

Bilayer vesicles as precursors for spherical fractal aggregates from the self-assembly of a C₆₀-fullerene-dyad in polar solvent

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Spherical fractal aggregates of $\sim 10 \mu\text{m}$ were formed from a π -electronic amphiphile, C₆₀-didodecyloxybenzene dyad when extracted from THF into water, necessitating a critical dielectric constant $\epsilon \geq 30$ in binary THF-water mixtures. Molecular dynamics simulations revealed the unit cluster to such a form involves an aggregation number ~ 90 with predominant soft associative molecular interactions which corroborated the octadecahedral model proposed for the cluster growth. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186992]

Understanding the intermolecular interactions in carbon nanomaterials is an important step towards the rational design of functional nanoscopic architectures.^{1,2} Precise control of the geometry of the self-assembled structures allows a fine-tuning of the functional properties of these materials towards building nanoelectronics.^{3,4} Fullerenes as nanoscopic carbon cages are proposed as promising materials for quantum computing nanodevices.^{5,6} Aggregation of C₆₀ has a geometric possibility of mimicking a dendrimeric type molecular growth to produce 3D spherical clusters through simple hydrophobic interactions.^{7,8} This communication reports the concentration and solvent polarity controlled structure architectures from the self-assembly of a C₆₀-dyad with a necessary hydrophobic-hydrophilic-hydrophobic network, supported by molecular dynamics simulations and a cluster growth model.

The dyad molecule [Fig. 1(a)] was synthesized as a pure [6,6] isomer and was confirmed from HPLC, NMR and other standard techniques. The chemical structure and the *ab initio* geometry optimized (B3LYP/3-21G*) dyad, 1-(3-carboxy)-(3,4-di(dodecyloxy)benzoic acid-4-carboxy phenyl ester) propyl-1-phenyl [6,6]-C₆₀ with hydrophobic-hydrophilic-hydrophobic (C₆₀-bridge-didodecyloxybenzene) network is depicted in Fig. 1. The calculated total dipole moment of the molecule was 8.9 D with the bridge benzene and the donor benzene being planar with respect to each other.

In a concentration range 0.01 to 1 mM, the dyad did not undergo molecular association leading to aggregate formation in neat THF (tetrahydrofuran) solvent. Thus the aggregates were prepared in binary solvents adopting two routes: (i) in THF-Water mixtures in the range 0-90% v/v from a 0.01 mM dyad solution, (ii) by extracting the dyad molecules from THF into water upon continuous stirring and nitrogen purging over a concentration range (0.01–1 mM). The water extracted dyad aggregates remained stable for several weeks.

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Figure 2 shows the UV-Visible spectra of the dyad aggregates in both binary solvent mixtures and water extractions clearly indicating red shifts of the 259, 328, and 431 nm bands along with line broadening and structureless absorption in the visible region. The origin of the structureless increased absorption is attributed to the enhanced vibronic coupling of the closely lying electronic states in the lower energy visible regions, such as at 431 nm.^{9,10} The characteristic absorption features further enabled the determination of the onset of aggregation at a critical dielectric constant of ~ 30 in the binary solvent mixture of THF-Water¹⁵ as depicted in the inset of Fig. 2.

The aggregate structures on a molecular level were examined with transmission electron microscopy (TEM, Philips CM12) and are illustrated in Fig. 3. Aggregation began in

