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Amphiphilic Diblock Dendrimers with a Fullerene Core

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Received July 18, 2003

Amphiphilic dendrimers with a C_{60} core have been obtained by cyclization of dendritic 1,3-phenylenebis(methylene)-tethered bis-malonate derivatives at the carbon sphere. The relative position of the two cyclopropane rings in the resulting bis-methanofullerene derivatives has been determined based on the molecular symmetry (C_s) deduced from the ^{1}H and ^{13}C NMR spectra. The hydrophobic−hydrophilic balance of these dendrimers has been systematically modified by changing the size of the polar headgroup in order to investigate the role of the amphiphilicity both at the air−water interface and during deposition onto solid substrates. Langmuir studies have revealed a conformational change in the dendritic structure with the size of the polar headgroup. Because of a better anchoring onto the water surface, the compounds with the largest polar headgroup adopt a more compact structure and the dendritic branches are forced to wrap the fullerene core. This model is nicely confirmed by the amount of fullerene−fullerene interactions within the Langmuir−Blodgett films as deduced from their absorption spectra.

Introduction

The past several years have seen a considerable interest in the use of dendrimers at surfaces and interfaces.[1] In particular, the preparation of Langmuir films from amphiphilic dendrimers has been investigated by several research groups.[2−5] Studies of the behavior of dendrimers at the air−water interface have yielded important information about their size, shape, compressibility, and flexibility.[2−5] In this respect, the Langmuir studies reported by Meijer and co-workers with poly(propylene imine) dendrimers modified with peripheral long hydrophobic chains are of particular interest.[3] They have shown that these compounds are able to arrange themselves in monolayers in which the dendritic poly(propylene imine) part acts as a polar headgroup and the alkyl chains packed together form a hydrophobic moiety, thus revealing the high flexibility of such dendrimers. Langmuir films have also been obtained with several amphiphilic dendritic molecules with a small polar headgroup at the focal point.[4] Even though this has been a convenient technique to directly determine the size of such compounds, the stability of the films appears to be a problem because of the difference in size between the hydrophobic and hydrophilic groups. As a result, their transfer onto solid substrates for the preparation of Langmuir−Blodgett films is rather difficult.[4] As part of this research, we have recently shown that the peripheral substitution of a diblock globular dendrimer with hydrophobic chains on one hemisphere and hydrophilic groups on the other one provides a perfect hydrophobic−hydrophilic balance allowing the formation of stable Langmuir films.[5] 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. In this paper, we report the synthesis of the new amphiphilic diblock dendrimers depicted in Figure 1.

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10.1021/jo035040a CCC: $25.00
Published on Web 11/15/2003

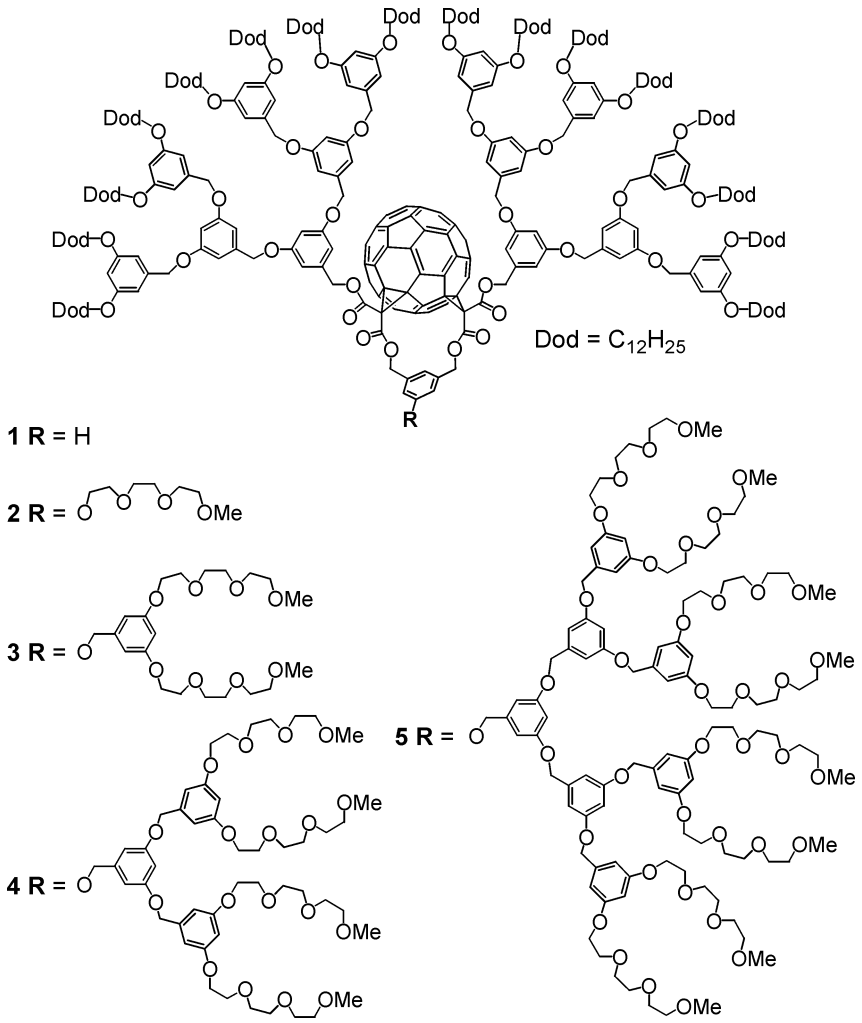

FIGURE 1. Fullerodendrimers **1**−**5**.

The hydrophobic−hydrophilic balance has been systematically modified by changing the size of the polar headgroup in order to investigate the role of the amphiphilicity both at the air−water interface and during deposition onto solid substrates. In the design of these compounds, it was also decided to use a fullerene sphere as a photoactive core unit in order to gain more insight into structural factors. Effectively, changes in the nanoenvironment of the C_{60} chromophore dramatically affect its electronic properties making it a sensitive probe to demonstrate shielding effects resulting from the presence of the surrounding dendritic shell.[6]

Results and Discussion

Synthesis. All of the fullerene derivatives reported in the present paper have been prepared by taking advantage of the versatile regioselective reaction developed by Diederich and co-workers,[7] which led to macrocyclic bis-adducts of C_{60} by a cyclization reaction at the C sphere with bis-malonate derivatives in a double Bingel[8] cyclopropanation. The cyclic fullerene bis-adduct **1** with no polar headgroup was obtained in two steps from **6**[9] and **7**[7b] (Scheme 1). Treatment of diacid **7** with alcohol **6** and *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of 4-(dimethylamino)pyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) gave bis-malonate **8** in 76% yield. Subsequent reaction with C_{60}, I_2, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the desired cyclization product **1** in 44% yield. The preparation of the amphiphilic fullerene derivative **2** bearing an ethylene glycol chain as the polar headgroup was achieved following a similar route. Reaction of bis-malonic acid **9**[10] with alcohol **6** under esterification conditions (DCC, DMAP, HOBt) yielded bis-malonate **10**.

