Unilamellar composite vesicles and Y-junctions from pristine fullerene C_{60}†

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We report here the first structurally defined aqueous phase nanovesicles and Y-junctions from a pristine C_{60} dispersion at a strictly defined [C_{60}]/[TX-100] concentration ratio, bearing a temporal dependence.

With the discovery of spherical bilayer vesicles from functionalized C_{60}, *i.e.*, from the potassium salt of pentaphenyl fullerene [$Ph_5C_{60}K$], a large number of self-assembled C_{60}-based supramolecules[1] have been reported. Synthesis of specific organized assemblies from C_{60} required complex synthetic modifications of the fullerene cage leading to degradation of the electronic structure and high electron affinity of C_{60}. The high electron accepting characteristics and the rich π electronic cloud concentrated at the cage periphery have enabled fullerene C_{60} to be a potential moiety in non-covalent synthesis.[2] Recently, Pantos and co-workers reported helical nanotubes of C_{60} from non-covalent interactions with naphthalenediimides in chloroform.[3] Nanofibres of fullerenes have been realized from the ball-and-socket interactions with calixarenes by Hubble and Raston.[4] A parallel stream of work to exploit C_{60}'s biological availability resulted in its solubilization in aqueous media. In this respect, water-soluble complexes of pristine C_{60} with β- and γ-cyclodextrins[5] and calixarenes[6] have been cited. Other preliminary studies include encapsulation and solubilization of C_{60} in vesicular and micellar media[7] without any structure details.

In bridging this gap, the present investigation reports the formation of unilamellar vesicles and Y-junctioned networks in an aqueous binary solution of pristine fullerene C_{60} and the non-ionic Triton X-100 surfactant in a confined molar ratio. In the process of direct bilayer formation, π–π and dipole–dipole interactions dictated the formation of vesicular assemblies. Structural evaluation of the vesicles suggested C_{60} to be an integral part of the bilayer architecture. A representative TEM image of the C_{60}:TX-100 system [TX-100 = 30 mM; C_{60} = 0.025 mM] in Fig. 1 shows the spherical vesicles with an average diameter of 110 nm. The dark outer ring as a characteristic of unilamellar vesicles maps well with that expected from a 2D projection of typical vesicular assemblies accounting for 8 nm, the vesicle's bilayer thickness (*cf.* Fig. 1(b)). The particle size distribution from light scattering (DLS) measurements revealed a mean diameter of the vesicles to be ~120 nm, corroborating the TEM data. An equilibration period of ~10 days was necessary for the formation of vesicles. On the other hand, upon DLS analysis, freshly prepared solutions showed signatures of ~70 nm particles. Therefore, we infer that the path to vesicle formation necessitated an equilibration period of ~7–10 days at 27 °C, implying the existence of dynamic phases in the medium.

Triton X-100, as a non-ionic neutral surfactant, predominantly forms micelles at a critical micellar concentration of 0.23 mM. Marsden and McBain reported the formation of periodic lamellar structures, able to diffract X-rays from a benzene–TX-100–water mixture.[8] A micelle-to-vesicle transition was observed in a TX-100–octanol mixture[9] when cetylpyridinium chloride was added. Our experiments strongly suggest that C_{60} plays the part of an aromatic additive to the TX-100 system, resulting in a bilayer-like arrangement.

Solubilization of C_{60} in aqueous TX-100 solution results in its encapsulation in the hydrophobic micellar core. During incubation, structure reorganization occurs resulting in a micelle-to-vesicle transformation. Such phase transformations are feasible with respect to a favorable hydrophilic–hydrophobic balance in