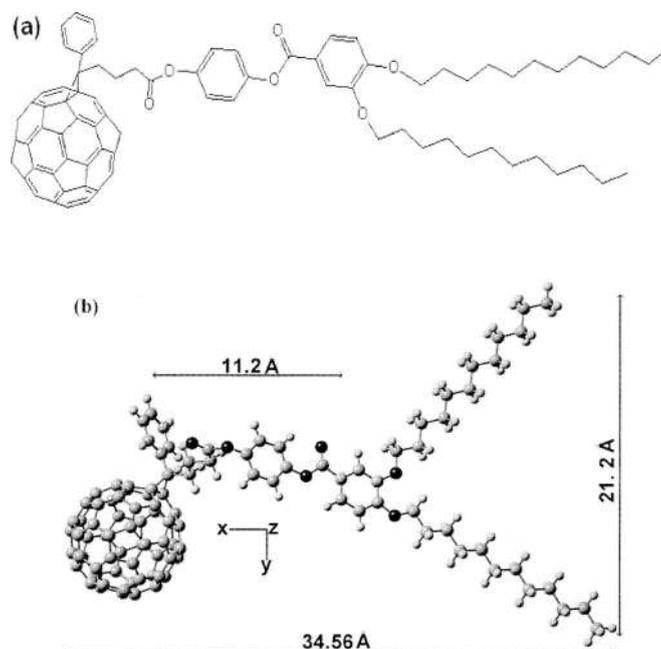


FIG. 1. (a) Chemical structure of the dyad, (b) *ab initio* (B3LYP/3-21G*) geometry optimized structure of the dyad showing the bridge and donor benzene rings to be planar (color codes: dark grey, carbon; light grey, hydrogen; black, oxygen).

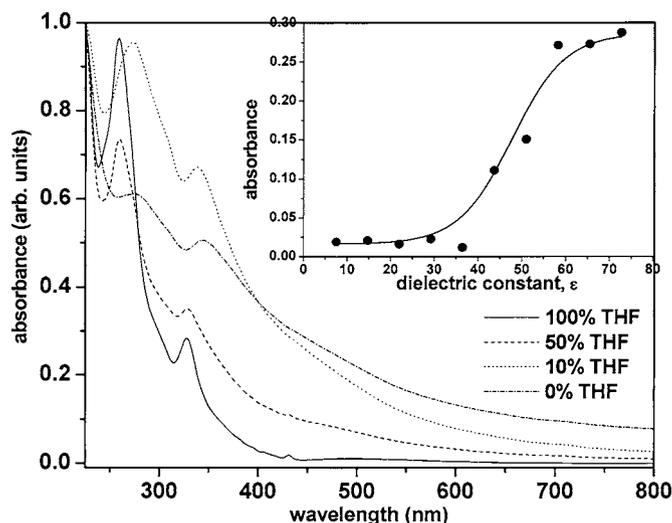


FIG. 2. Electronic absorption spectra of the dyad in binary THF-water mixtures and in water extraction. Inset shows the absorbance vs dielectric constant profile indicating the critical dielectric constant ($\epsilon \geq 30$) for aggregation in THF-Water mixture according to $\epsilon_{mix} = f_A \epsilon_A + f_B \epsilon_B$; f being the volume fraction of THF (A) and water (B), respectively.

60%-40% THF-water solvent with formation of fibers [Fig. 3(a)]. On increasing the water concentration to 50%, spherical bilayer vesicle growth was observed upon immobilizing them on to carbon-coated copper grids. The vesicles are seen with a uniform diameter of ~ 90 nm in Fig. 3(b) and their electron diffraction pattern in Fig. 3(c) reveals them to be crystalline domains, indexed to a simple cubic lattice according to JCPDS File No. 79-1715. A cross-section of the shown open vesicles show two types of domains; (i) the outer thinner core-shell made of hydrophobic alkyl tails and (ii) the thicker central core-shell C_{60} cages with greater aggregation. The alkyl tail parts as a result of desolvation on TEM grids are less visible; nevertheless, the vesicles are mostly bilayers

