of the N-Pt-N and N-Pt-O angles for approaches I and II, respectively, as shown for **2** in Figure 1. To assess the effect of nuclear relaxation, we re-optimized the geometry of **2** during H_2O approach II at the E_{MP2} minimum (Pt ··· O 3.5 Å). The energy gain from nuclear relaxation amounted to $-0.05\,kcal\,mol^{-1}$ and was considered negligible. The geometry of the systems was therefore not re-optimized. The basis set superposition error (BSSE) was evaluated using the counterpoise method[22, 23] for the approaches I/**2** and II/**2**. For the interactions of **1**, the BSSE was assumed to be the same as for the corresponding approach of **2** at the same Pt ··· O distance. The atomic charges used for the estimation of E_{ES} were determined from fits to the MP2 electrostatic potential for the isolated species using the Merz–Kollman routine[24] implemented in GAUSSIAN94, with a van der Waals radius of 2.3 Å for Pt. A check calculation using the CHELPG routine[25] yielded only slightly different E_{ES} curves. The CCDC crystal structures (Figures 3, 4) were drawn using the program Insight II.[26]

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Investigations of Thin Films with Amphiphilic Dendrimers Bearing Peripheral Fullerene Subunits**

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Dedicated to Dr. Antoine Skoulios
on the occasion of his 65th birthday

The preparation and study of fullerene derivatives are being intensively pursued, with the aim of generating new supramolecular assemblies and advanced materials.[1] Incorporation of fullerenes into thin ordered films appears as an important issue in the applications of this carbon allotrope.[2] However, monolayers of fullerene 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 Langmuir–Blodgett (LB) multilayers of fullerenes have failed.[3, 4] Whereas functionalization of the fullerene sphere with hydrophilic addends leads to significant improvements,[4, 5] fullerene derivatives with good spreading characteristics and reversible compression/expansion behavior are quite rare.[6, 7] In a collaborative work among the research groups of Diederich, Stoddart, Echegoyen, and Leblanc, dendrimers with a fullerene core and peripheral acylated glucose units have been investigated.[6] These derivatives show reversible behavior of fullerene monolayers in successive compression/decompression cycles, the dendritic portion preventing the irreversible aggregation

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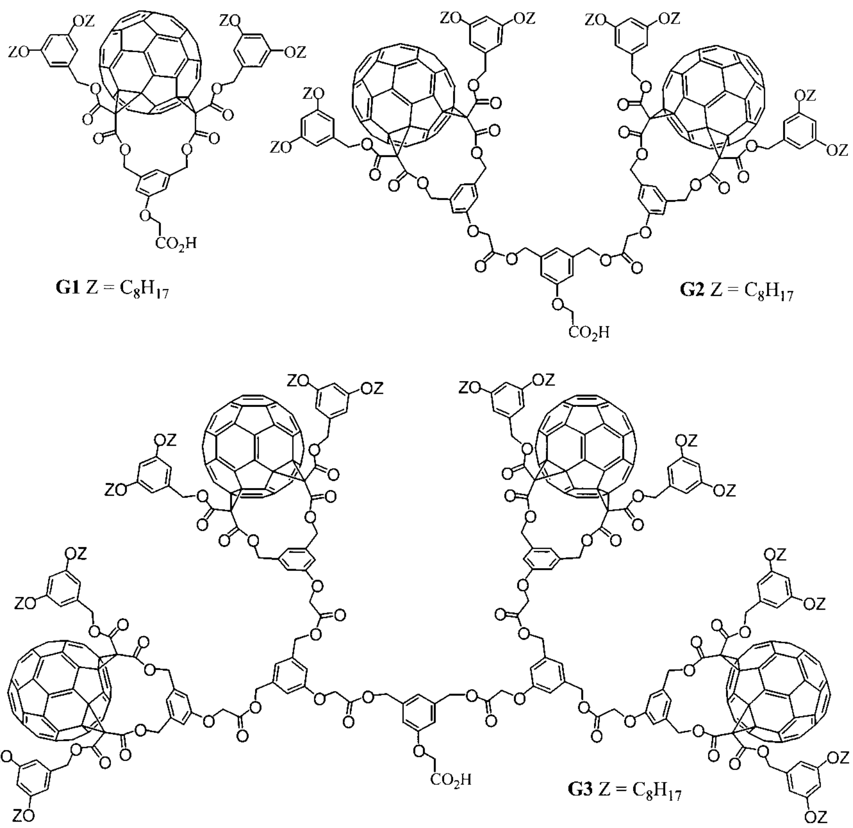
of the fullerene moieties. We have recently shown that the encapsulation of the fullerene sphere in a cyclic addend also prevents the aggregation encountered with amphiphilic fullerene derivatives.[7] As a part of this research, we now report on investigations of Langmuir and LB films of the amphiphilic dendrimers with peripheral fullerene units **G1**–**G3**.[8] Whereas Langmuir films with dendrimers have been reported, the incorporation of dendrimers in LB films has been scarcely considered.[6, 9] Compounds **G1**–**G3** are all able to form stable Langmuir films at the air–water interface, and a reversible compression/decompression behavior has been observed for all compounds. The Langmuir films of **G1** and **G3** were transferred, forming LB films with high efficiency, in spite of a molecular mass of 7704.6 g mol^{-1} (**G3**).



