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Amphiphilic and Mesomorphic Fullerene-Based Dendrimers

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Summary: Growing attention is currently devoted to large dendritic structures for applications in nanotechnology and materials science. In this respect, the incorporation of such compounds into thin ordered films appears to be an important issue. One of the most widely pursued approaches to structurally ordered dendrimer assemblies has been the preparation of Langmuir films at the air-water interface. We report on the case of a diblock globular fullerene-based dendrimer and show that peripheral substitution of the dendrimer with hydrophobic chains on one hemisphere and hydrophilic groups on the other provides the required hydrophobic/hydrophilic balance allowing the formation of stable Langmuir films. A second approach has been to consider the case of fullerene containing dendrimers terminated by mesogenic groups such as cyanobiphenyl subunits. Whatever the generation is, up to the fourth one, all these compounds exhibit a well-defined liquid crystalline smectic A phase. The molecular organisation within the smectic layers is found to be monolayered or bilayered depending on the generation. For the smallest dendrimers, the organisation is mainly governed by the size of the fullerene moiety, whereas for the higher ones, it is governed by the interactions between the terminal mesogenic groups. These two approaches appear particularly interesting for functional groups such as fullerenes, which are not well adapted to be organised in nanoscale architectures. The present study shows that fullerenes can indeed be introduced into different types of ordered structure when they have been chemically adequately modified.

Introduction

Fullerenes and their derivatives have shown a wide range of chemical and physical properties that make them attractive candidates for a variety of interesting features in supramolecular chemistry and materials science[1]. An important issue for applications of this new carbon allotrope appears to be its incorporation into well-ordered structures such as Langmuir-

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Blodgett (LB) films or liquid crystals.

Monolayers of C_{60} itself at the air-water interface are difficult to achieve due to strong fullerene-fullerene interactions and three-dimensional aggregation and all attempts to create defined LB multilayers of fullerenes have failed.[2-4]. Whereas the functionalisation of the fullerene sphere with hydrophilic addends leads to significant improvements[4-5], fullerene derivatives with good spreading characteristics and reversible compression/expansion behaviour are quite rare[6-7]. In a collaborative work amongst the research groups of Diederich, Stoddart, Echegoyen and Leblanc, dendrimers with a fullerene core and peripheral acylated glucose units have been prepared and studied[6]. These fullerene derivatives have shown for the first time a reversible behaviour of fullerene monolayers in successive compression/decompression cycles, the dendritic part of the compounds preventing the irreversible aggregation of the fullerene moieties. We have recently shown that the encapsulation of the fullerene sphere in a cyclic addend is also able to prevent the aggregation usually observed for amphiphilic fullerene derivatives[7].

Fullerene-containing liquid crystals appear to be another important class of materials for technological applications. However, the liquid crystalline ordering of fullerenes is difficult since the C_{60} subunit does not behave as a mesogenic unit[8]. During the last few years, several approaches have been developed for the preparation of fullerene-containing liquid crystalline derivatives.

The first C_{60}-containing thermotropic liquid crystal was described in 1996.[9] The functionalization of C_{60} with a malonic ester bearing two mesogenic cholesterol subunits resulted in a fullerene derivative with liquid crystalline properties. A mesophase was observed from 146 to 190°C and identified as a monotropic smectic A phase. More recently, the same group has shown that a dendritic addend exhibits similar mesogenic properties[10]. In this case, the C_{60} core is buried in the middle of the dendritic structure and thus prevents unfavourable effects of the C_{60} unit such as aggregation or steric hindering.

In this paper, we will present recent results obtained in our laboratories regarding both ways of introducing fullerene groups into ordered structures. Langmuir-Blodgett films containing fullerene will be considered in a first part, whereas smectic liquid-crystalline structures containing C_{60} will be in a second one. In both cases, the nanostructures are obtained with fullerene-based dendrimers.