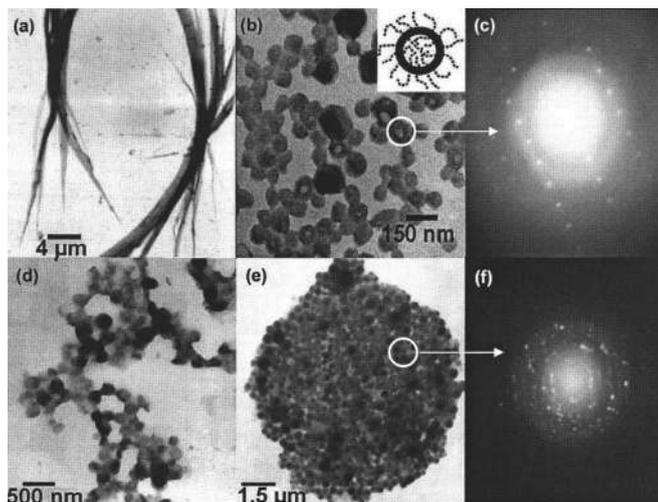


FIG. 3. Transmission electron micrographs of (a) 60%-40% (b) 50%-50% THF-Water mixtures from 0.01 mM dyad solution (c) the diffraction pattern from b; (d) 0.01 mM and (e) 1 mM water extracted fractal aggregates (f) the diffraction pattern from e. Inset in (b) is a structure scheme for the bilayer vesicle.

with a C_{60} head-to-head conformation. The actual form assumed by an aggregate depends on the individual molecular constitution and can be explained by simple geometric considerations. In a first-order approximation, the geometry of a moderately amphiphilic molecule is described by the critical packing parameter ' p ' which is defined as the ratio of the hydrophobic volume (v_s) to the product of the head group area (a) and chain length (l_s) as $p = v_s / a l_s$. The critical packing parameter determines the preferred curvature of the aggregate formed.^{11,12} Thus, with a packing parameter of ~ 0.52 obtained from the molecular modeling, the dyad forms a truncated cone-shaped geometric packing favoring the formation of bilayer vesicles. Further these bilayer

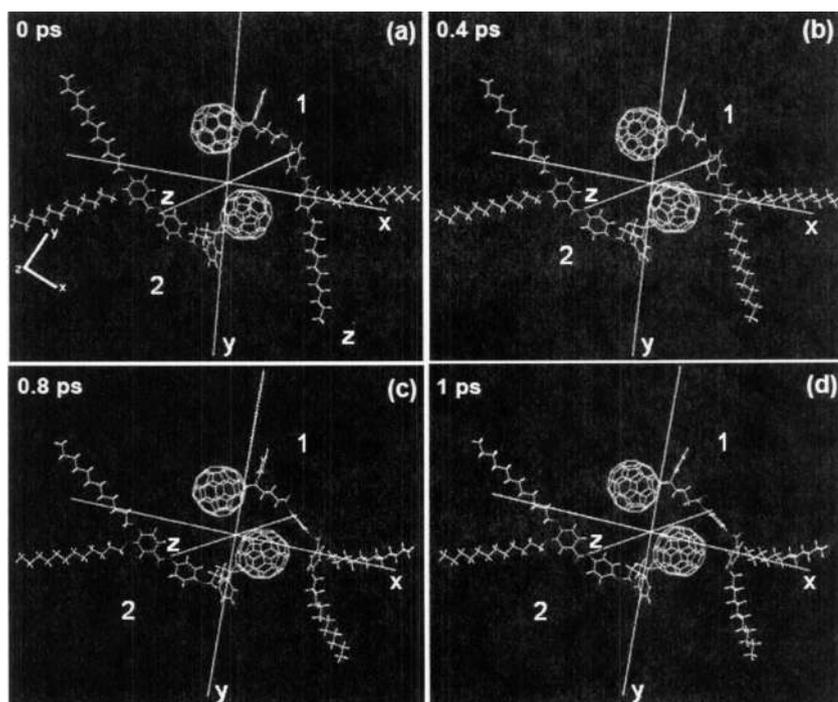
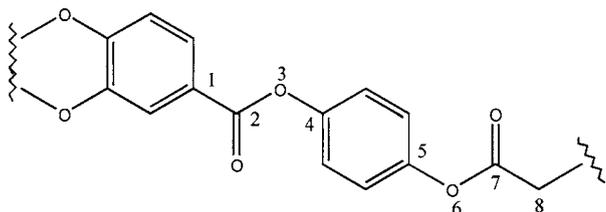


FIG. 4. Snapshots focusing on typical interactions between a two-dyad molecule system at (a) 0 ps, (b) 0.4 ps, (c) 0.8 ps, and (d) 1 ps.

