Amphiphilic Diblock Dendrimers: Synthesis and Incorporation in Langmuir and Langmuir−Blodgett Films[†]

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Received January 18, 2001

Abstract: A new dendron with peripheral long alkyl chains and containing five C_{60} units in the branching shell has been prepared and attached to a Fréchet-type dendron functionalized with ethylene glycol chains. The peripheral substitution of the resulting 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. Furthermore, a perfect reversibility has been observed in successive compression/decompression cycles. The diblock structure of the dendrimer has been also crucial for the efficient transfer of the Langmuir films in order to obtain well-ordered multilayered Langmuir−Blodgett films. This approach appears particularly interesting since functional groups not well adapted for the preparation of Langmuir and Langmuir−Blodgett films such as fullerenes can be attached into the branching shell of the dendritic structure and, thus, efficiently incorporated in thin ordered films.

Introduction

Growing attention is currently devoted to large dendritic structures for applications in nanotechnology and materials science.[1] In this respect, the incorporation of such compounds into thin ordered films appears as an important issue,[1n,2−6] and one of the most widely pursued approaches toward structurally ordered dendrimer assemblies has been the preparation of Langmuir films at the air−water interface.[3−6] For example, successful preparation of Langmuir monolayers has been achieved with poly(propyleneimine) dendrimers substituted with peripheral long alkyl chains. In this case, thanks to the high flexibility of the dendrimer, the compounds are able to adopt a cylindrical amphoteric shape, in which the dendritic poly(propylene imine) part acts as a polar headgroup and the alkyl chains packed together form a hydrophobic moiety.[4] It has also been shown that dendrimers with peripheral polar headgroups can be used for the preparation of thin ordered films at the air−water interface.[3] Such a strategy appears limited however, since for high generation numbers, the dendrimer should be water-soluble due to the presence of too many polar units. Langmuir films have also been obtained with amphiphilic dendritic molecules with a small polar headgroup at the focal point.[5] However, the stability of the films appears to be a problem due to the difference in size between the hydrophobic and hydrophilic groups.[3b,5] Another interesting approach based on amphiphilic cylinders has been also recently proposed by Schlüter and co-workers.[6]

As part of this research, we have recently shown that fullerene functionalized dendrons with peripheral octyl chains and a carboxylic acid at the focal point are able to form Langmuir films at the air−water interface.[5d] 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 hydrophobic and hydrophilic groups, the preparation of multilayered films was found to be difficult and the transfer ratio not too good (∼0.7−0.8). We now report on the synthesis of a diblock globular dendrimer[7] and show that the peripheral substitution of the dendrimer with hydrophobic

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[†] Dedicated to Prof. Maurice Gross on the occasion of his 60th birthday.

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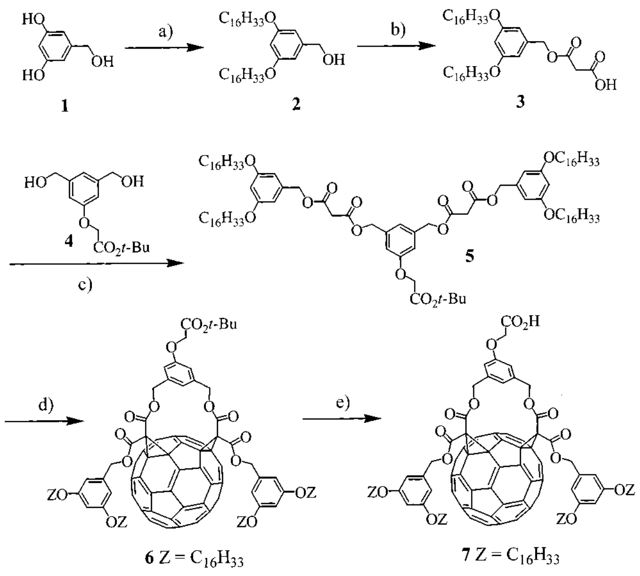
10.1021/ja010155m CCC: $20.00

Scheme 1. Preparation of Compound **7**[a]