(6) (a) Rio, Y.; Accorsi, G.; Nierengarten, H.; Rehspringer, J.-L.; Hönerlage, B.; Kopitkovas, G.; Chugreev, A.; Van Dorsselaer, A.; Armaroli, N.; Nierengarten, J.-F. *New J. Chem*. **2002**, *26*, 1146. (b) Rio, Y.; Accorsi, G.; Nierengarten, H.; Bourgogne, C.; Strub, J.-M.; Van Dorsselaer, A.; Armaroli, N.; Nierengarten, J.-F. *Tetrahedron* (Symposium-in-Print on Recent Developments in Dendrimer Chemistry) **2003**, *59*, 3833. (c) Nierengarten, J.-F.; Armaroli, N.; Accorsi, G.; Rio, Y.; Eckert, J.-F. *Chem.*−*Eur. J*. **2003**, *9*, 36.

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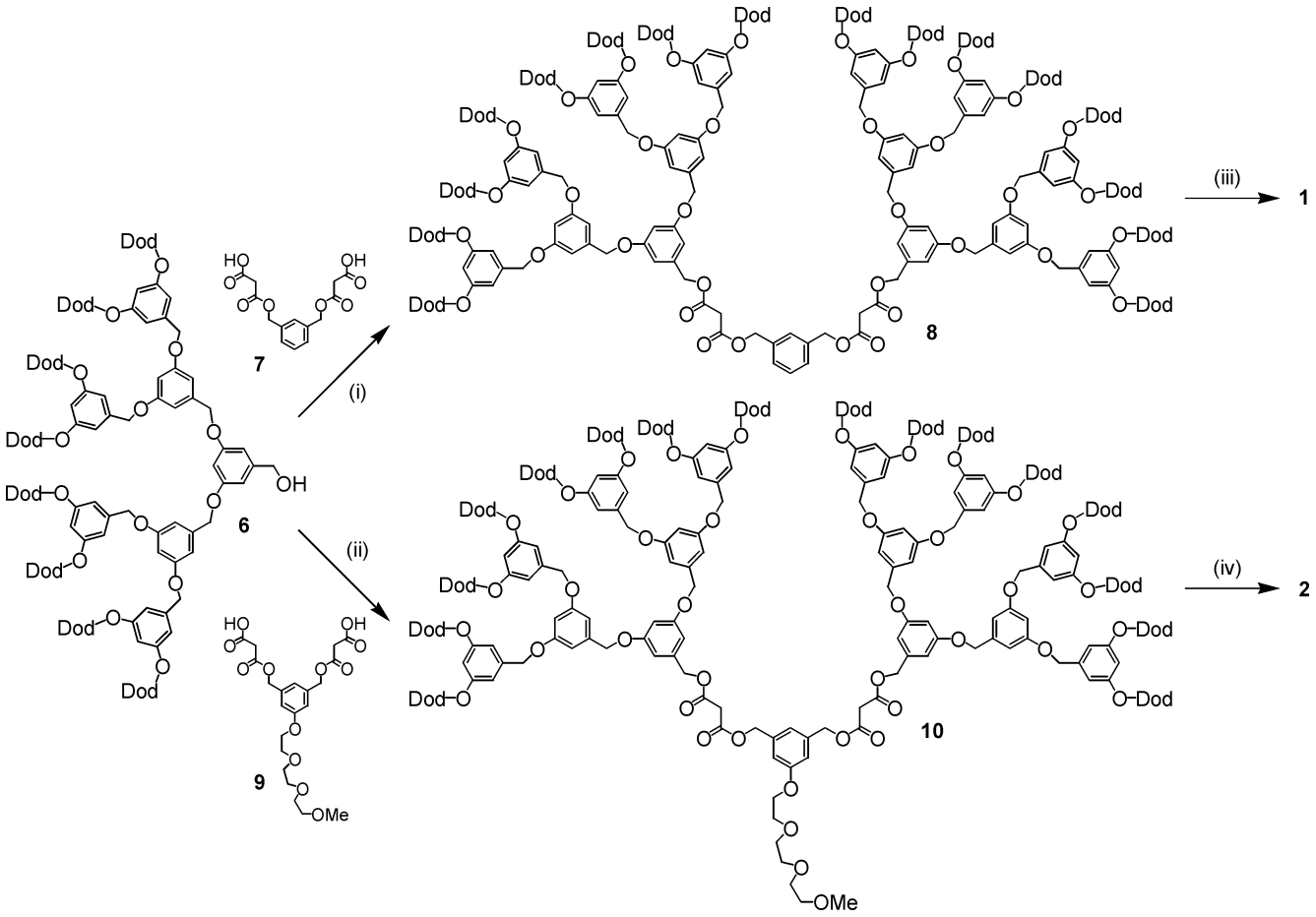
SCHEME 1. Preparation of Fullerodendrimers 1 and 2[a]



[a]Reagents and conditions: (i) DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to room temperature, 24 h (76%); (ii) DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to room temperature, 24 h (70%); (iii) C_{60}, I_2, DBU, toluene, rt, 24 h (44%); (iv) C_{60}, I_2, DBU, toluene, rt, 24 h (42%).

Fullerodendrimer **2** was then obtained in 42% yield by reaction of **10** with C_{60}, I_2, and DBU in toluene at room temperature.

The preparation of the fullerene derivative bearing two triethylene glycol chains is depicted in Scheme 2. Treatment of bromide **11**[11] with dimethyl 5-hydroxyisophthalate in the presence of K_2CO_3 in DMF at 70 °C afforded **12** in 82% yield. Lithium aluminum hydride (LAH) reduction then gave diol **13**, and subsequent treatment with Meldrum's acid[12] (2,2-dimethyl-1,3-dioxane-4,6-dione) afforded diacid **14** in 98% yield. Reaction of alcohol **6** with diacid **14** under esterification conditions using DCC, DMAP, and HOBt in CH_2Cl_2 gave bis-malonate **15** in 43% yield. Finally, reaction of **15** with C_{60}, I_2, and DBU in toluene at room temperature afforded the bis-adduct **3** in 33% yield.

