Ordering Fullerene Materials at Nanometer Dimensions

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ABSTRACT

The combination of the hydrophobic fullerene core with hydrophilic functional groups of both ionic and nonionic nature produces organized structures with sizes that range from nanometer to micrometer length scales. The driving force toward this spontaneous organization is the amphiphilic character of the fullerene derivatives. To control both shape and size of the supramolecular assemblies and ultimately their function, important parameters that must be tuned are (i) the balance between the hydrophobic and the hydrophilic moieties, (ii) the effect of the environment, typically provided by simple solvents, (iii) the interface on which the aggregation occurs or, more precisely, surface templating effects, and (iv) the solvation process.

In recent years one-, two-, and three-dimensional assemblies the order and organization of which follow supramolecular principles have assumed remarkable importance. The goal to achieve is to control both the organization of the assemblies and their physical and chemical properties through simple external parameters or variables with the intent of creating new tailored materials.[1] Among the tools exploitable for the creation of new assemblies are hydrophilic and hydrophobic forces.

Nature has long used these interactions to create a formidable array of structures that range from micelles of various shapes to vesicles and bilayers. Apart from the effect of the size of the forces, the formation of one particular spatial arrangement over another is governed by molecular geometrical features, as in the case of phospholipids.[2]

C_{60} is a strongly hydrophobic and bulky compound with a perfect icosahedral symmetry. It remains deeply fascinating for chemists who have developed numerous ways to use it as a building block for the construction of architectures of high complexity (i.e., core–shell structures, dendrimers, liquid crystals, etc.).[3]

This all-carbon cage is virtually insoluble in polar media (and has an equally strong and evident penchant toward solvents able to establish interactions with its π-electron system). The versatile methodologies to functionalize the fullerene core and the protocols to attach a wide range of polar/hydrophilic groups to the cage have led to improved fullerene solubility in polar media and even to fullerene dispersibility in water. The polar/hydrophilic functionalities have also become a critical element to promote and modulate supramolecular aggregation, a process where factors such as growth, arrangement, and dimensions are being regulated. This aspect seems crucial in the light of engineering extended one-, two-, and three-dimensional ensembles at the molecular level.

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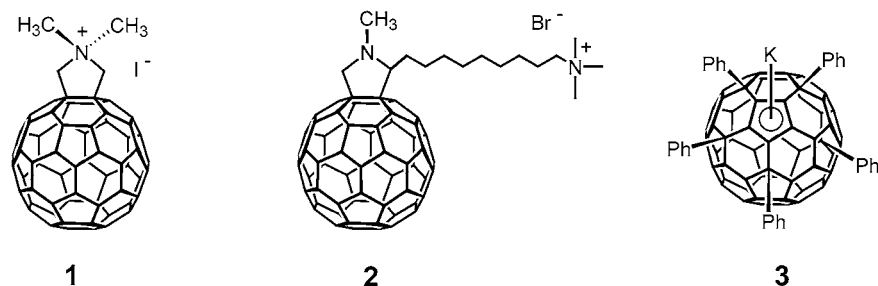⊥ E-mail: Francesco.zerbetto@unibo.it.
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Dirk M. Guldi graduated from the University of Cologne (Germany) in 1988, from where he received his Ph.D. in 1990. In 1992, after a postdoctoral appointment at the National Institute of Standards and Technology, he took a research position at the Hahn-Meitner-Institute, Berlin. After a brief stay as a Feodor-Lynen Stipend (Alexander von Humboldt Foundation) at Syracuse University, he joined in 1995 the faculty of the Notre Dame Radiation Laboratory where he was promoted to Associate Scientist in 1996. In 1999, he completed his Habilitation at the University of Leipzig (Germany). Since 2004, he has been Professor of Physical Chemistry at the Friedrich-Alexander University in Erlangen (Germany). He was awarded with the Heisenberg-Prize (1999; Deutsche Forschungsgemeinschaft), Grammaticakis-Neumann-Prize (2000; Swiss Society for Photochemistry and Photophysics), JSPS Fellowship (2003; The Japan Society for the Promotion of Science) and JPP-Award (2004; Society of Porphyrins and Phthalocyanines). His primary research interests are in the areas of new multifunctional carbon-based nanostructures within the context of light-induced charge separation and solar-energy conversion.