TABLE I. Molecular parameters for the incoming dyad molecule at 0 and 1 ps simulation times with a part of dyad skeleton labeled for clarity.

Parameter	Atoms	0 ps	1 ps
Distance between C ₆₀ of molecule 1 and bridge benzene of molecule 2	C-C	5 Å	3.6 Å
Dihedral angle	C8-C7-O6-C5	0.5°	122.4°
	C4-O3-C2-C1	176.3°	-116.5°
Angle	C4-O3-C2	125.3°	119.1°
	C5-O6-C7	121.9°	128.8°



vesicles being irreversible, serve as precursors towards the formation of spherical dyad aggregates in highly polar conditions.

Following the above mentioned procedure, the water extracted dyad aggregates show well defined spherical clusters of diameter 120 nm as in Fig. 3(d). A ten fold increase in concentration resulted in the formation of giant fractal aggregates of micron size [cf. Fig. 3(e)]. A set of points is a fractal, if it exhibits self-similarity over all scales. Adopting to the Hausdorff box-counting method, the fractal structure in Fig. 3(e) was analyzed. A fractal dimension of 1.85 led to a deduction of the aggregation mechanism to be diffusion limited

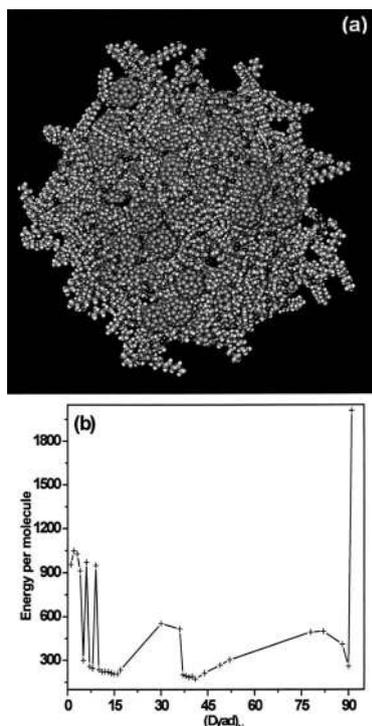


FIG. 5. (a) Space filling model of 90 molecule dyad cluster tending towards a spherical geometry. (b) Calculated energy (normalized to one molecule) of dyad clusters.

with a diffusion coefficient $\sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ as against $\sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for pristine C₆₀ aggregates.^{13,14} The water extracted aggregate structure and dynamics were further investigated by dynamic light scattering experiments, which indicated the molecules to undergo a stretched exponential decay with time¹⁵ and their sizes increased from 110 to 250 nm with increasing dyad concentration, complimenting the geometry and size obtained from TEM.

