Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information : Novel Catanionic Vesicles from Calixarene and Single-Chain Surfactant

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I. Material and Methods

Synthesis of Calixarene: *p*-Sulfonatocalix[4]arene (SC4) was prepared by *ipso*-sulfonation of *p-tert* butylcalixarene in H2SO4 at 80 °C. The pentasodium salt (SC4Na) of SC4 was obtained by neutralization of the acid form of SC4 with Na2CO3 in H2O. Finally, the sodium salt was purified by recrystallization three times from water/methanol mixtures.

Sonication procedure. The vesicles were prepared as follows: a certain amount of p-SC4 and TTABr was dispersed in 40 mL of water at 60 ºC. Then the solution was sonicated using a Branson Sonifier 450 with a probe containing a 13 mm flat tip. The tip was submerged approximately two-thirds of the sample height and the power monitor indicated 20%. After every 5 min of sonication, the sample was left at rest during 2 min. The sonication time was always 30 min in total. Samples were then equilibrated to room temperature and filtered through a 0.45 μm pore size filter in order to eliminate possible titanium particles.

NMR. The ^{1}H NMR spectra in D_2O solution were measured with a Varian Mercury 300 MHz NMR spectrometer.

Zeta-potential measurement. Vesicle electrophoretic mobilities were measured using a Malvern Zetasizer 2000. The ζ-potentials were calculated using the Smoluchowski equation. All samples were filtered prior to the measurement that was performed at 25 °C.

TEM. Vesicles were imaged with a PHILIPS CM-12 transmission electron microscope at 100kV using the negative staining method. A drop of vesicle solution was spread on a 200-mesh copper grid coated with a Formvar film, and the extra droplet was instantly wiped off by filter paper. After being naturally desiccated, a drop of 2% phosphotungstic acid solution was dropped on the copper grid for about 60 s and the

extra droplet was also removed. Then the grid was dried naturally for about 3 h before TEM observation.

Lyophilization. The sample is cooled with liquid nitrogen, causing ice crystals to nucleate and grow. The sublimation of the ice with a TELSTAR lyophilizator yielded a freeze-dried powder.

Light scattering. Light scattering was performed using an ALV SP-86 goniometer, ALV 5000 Multi-tau correlator and a Coherent Sapphire optically pumped semiconductor laser operating at a wavelength of 488 nm and a power of 200 mW. The correlation functions were accumulated for 100 s and analysed using the ALV Correlator Software (ALV-5000/E version 3.0) based on the CONTIN algorithm adapted to the specific correlator noise. Temperature was fixed to 25 ºC. The logarithmically sampled relaxation time spectra (amplitude vs. log(τ)) were obtained from the CONTIN inversion of the normalised correlation functions. Assuming homodyne light beating, the distribution of diffusivities were obtained applying the relation $D = 1 / (q^2 \square$, and transformed using the Stokes-Einstein relation, the electrolyte solvent viscosity η_0 and refractive index n at the actual temperature T in order to yield the hydrodynamic radius $R_H = kTq^2\tau / 6\pi\eta_0$ where k is the Boltzmann constant, $q = (4\pi n/\lambda)\cdot\sin(\theta/2)$ is the scattering vector as a function of wavelength in vacuum, λ, and scattering angle θ. Measurements were performed at angles between 30 and 150º with increments of 15º.

Light Microscopy. An Axioplan Universal light microscope from Carl Zeiss, equipped with differential interference contrast (DIC) lenses and a video-camera system, was used.