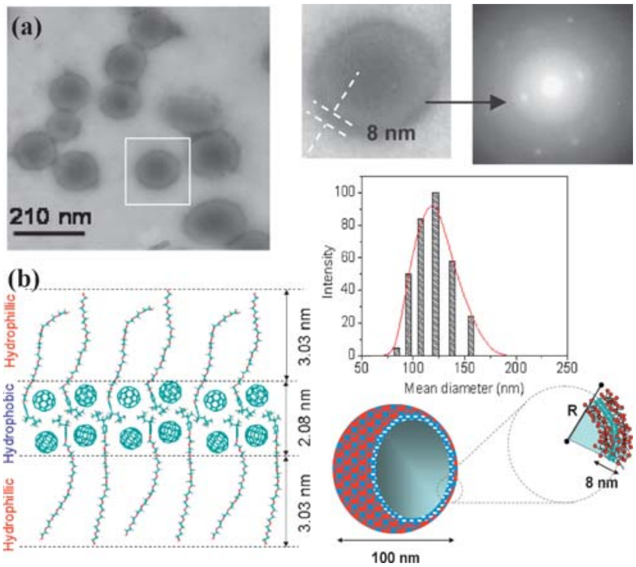

Fig. 1 (a) TEM image of C_{60}:TX-100 vesicles. To the right is shown the SAED pattern and the distribution profile from DLS measurements, evidencing the most probable diameter as 120 nm. (b) Schematic of the proposed vesicle bilayer corresponding to 8 nm.

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conjunction with appropriate dipole–dipole and π–π interactions between the C_{60}–TX-100 as well as between the TX-100 molecules. At a concentration ratio 30 : 0.025 mM of TX-100 : C_{60}, the system reorganized into a bilayer structure with the hydrophobic moieties towards the interior encompassing C_{60}, while the polar polyoxyethylene (POE) chains were exposed to the aqueous environment. The UV-visible absorption of the fresh solutions (see ESI†) revealed C_{60} to exist as monomeric species. After the incubation period the symmetrical stacking of the individual monolayers make up the bilayer wall thickness to be 8 nm, in line with the TEM results. The conceived vesicular microstructure is illustrated schematically in Fig. 1(b). The selected area electron diffraction (SAED) pattern of the vesicular structures, as shown in Fig. 1 clearly evidences the presence of C_{60} in the bilayer region, indexed as a simple cubic lattice (JCPDS 79-1715).

The C_{60} : TX-100 bilayers were simulated using the Hyperchem professional (version 7.5, Hypercube Inc.) program package with geometry optimized structures of TX-100 and C_{60} obtained using the *Gaussian 03* program at the B3LYP/3-21G level. An MM+ force field was used to perform dynamics in the NVE ensemble at constant temperature *in vacuo*. Simulations were carried out for 1 ps on a 1 : 1 C_{60} : TX-100 system and for 2 ps on a 4 : 4 C_{60} : TX-100 bilayer arrangement, with a time step of 1 fs (*cf*. Fig. 2). Associative π–π interactions between the curved π-surface and the flat π-surface of TX-100's phenyl ring were visualized at different simulation times upon approach of the TX-100 molecule towards one of the 6-membered rings of C_{60}. An equilibrium distance of 3.654 Å had the minimum energy configuration (Fig. 2(c)) which complies with the fullerene–aromatic ring interactions and Hunter–Sanders rule.[10] The molecular conformations reveal the phenyl ring of TX-100 to lie above the 5:6 ring fusion. The 5:6 ring fusions represent centers of positive charge on the C_{60} surface and the 6:6 fusions represent the centers of negative charge.[11] Thus, the electrostatic interaction between the electropositive 5:6 fusion and the electronegative aromatic π system is also a dominant interaction in addition to π–π interactions. Simulations done with a single C_{60} : TX-100 couple revealed a geosynchronous satellite-like rotation of C_{60} around TX-100's phenyl ring (*cf*. Fig. 2(a) and (b)). Simulations of a C_{60} : TX-100 bilayer assembly in Fig. 2(d–f) reveal the arrangement to be stable with the above said interactions remaining intact. The predominant mode of interaction therefore was π–π stacking, acting as the driving force for self-assembly towards the formation of unilamellar vesicles.