Fullerodendrimers **4** and **5** were obtained from **16**[11] and **21**,[11] respectively, by following a synthetic route similar to the one used for the preparation of compound **3** (Schemes 3 and 4). Diacids **19** and **24** were prepared by alkylation of dimethyl 5-hydroxyisophthalate with the corresponding bromide followed by LAH reduction and subsequent reaction with Meldrum's acid.

Treatment of **19** and **24** with **6** under DCC-mediated esterification conditions afforded the corresponding bis-malonates **20** and **25** in moderate yields. Actually, the yields were limited by abnormally high proportions of *N*-acyldicyclohexylurea byproducts resulting from the rearrangement of the activated acid intermediates.[13] This is a clear indication that the reaction of the alcohol with the activated acid is slow. The latter observation results certainly from the reduced accessibility of the reactive groups located at the focal point of dendritic moieties for both reactants. Finally, treatment of C_{60} with **20** and **25** in the presence of I_2 and DBU in toluene gave the targeted bis-adducts **4** and **5**, respectively.

Fullerodendrimers **1**−**5** have been characterized by ^1H and ^{13}C NMR, UV−vis spectroscopy, and IR spectroscopy. In addition, the structures of **1**−**5** have also been confirmed by MALDI-TOF mass spectrometry. The relative position of the two cyclopropane rings in **1**−**5** on the C_{60} core has been determined based on the molecular symmetry (C_s) deduced from the ^1H and ^{13}C NMR spectra. It is also well established that the 1,3-phenylenebis(methylene)-tethered bis-malonates produce regioselectively the C_s symmetrical cis-2 addition pattern at C_{60}.[7,14] As

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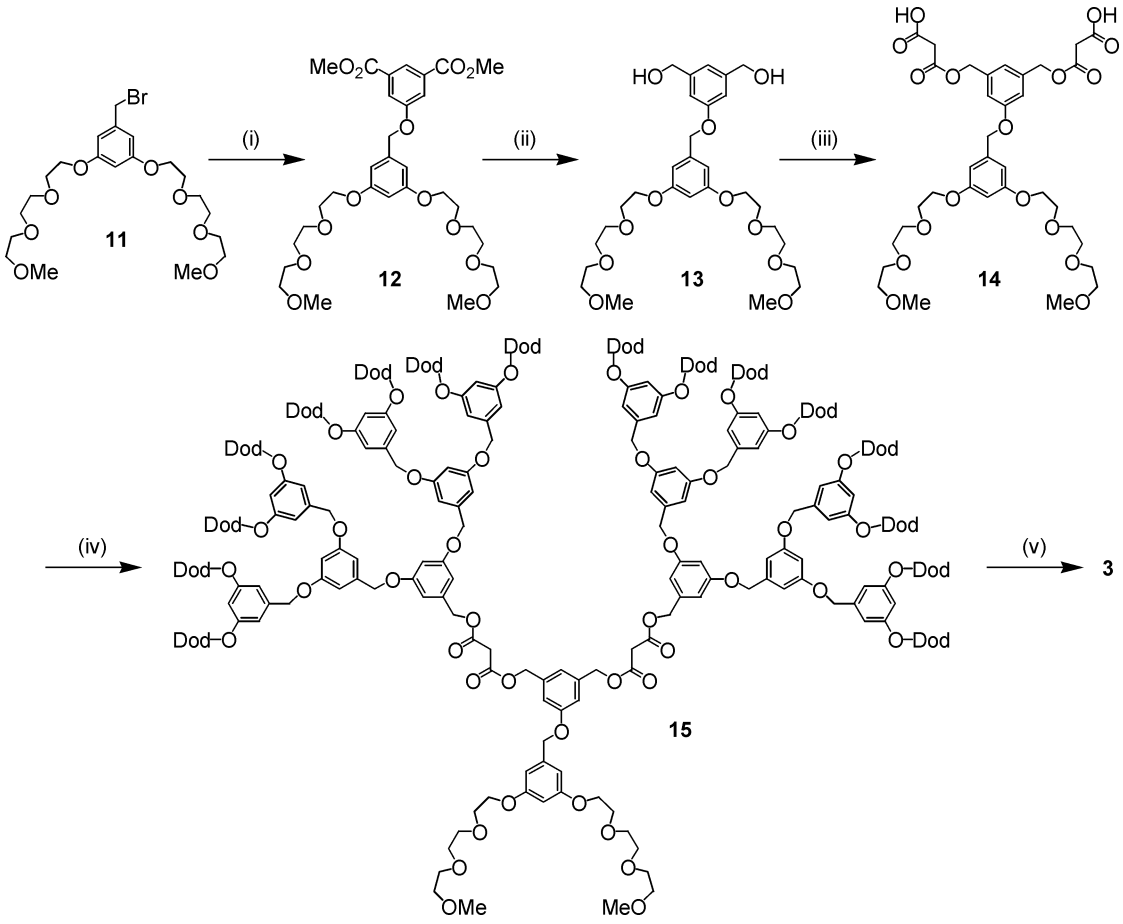
SCHEME 2. Preparation of Fullerodendrimer 3[a]



[a] Reagents and conditions: (i) dimethyl 5-hydroxyisophthalate, K_2CO_3, 18-crown-6, acetone, Δ, 48 h (82%); (ii) LAH, THF, 0 °C, 6 h (88%); (iii) Meldrum's acid, 120 °C, 4 h (quantitative); (iv) **6**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to room temperature, 24 h (53%); (v) C_{60}, I_2, DBU, toluene, rt, 24 h (33%).

typical examples, the ^{13}C NMR spectra of compounds **1** and **5** recorded in $CDCl_3$ are shown in Figures 2 and 3.

The spectrum of **1** is in full accordance with the proposed molecular structure. The 32 expected fullerene resonances are clearly observed: two at $\delta = 66.77$ and 70.57 for the two different sp^3 C atoms and 30 between $\delta = 134$ and 146 for the 30 different sp^2 C atoms. It is worth noting that four of the resonances seen in the sp^2 region show half-intensity signals. Actually, the latter observation is an unambiguous proof for the C_s symmetry of compound **1**. Effectively, for such a C_{60} derivative, there are 26 pairs of equivalent sp^2 fullerene C atoms and four unique ones. The 35 expected non-fullerenic signals are also observed for C_s symmetrical **1**. Interestingly, the aromatic C atoms of the dendritic wedges appear as four groups of three signals having a 4:2:1 relative intensity in perfect agreement with their branched structure. The ^{13}C NMR spectrum of fullerodendrimer **5** shows the same characteristic features as **1** with additional signals arising from the additional dendritic unit. It can be noted that the patterns seen for the fullerene C atoms in the sp^2 region are nearly identical for both **1** and **5**. Actually, the same pattern is also observed in the ^{13}C NMR spectra of **2**−**4**, thus showing that the relative position of the two cyclopropane rings on the C_{60} core is the same for the five compounds.

