

Electronic supplementary Information (ESI)

Photoresponsive Self-Assemblies based on Fatty Acids

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Experimental Procedure

1.1 Materials and samples preparation

All chemicals were purchased from Sigma-Aldrich and used as received. 1M choline hydroxide solution was prepared in ultrapure water from the commercially choline hydroxide solution (Choline hydroxide, 46% weight in water). 12-hydroxystearic acid (12-HSA, purity>75%) was weighted exactly in a tube and ultrapure water was added to reach a final concentration of 8 g/L (0.8% weight in water). Then, the desired volume of the 1M choline hydroxide solution was incorporated to obtain a molar ratio of 1.6 between the counter-ion choline and 12-HSA. A 50 mM PAG (diphenyliodonium nitrate) solution was prepared in ultrapure water. Then, an appropriate volume of 50 mM PAG solution was added to the 12-HSA/choline sample to reach a final concentration of 10 mM PAG before leaving to stir one hour at room temperature. After PAG addition, all the flasks containing the samples were protected from light by aluminum foil. The PAG has reported λ_{max} values of 203 and 226 nm.¹ Irradiated samples did not undergo any changes when stored under ambient conditions, which facilitated subsequent tests.

1.2 Methods

UV irradiation

All samples were irradiated with UV light from a 15 W Herloba UV lamp (wavelength 254 nm). 300 μ L of solution was placed in 1-mm path length quartz cells (Helma Analytics) and positioned horizontally at approximately 5 cm from the UV lamp.

pH measurements

A calibrated pH probe (TIM900 Titration Manager, Radiometer) was used for the pH measurements. The stated accuracy of the pH measurements is +/- 0.1. The pH measurements were performed at room temperature.

Small Angle Neutron Scattering measurements

Small Angle Neutron scattering (SANS) experiments were performed at Laboratoire Léon Brillouin (Laboratoire mixte CEA/CNRS, Saclay, France) on the PACE spectrometer. Three configurations were chosen to get a Q-range lying between 0.005 and 0.3 Å⁻¹ (respectively, 5 Å at 1m, 5 Å at 4.7m and 13 Å at 4.7m) with a significant overlap between the three configurations. The neutron wavelength was set to the desired value with a mechanical velocity selector ($\Delta\lambda/\lambda \approx 0.1$). Samples were prepared with deuterated water and were held in flat quartz cells with a 2 mm optical path length. The temperature was controlled by a circulating fluid to within $\pm 0.2^\circ\text{C}$. The azimuthally averaged spectra were corrected for solvent, empty cell, as well as background noise, and were normalized to the incoherent H₂O signal by using PASINET software package provided at the beamline.

TEM measurements

A drop of the sample was first placed on a carbon-coated TEM copper grid (Electron Microscopy Sciences, Germany). Samples were stained with uranyl acetate. The excess of liquid was blotted with a filter paper after and the TEM grid was then air-dried at room temperature. The specimen was inserted into a sample holder (EM21010, JEOL gmbH, Eching, Germany) and transferred into a JEOL JEM-2100 (JEOL gmbH, Eching, Germany). The TEM was operated at an acceleration voltage of 200 kV. All images were recorded digitally by a bottom-mounted 4k CMOS camera system (TemCam-F416, TVIPS, Gauting, Germany) and processed with a digital imaging processing system (EM-Menu 4.0, TVIPS, Gauting, Germany).

Fourier Transform Infrared Spectroscopy (FT-IR) measurements

FT-IR spectra were recorded on a Nicolet Magna IR 550 Serie II (nitrogen cooled mercury-cadmium-telluride detector, KBr beamsplitter) with a resolution of 2 cm⁻¹ at room temperature. Samples were spread on the selenium chloride crystal. The instrument was continuously purged with dry air. To improve single to noise ratio, 200 scans were averaged for each sample. The baseline subtraction and offset corrections were done by using the Galactic GRAM/AI 7.0 software.

Foaming properties measurements

Foam samples were prepared by vigorous handshaking of glass containers containing 2 mL of the 12-HSA solution. The mixture was agitated for 30 seconds and all foam samples were produced by the same operator. The foamability and the foam stability were studied by visual inspection.

Additional Results

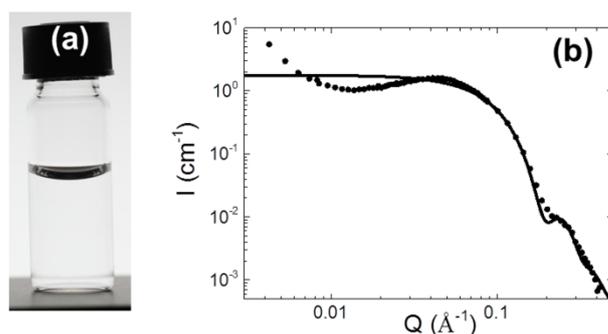


Figure SI.1: (a) Photograph of the 12-HSA/choline dispersion before the addition of PAG. (b) SANS intensity profile for the 12-HSA/choline dispersion before the addition of PAG at 25°C. The black line corresponds to the form factor of a sphere with a diameter of about 4.4 nm.