[a] Reagents and conditions: (a) K_2CO_3, DMF, 70 °C, 48 h (63%); (b) Meldrum's acid, 115 °C, 4 h (99%); (c) DCC, DMAP, CH_2Cl_2, 0 °C to room temperature, 24 h (83%); (d) C_{60}, I_2, DBU, toluene, room temperature, 15 h (59%); (e) CF_3CO_2H, CH_2Cl_2, room temperature, 35 mn (99%).

chains on one hemisphere and hydrophilic groups on the other provides the perfect hydrophobic/hydrophilic balance allowing the formation of stable Langmuir films. Furthermore, transfer experiments of the resulting monolayers onto solid substrates have been carried out and the deposition occurs regularly with a transfer ratio of 1. This approach appears particularly interesting since functional groups not well suited for the preparation of Langmuir and LB films such as fullerenes[8] can be attached into the branching shell of the diblock dendritic structure and, thus, be efficiently incorporated in thin ordered films.

Results and Discussion

Synthesis. The fullerene derivative **7** was prepared according to the procedure we developed for the synthesis of the corresponding derivative bearing octyl chains (Scheme 1).[9] The monoester **3** of malonic acid was prepared by alkylation of 3,5-dihydroxybenzyl alcohol (**1**) with 1-bromohexadecane in DMF at 70 °C with K_2CO_3 as base followed by reaction of the resulting 3,5-dihexadecyloxybenzyl alcohol (**2**) with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) at 115 °C. Diol **4** was prepared in two steps from dimethyl 5-hydroxyisophthalate as previously reported.[9] *N,N′*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of **4** with **3** in CH_2Cl_2 gave bis(malonate) **5** in 83% yield. The functionalization of C_{60} was based on the highly regioselective reaction developed in the Diederich group,[10] which led to macrocyclic bis(adducts) of C_{60} through a macrocyclization reaction on the fullerene sphere with bis(malonate) derivatives in a double Bingel addition.[11] Treatment of C_{60} with **5**, I_2, and diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded **6** in 59% yield. It is well established that the 1,3-benzenedimethanol-tethered bis(malonates) yield regioselectively a cis-2 addition pattern on the C_{60}.[10,12] Effectively, all the spectroscopic data obtained for **6** are in agreement with a cis-2 addition pattern. In particular, the UV/visible spectra of the bis-cyclopropanated fullerene derivative **6** shows all the characteristic features of a cis-2 bis(adduct).[10,13] Finally, selective cleavage of the *tert*-butyl ester moiety[14] of **6** with CF_3CO_2H in CH_2Cl_2 afforded carboxylic acid **7** in a quantitative yield.

Compound **8** was prepared according to a previously reported procedure.[15] DCC-mediated esterification of **4** with **8** in CH_2Cl_2 gave bis(malonate) **9** in 90% yield (Scheme 2). Treatment of C_{60} with **9**, I_2, and DBU in toluene at room temperature afforded the C_s symmetric cis-2 bis(adduct) **10** in 21% yield. Cleavage of the *p*-methoxybenzyl (PMB) protecting groups[16] with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in CH_2Cl_2 in the presence of a small amount of water gave tetraalcohol **11** in 85% yield.

Reaction of acid **7** with **11** under esterification conditions using DCC, 4-(dimethylamino)pyridine (DMAP), and 1-hydroxybenzotriazole (BtOH) afforded fullerodendron **12** in 65% yield (Scheme 3). Selective cleavage of the *tert*-butyl ester moiety with CF_3CO_2H in CH_2Cl_2 then gave **13** in 96% yield. Thanks to the presence of the four hexadecyloxy substituents per peripheral fullerene subunit, **12** and **13** are highly soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene, or THF, and complete spectroscopic characterization was easily achieved. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra also confirmed the structures of **12** and **13**, with no peaks corresponding to defected dendrons being observed. For **12**: m/z 10 702 (MH$^+$, calcd for $C_{734}H_{681}O_{75}$: 10 702.4), 10 724 (M + Na$^+$, calcd for $C_{734}H_{680}O_{75}Na$: 10 724.4). For **13**: m/z 10 647 (MH$^+$, calcd for $C_{730}H_{673}O_{75}$: 10 646.3), 10 671 (M + Na$^+$, calcd for $C_{730}H_{672}O_{75}Na$: 10 668.3)].