G1 $Z = C_8H_{17}$

G2 $Z = C_8H_{17}$

G3 $Z = C_8H_{17}$

Compounds **G1**–**G3** form high-quality Langmuir films at the air–water interface. Isotherms taken at 20 °C are depicted in Figure 1. Compounds **G1** and **G3** can withstand pressures up to $\Pi \approx 20$ mN m^{-1}, the collapse of the film indicated by a change of compressibility, while the **G2** film begins to collapse around 30 mN m^{-1}. These isotherms are perfectly reversible upon multiple compression–decompression cycles and no hysteresis is observed as long as the collapse pressure is not exceeded. The molecular areas for **G1**–**G3**, extrapolated to zero pressure, are 140 ± 7 Å^2, 310 ± 15 Å^2, and 560 ± 30 Å^2, respectively. The values are in the expected 1:2:4 proportion given the structure of the dendrimers, and are in good agreement with the values estimated by molecular modeling.

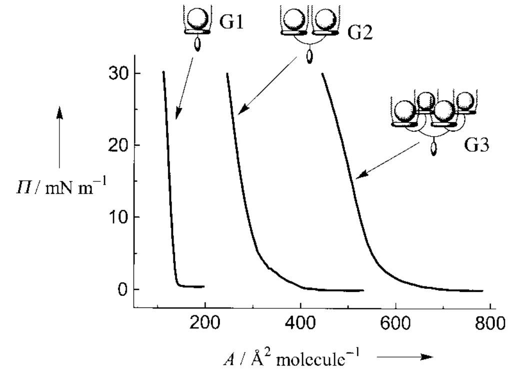


Figure 1. Pressure (Π)–area (A) isotherms for **G1**, **G2**, and **G3** (shown schematically) at 20 °C.

The spreading behavior of **G1**–**G3** shows no significant dependence on compression speed or temperature up to 50 °C. Observation of the Langmuir films by Brewster angle microscopy (BAM) shows high-quality films for all compounds (Figure 2). When the surface pressure reaches $\Pi \approx 10$ mN m^{-1}, and as long as the films do not enter the collapse regime $\Pi \approx 20$ mN m^{-1}, only homogeneous surfaces were observed. Figure 2 a shows a BAM image of the **G1** film at a molecular area $A \approx 180$ Å^2. All the water surface is covered with molecules, except for small circular domains (black regions), which shrink and disappear when $A \approx 140$ Å^2. Figure 2 b shows the films become uniform. The stripes that can be seen are interferences due to the laser light. Contrary to **G1**, **G2** and

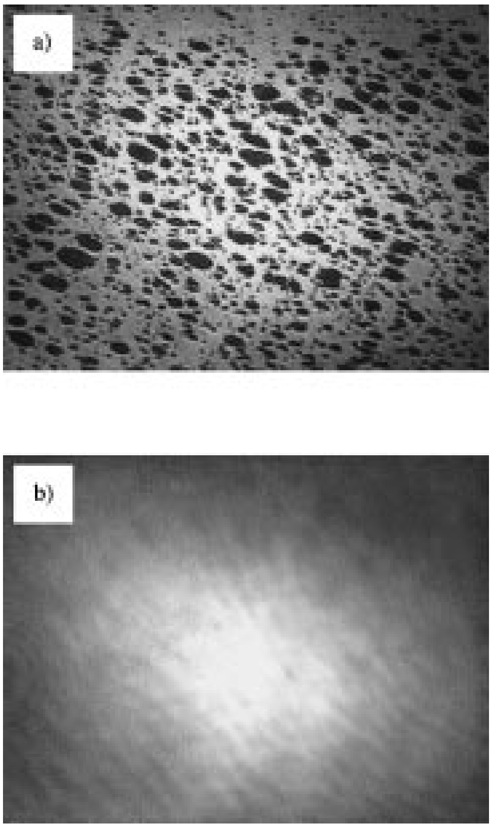


Figure 2. Brewster angle microscopy images for **G1** at $A \approx 180$ Å^2 (a), $A \approx 150$ Å^2 (b).