Langmuir-Blodgett Films of Amphiphilic Diblock Fullerene Based-Dendrimers

We have shown recently that fullerene functionalised dendrons with peripheral octyl chains and a carboxylic acid at the focal point are able to form Langmuir films at the air-water interface[11]. We also succeeded in forming Langmuir-Blodgett (LB) films by transferring the monolayers onto hydrophobic substrates. However, due to the difference in size between the the hydrophobic and hydrophilic groups, the preparation of multilayered films was found to be difficult and the transfer ration not too good (~~0.7-0.8). Thus, it was decided to consider the case of a diblock globular dendrimer (figure 1) where the peripheral substitution of the dendrimer is obtained with hydrophobic chains on one hemisphere and hydrophilic groups on the other, in order to provide the perfect hydrophobic/hydrophilic balance allowing the formation of stable Langmuir films[12].

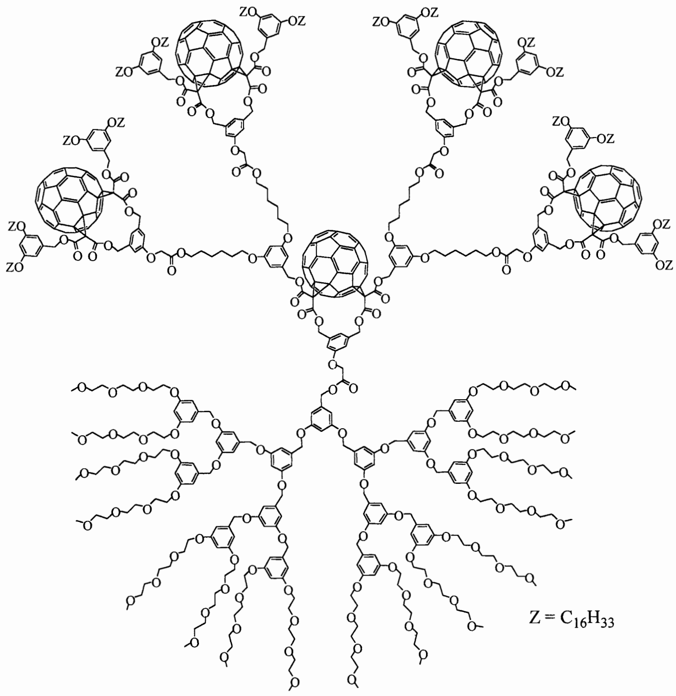

Figure 1. Chemical structure of the amphiphilic dendrimer considered in the present study.

This compound is able to form Langmuir films at the air-water interface. The molecular area extrapolated to zero pressure is 610 ± 30 Å^2 in good agreement with the value estimated by molecular modelling. The films are stable and a perfect reversibility has been observed in successive compression/decompression cycles (figure 2).

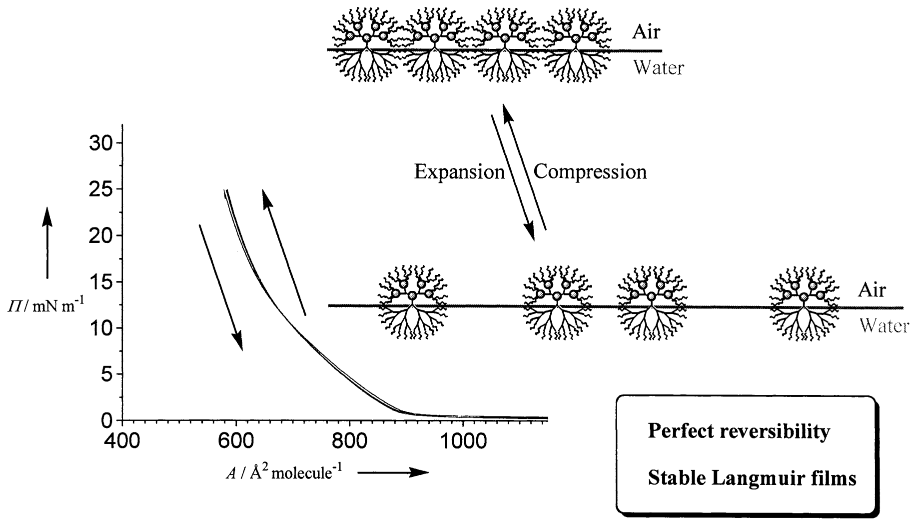

Figure 2. Four successive compression/decompression cycles with a monolayer of the amphiphilic dendrimer (25°C; compression/decompression speed, 5 mm mn^{-1}) showing the perfect reversibility of the process.