Compound **14** was prepared in nine steps as previously described.[17] Treatment of **14** with **13** under DCC-mediated esterification conditions afforded the targeted amphiphilic dendrimer **15** in 20% yield (Scheme 4). This low yield is certainly due to the poor accessibility of the reactive groups

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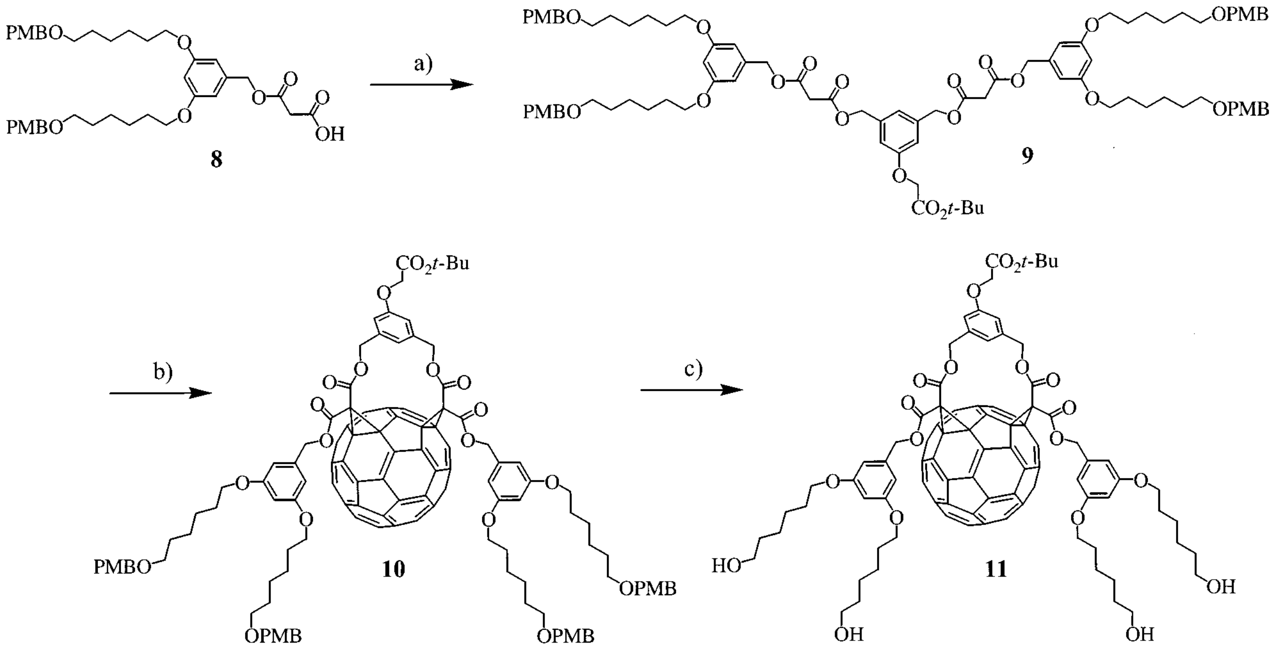
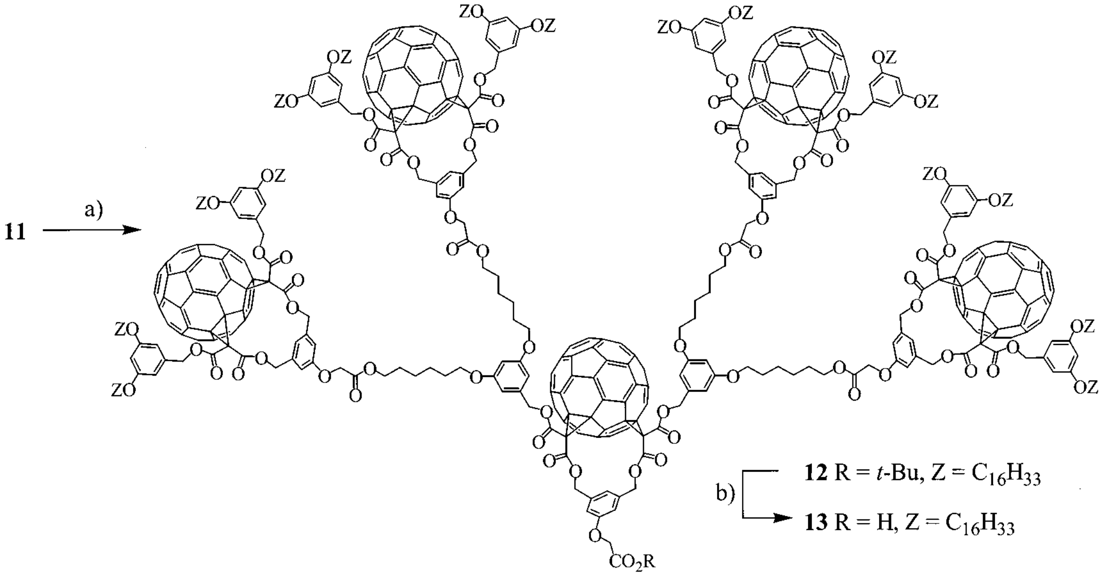
Scheme 2. Preparation of Compound **11**[a]