G3 do not spread uniformly and the molecules spontaneously form islands which are almost defectless. Upon compression, these islands coalesce, yielding good-quality films (the BAM picture of the **G2** and **G3** films at the end of the compression looks exactly like the picture depicted in Figure 2b for **G1**). We emphasize that in spite of the fact that the **G2** and **G3** molecules seem to aggregate when they are spread on water, the isotherms are perfectly reversible as long as Π remains below 20 $\mathrm{mN\,m^{-1}}$.

Although we could not succeed in transferring the **G1**–**G3** monolayers on hydrophilic substrates, we have been able to easily transfer **G1** and **G3** onto silicon or glass substrates covered with a monolayer of octadecyltrichlorosilane. The transfer ratios (TR) for the first layer were 1.0 ± 0.05 for **G1** and 0.8 ± 0.1 for **G3**, while subsequent layers had a slightly smaller TR (0.9 for **G1** and 0.7 for **G3**). Since the Langmuir films were stable, this should indicate defects were present. Nevertheless, all LB films had a very good appearance, with a uniform brown color for the multilayer films. Films of **G1** gave the best results, followed by **G3**. It was not obvious that a large molecule such as **G3** would allow for the processing of LB films. Compound **G2** could not be transferred by the vertical dipping method (LB), due, we believe, to the lack of rotational symmetry of this molecule. Effectively, **G1** and **G3** are cone-shaped, while **G2** is fanlike. A monolayer of **G2** was deposited on a hydrophilic silicon substrate by the Langmuir–Schaefer (LS) method.[10]

Figure 3 shows the grazing X-ray patterns for two LB films of **G1**. The monomolecular film shows only two Kiessig fringes, the best fit giving a thickness of 21.0 ± 0.5 Å and a roughness of about 4 Å. The expected average layer thickness was found to be somewhat smaller than 21 Å for the multilayer films, which is suprising since all layers have the same quality and an almost constant transfer ratio. This apparent contradiction is solved if the overall thickness of multilayer films is measured as a function of the number of layers. Odd layers (downstroke) increase the film thickness by 21 Å, whereas even layers (upstroke) increase by only 17 Å. We believe that this indicates that the molecules of even layers do not deposit atop odd ones, but partially wedge themselves in between (Figure 4). Molecular modeling shows this is indeed reasonable, and suggests that intermolecular hydrogen bonds could take place as schematically depicted in Figure 4 providing additional stabilization of the films. The IR spectra of the multilayer films of **G1** show a signal at 3340 $\mathrm{cm^{-1}}$, in good agreement with the presence of such hydrogen bonds.[11]

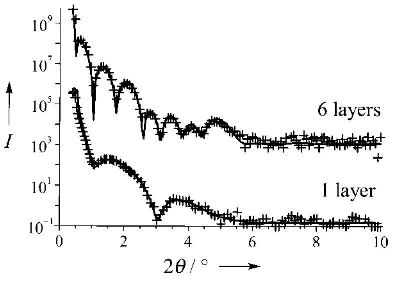


Figure 3. Grazing incidence X-ray patterns for LB films of **G1** (6 layers: upper curve; 1 layer: lower curve), together with the best fit (continuous line) to the data. Overall thickness and film roughness, as deduced from the fits, are 21.0 ± 0.5 Å and 4 Å for the 1-layer film, and 104 ± 1 Å and 6 Å for the 6-layer film (see text). Not all data points are plotted and the upper curve has been shifted for clarity.

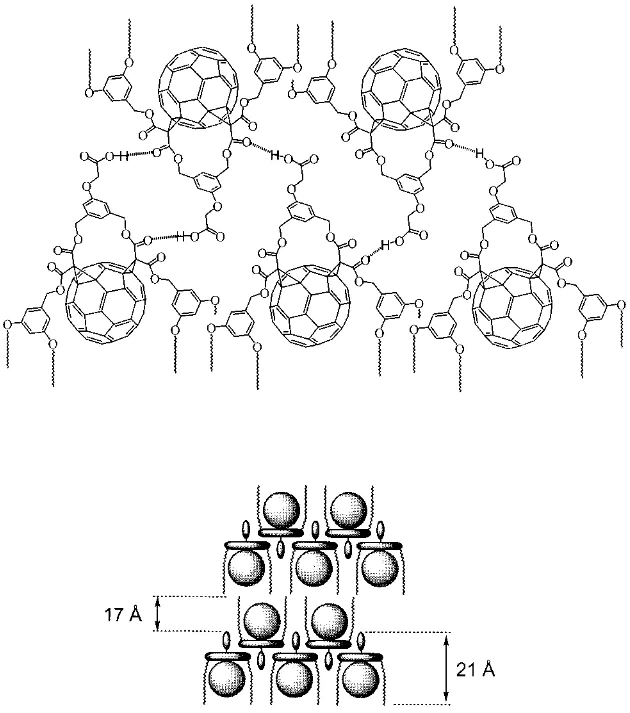


Figure 4. Schematic model of the structure of the multilayer LB films.