The colors and, accordingly, the absorption spectra of C_{60} bis-adducts are highly dependent on the addition pattern and are characteristic for each of the regioisomers.[14] The orange color and the UV−vis spectra of **1**−**5** are indeed fully consistent with those of previously reported analogous cis-2 bis-adducts.[7,15] As a typical example, the UV−vis spectrum of fullerodendrimer **1** in CH_2Cl_2 is shown in Figure 4. The absorption spectrum is much less resolved than that of plain C_{60}. In the UV only one distinct band is present ($\lambda_{max} = 263$ nm) with two shoulders above 300 nm, compared with the two well-distinct bands observed for the parent C_{60} in the same region.[16] In the visible spectral region, the spectrum is very broad and the band corresponding to the lowest-allowed singlet transition, which is very sharp and well distinguishable for C_{60}, is barely detectable at about 437 nm.

Langmuir Films. Compound **1** with no polar headgroup does not form any Langmuir film, even when compressed down to unrealistic molecular areas. In contrast, Langmuir films have been obtained with dendrimers **2**−**5**. Regardless of its size, the polar headgroup of these compounds is responsible for an attractive interaction with the aqueous subphase thus forcing the

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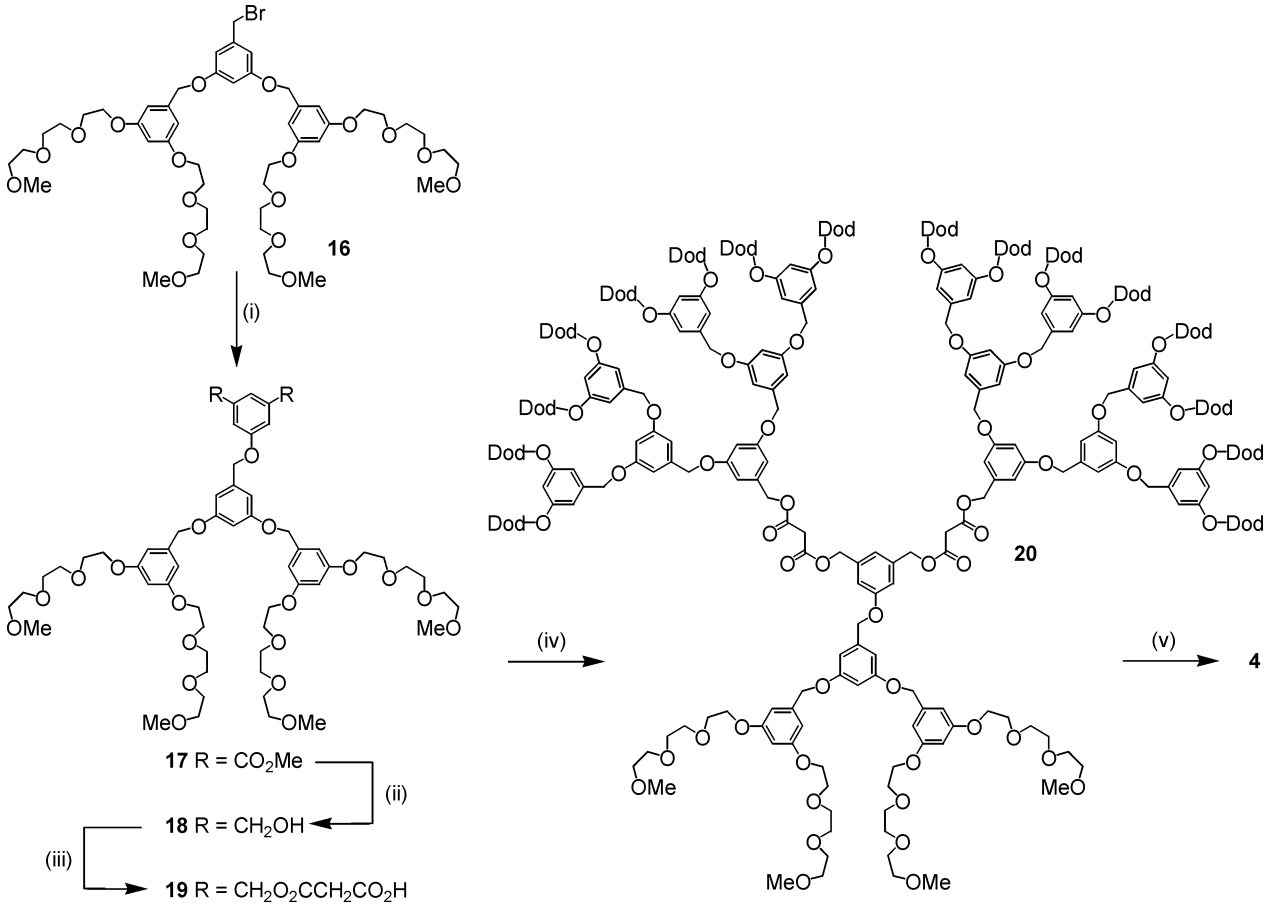
SCHEME 3. Preparation of Fullerodendrimer 4[a]