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Scheme 1

1   **2**   **3**

In this Account, we discuss the concepts the exploitation of which results in the ordered association of fullerene derivatives. The main scope is to describe the preparation and characterization of spheres, vesicles, needles, rods, and tubules of nanometer dimensions the molecular building blocks of which are ionic fullerene derivatives. The focus is on phenomena that determine the shape of the final ensemble and take place in solution, on surfaces, and in general at interfaces.

Solution

Solid samples of functionalized fullerene can be directly introduced into aqueous media. The individual molecules extracted from amorphous solids diffuse into the liquid phase. Dipolar interactions between the ionic moiety and water molecules are responsible for the solvation process, which is usually further increased by ultrasonic treatment. For pristine fullerenes, the lack of dipolar interactions completely prevents dissolution.

Solvent variations promote the self-assembly—into either nanorods or vesicles—of fullerenes functionalized with an ionic group. Transmission electron microscopy (TEM) was used for the characterization and the morphological study of the nanostructures. Nanorods were detected in benzene solution when $C_{60}-N,N$-dimethylpyrrolidinium iodide (compound **1**, Scheme 1) was dissolved in a biphasic mixture of dimethyl sulfoxide (DMSO), water, and benzene.[4] The dimensions of the nanorods ranged between 14 and 120 nm in diameter and were over 70 nm in length. Instead, vesicles formed when the same fullerene salt was dispersed in water with the help of sonication.

TEM analysis of an aqueous solution of a fullerene derivative with a structure similar to **1** but bearing a long alkyl side chain on the pyrrolidine ring (compound **2**, Scheme 1) revealed the formation of long fiberlike nanostructures with a diameter less than 20 nm.[5] Interestingly, the electrochemistry of **2** in aqueous solutions was found to differ from that of the same compound in a film, in agreement with what one would expect on the basis of a different degree of association.

Using laser light scattering, Chu, Nakamura, and colleagues investigated the behavior of the potassium salt of pentaphenyl fullerene anion in water (compound **3**, Scheme 1). Pentaphenyl fullerene anions organize into bilayers that form stable spherical vesicles, the average hydrodynamic radius of which was estimated to be ~17 nm.[6] The authors found that vesicle formation did not depend on the concentration and occurred even in a very dilute solution (10^{-7} M). This is similar to what happens for phospholipids where the phenomenon has long been understood and is by-and-large governed by geometrical parameters such as molecular volumes and solvent-exposed areas.[2] Of course, the ratios of volumes and exposed surface areas of the hydrophobic and hydrophilic parts of fullerene derivatives are remarkably different from those of phospholipids (see below).

The data available to date reveal that fullerene amphiphiles tend to aggregate either into spherical or into linear (nano)structures. Inspection of the morphologies obtained in water suggests that short organic side chains favor spherical structures, while long chains favor linear formations. The solvent, however, does play a role, a lower polarity favoring linear aggregates.

This notion was further confirmed through the investigation of the supramolecular behavior in aqueous media of three fullerene derivatives. In derivative **4** (Scheme 2), the fullerene core carries a short organic side chain that is terminated by an ionic ammonium group. After solubilization assisted by ultrasonication, **4** forms exclusively spherical nanostructures with an average diameter of 800 nm (Figure 1).[7]

In derivatives **5** and **6**, the fullerene core carries a long side chain. Compound **6** has a second charge located on the nitrogen atom of the pyrrolidine ring, which was introduced to enhance its hydrophilicity and therefore its solubility in water. Differently from **3**, these two systems form rodlike supramolecular nanostructures. The nanorods are several micrometers long, have a diameter of about 4 nm, and form uniform bundles (see Figure 1). These observations corroborate the hypothesis that the size of the functional group attached to C_{60} determines the shape of the final aggregate.

Although, in principle, solubility could be an important factor for the self-assembly geometry, there is no evidence in this direction. In fact, **3** is relatively soluble in water, while **4** is almost insoluble, and yet they aggregate in similar ways.

The solvent, however, may affect the position and the folding of the side chain and effectively make the distance between its tail end and the fullerene core shorter. As in the case reported by Tour and co-workers for short chain compounds,[4] solvent polarity could turn the aggregation of derivatives with long chains from nanorods to vescicles.

