



BIPHASIC NANOCABLES FROM AN ORGANOFULLERENE DERIVATIVE AT AIR-WATER INTERFACE

S. Shankara Gayathri and Archita Patnaik

*Department of Chemistry
Indian Institute of Technology-Madras, Chennai 600 036*

ABSTRACT

A fullerene derivative with Donor – Bridge – Acceptor structure has been designed and synthesized. The redox active chromophore in the adduct showed increased absorption relative to pristine C₆₀ and the HOMO – LUMO gap was experimentally found to be 1.7 eV, as against a gap maximum of 1.8 eV for the pristine C₆₀. The transmission electron microscopic images of the 2-D surface structure of the spread monolayers on carbon coated copper grids revealed the formation of uniform diameter (~ 200 nm) biphasic nanocables with distinct ridges comprising of fullerene molecules, which further self-organized into a vesicular nanowire assembly.

1. INTRODUCTION:

Self assembly at different length scales offers rich possibility to construct nano-structured materials. During the past decade there has been a large interest in the properties of supramolecular assemblies, prepared on planar substrata according to the Langmuir-Blodgett technique. The high local concentration of the chromophores in those assemblies promotes molecular aggregation and inter- and intralayer electron and energy transfer¹. Numerous efforts have been devoted to the elaboration of well ordered thin films containing C₆₀, in particular using Langmuir-Blodgett techniques²⁻⁵. These studies have revealed that these compounds, due to their strong hydrophobic character exhibit a strong tendency to form three dimensional aggregates at gas-water interface. One of the strategies to avoid such aggregation is to functionalize C₆₀ with polar groups to obtain amphiphilic derivatives^{6,7}.

Here we report interfacial properties and the surface film structure of a methanofullerene derivative with Donor – Bridge – Acceptor (dyad) structure by measuring its pressure-area isotherms. Strong evidence towards self organization of the surface network leading to aggregate formation at the air-water interface were obtained from the prominent red shifts in the UV absorption features. The transmission electron microscopic images of the transferred films further allowed us reach a better understanding of the formed biphasic microcables and nanosized vesicles based upon a molecular skeleton with a balance between the hydrophobic and hydrophilic moieties. Thus by changing / controlling the surface molecular density, the microstructure of the assemblies could be controlled.

2. EXPERIMENTAL

The dyad was synthesized according to the procedure reported elsewhere⁸. The purity of the dyad was determined by ¹H, ¹³C NMR and by elemental analysis.

The pressure-area (π - A) isotherms were recorded using a commercial Teflon trough (772.5 cm² KSV 5000, Standard trough). The ultrapure water with resistivity 18 M Ω cm Millipore MilliQ system and used as subphase. The Carbon disulphide (99+%, Aldrich Chemical Co. Inc, USA) was used as a spreading solvent for the film preparation. 1 x 10⁻³ M, and 0.1 x 10⁻³ M solutions of dyad were used for acquiring pure monolayers. The π - A isotherms were recorded

at 25 °C after 100 μ L of the appropriate solutions uniformly spread over the water subphase. The compression speed was 10 mm/min. The surface pressure was recorded by a Pt-Wilhelmy balance with an accuracy ± 0.05 mN/m.

The Langmuir films of the dyad were deposited onto Carbon coated Copper grids (EMS, Washington, PA) and Quartz substrates by vertical dipping method. The quartz plates used were cleaned by acetone, chloroform, Millipore water, followed by a pretreatment with “piranha” solution. The deposition pressures were 10 mN/m and 40 mN/m for 1×10^{-3} M solution and 8 mN/m for 0.1×10^{-3} M solution.

Electronic absorption spectra were recorded on a Cary 5E double beam spectrophotometer.

Transmission electron microscopic (TEM) measurements were performed using a Philips CM12 transmission electron microscope, equipped with 100 kV electron gun.

3. RESULTS AND DISCUSSION:

3.1. Electronic Structure of the Dyad:

The geometry optimized structure of the dyad is shown in figure 1, which was optimized using the G98W program¹⁰ employing the Becke's three parameter exchange functional¹¹ combined with the Lee, Yang, and Parr's correlation function (B3LYP)¹¹. Molecular geometry optimization was done at the density functional level of electronic structure theory using 3-21G basis set. The frontier HOMO and LUMO for the dyad showed that the majority of the electron distribution of HOMO was found to be located on the oxygens of the donor moiety. On the other hand, the majority of the electron distribution of the LUMO was located on the C₆₀ spheroid. This observation suggests the existence of charge transfer transition from the donor entity to the C₆₀ entity. The orbital energies along with the HOMO-LUMO gap (gas phase) of the dyad and PCBM ([6,6]-phenyl-C₆₁-butyric acid-methyl ester, a model compound) are shown in figure 2.