The onset of the surface being quite progressive, one could have expected the existence of some liquid condensed phases in the Langmuir film. Brewster angle microscopy (BAM) reveals that this is actually not the case and that the molecules already associate to form islands at large molecular areas, as seen in figure 3a. Still, these islands fuse together in a nice and reversible way and finally yield a very homogeneous film, as clearly shown in figure 3b. It is noteworthy that the five C_{60} units are buried in the middle of the dendritic structure, which is capable of providing a compact insulating layer around the carbon spheres, thus preventing the irreversible three-dimensional aggregation resulting from strong fullerene-fullerene interactions as usually observed with C_{60} derivatives[13]. The polar head-group causes an attractive interaction with the aqueous subphase, forcing the molecules to a two-dimensional arrangement on the water surface. In the case of the present dendrimer, it seems there exists a perfect hydrophilic/hydrophobic balance provided by the 16 triethylene glycol units in the diblock dendrimer, allowing the preparation of stable Langmuir films. Therefore, the functionalisation of the branching shell of a diblock dendrimer structure is an efficient strategy for the incorporation of functional groups in thin ordered films.

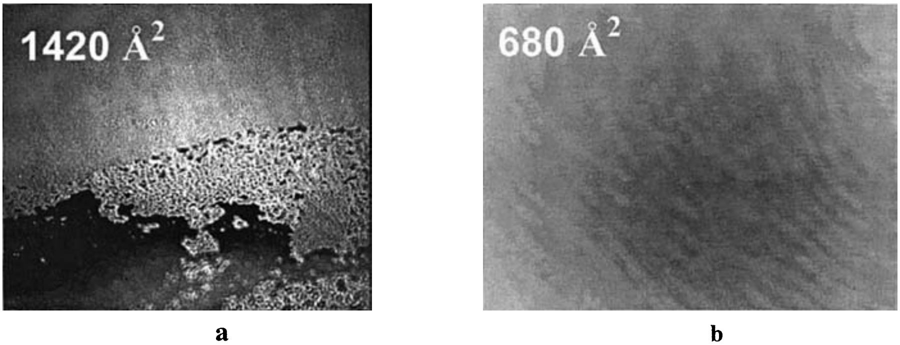

Figure 3. Brewster angle microscopy images for the diblock dendrimer at large molecular areas (a) showing the formation of islands, and at smaller molecular areas (b) showing the formation of an homogeneous film.

Transfer experiments of the Langmuir films onto solid substrates and the preparation of LB films were investigated. The deposition of films of the diblock dendrimer occurred regularly on fused silica slides or silicon wafers with a transfer ratio of 1 ± 0.05. Once again, the

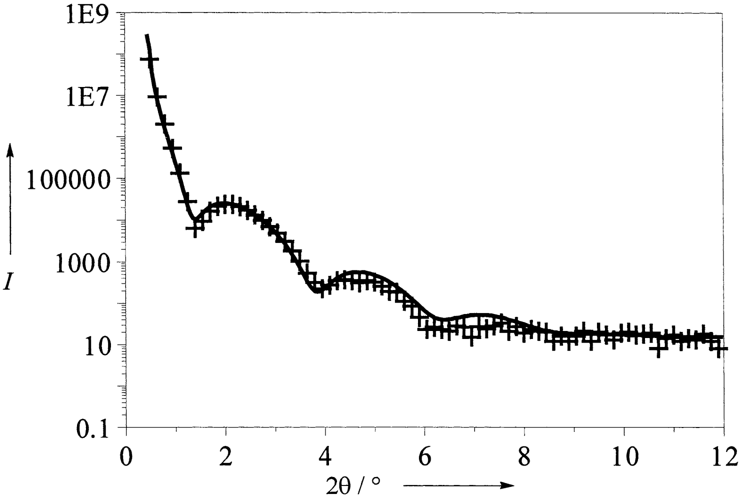

Figure 4. Grazing incidence X-ray pattern of a monolayer, together with the fit (continuous line) of the data.