All the molecules discussed above have two elements of ordering, the hydrophobic fullerene cage and the

Scheme 2
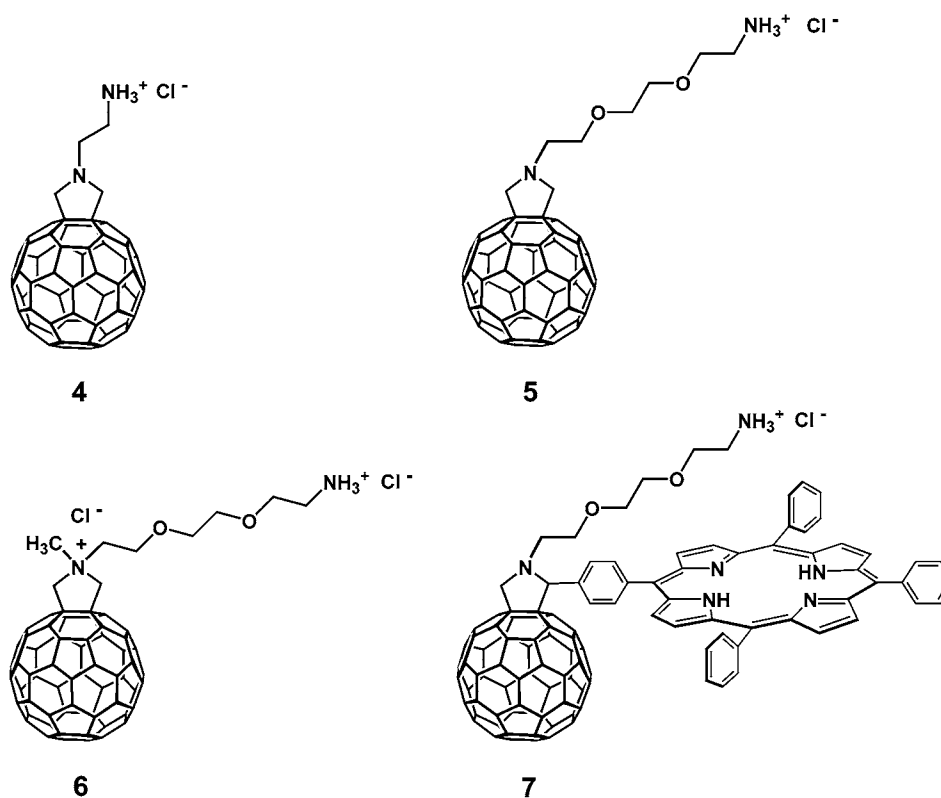
hydrophilic ionic group. In **7**, Scheme 2, a third element of ordering was added. It is known that porphyrin groups favor π-stacking interactions among themselves and with fullerenes. Sonication-assisted solubilization of **7** in water led to a completely different nanostructure. The nanotubules presented in Figure 1 and observed by TEM analysis have uniform dimensions typically reaching 30 nm in diameter and 500 nm in length. In this case, the strong interactions that favor the formation of nanoaggregates are either porphyrin–porphyrin or C_{60}–porphyrin that are several times larger than the C_{60}–C_{60} interactions.
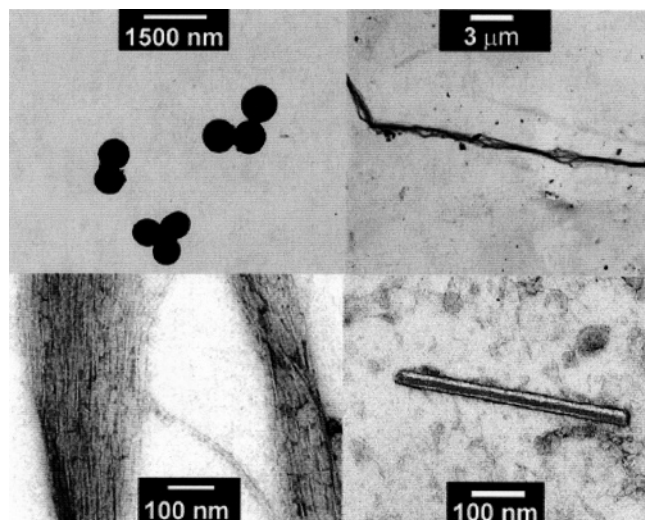
FIGURE 1. Nanostructures obtained from compounds **4** (top left), **5** (top right), **5** (higher magnification, bottom left), and **7** (bottom right).