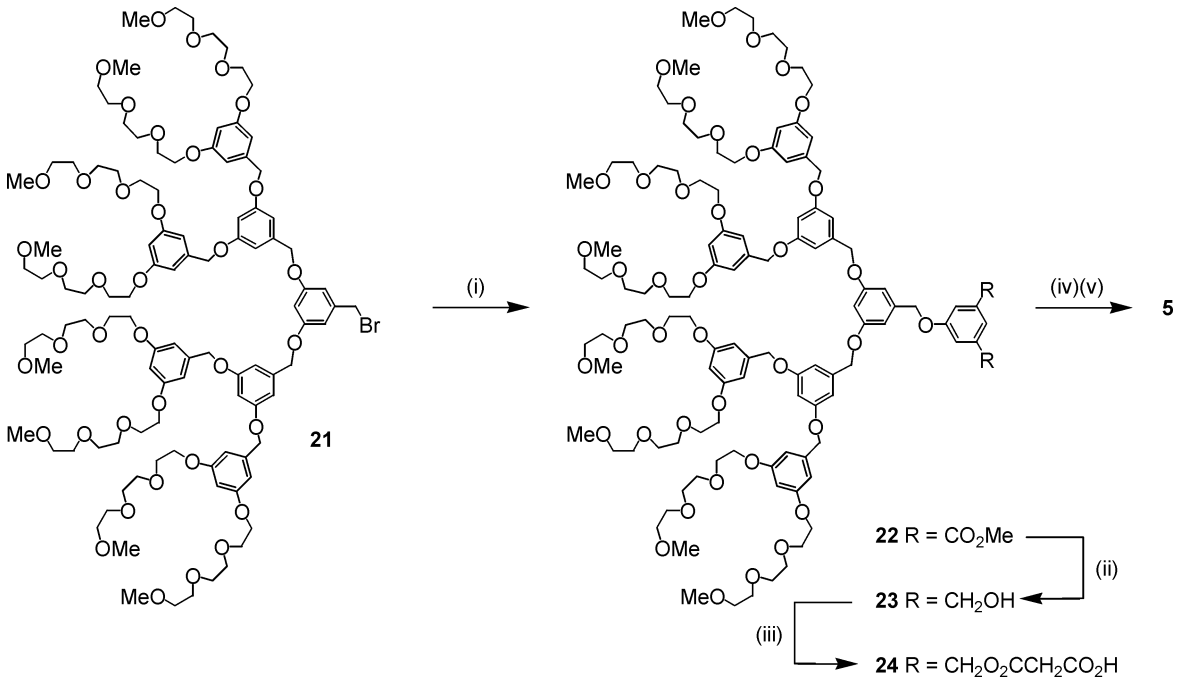
[a] Reagents and conditions: (i) dimethyl 5-hydroxyisophthalate, K_2CO_3, 18-crown-6, acetone, Δ, 48 h (87%); (ii) LAH, THF, 0 °C, 6 h (89%); (iii) Meldrum's acid, 120 °C, 4 h (quantitative); (iv) **6**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to room temperature, 24 h (41%); (v) C_{60}, I_2, DBU, toluene, rt, 24 h (30%).

molecules toward the water surface in a two-dimensional arrangement. The pressure/area (Π/*A*) isotherms of fullerodendrimers **2**−**5** are depicted in Figure 5.

The four compounds exhibit a similar behavior: the surface pressure Π increases smoothly at molecular areas between 400 and 500 Å^2 before taking a sharper rise between 250 and 350 Å^2, depending on the compound. The general shape of the isotherms indicates that the films are at first in a liquid-condensed phase. The rather big molecular areas at which the molecules start to physically interact are not surprising given the size of these molecules and the fact that alkyl chains and C_{60} will initially tend to segregate, pushing the alkyl chains away from the core. The molecules have, therefore, a rather large radius on the water surface before being forced to adopt a more compact conformation because of the compression. Such behavior has already been observed.[5] Final molecular areas, A_0, extrapolated at zero surface pressure are 307 ± 3 (**2**), 320 ± 3 (**3**), 295 ± 3 (**4**), and 280 ± 3 Å^2 (**5**) which are in good agreement with the value which can be estimated by molecular modeling. Interestingly, the A_0 values are smaller for the two compounds with the largest polar headgroup (**4** and **5**). The latter observation could be ascribed to a conformational change in the dendritic structure when the anchoring on the water surface is stronger. The repulsion of the $C_{12}H_{25}$-terminated dendrons from the water surface must be more effective in the case of **4** and **5**, and as a result, the molecules adopt a more compact structure. In other words, the two $C_{12}H_{25}$-terminated dendritic branches are forced to wrap the fullerene core. In contrast, for compounds **2** and **3** the dendritic structure may be less densely packed around the central fullerene core because of the weaker anchoring on the water surface. This model is further supported by observations done on the Langmuir−Blodgett films prepared from the Langmuir films of compounds **2**−**5** (discussed later). The larger molecular area observed for compound **3** compared to **2** seems, however, to be in contradiction with the proposed model. Actually, it must be noted that the unique ethylene glycol subunit in **2** is directly connected to the bridging phenyl ring, whereas the two polar chains in **3** are separated from the core unit by an additional benzylic moiety. Therefore, even if the anchoring on the water is weaker for **2** compared to **3**, the two dodecyloxy-functionalized dendrons are closer to the aqueous surface in the case of **2**. As a result, the repulsion of the dendritic branches from the water surface must be slightly more effective for **2**. Therefore, this compound adopts a more compact structure and its molecular area is smaller.

Upon further compression all films reach a final collapse pressure Π_c which strongly depends on the size of the polar headgroup. Let us mention here that the isotherms of **2**−**5** showed excellent reversibility (no

SCHEME 4. Preparation of Fullerodendrimer 5[a]



[a] Reagents and conditions: (i) dimethyl 5-hydroxyisophthalate, K_2CO_3, 18-crown-6, acetone, Δ, 48 h (85%); (ii) LAH, THF, 0 °C, 6 h (91%); (iii) Meldrum's acid, 120 °C, 4 h (quantitative); (iv) **6**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to room temperature, 24 h (**25**: 35%); (v) C_{60}, I_2, DBU, toluene, rt, 24 h (36%).