[a] Reagents and conditions: (a) **4**, DCC, DMAP, BtOH, CH_2Cl_2, 0 °C to room temperature, 48 h (90%); (b) C_{60}, I_2, DBU, toluene, room temperature, 24 h (21%); (c) DDQ, CH_2Cl_2, H_2O, room temperature, 1 h (85%).

Scheme 3. Preparation of Compound **13**[a]



[a] Reagents and conditions: (a) **7**, DCC, DMAP, BtOH, CH_2Cl_2, 0 °C to room temperature, 96 h (65%); (b) CF_3CO_2H, CH_2Cl_2, room temperature, 2 h (96%).

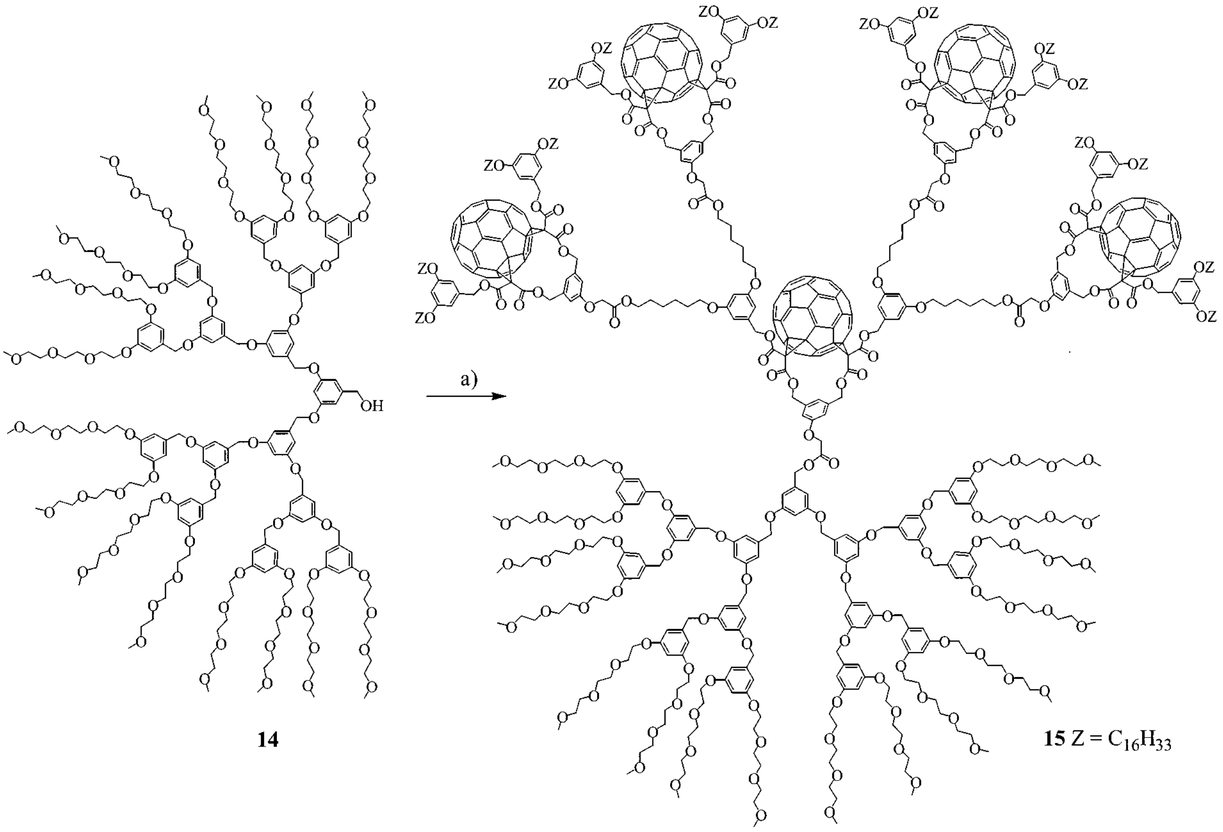
located at the focal points of both dendrons. The NMR spectra of **15** are fully consistent with the proposed structure and show clearly the presence of both kinds of dendritic branches. The structure of **15** is also confirmed by MALDI-TOF mass spectrometry, which displays the sodium molecular ion peak at m/z 14 837 ($M + Na^+$, calcd for $C_{947}H_{986}O_{153}Na$: 14 839.1).