Optical microscopic investigations of the aged vesicular solutions as a spongy precipitate revealed branched fibrous networks of tubular structures with diameters ranging from 2–2.5 μm with several micrometres length. The networks in Fig. 3(a) resemble typical worm-like (or thread-like) micelles from non-ionic micelles and are found to be associated with end-caps and Y-junctions, similar to topological defects of tubular structures.[12] Fig. 3(c) shows the confocal Raman image of one of the Y-junctions. An intense fluorescence emission around 570 nm, along with weak overlapping emissions at 619, 648, 679 and 717 nm were observed, as shown in Fig. 3(e). The confocal depth scanning of the structures in Fig. 3(d) revealed the presence of hollow channels in the tubes. Pristine fullerene C_{60} has been found to show solvent dependent fluorescence emission characteristics.[13] In the present case, the intense band around 570 nm tallies with the earlier reported values in polar solvents such as DMSO and pyridine.[14] The presence of the 570 nm band suggests that C_{60}, even though it is localized in the non-polar core of the bilayer, experiences a slight polar micro-environment, possibly due to water leakage or because of its proximity to the polar POE

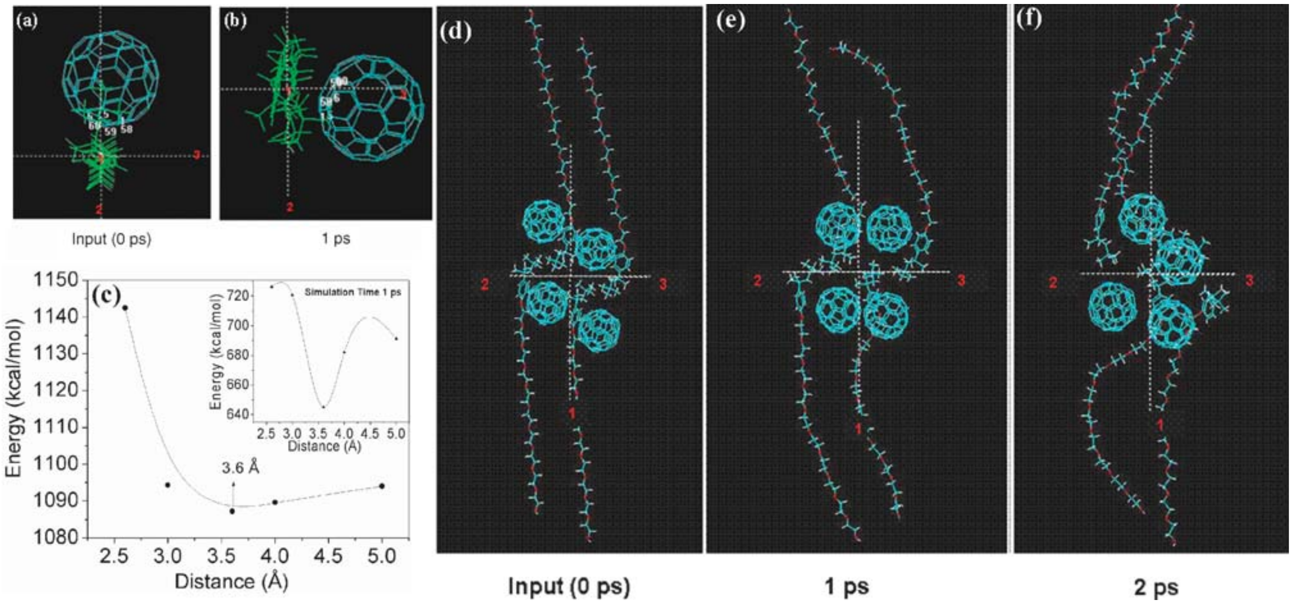

Fig. 2 Snapshots showing typical interactions between fullerene C_{60} and Triton X-100 at various simulation time intervals with a 1 fs time step. (a) and (b) show the satellite-like rotation of C_{60} around TX-100's phenyl ring (the TX-100 molecule is highlighted in green). (c) Shows the total energy *vs*. TX-100–C_{60} distance (between the planar 6-membered rings). (d)–(f) show the bilayers constituted from 4 pairs of TX-100 and C_{60} through hydrophobic interactions. The molecular dimensions were obtained from B3LYP-3-21G optimized structures found using the *Gaussian 03* package.

