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Well-defined self-assembling supramolecular structures in water containing a small amount of C_{60}

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In this communication, we report for the first time on the spherical bilayer vesicle formation of a dendritic C_{60}-amphiphile–surfactant hybrid in aqueous solutions.

Amphiphilic fullerene derivatives consisting of polar functions, such as carboxylic acid groups,[1–5] amines and ammonium surfactants,[6–10] and starlike fullerene derivatives like $C_{60}[(CH_2)_nSO_3Na]_6$,[11] have a propensity to aggregate in aqueous solutions. In an effort to preserve as many double bonds as possible and thus retain a high potential for scavenging deleterious radicals in biological systems,[12] a very water-soluble [60]fullerene monoadduct which is a methano[60] fullerene dendrimer with 18 carboxylic acid groups as shown in Fig. 1 was synthesized by Hirsch and coworkers[13] (this molecule will be referred to as DA[2] in the following). This dendritic amphiphilic compound exhibits two important properties investigated.[2,13] One is the solubility of 8.7 mg C_{60} per mL in an aqueous solution buffered to pH = 7.4,[13] another is the fact that it does not form extended aggregates in water. At pH > 5 no aggregation at all is observed. This is in contrast to many other water soluble fullerene derivatives.[2]

In this communication, we report for the first time on the spherical bilayer vesicle formation of DA–surfactant hybrids in aqueous solutions. The aims of these investigations were: a) to modulate the aggregation behavior of DA by interaction with the added single-chain co-surfactant tetradecyltrimethylammonium hydroxide (TTAOH) and to study what type of aggregates (micelles *versus* spherical bilayer vesicles) are formed; b) to modulate the solubility of DA which should be different from that in the aqueous solution buffered to pH = 7.4.[13]

TTAOH stock solution (pH = 12–13) was prepared from tetradecyltrimethylammonium bromide (TTABr, 120 mmol L^{-1}) by strong base anion exchange (Ion exchanger III, Merck) at 40 °C until no bromide ions could be detected upon precipitation with $AgNO_3$ in excess HNO_3. The resulting ion exchange with hydroxide was >99%. The concentration of the resulting clear micellar stock solution of TTAOH was 117.4 mmol L^{-1} as determined by acid–base titration. The critical micelle concentration, cmc, of TTAOH was determined to be 1.8 mmol L^{-1} by using surface tension measurements. DA was synthesized according to the procedure described previously.[13a] The purity estimated by chromatographic and electrophoretic methods was higher than 93%.

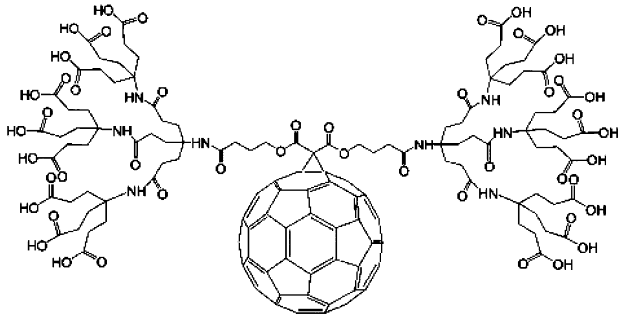

Fig. 1 The structure of the dendritic methano[60]fullerene octadeca-acid (DA).[13]

In order to compare the solubility of DA in TTAOH micellar solution with that in phosphate buffer solution at pH = 7.4, we tested the solubility of DA in 10 mmol L^{-1} TTAOH micellar solution. We found out that under these conditions the solubility of DA increases considerably to at least 275.4 mg mL^{-1}, which corresponds to an equivalent of 70.1 mg of C_{60} per mL water. The clear red solutions of DA prepared in this way were stable for at least two weeks at room temperature (~23 °C).

So far no imaging studies of DA aggregates have been carried out. Here change in supramolecular ordering of TTAOH micelles induced by DA was clearly observed by Freeze–fracture Transmission Electron Microscopy (FF-TEM) and dynamic laser light scattering (DLLS). Two typical FF-TEM micrographs for 2 and 5 mg mL^{-1} DA in 10 mmol L^{-1} TTAOH micellar solutions are shown in Fig. 2, respectively. The features of the vesicular structures in the two samples are apparent. Only perfectly spherical bilayer vesicles throughout the samples can be seen in these two representative images. The dimensions of spherical bilayer vesicle are similar to those of the single-tailed cationic/anionic (catanionic) surfactants[14] and natural lipids such as lecithin.[15] We varied DA concentration from 0.5 to 5.5 mg mL^{-1}; six samples were used to characterize the shape and size of the superstructures. The perfectly spherical bilayer vesicles were observed by FF-TEM in all samples. As a consequence the formation of spherical bilayer vesicles is induced by the DA co-surfactant, whereas under normal conditions TTAOH forms micelles in water. The unilamellar vesicles have diameters ranging from about 30 nm to more than 400 nm. The vesicles completely disperse and do not tend to aggregate with each other. This is in contrast to the supramolecular nanostructures formed by an amphiphilic hexakis-adduct of C_{60} in phosphate buffer (pH = 7.4) where vesicles and smaller cylindrical aggregates of about 5 to 200 nm in length were observed by FF-TEM and Cryo-TEM;[3] no other nanostructures are detected in the DA/TTAOH hybrid aggregates.