For multilayer films, the presence of low-angle Kiessig fringes indicate that the overall quality of the films is good. Atomic force microscope (AFM) observations using the tapping mode performed on a 13-layer LB film showed, on average, only one defect higher than 5 nm on a 1.25×1.25 $\mathrm{\mu m^2}$ area (see Supporting Information). Even if the inner structure of thick films is more poorly defined due to rather high roughness, the feature around $2\theta \approx 5°$ in the X-ray pattern of the 6-layer film indicates the emergence of a Bragg peak. This peak corresponds to an average layer spacing of ≈ 18 Å, in agreement with simulations of the electronic density along the z axis calculated according to the model proposed in Figure 4. The broadness of the peak can be ascribed to the small number of layers. Lastly, a plot of the UV/Vis absorbance, obtained from the spectra of the LB films against the layer number, results in a straight line, indicating effective stacking of the layers. In fact, the **G1** films could be considered as self-healing, a subsequent layer being able to compensate for an imperfect previous one, leading to a macroscopically homogeneous film.

In conclusion, we have shown that fullerene-based amphiphilic dendrimers can form stable Langmuir films and some of them can be readily transferred onto solid substrates, yielding high-quality LB films. The preparation of mixed LB films using those fullerene-based derivatives and amphiphilic conjugated oligomers is now under investigation for photovoltaic applications. Special emphasis is placed on the control of the film morphology for a better understanding of the photovoltaic device performances.

Experimental Section

The synthesis of **G1**–**G3** has been recently reported.[8]

Langmuir and LB films: Spreading solutions were prepared by dissolving **G1**–**G3** in $CHCl_3$ (1.0–3.0 mg mL^{-1}). Stock solutions proved stable for several months at room temperature. Stock solution (50 µL) was spread on the water surface with a microsyringe, and the film was left for 15–20 min to equilibrate before the compression was started. Data were collected with a KSV LB5000 system (KSV Instruments, Helsinki, Finland) using a symmetrical compression Teflon trough and hydrophilic barriers in a dust-free environment. The whole setup was in a Plexiglas enclosure resting on a vibration-free table, and the trough temperature was controlled to ±0.1 °C. All isotherms were taken at 20 °C unless otherwise specified. Ultra pure water ($\rho = 18.2\,M\Omega\,cm^{-1}$) obtained from a Milli-RO3 Plus system combined with a Milli-Q185 Ultra Purification system from Millipore was used for the subphase. Surface pressure was measured by the Wilhelmy plate method. The monolayers were compressed with speeds ranging from 1.2 to 10 Å^2 molecule^{-1} min^{-1}, with almost no incidence of the barrier velocity on the observed behavior.

LB films were obtained by transfer on glass slides or silicon wafers (100) rendered hydrophobic through silanization of the surface with octadecyltrichlorosilane. The vertical dipping method was used for **G1** and **G3**, while **G2** could only be transferred with the horizontal (LS) method. Dipping parameters were not very stringent and usually kept around the following values: trough 30–40 °C, dipping speed ≈0.5–4 mm min^{-1}. Transfers were performed at surface pressures 12, 15, and 22 mN m^{-1} for **G1**, **G2**, and **G3**, respectively. It has been possible to build Y-type multilayer films of **G1** and **G3**.

Grazing incidence X-ray analysis (GIXA): The studies of LB films were performed on a X'PERT-MPD device (Philips), equipped with a programmable divergence slit (1/32°), a Soller slit collimator, a flat Ge monochromator, and proportional Xe detector. A nickel-filtered $Cu_{K\alpha}$ line (λ = 0.1542 nm) was used.

All measurements were recorded immediately after the film transfer, but the diffraction patterns remained stable for as long as several weeks without special care being taken for the storage of the film.

BAM: BAM was performed using a BAM2plus (Nanofilm Technologies GmbH) illuminated by an Ar laser. Images were recorded on a CCD camera of field 620 µm × 500 µm.

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Acetamidoglycosylation with Glycal Donors: A One-Pot Glycosidic Coupling with Direct Installation of the Natural C(2)-*N*-Acetylamino Functionality[**]

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The 2-*N*-acetylamino-2-deoxy class of carbohydrates is ubiquitous among biologically important complex oligosaccharides and glycoconjugates, including, inter alia, glycosaminoglycans, peptidoglycans, and blood group antigens.[1] As a result, the efficient preparation of this group of glycosides

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