The intensity scattered by objects in solution can be described as a product of structure factor $S(Q)$, characteristic of the correlations between objects, by a form factor $P(Q)$, that describes the shape of the objects. At large Q , the scattering curves scatter like Q^{-4} that is characteristic of a Porod behavior corresponding to the surface scattering of 3-D objects. The main equations used to fit the data of our system and consequently get further information on the objects in solution are those for lipids embedded in flat membranes or micelles.² The form factor of a completely filled spherical object of radius R like micelles is given by $P_{\text{sphere}}(Q) = 9[(\sin(QR) - QR\cos(QR))/(QR)^3]^2$. For centrosymmetrical objects like spheres, it is often considered that the structure factor $S(Q) \sim 1$ at large Q . Consequently the radius of the micelle can be estimated from the form factor. The line corresponds to the best fit of the data according to a form factor $P(Q)$ of a sphere with a diameter of about 4.4 nm. It confirms the presence of micelles in the lipid dispersion before adding PAG. At intermediate Q around 0.045 \AA^{-1} , there is a broad correlation peak. At low Q , there is a decrease of the scattering when going towards lower Q , showing that the system has a low isothermal compressibility. Such low compressibility, associated with the correlation peak, arises from a structure factor $S(Q)$ associated with a homogeneous dispersion of a repulsive negative system. As they are charged, micelles strongly electrostatically repel each other over large distances.

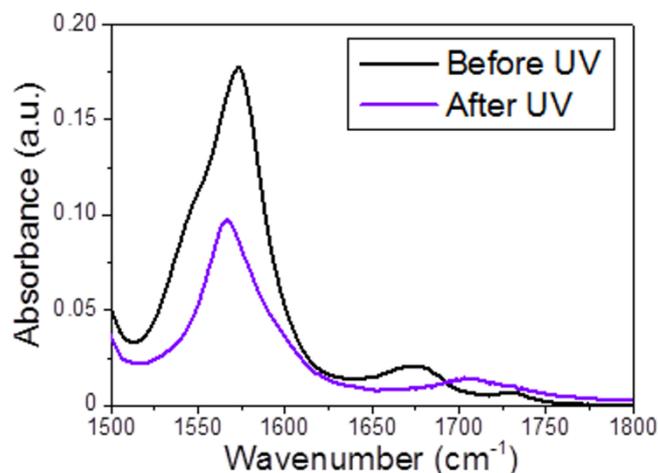


Figure SI.2: FT-IR spectra for the 12-HSA/choline dispersion with PAG before and after 12 hours of UV irradiation at room temperature.

From the FT-IR spectra, we estimated the portions of protonated and deprotonated 12-HSA in the solution after 12 hours of UV irradiation. The proportion of protonated 12-HSA was around 25% and the proportion of deprotonated 12-HSA was around 75% in solution.

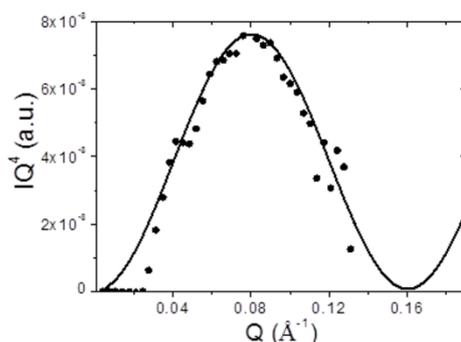


Figure SI.3: SANS intensity profile for the 12-HSA/choline dispersion in the presence of PAG after 12 hours of UV irradiation at 25°C displayed in the Porod representation. The black line corresponds to the best fit of the data according to a previously published model corresponding to the form factor of a flat membrane with a thickness of 4 nm.³

In the case of lamellar structure, the main features of the SANS spectra can be described in terms of the form factor of a randomly oriented planar membrane of well-defined thickness δ namely the function $P_{\text{planar membrane}}(Q) = \sin^2(Q \delta/2)/Q^4$ in order to estimate the value of the membrane thickness δ . The line corresponds to the best fit of the data according to a bilayer form factor model. The fit obtained cannot describe the data in the Q range where the

structure factor effects are important. However this bilayer form factor model has been shown to be useful to describe lamellar systems.⁴

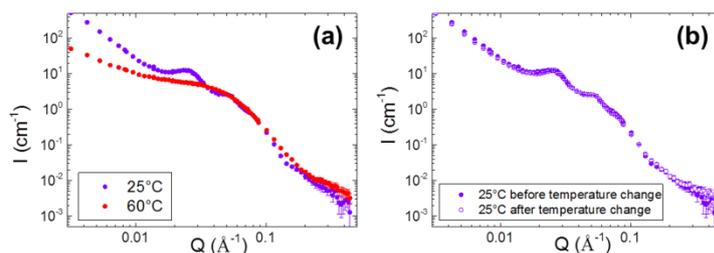


Figure SI.4: (a) SANS intensity profile for the 12-HSA/choline dispersion in the presence of PAG after 12 hours of UV irradiation at 25°C and after increasing the temperature at 60°C. (b) Comparison of the SANS intensity profile for the 12-HSA/choline dispersion in the presence of PAG after 12 hours of UV irradiation at 25°C and after temperature change from 60°C to 25°C.

The SANS spectrum obtained at 60°C (Fig. SI4.a) corresponds to the presence of spherical micelles with a diameter of about 4.8 nm with a polydispersity of 30%.

References

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