perfect hydrophilic/hydrophobic balance also appeared crucial for efficient transfers of the Langmuir films in order to obtain well-ordered multilayered LB films. The structural quality of mono- and multilayer films was investigated by grazing X-ray diffraction. The presence of low-angle Kiessig fringes in the grazing X-ray patterns indicates that the overall quality of the films is good. The fit obtained for a monomolecular film gives a thickness of 36 ± 1 Å and a roughness of ~ 2 Å (figure 4). For the multilayer films, the average layer thickness was found to be ~ 36 Å, indicating no or little interpenetration of successive layers. The excellent quality of the LB films is also deduced from the plot of their UV/visible absorbance as a function of the layer number, which results in a straight line, indicating an efficient stacking of the layers (figure 5). It is worth stressing the quality of the stacking and, as a consequence, the quality of the multilayered films obtained with such a megamolecule.

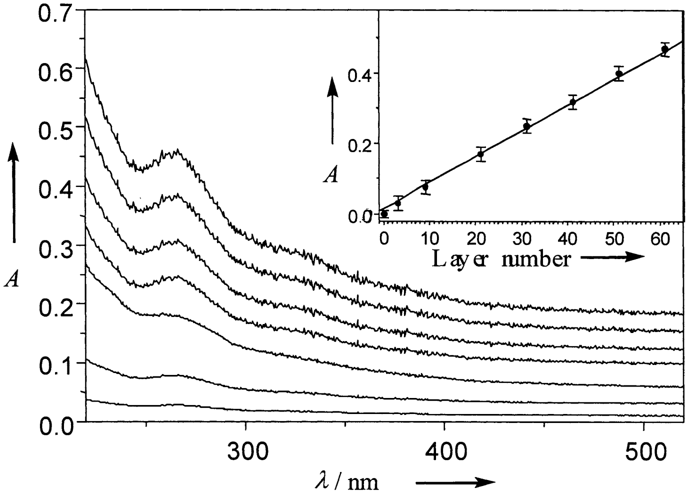

Figure 5. UV-visible spectra of the LB films of the diblock dendrimer (from bottom to top: 3, 9, 21, 31, 41, 51 and 61 layers). The inset shows the plot of the absorbance at 265 nm against the layers number.

Fullerene-Containing Liquid Crystalline Dendrimers

Two main objectives motivate the research in fullerene-containing thermotropic liquid crystals: 1) the understanding of how a sphere-like structure can be incorporated into liquid-crystalline phases (this study will lead to a better understanding of the structure-organization relationship for fullerene-based supramolecular assemblies), and 2) the design of new anisotropic materials.