Absorption spectra of the dyad showed a characteristic feature at 431 nm, observably red shifted from that in pristine C₆₀. Further, appearance of the 697 nm feature indicated the characteristic of [6,6]-closed C₆₀ mono-adducts⁹. The band gap estimated from the electronic absorption spectra as 1.7 eV was comparable / less than the pristine C₆₀ (1.8 eV) implying the dyad to be a good electron transport medium with distinct redox active nature.

3.3. Langmuir and Langmuir-Blodgett film studies:

Figure 3 shows the π - A isotherm of the dyad at two different concentrations recorded at 25 °C. The isotherms show two distinct regions for 1×10^{-3} M concentration withstanding a surface pressure of 60 mN/m. On dilution to ten times, the isotherm shows a single phase withstanding a pressure of 12 mN/m. The limiting area per molecule A₀ (obtained by extrapolating the linear portion of the isotherm to zero pressure) for both the concentrations correspond to 106 Å²/molecule which is in agreement with the theoretically predicted area of C₆₀, i.e. 90 Å²/molecule¹³ indicating the formation of a true monolayer. This monolayer, however, underwent reorganization upon further compression (in the case of 1×10^{-3} M concentration). As seen in the figure 3 the isotherm follows a steeper trajectory resulting in a molecular area of 62 Å²/molecule, indicative of the formation of multilayer / aggregates at the air – water interface, further confirmed from the UV-Visible features in the transferred film (figure 4). The spectrum exhibits absorption bands at 221, 269 and 336 nm, red shifted compared to those in bulk solution (219, 259 and 328 nm) of the dyad. Pure C₆₀ shows a characteristic 450 nm band indicative of its aggregates¹⁴. However, in the present experiments, the dyad film structure

transferred at 10 mN/m shows a structureless spectrum with appreciable absorption implying the presence of aggregates probably due to the lack real amphiphilic character on account of a less polar alkoxy and ester functionalities.

3.4. Transmission Electron Microscope studies:

Figure 5 shows the TEM of the dyad transferred at 10 mN/m, indicating the closed bilayer vesicles formed from the self-organized hydrophobic – hydrophilic – hydrophobic dyad network culminating in biphasic cables. These biphasic nanocables are found to be of uniform diameter (~ 200 nm) with distinct ridges comprising of fullerene molecules (figure 5a) and each subunit of the cable has a ~ 36 nm diameter C_{60} peripheral amorphous layer connected through van der Waal's interaction. As seen from the figure 5b, the bilayer structure further self-organizes into a vesicular nanowire assembly.

The electron diffraction pattern of the above molecular organization showed d-spacings of 3.2 and 2.03 Å respectively for (331) and (444) reflections from a cubic lattice of C_{60} -dyad with the lattice parameter $a = 14.04$ Å. However, the dyad molecules transferred at a surface pressure of 40 mN/m formed intertwined nanowires / flat plates / sheets due to the resistance of curvature in the condensed phase at larger molecular density. The minor existence of the bilayer vesicles at this pressure further indicated the presence of a liquid condensed phase along with the solid phase with long range order. Thus by changing the surface molecular density, the importance of aggregation could be visualized in controlling the microstructure, mostly through weak intermolecular hydrophobic- hydrophobic interactions.

4. CONCLUSIONS:

The dyad molecule shows a considerable decrease in the band gap with existence of charge transfer transition from the donor entity to the C_{60} entity as shown from the ab initio calculations and UV-Vis studies. The pressure-area isotherms at air-water interface reveal the formation of spatially oriented aggregates. When analysed by TEM, the latter revealed the formation of C_{60} -bilayer vesicles at lower surface molecular density which transformed into intertwined nanowires at higher surface densities. Such materials with directed structure in constricted dimensions could be ideal medium for directional electron transport through single molecular skeleton.

5. REFERENCES:

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FIGURES

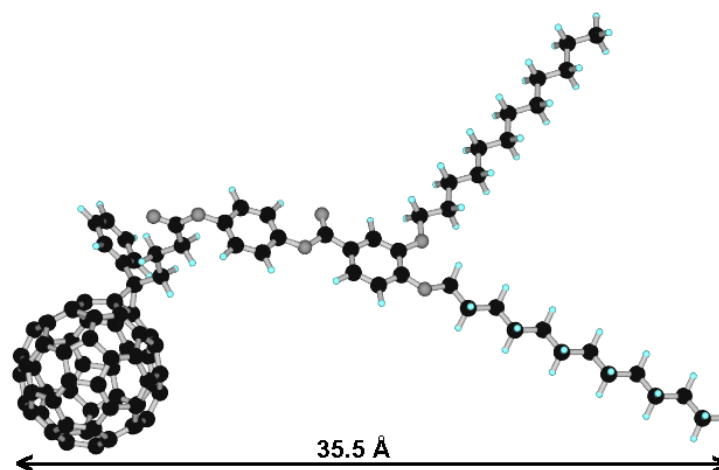


Figure 1. Energy minimized / geometry optimized (B3LYP/3-21G) structure of the Donor-Bridge-Acceptor dyad. (Atom color code: Black = Carbon, Grey = Oxygen, Blue = Hydrogen)