Langmuir and Langmuir–Blodgett Films. Compounds **13** and **15** are both able to form Langmuir films at the air–water interface. The general shapes of the isotherms obtained at 25 °C for both **13** and **15** are similar and the molecular areas extrapolated to zero pressure (610 ± 30 Å^2 for **13** and 680± 30 Å^2 for **15**) in good agreement with the values estimated by molecular modeling (Figure 1).

The stability of both films and their behavior upon successive compression/decompression cycles is different however. Effectively, for **13**, the films are not very stable and the isotherm show poor reversibility, even when the highest pressure is kept below the collapse value. In contrast, the Langmuir films of **15** are stable and a perfect reversibility has been observed in successive compression/decompression cycles (Figure 2). The onset of the surface pressure being quite progressive (Figure 2), one could have expected the existence of some liquid condensed phase 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 seen in Figure 3b.

It is noteworthy that the five C_{60} units of **13** or **15** are buried in the middle of the dendritic structure, which is capable of

Scheme 4. Preparation of Compound **15**[a]



[a] Reagents and conditions: (a) **13**, DCC, DMAP, BtOH, CH_2Cl_2, 0 °C to room temperature, 96 h (20%).

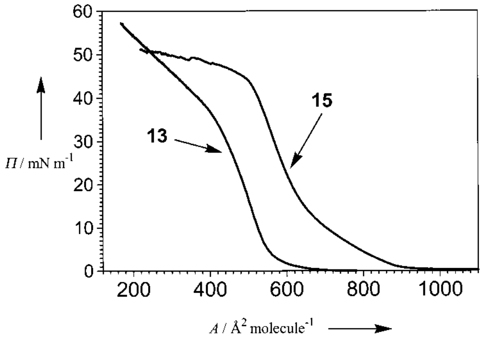


Figure 1. Pressure−area isotherms for **13** and **15** at 20 °C.

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 amphiphilic C_{60} derivatives.[8] For both **13** and **15**, the polar headgroup causes an attractive interaction with the aqueous subphase, forcing the molecules to a two-dimensional arrangement on the water surface. However, for **13**, due to the small size of the polar headgroup relative to the large hydrophobic moiety, the interaction with the aqueous layer is certainly not strong enough to stabilize the films. In contrast, a perfect hydrophilic/hydrophobic balance is provided by the 16 peripheral long alkyl chains and 16 triethylene glycol units in the diblock dendrimer **15**, allowing the preparation of stable Langmuir films. Therefore, the functionalization of the branching shell of a diblock dendritic structure is an efficient strategy for the incorporation of functional groups in thin ordered films.

Transfer experiments of the Langmuir films onto solid substrates and the preparation of LB films were investigated for both **13** and **15**. The deposition of films of **15** occurred regularly on quartz slides or silicon wafers with a transfer ratio of 1 ± 0.05. The diblock structure of dendrimer **15** providing the perfect hydrophilic/hydrophobic balance also appeared crucial for efficient transfers of the Langmuir films in order to obtain well-ordered multilayered LB films. Effectively, the transfer of the Langmuir films of the dendrimer **13** with the small polar headgroup was found to be difficult with a transfer ratio of about 0.5−0.7.