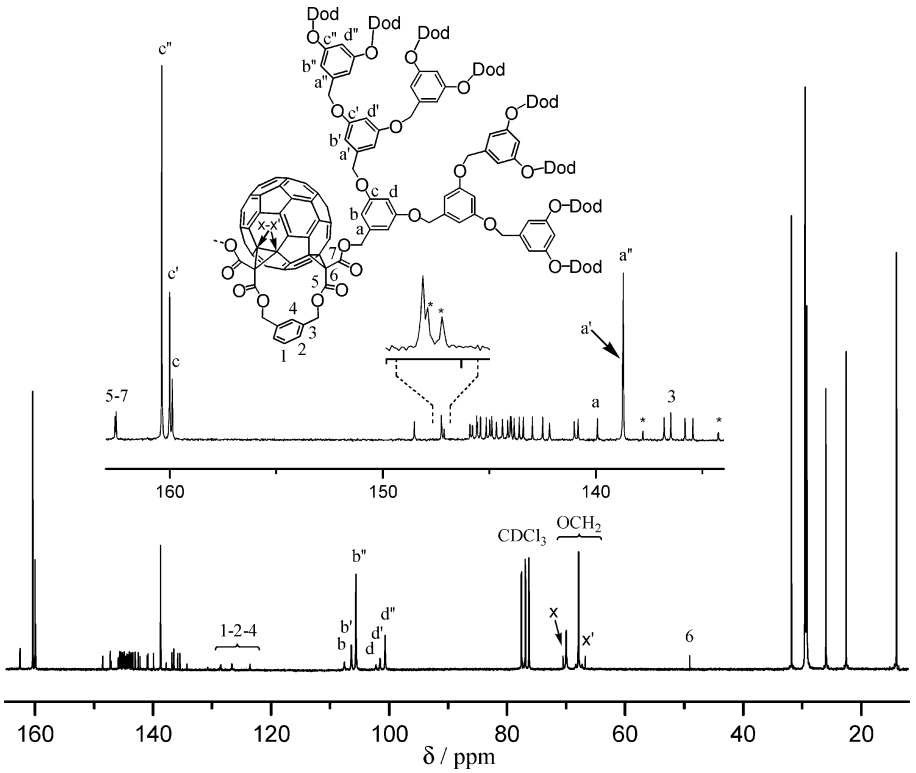


FIGURE 2. ^{13}C NMR spectrum ($CDCl_3$, 50 MHz) of fullerodendrimer **1** (∗ indicates the four sp^2 fullerene C atoms showing half-intensity signals).

hysteresis) as long as the collapse pressure was not exceeded. The following Π_c values have been taken at the point where the compressibility of the film starts to decrease: 10.5 ± 1.0 (**2**), 30.5 ± 1.0 (**3**), 41 ± 1.0 (**4**), and 42.5 ± 1.0 $mN \cdot m^{-1}$ (**5**). For a given compound, the Π_c values obtained from different films did not vary significantly. Changes in the collapse pressure with the number of ethylene glycol subunits show how critically the strength of the polar headgroup needs to match that of the hydrophobic part. Put in an Orwellian style: no head, no film; small head, weak films. The only films able to withstand a significant compression before collapsing are

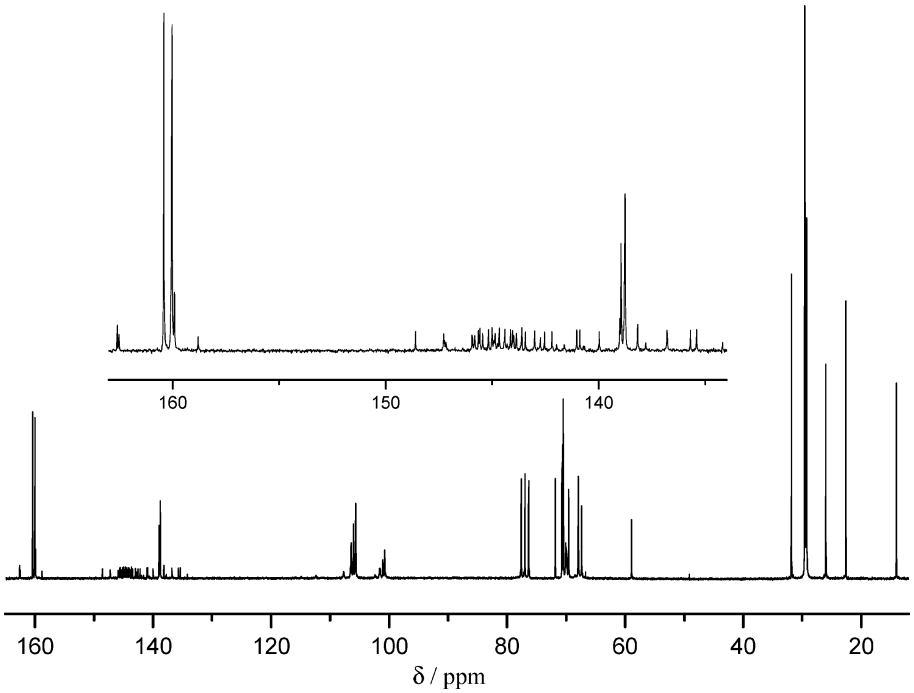


FIGURE 3. ^{13}C NMR spectrum ($CDCl_3$, 50 MHz) of fullerodendrimer **5**.

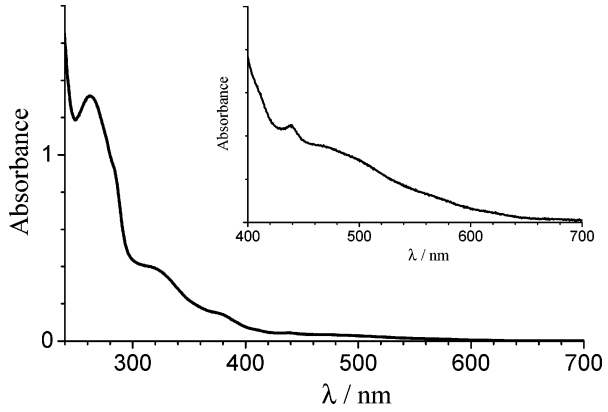


FIGURE 4. Absorption spectrum of fullerodendrimer **1** recorded in CH_2Cl_2 solution.

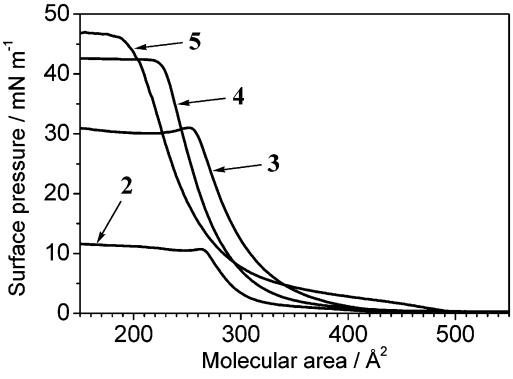


FIGURE 5. Pressure/area isotherms of compounds **2**−**5** taken on pure water at 20 °C. The collapse pressure increases with the size of the polar headgroup.

those for which the hydrophilic force anchoring the molecules on the water balances the hydrophobic forces. It is interesting to note that there is no significant improvement of the collapse pressure when going from compound **4** with four ethylene glycol chains to compound **5** with eight chains. This is because even perfectly anchored films will start buckling because of their limited rigidity.