Theoretical calculations to deduce the structure of such water extracted dyad aggregates have been performed only on pristine C₆₀ in literature,^{16,17} where the smallest unit cluster was found to be (C₆₀)₁₃. Hence, a molecular dynamics simulation was performed to provide an insight into the molecular interactions leading to a definite aggregate geometry and size upon self-assembly. Simulations were performed using *Hyperchem's* (Hypercube Inc.) force field with Lennard-Jones interactions of the dyad atoms. The dyad structure was fully optimized using GAUSSIAN 03¹⁸ program at B3LYP/3-21G* level of theory. Molecular mechanics, using MM⁺ force field was used to perform dynamics calculations in the NVE ensemble at constant temperature in vacuo. Simulations were carried out over 1 ps with a time step of 1 fs. Associative molecular interactions focusing on the van der Waals, π -stacking and electrostatic interactions, etc., were visualized at different simulation times upon approach of the second dyad molecule along the z -axis towards the first with a distance of 5 Å. This distance was used considering a nearest neighbor distance of ~ 1 nm adopted by a C₆₀ cubic lattice in the first coordination sphere. Polarization contribution from water was neglected owing to the fact that the dipole moment of the solvent water did not contribute to the dyad monomer's solubility in it. Further, columbic interactions in water bound system are exaggerated due to an insufficient screening by the SPC (single point charge) of the water molecule.¹⁹ Figures 4(a)–4(c) illustrate the snapshots of spatial orientations of the two-molecule system at different simulation times. The π - π interaction between the C₆₀ and the bridge benzene became predominant with negligible C₆₀-C₆₀ van der Waals interactions at 0.4 ps [cf. Fig. 4(b)]. The resultant structure in Fig. 4(d) at 1 ps deviates drastically from its monomeric planar configuration between the bridge and the donor benzenes. Table I shows the change in molecular parameters with the approach of the second molecule clearly indicating the molecular interactions. However, with increasing number of dyad molecules tending to clus-

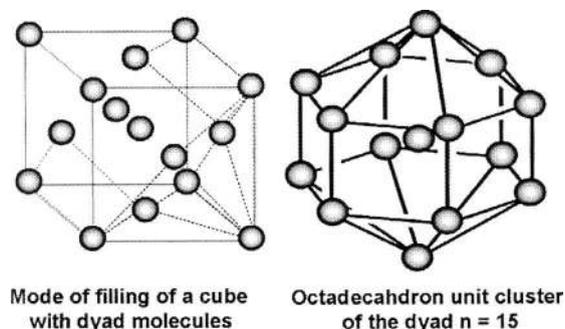


FIG. 6. The octadecahedral unit cluster of the dyad resulting from a specific arrangement of dyad molecules in a cube.

TABLE II. A comparison of the aggregation numbers obtained from our proposed octadecahedral model and molecular dynamics calculations.

No. of octadecahedra stacked (N)	No. of dyad molecules in aggregate according to proposed model	No. of dyad molecules in the energy minimized clusters
1	15	15
2	25	25
3	35	36
4	42,45	41
5	52,55	52
6	59, 62, 65	65
7	69, 72, 75	72
8	76, 79, 82, 85	78
9	83, 86, 89, 92, 95	90

terize, the hydrophobic C_{60} - C_{60} and C_{60} -(CH_2)-chain interactions become prevalent. The computed energies of the clusters normalized per molecule in Fig. 5(b) signify lowest energy configurations for aggregation numbers 15, 41, and 90; the latter tending towards a spherical cluster as shown in Fig. 5(a).

Considering a unit cluster (N) of the dyad aggregate with an aggregation number, $n=15$ obtained with minimum energy from the molecular dynamics simulations, an octadecahedral model is proposed for the growth of the dyad clusters. In this model, a cube was arranged with dyad molecules at its corners, face centers and at the body center resulting in an octadecahedron with (dyad) $_{15}$ unit as shown in Fig. 6. Using a Young's diagramlike approach,²⁰ an array of these octadecahedra is stacked in various permutations from which increasing N in a periodic fashion gives different cluster numbers as listed in Table II. The combinations match very well with the aggregation numbers obtained from the molecular dynamics calculations.