The structural quality of mono- and multilayer films of **13** and **15** was investigated by grazing incidence X-ray diffraction. The quality of the LB films made with **13** was not too good and only allowed an estimation of their thickness, the roughness being always in the 3-Å range. Monolayers of **13** were ∼20 Å thick, and the average value of the layer thickness was found to be somewhat smaller than expected for the multilayer films (∼18 Å). This smaller value is probably the result of a partial interpenetrating of the successive layers within the film.[5d]

For LB films of **15**, the presence of low-angle Kiessig fringes in the grazing X-ray patterns indicates that the overall quality of the films is good. The best fit of the grazing X-ray pattern 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 prepared with **15** 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.

Conclusion

The peripheral substitution of a globular dendrimer with hydrophobic chains on one hemisphere and hydrophilic groups

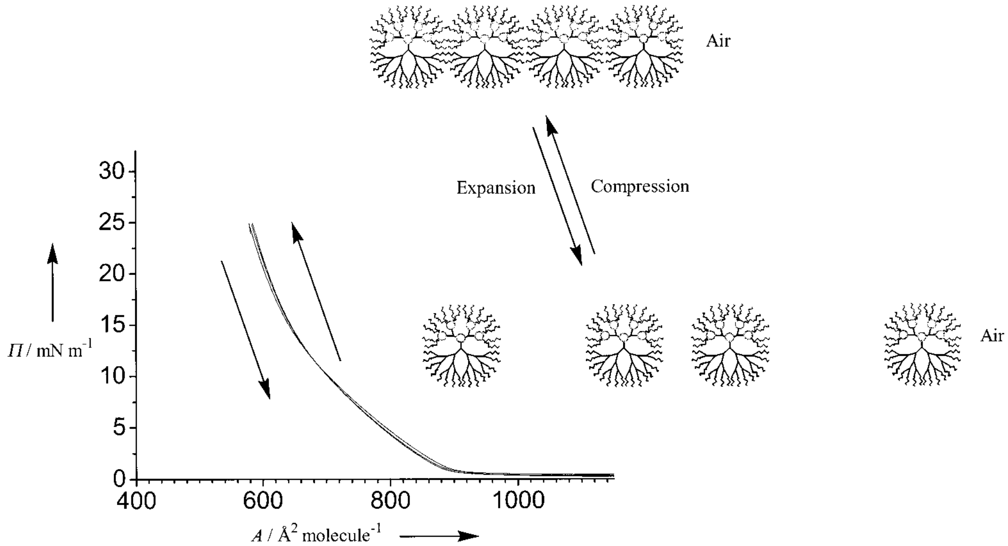


Figure 2. Four successive compression/expansion cycles with a monolayer of **15** (25 °C; compression/decompression speed, 5 mm mn^{-1}) showing the perfect reversibility of the process.

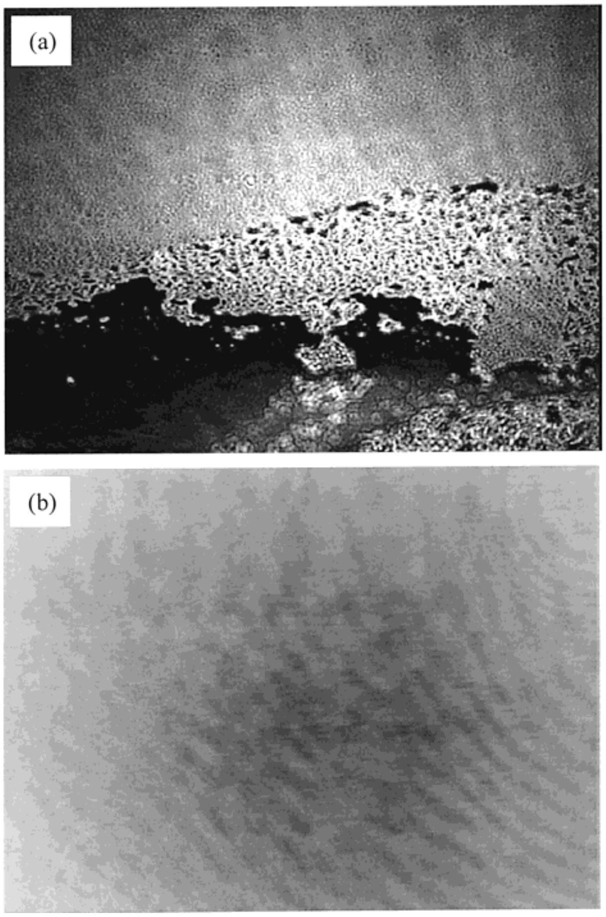


Figure 3. Brewster angle microscopy images for **15**: (a) $A = 1420$ Å^2; (b) $A = 680$ Å^2.