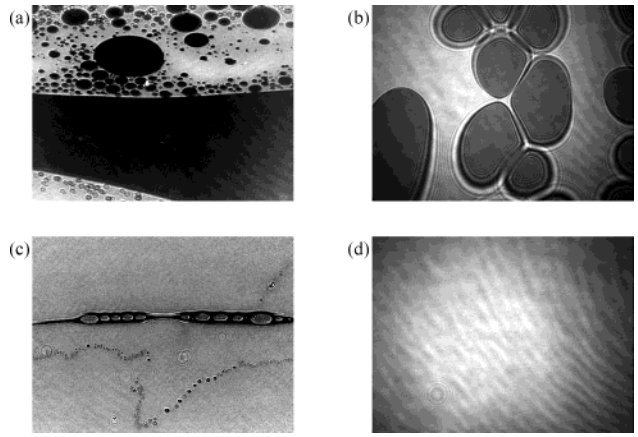


FIGURE 6. Brewster angle microscopy images for Langmuir films: (a) **2** at $A = 840$ Å^2; (b) **3** at $A = 900$ Å^2; (c) **5** at $A = 530$ Å^2; (d) **5** at $A = 211$ Å^2. The dark areas are the water subphase, the fringes are caused by the laser light.

Microscopy at the Brewster angle (BAM) allows for visual observation of film formation at a microscopic level. Except for **1**, observations reveal a very similar behavior for the different compounds. At large molecular areas, the films are in the liquid-expanded state, with the molecules assembled in smooth-edged domains surrounded by water (Figure 6a). These domains are not solid, and lots of "holes" remain through which water can be seen (Figure 6b). Upon further compression, being liquid, all of these domains gently merge together (Figure 6c) and the final film exhibits no defects (Figure 6d). It must be emphasized that just before the final collapse, films from all compounds were identical to the one pictured in Figure 6d.

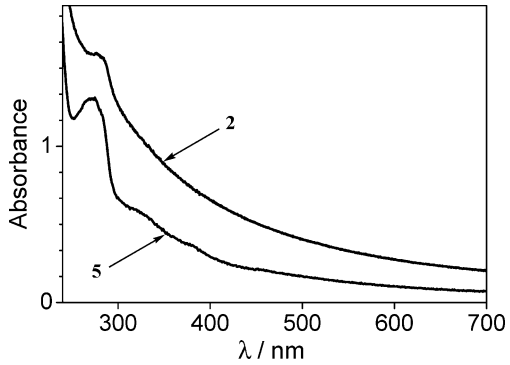


FIGURE 7. Absorption spectra of LB films of **2** and **5**.

Langmuir−Blodgett Films. When the Langmuir−Blodgett (LB) technique is used, it has been possible to transfer the Langmuir films made from **2**−**5** and to obtain multilayers on solid substrates. In accordance with previous observations,[5] transfer is more efficient upon increasing the size of the polar headgroup. The excellent quality of the LB films prepared from these amphiphilic dendrimers is deduced from the plot of their UV−vis absorbance as a function of the layer number which results in straight lines, indicating an efficient stacking of the layers.[17] The UV−vis spectra of the LB films obtained from **2** and **5** are shown in Figure 7.

The main feature of the UV−vis spectrum of the LB film of **2** is the broadening of the absorption in the film compared to that of the solution. The latter observation is indicative of fullerene−fullerene interactions within the LB films.[18] Because of the presence of the dendritic subunits around the C_{60} core within a layer, we believe that these fullerene−fullerene interactions may be the result of the contact of carbon spheres from neighboring layers rather than from within the layers. The absorption spectra of LB films prepared from compound **3** (not shown) are also broad. Remarkably, a clear evolution can be seen by going from **2** to **5**: the broadening of the absorption spectrum seen for **2** is almost vanished for **4** and **5**. Actually, the UV−vis spectra of LB films of **4** and **5** are close to the ones recorded in CH_2Cl_2 solutions suggesting limited fullerene−fullerene interactions within the LB film. This observation is in full agreement with the more compact structures proposed for **4** and **5** at the air−water interface compared to **2** and **3**. The latter hypothesis was also confirmed by computational studies.[19] As shown in Figure 8, the calculated structure of fullerodendrimer **5** reveals that the dendritic shell is effectively able to completely cover the fullerene core (the calculations have been performed in the absence of solvent, our aim being only to estimate the possible degree of isolation).

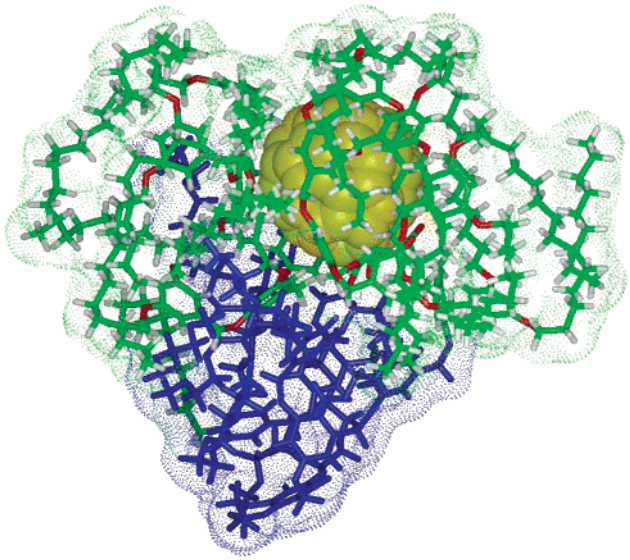


FIGURE 8. Snapshot of the theoretical structure of fullerodendrimer **5** at 300 K obtained from a molecular dynamics calculation.[19]

Conclusion

Amphiphilic diblock dendrimers with a C_{60} core have been obtained by cyclization of dendritic bis-malonate derivatives at the carbon sphere. All of the amphiphilic derivatives show good spreading characteristics and a reversible behavior upon successive compression−expansion cycles. The Langmuir studies have revealed a conformational change in the dendritic structure with the size of the polar headgroup. Because of a better anchoring onto the water surface, the compounds with the largest polar headgroup adopt a more compact structure and the dendritic branches are forced to wrap the fullerene core. This model is nicely confirmed by the amount of fullerene−fullerene interactions within the LB films as deduced from their absorption spectra. On the one hand, the results obtained in this systematic study show some of the fundamental architectural requirements for obtaining stable Langmuir films with amphiphilic dendrimers. On the other hand, it is worth noting that the fullerene chromophores are almost isolated from external contacts by the dendritic structure thus paving the way toward ordered thin films of isolated functional molecular units. This appears to be an important finding for future nanotechnological applications, in particular, for data storage at a molecular level.