The redox behavior of the water extracted aggregates spin coated on indium-tin oxide (ITO) electrode of 0.5 cm² surface area is shown in Fig. 7. Although, fullerene derivatives dissolved in organic solutions form multiply charged

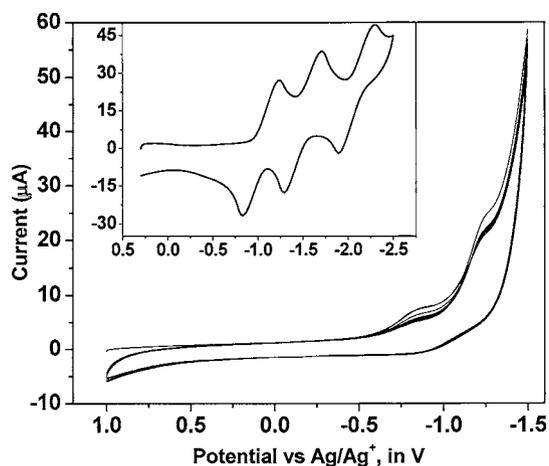


FIG. 7. Electrochemical behavior of the spin cast film of the 0.01 mM water extracted dyad aggregate on ITO electrode in acetonitrile. CE, Pt; RE, Ag/Ag⁺; SE, tetrabutylammonium hexafluorophosphate (0.1 M). Inset shows the reversible waves of the C₆₁-acceptor on GC electrode.

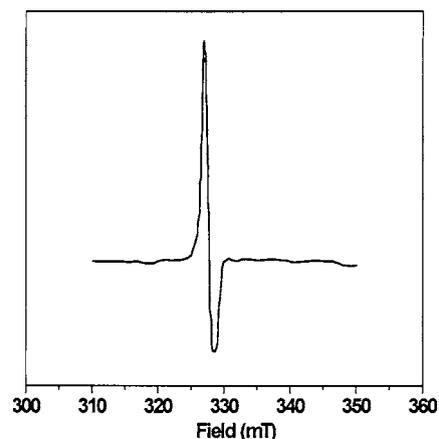


FIG. 8. EPR signature of the radical anion (C_{61}^{1-}) of the spin cast film of the 0.01 mM water extracted dyad aggregate on ITO electrode obtained by electroreduction.

anions upon reduction, the electrochemistry of their films are rather complicated.^{21,22} With tetrabutylammonium hexafluorophosphate as the supporting electrolyte, the electrode exhibited redox responses that could be attributed to the generation of monoanion C_{60}^{1-} and the dianion C_{60}^{2-} . The potential cycling caused the irreversible appearance of C_{60}^{1-} and C_{60}^{2-} ions within the potential window of ITO electrode at half-wave potentials -0.83 and -1.19 V, anodically shifted with respect to the acceptor at -1.03 and -1.48 V. Literature reports on the redox properties of aggregates of C_{60} and its derivatives are scarce. However, cyclic voltammetric behavior of a supramolecular host-guest complex, C_{60}/γ -CD in water showed one-electron reduction waves corresponding to -0.62 and -1.03 V with the second reduction being irreversible.^{23,24} The dyad clusters in the present study thus exhibit a good charge transport medium with a probable rectifying nature. In corroboration with these results, the EPR spectrum in Fig. 8 confirmed the presence of C_{60}^{1-} radical anion at $g=1.986$ with a line width of 0.5 mT.

In conclusion, we have demonstrated that solvent polarity, molecular density and the method of preparation strictly govern the aggregate geometry and size, resulting in bilayer spherical nano-vesicles as precursors for the spherical clusters in a complete water extracted phase. Molecular dynamics simulations revealed such spherical clusters with aggregation number ~ 90 to have been formed predominantly from non-covalent interactions. Accordingly, an octadecahedral model was proposed for the dyad cluster growth. Following diffusion limited growth; the giant fractal aggregates with a fractal dimension 1.85 resulted from spherical clusters with a translational diffusion coefficient of $\sim 10^{-8}$ cm² s⁻¹. The above results thus represent a holistic approach towards establishing the structure and size, the dynamics and a probable potential application of the aggregates obtained from a suitable design of a donor-bridge-acceptor based fullerene- C_{60} -didodecyloxybenzene dyad.

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