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 architectural 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 ordered films.

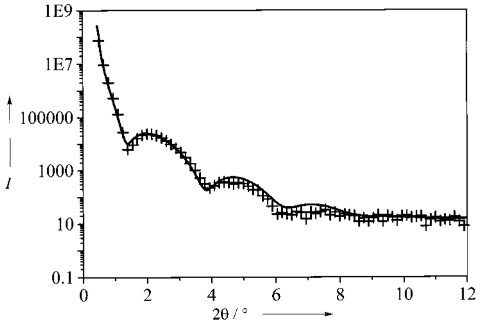


Figure 4. Grazing incidence X-ray pattern of a monolayer of **15**, together with the best fit (continuous line) to the data.

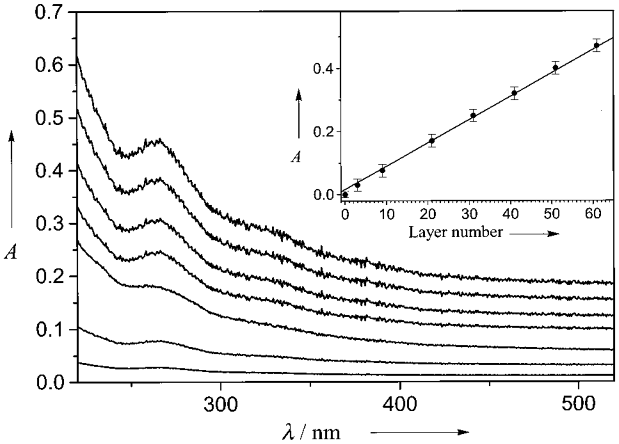


Figure 5. UV−visible spectra of the LB films of derivative **10** (from bottom to top: 3, 9, 21, 31, 41, 51, and 61 layers). The inset shows the plot of the absorbance at 265 nm against the layer number.

Experimental Section

Langmuir and LB Films. Spreading solutions were prepared by dissolving the compounds in $CHCl_3$ (Analysis Grade from Carlo Erba) at 1.0−3.0 mg mL^{-1} concentrations. Stock solutions proved stable for several months when stored at room temperature. For a typical experiment, 50 μL of the stock solution was spread on the water surface with a microsyringe, and the film was then left for 15−20 min to equilibrate before the compression 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. Ultrapure water ($\rho = 18.2$ MΩ cm) 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 with 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 quartz slides or silicon wafers (100). Vertical dipping method was used for **13** and **15**. Dipping parameters were not very stringent and usually kept around the following values: trough temperature $T \approx 20-30$ °C; dipping speed $V_{\text{dip}} \approx 0.5-4$ mm min^{-1}. Transfers were performed at surface pressures of 22 mN m^{-1}. BAM has been performed using a BAM2plus setup from Nanofilm Technologies GmbH. Illumination came from an argon laser; images were recorded on a CCD camera. The field is 620 μm width × 500 μm height. The grazing incidence X-ray studies of LB films were performed on a device equipped with a programmable divergence slit (1/32°), a Soller slit collimator, a flat Ge monochromator, and a proportional Xe detector. Nickel-filtered Cu Kα line (wavelength 0.1542 nm) was used. All measurements were recorded immediately after the LB transfer.

Acknowledgment. This work was supported by the CNRS and the French Ministry of Research (ACI Jeunes Chercheurs). J.-F.E. thanks the DGA for a doctoral fellowship, Y.R. thanks the French Ministry of Research for a doctoral fellowship, and M.d.P.C. thanks DGAPA-UNAM and CONACyT for a post-doctoral fellowship. We further thank Dr. A. Van Dorsselaer and H. Nierengarten for the MS spectra, M. Schmitt for the NMR measurements, and L. Oswald for technical assistance.

Supporting Information Available: Synthetic procedures and full characterization of all new molecules. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

JA010155M