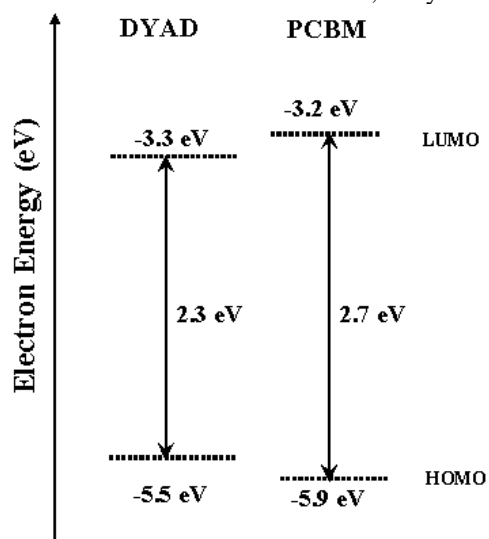


Figure 2. Orbital energies and the HOMO-LUMO gap (gas phase) of the dyad and the PCBM (acceptor, model compound), calculated with B3LYP/3-21G.

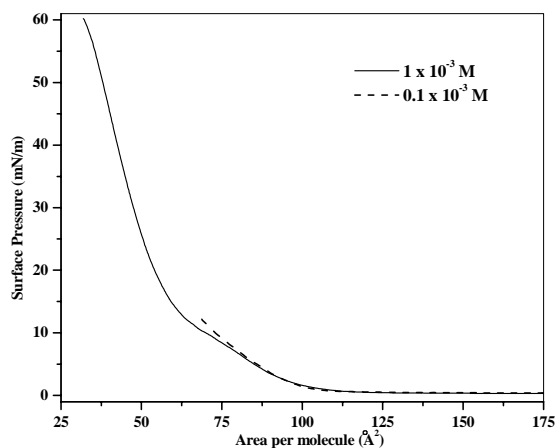


Figure 3. π - A isotherms of the dyad at two different concentrations at the air-water interface at 298 K.

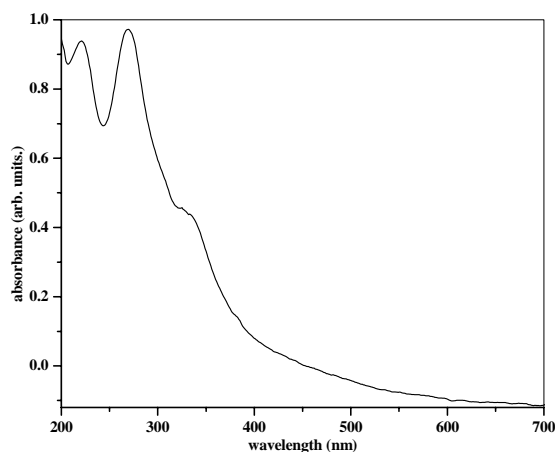


Figure 4. UV-Visible spectrum of the monolayer transferred film of the dyad at 10 mN/m by vertical dipping method.

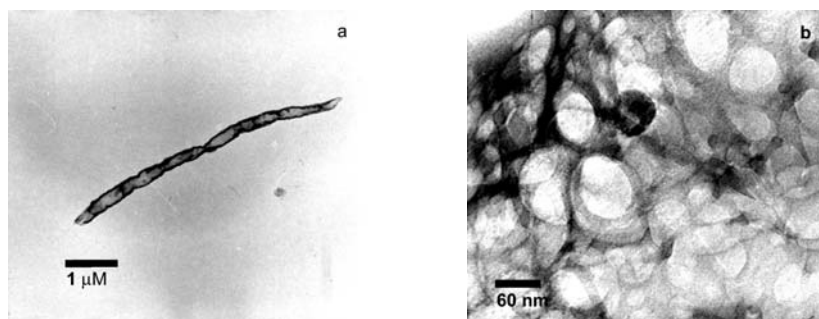


Figure 5. TEM image of the transferred films of the dyad at a surface pressure of 10 mN/m showing a) biphasic cables b) nanovesicular network.