfactant, cetylammonium bromide (CTAB). Vesicles formed from a mixture of 16azo16 and CTAB (10 : 1) are similar in shape to those previously obtained using 16azo16 alone. However, as shown by the DIC images in Fig. 3, upon irradiation the vesicles rapidly deform (within ~30 s) and rupture to transform into much smaller birefringent objects (Fig. 4). The exact nature of the latter could not be unambiguously determined as they were not resolved either by optical microscopy or by cryofracture TEM. It is likely that the vesicles are transformed into a mixture of micelles and small crystallites. The vesicles are not spontaneously re-formed after irradiation is halted, despite the reversible nature of the *E*, *Z* isomerisation.

In the absence of UV irradiation, the vesicular aggregates formed by 16azo16 in the presence of CTAB display exceptional thermal stability. Indeed, heating a suspension of the vesicles in water to 80 °C did not provoke any change in the aggregate morphology or size distribution, as evidenced by optical microscopy. We can therefore attribute the light-induced collapse of the

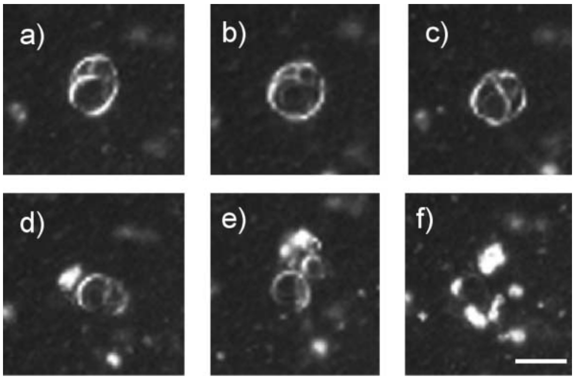

Fig. 4 Rupturing of vesicles under irradiation. Images are taken every 10 s. Scale bar 15 μm.

vesicles to the destabilisation of the lamellar structure due to a change in the surface curvature induced by E,Z isomerisation.

In conclusion, we have unambiguously shown that a cationic gemini surfactant having azobenzene spacer can reversibly change its conformation at the air–water interface, allowing us to modulate the surface pressure using a remote external stimulus, namely UV irradiation. In solution, 16azo16 spontaneously forms vesicles which, when prepared in the presence of a small amount of CTAB, readily rupture upon UV irradiation. Current effort is oriented towards rendering the system completely reversible and to investigate its potential in the controlled release of substances in aqueous environments.

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Notes and references

† All compounds exhibited satisfactory ^{1}H, ^{13}C and MS spectra. Full experimental details of the synthesis will be published elsewhere.

1 (*a*) T. Kunitake, N. Nakashima, M. Shimomura and Y. Okahata, *J. Am. Chem. Soc.*, 1980, **102**, 6642; (*b*) T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami and K. Takarabe, *J. Am. Chem. Soc.*, 1981, **103**, 5401; (*c*) W. F. Mooney, P. E. Brown, J. C. Russel, S. B. Costa, L. G. Pedersen and D. G. Whitten, *J. Am. Chem. Soc.*, 1984, **106**, 5659; (*d*) D. A. Holden, H. Ringsdorf, V. Deblauwe and G. Smets, *J. Phys. Chem.*, 1984, **88**, 716; (*e*) K. Nishiyama and M. Fujihira, *Chem. Lett.*, 1988, 1257; (*f*) S. D. Evans, S. R. Johnson, H. Ringsdorf, L. M. Williams and H. Wolf, *Langmuir*, 1998, **14**, 6436; (*g*) H. C. Kang, B. M. Lee, J. Yoon and M. Yoon, *J. Colloid Interface Sci.*, 2000, **231**, 255.

2 (*a*) M. Haubs and H. Ringsdorf, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 882; (*b*) I. R. Dunkin, A. Gittinger, D. C. Sherrington and P. J. Wittaker, *J. Chem. Soc., Chem. Commun.*, 1994, 2245; (*c*) Z. Li and A. G. Kutateladze, *J. Org. Chem.*, 2003, **68**, 8236; (*d*) J. Eastoe, M. S. Dominguez, H. Cumber, P. Wyatt and R. K. Heenan, *Langmuir*, 2004, **20**, 1120.

3 O. Karthaus, M. Shimomura, M. Hioki, R. Tahara and H. Nakamura, *J. Am. Chem. Soc.*, 1996, **118**, 9174.

4 J. Eastoe, M. S. Dominguez, P. Wyatt, A. Beeby and R. K. Heenan, *Langmuir*, 2002, **18**, 7837.