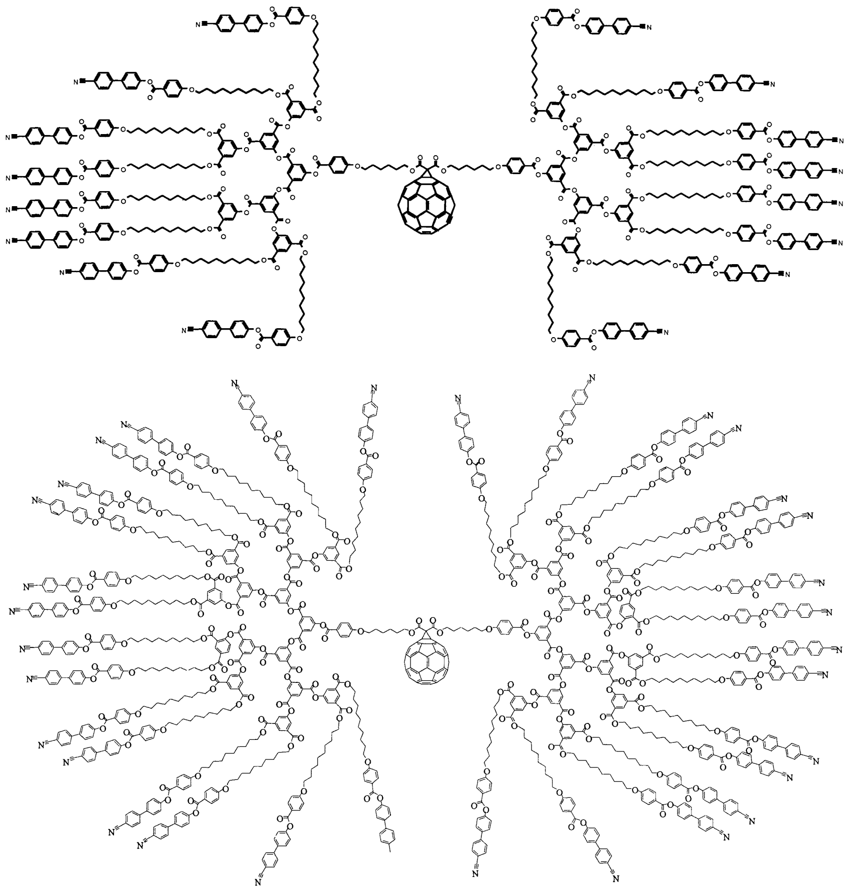

Figure 6. Chemical structures of the dendrimers of third and fourth generation containing 16 and 32 mesogenic cyanobiphenyl terminal groups.

In order to circumvent the size and the shape of C_{60}, which decrease naturally the liquid-crystalline potentiality of the corresponding materials, the use of dendritic addends could be an interesting means for the elaboration of fullerene-containing liquid crystals with tailor-made properties, which could be controlled *via* the dendrimer generation. This is the case of the two dendrimers presented in figure 6, where the dendritic part is ended by a large number of mesogenic groups.

Both compounds exhibit a smectic A phase as revealed by the X-ray diffraction patterns (figure 7) which contain, in the low angle region, two sharp reflections, the corresponding spacing being in the 1:2 ratio, and, in the wide angle region, a diffuse signal corresponding to the liquid-like arrangement of the mesogenic groups. The layer spacing is very similar for the two compounds and ranges between 55-56 Å. This value is rather small compared to the size of the dendrimers. In addition to the X-ray diffraction signals characteristic of a smectic A phase, one should mention the presence of diffuse bands corresponding to spacings of 22 and 29 Å respectively. It is also important to remark that the intensity of the Bragg reflections decreases as the generation number increases, and that these reflections are not as sharp as for the low generations.

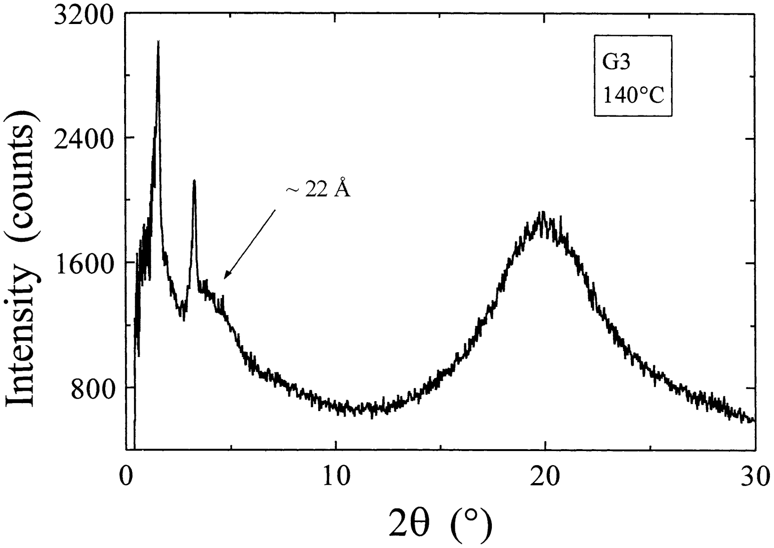

Figure 7. X-ray diffractogram pattern of the third generation dendrimer in the smectic A phase recorded at 150°C.