Interface

A straightforward technique able to generate two-dimensional molecular networks is to spread an aqueous solution of amphiphilic C_{60} derivatives at the air–water interface. Numerous studies have demonstrated the great success of this approach.[8] A single-monolayer, tightly packed coverage was found when the balance between hydrophilicity and hydrophobicity is appropriate. The hydrophilic groups interact with the aqueous phase, which, in turn, drives the fullerene core at the air–water interface. The balance between hydrophobic and hydrophilic interactions is so delicate that it was possible to trigger and observe phase transitions in the closely packed monolayer.[9] The structural rearrangements took place when the surface pressure was in the medium-to-high range. The investigations were carried out measuring both surface-area/surface-pressure isotherms and Brewster angle/atomic force microscopy (AFM) images. The products of the (possibly) cooperative rearrangements are uniformly oriented rods, which are several hundred micrometers long and have an outside diameter of ~1.1 $\pm$ 0.2 μm. The inner structural details of these fibers depends on the hydrophilic functionality. For instance, for the $[Ru(bpy)_3]^{2+}$/trioxyethylene system (**8**) (bpy = 2,2'-bipyridine), Scheme 3, the rods are 1.0 $\pm$ 0.2 μm wide clusters, which, in turn, consist of smaller clusters with diameters of 100 $\pm$ 20 nm (Figure 2a–c); for the all equatorial *e,e,e*-$C_{60}[C(COOH)_2]_3$ (**9**), the rods are formed from well-ordered layers where the fullerenes arrange into a hexagonal pattern (Figure 3a–d). At the air–water interface, both molecules arrange to form fibrous rods.

Scheme 3

8

9
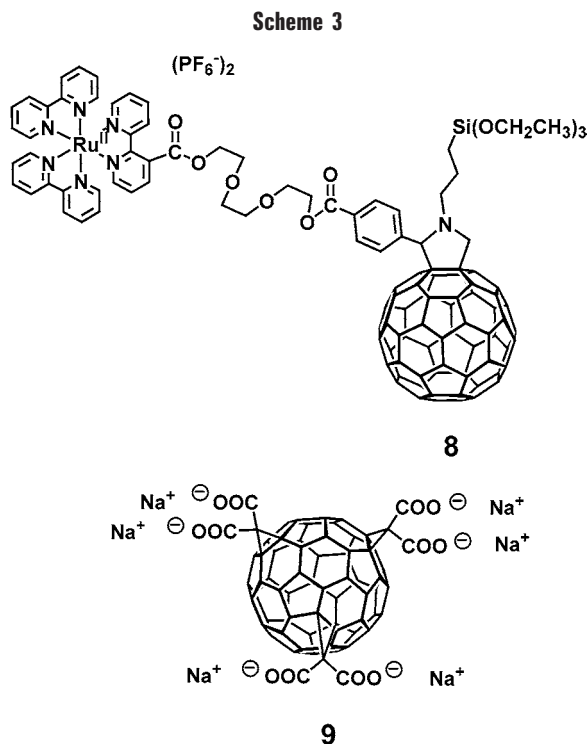
The side groups, however, play a fundamental role that drives the supramolecular organization. In **8**, the charged [Ru(bpy)$_3$]$^{2+}$ groups establish spherical repulsive Coulomb interactions between themselves. To reduce the C$_{60}$–water phobic interactions, individual molecules assemble together in the thermodynamically favored shape of spherical clusters. In **9**, the presence of six polar termini in the all-equatorial arrangement promotes the formation of hexagonal patterns.
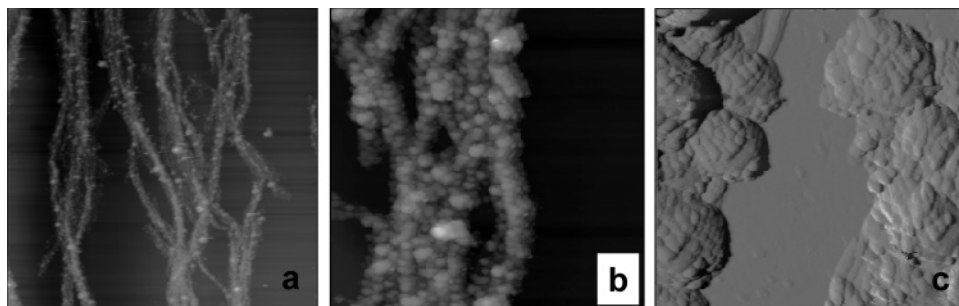
Surface

Film growth, for example, on polyelectrolyte surfaces also induces nanocrystalline morphology.[10] This is an alternative to forcing structural ordering in solution or at the air–water interface.