II. Dynamic Light Scattering data

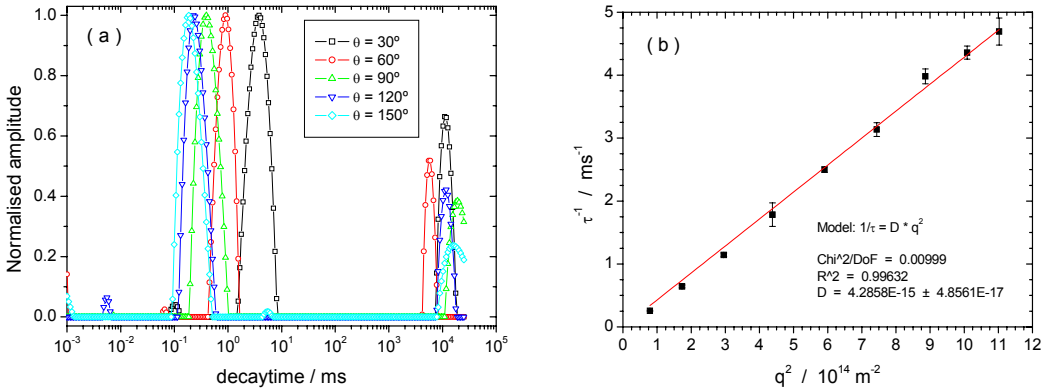

Fig. 1 DLS data of negatively charged catanionic vesicles a few hours after preparation: (a) angular dependence; (b) determination of the diffusion coefficient of the vesicles.

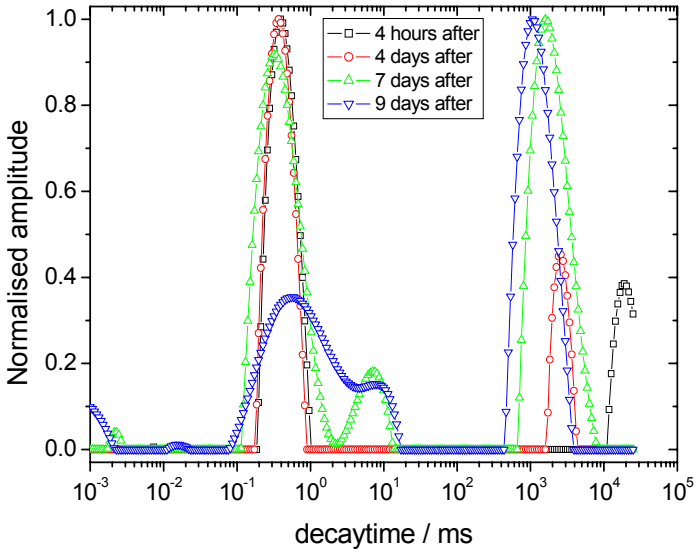

Fig. 2 Time evolution of the DLS for negatively charged vesicles.

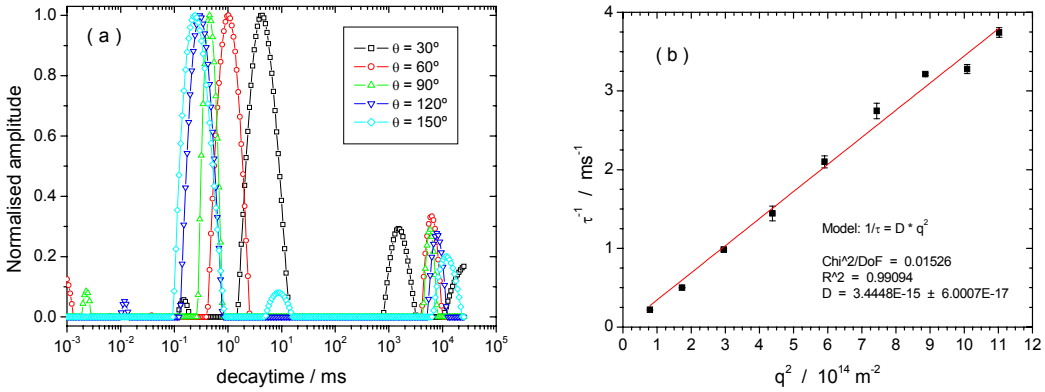

Fig. 3 DLS for negative vesicles after lyophilization, measured 3 days after redispersion: (a) angular dependence; (b) determination of the diffusion coefficient of the vesicles