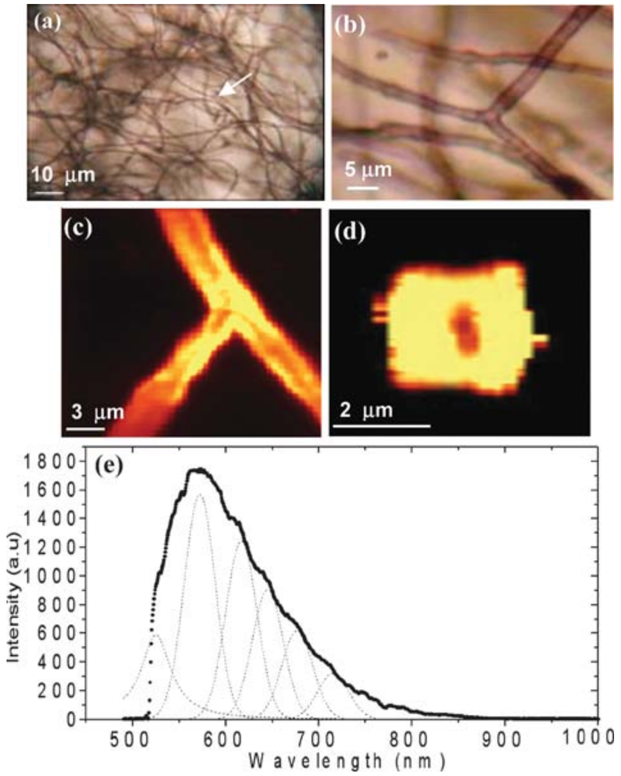

Fig. 3 (a) Optical image of the Y-junctioned network; (b) a single Y-junction; (c) the confocal Raman image of the Y-junction; and (d) the confocal depth scanning image of the tube showing the hollow nature. (e) Fluorescence emission of the tubules at an excitation λ = 514.2 nm.

chains of TX-100. This observation is further corroborated by the hollow nature of the tubes enclosing a channel of water molecules. The dimensions of the tubes were of microns in diameter, suggesting the presence of multi-bilayered walls. Therefore, a fused vesicle mechanism (Scheme S1, ESI†) for the formation of giant tubes[15] with Y-junctions has been proposed. The C_{60} : TX-100 vesicles over a period of time aggregated due to stacking compression and formed multi-bilayers. The bilayer stacks ended up in hollow tubes that progressed in length by the formation of end caps.[16] The optical images of the tubules showed constriction signatures (Fig. 3(b)) along the length of the tube that corroborated the above mechanism (see ESI†).

In conclusion, we have reported the formation of spherical unilamellar vesicles and Y-junctioned networks of hollow tubes in a strictly configured concentration range of the non-ionic TX-100 and pristine C_{60} composite system. The bilayer architecture constituted monomeric C_{60} as an integral part, involved in π–π interaction with the phenyl ring of TX-100 along with electrostatic interactions to induce the self-organization process. The formed vesicles can be used as encapsulants for C_{60} with its anti-oxidant and anti-carcinogenic activity, while the Y-junction hollow tubules can act as microfluidic devices. It is anticipated that self-assembly and fine-tuning of the [C_{60}] to [surfactant] ratio will lead to the construction of a wide range of supramolecular architectures, fostering innovative avenues for the development of biologically inspired materials.

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