An important requisite is the presence of ionic functionalities in the molecule, such as a pyrrolidinium ion, which bestow amphiphilic character to the C$_{60}$ derivative.[11] The functionalization of C$_{60}$ can be either flexible as in the case of oligo(ethylene glycol) (**10**) or rigid as in the case of an androstane bridge (**11**), Scheme 4.[12] Orderly

assemblies were found in both systems, but strong differences emerge. For **10**, topographic images of the surfaces show fine-grained structures with two-dimensional aggregates of 20−50 nm sizes that develop into a continuous uniform film in a way found not only for fulleropyrrolidinium salts such as **10** but also for other monofunctionalized fullerene derivatives (Figure 4a). System **11**, instead, reveals a surprisingly high level of intermolecular organization characterized by linear aggregates, typically 10 nm in height and 1−3 micrometers in length (Figure 4b). The organization is the outcome o f the structural anisotropy, which is larger for the rigid compound **11**. Water inhibits the formation of the rods for **11**. In this solvent, films with regular grain morphology (i.e., 20−50 nm sized nanoaggregates) are obtained. When only 10 vol % of water is added to the DMSO solution, an intermediate morphology appeared characterized by a two-dimensional network of spaghetti (Figure 4).

While many questions about the internal structure of these supramolecular aggregates remain open, it is instructive to examine them in the light of the models that have been used to explain the formation of ordered supramolecular structures of ionic amphiphiles. Israelachvili and co-workers[2] showed that single chains form micelles when they have a large ratio of the surface area of the water-exposed head to the molecular volume. The hydrophibic core of the fullerene derivatives, namely, C$_{60}$, is very large, and the structure of functionalized C$_{60}$ differs substantially from the amphiphilic chains for which the theory was developed. Indeed, the molecules discussed here may perhaps be considered an even more extreme case than the peptide amphiphiles recently investigated,[13] where the phobic and philic parts have similar geometrical shape, which makes the application of the theoretical treatment of ref 2 inaccurate. In the model of Israelachvili et al., the aggregation of wedgelike molecules is governed by the critical parameter $v/(a_0l_c)$, where v is the molecular volume, a_0 is the optimal water-exposed surface of the amphiphile, and l_c is the length that the chain assumes in the aggregates. At small values of the ratio, micelles form; as the ratio increases and reaches 0.5, cylindrical systems appear. Finally when $v/(a_0l_c) = 1$, planar bilayers are found.

In more recent work,[14] the aggregation "proceeds" from cones and the critical driving parameter are two angles,
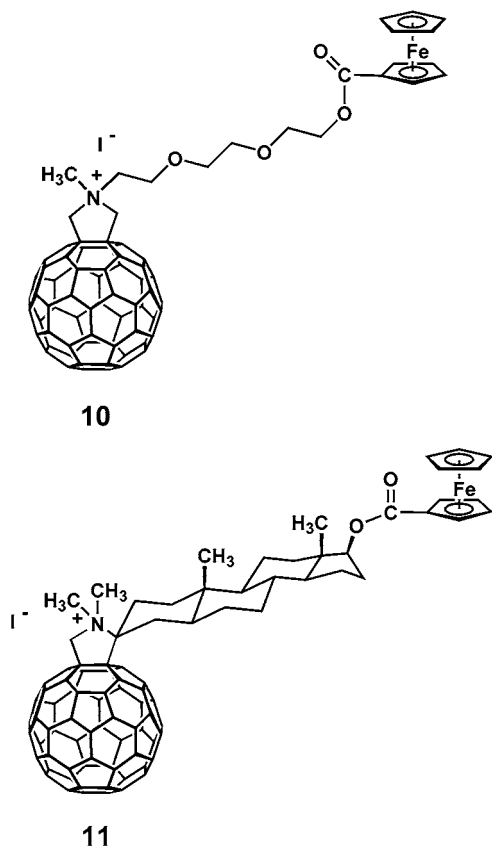