DLLS measurements are carried out for a series of samples, which reveal the aggregate formation in the DA–TTAOH hybrids. The sizes of the aggregates with the hydrodynamic radius (R_h) of the particles from the characteristic line width Γ were obtained by the CONTIN analysis method for the DLLS data.[16] The aggregates have the size distribution consisting of two large peaks with average R_h values about 48 nm with a polydispersity of 0.11 at the first peak and the second peak around 310 nm with a polydispersity of 0.12, which could be attributed to the spherical bilayer vesicles with a variety of different sizes but well-defined shape. Fig. 3 shows plots of the relative intensity contribution $\Gamma G(\Gamma)$ as a function of the apparent hydrodynamic radius R_h for 1.5 mg mL^{-1} at scattering angle of 45° and 5.0 mg mL^{-1} at 60 °C in TTAOH micellar solution.

In buffer solutions at pH = 7.4, the electrostatic repulsion between the deprotonated carboxylic acid groups is strong enough to preclude major formation of aggregates and the hydrophilic–hydrophobic interaction plays an important role in the vesicle and smaller cylindrical aggregate formation. However, the current case in the absence of electrostatic repulsion stabilizes the DA–TTAOH hybrid aggregates. Closed spherical bilayer vesicles form spontaneously. The driving force for the self-assembly process in solution could be the hydrophilic–hydrophobic interaction like the behavior of salt-free surfactant solutions[18] but the architecture of the system studied here is significantly different from those of traditional chain-based surfactant systems because their flexible hydrocarbon chains are replaced by the rigid fullerene core.

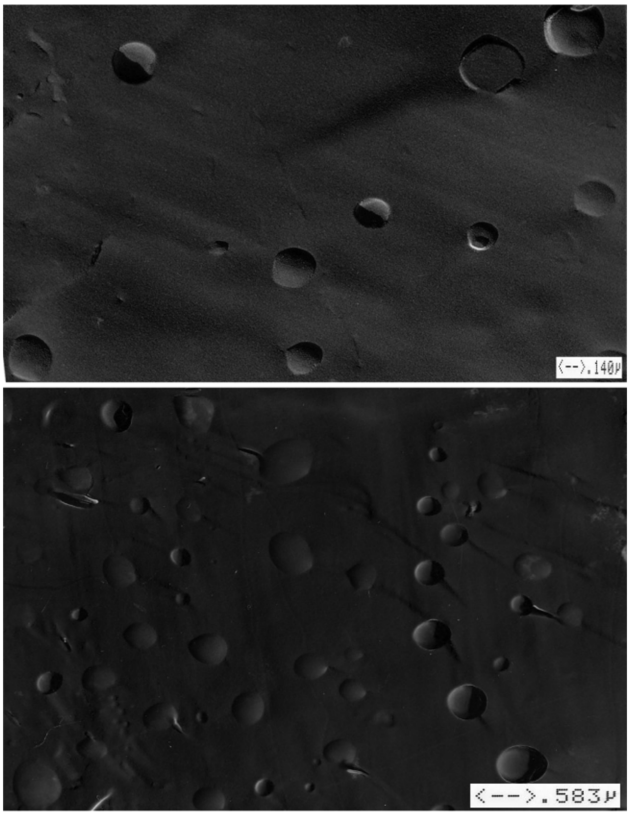

Fig. 2 FF-TEM images of two samples: 2 mg mL^{-1} (top) and 5.0 mg mL^{-1} (below) DA in 10 mmol L^{-1} TTAOH micellar solution. In the top image (the bar represents 0.140 μm), bilayer vesicles with diameters ranging from 30 to 340 nm; in the lower image (the bar represents 0.583 μm), unilamellar vesicles with diameters ranging from 30 to about 480 nm. Freeze from room temperature in liquid propane cooled by liquid N_2; further details are analogous to ref. 17

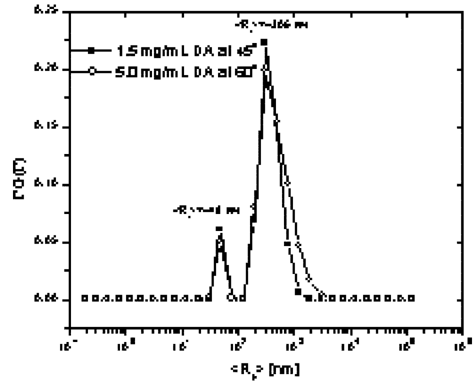

Fig. 3 Apparent hydrodynamic radius distributions of Spherical bilayer vesicles in water. $c_{DA} = 1.5$ mg mL^{-1} and $c_{DA} = 5.0$ mg mL^{-1} in TTAOH micellar solution.

To conclude, the solubility of DA in a micellar solution of TTAOH increases and the supramolecular nanostructure transition was induced by the dendritic C_{60}-amphiphile, whereas TTAOH forms usually micelles in the presence of DA induced assembly of spherical bilayer vesicles. This concept of mixing traditional surfactant aggregates used as a primary framework with C_{60}-amphiphiles to give new altered nanostructures in water could provide a rapid one-step entry to hybrid nanoarchitectures, whose size regimes are inaccessible by traditional methods. Therefore, analogous surfactant self-assembly templating routes may broaden the scope of functionalized fullerenes and attract considerable interest from both structures and applications.

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