To describe the molecular organization, it is necessary to realize that these dendrimers are mainly constituted by the branching nodes and by the 16 and 32 mesogenic moieties including the aliphatic spacers; the fullerene moiety represents henceforth a minor part. It is reasonable to admit that the structure is governed essentially by the polar cyano mesogenic groups. The latter should tend to form an anisotropic micro-domain and tend to be oriented parallel to one another. However, due to the fact that these groups are attached to one of their extremity and due also to the fact that the branching nodes are rather voluminous, their parallel orientation is far from being optimized. As it is shown in a molecular simulation, free space is available between the terminal cyano groups[14]. Such a conformation is therefore very favorable for an inter-penetration of mesogenic groups of adjacent layers. Thus, the molecular organization can be schematized as illustrated in Figure 8 for the dendrimer of third generation (the molecular organization of the dendrimer of fourth generation is similar, the only difference lying in the number of mesogenic groups). The central part of the layer is constituted by the fullerene moiety embedded by the important branching part, and the layer interface is formed by the mesogenic cyano groups oriented in one main direction and partially interdigitated from one layer to the adjacent one. This interdigitation is in agreement with the decrease in intensity of the Bragg signals corresponding to the layering and to their simultaneous small broadening; this is similar to X-ray investigations of the smectic A to nematic transition where the interface between the layers becomes more and more diffuse as the transition temperature is approached.[15] Let us remark that such an organization and the good space filling are presumably made possible thanks to the presence of rather long aliphatic spacers and to a large number of ester groups which ensure the necessary flexibility to the dendrimer. Finally, in such a structure, the diffuse X-ray signals corresponding to spacings of 22 and 29 Å may be

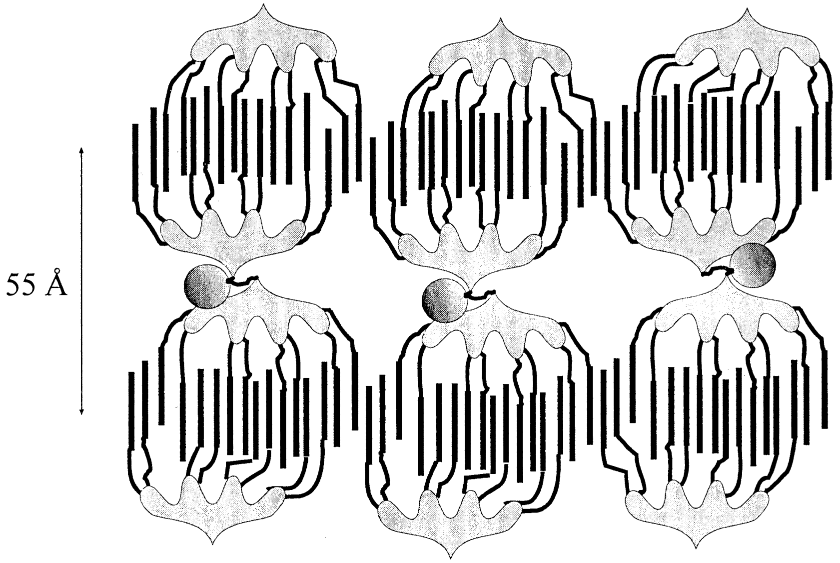

Figure 8. Schematic representation of the supramolecular organisation of the dendrimer of third generation within the smectic A layers. The full circles represent the C_{60} groups, the vertical full rectangles the mesogenic groups, the wavy lines the aliphatic spacers and the rest the dendritic part.

attributed to the mean average distance between the fullerene moieties within the smectic layers, this distance increasing as expected with the size of the dendrimer. This indicates that the expansion of the dendritic volume takes place in two dimensions essentially, as the dendrimer generation increases.

Conclusion

The above examples show how fullerene moieties can be incorporated into ordered nanostructures. In the case of LB films, the peripheral substitution of a globular dendrimer with hydrophobic chains on one hemisphere and hydrophilic groups on the other provides the perfect hydrophobic/hydrophilic balance allowing the formation of stable Langmuir films. On one hand, this approach shows some of the fundamental architecture requirements for obtaining stable films with amphiphilic dendrimers. On the other hand, functional groups not well adapted for the preparation of Langmuir and LB films such as fullerenes can be attached into the branching shell of the dendritic structure and, thus, efficiently incorporated in thin order films.

In the case of liquid-crystalline dendrimers, the fullerene moiety is embedded by an important branching part surrounded by a large number of mesogenic cyano groups. The latter ensure the formation of a mesomorphic phase, whereas the bulkiness of the branching part prevents the C_{60} groups from aggregation. Once more, functional groups such as fullerenes which are not intrinsically mesogenic can however be incorporated into ordered structures such as smectic mesophases and participate to the production of new mesomorphic materials with very interesting physical properties associated to the C_{60} units.

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