FIGURE 2. Two-dimensional AFM images of dyad **8** transferred from the water surface to a quartz plate at 70 mN/m and scanned perpendicular to the fibers: (a) 75 μm × 75 μm, (b) 20 μm × 20 μm; (c) 2.6 μm × 2.6 μm.
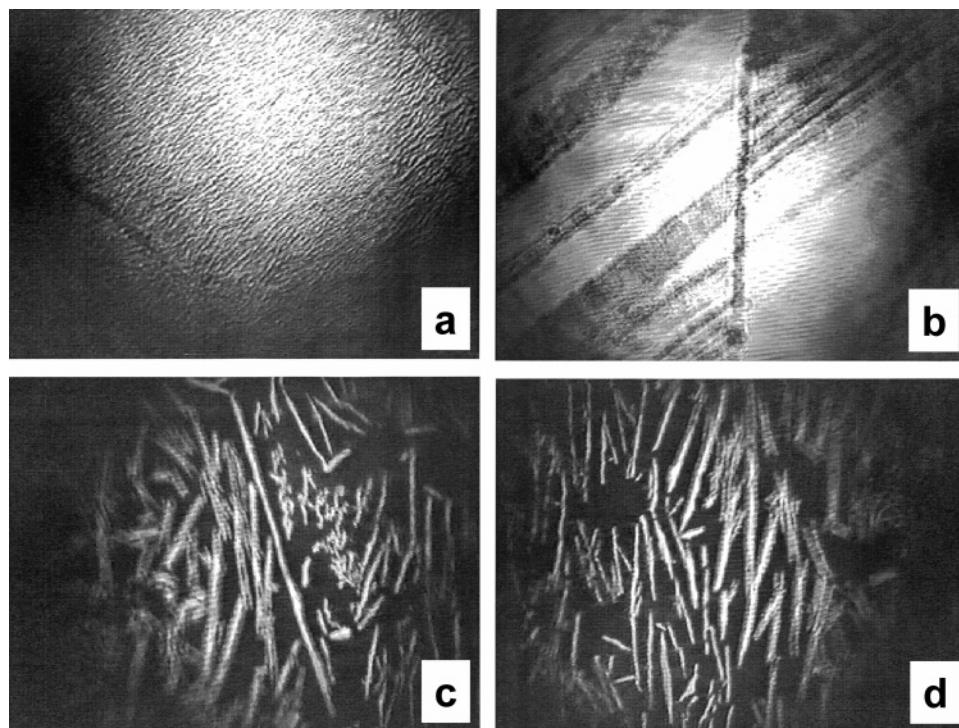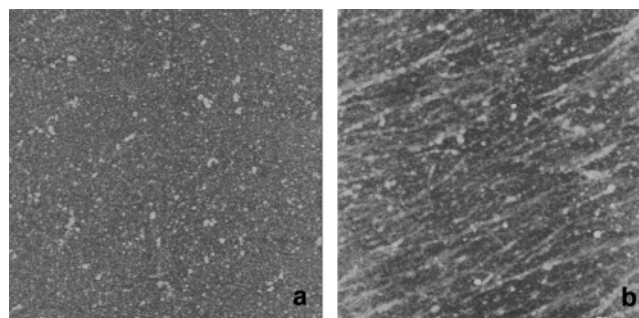
FIGURE 3. Brewster angle microscopic (BAM) images of the tris adduct **9**, compressed on the water surface in a Langmuir balance to (a) 50 and (b) 70 mN/m and (c,d) after expansion to 0 mN/m. The scale is 200 μm.

Scheme 4

10

11

FIGURE 4. AFM images of films of (a) **10** and (b) **11** film adsorbed from dimethyl sulfoxide (DMSO) on poly(diallyl-dimethylammonium)/ poly(styrene-4-sulfonate) polyelectrolyte layer (5 μm $\times$ 5 μm).

The size of the fullerenic core hardly lends itself to either one of theoretical approaches, which tend to assume that the hydrophobic core tapers off (even to a point). The models could still be applicable if the aggregating units are formed by more than one fullerene derivative, where the individual molecules are arranged to form a truncated cone or a wedge. More modeling work is obviously required and will be carried out in the future.

According to the presently available data,[15] we can conclude that short ionic groups attached to a fullerene core favor the formation of spherical aggregates, while long ionic groups favor linear aggregates. Furthermore, the presence of an additional porphyrin group introduces an extra element of ordering, which results in shortening and shaping of the nanostructures. In general, fine tuning of the geometrical characteristics of the monomers appears in line with what takes place in the assembly of supramolecular structures of lipids and ionic amphiphiles based on alkyl chains. Similar models will be explored

α and γ; α is the angle formed by the centers of the circles of two adjacent cones and their conjoint apex, and γ is a dihedral angle function of the curvature on the external hydrophilic surface.[14]

elsewhere with the intent of predetermining the final shape and morphology of the nanostructures.

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