(16) Armaroli, N.; Boudon, C.; Felder, D.; Gisselbrecht, J.-P.; Gross, M.; Marconi, G.; Nicoud, J.-F.; Nierengarten, J.-F.; Vicinelli, V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3730.

(17) The structural quality of the LB films was also probed by preliminary grazing incidence X-ray diffraction measurements. In all of the spectra, many Kiessig fringes can be seen, which is evidence that the film roughness is quite low (typically $R \approx 5.5$ Å). Further experiments are still in progress and will be reported in due time.

(18) (a) Guldi, D. M.; Hungerbühler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 13487. (b) Jonas, U.; Cardullo, F.; Belik, P.; Diederich, F.; Gügel, A.; Harth, E.; Herrmann, A.; Isaacs, L.; Müllen, K.; Ringsdorf, H.; Thielgen, C.; Uhlmann, P.; Vasella, A.; Waldraff, C. A. A.; Walter, M. *Chem.−Eur. J.* **1995**, *1*, 243. (c) Guldi, D. M. *J. Phys. Chem. A* **1997**, *101*, 3895. (d) Guldi, D. M.; Hungerbühler, H.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1783. (e) Felder, D.; Guillon, D.; Lévy, R.; Mathis, A.; Nicoud, J.-F.; Nierengarten, J.-F.; Rehspringer, J.-L.; Schell, J. *J. Mater. Chem.* **2000**, *10*, 887. (f) Felder, D.; Gutiérrez Nava, M.; Carreon, M. P.; Eckert, J.-F.; Luccisano, M.; Schall, C.; Masson, P.; Gallani, J.-L.; Heinrich, B.; Guillon, D.; Nierengarten, J.-F. *Helv. Chim. Acta* **2002**, *85*, 288.

(19) The molecular dynamics (MD) studies have been performed on SGI Origin 200 and Octane workstations using the Discover 3 software from Accelrys (www.accelrys.com) with the pcff force field. The previously minimized structures were allowed to equilibrate for 500 ps at a 300 K isotherm by the MD simulation (in the NVT ensemble with a time step of 1 fs).

Experimental Section

General. Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over sodium benzophenone ketyl. Compounds **6**,[9] **7**,[7b] **9**,[10] **11**,[11] **16**,[11] and **21**[11] were prepared as previously reported.

General Procedure for the Synthesis of Diesters 12, 17, and 22. A mixture of dimethyl 5-hydroxyisophthalate (1 equiv), the appropriate bromide (1 equiv), K_2CO_3 (5 equiv), and 18-crown-6 (0.5 equiv) in acetone was refluxed for 48 h. The resulting mixture was diluted with CH_2Cl_2, filtered, and evaporated. The crude product was then purified as outlined in the following text.

Diester 12. This compound was prepared from **11** and purified by column chromatography (SiO_2, acetone/CH_2Cl_2 4:1) to give **12** (82%) as a colorless glassy product. IR (CH_2Cl_2, cm^{-1}): 1725. ^1H NMR ($CDCl_3$, 200 MHz, δ): 8.30 (t, J = 1.5 Hz, 1 H), 7.82 (d, J = 1.5 Hz, 2 H), 6.60 (d, J = 2 Hz, 2 H), 6.46 (t, J = 2 Hz, 1 H), 5.07 (s, 2 H), 4.12 (m, 4 H), 3.95 (s, 6 H), 3.85 (m, 4 H), 3.75−3.50 (m, 16 H), 3.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 165.22, 159.57, 158.02, 137.79, 131.15, 122.48, 119.39, 105.34, 100.63, 71.32, 70.19, 70.03, 69.93, 69.53, 69.02, 66.91, 58.33, 51.77. Anal. Calcd for $C_{31}H_{44}O_{13}$: C, 59.60; H, 7.10. Found: C, 59.62; H, 7.26.

Diester 17. This compound was prepared from **16** and purified by column chromatography (SiO_2, acetone/CH_2Cl_2 3:7) to give **17** (1.07 g, 87%) as a colorless glassy product. IR (CH_2Cl_2, cm^{-1}): 1725 (C═O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 8.30 (t, J = 1.5 Hz, 1 H), 7.82 (d, J = 1.5 Hz, 2 H), 6.66 (d, J = 1.5 Hz, 2 H), 6.59 (d, J = 1.5 Hz, 4 H), 6.56 (t, J = 1.5 Hz, 1 H), 6.45 (t, J = 1.5 Hz, 2 H), 5.08 (s, 2 H), 4.96 (s, 4 H), 4.12 (m, 8 H), 3.95 (s, 6 H), 3.82 (m, 8 H), 3.75−3.50 (m, 32 H), 3.38 (s, 12 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 164.9, 159.3, 159.3, 157.8, 138.4, 137.8, 130.9, 122.2, 119.1, 105.5, 105.1, 100.9, 100.8, 71.1, 70.0, 69.8, 69.7, 69.3, 69.2, 68.8, 66.7, 58.1, 51.6. Anal. Calcd for $C_{59}H_{84}O_{23}$: C, 61.02; H, 7.29. Found: C, 61.13; H, 7.56.

Diester 22. This compound was prepared from **21** and purified by column chromatography (SiO_2, acetone/CH_2Cl_2 1:1) to give **27** (85%) as a colorless glassy product. IR (CH_2Cl_2, cm^{-1}): 1725 (C═O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 8.30 (broad s, 1 H), 7.82 (broad s, 2 H), 6.68 (broad s, 4 H), 6.60 (broad s, 13 H), 6.45 (broad s, 4 H), 5.03 (s, 2 H), 4.96 (s, 12 H), 4.11 (m, 16 H), 3.95 (s, 6 H), 3.82 (m, 16 H), 3.75−3.50 (m, 64 H), 3.38 (s, 24 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 165.1, 159.4, 159.4, 158.0, 138.6, 138.5, 137.9, 122.4, 119.3, 105.6, 105.3, 100.8, 100.3, 71.2, 70.1, 69.9, 69.8, 69.4, 69.2, 68.9, 66.8, 50.7. Anal. Calcd for $C_{115}H_{164}O_{43}$: C, 61.81; H, 7.40. Found: C, 61.83; H, 7.69.

General Procedure for the Preparation of Diols 13, 18, and 23. A 1 M $LiAlH_4$ solution in THF (2 equiv) was added to a stirred solution of the appropriate diester (1 equiv) in THF at 0 °C. The resulting mixture was stirred for 6 h at 0 °C, and then MeOH was carefully added. The reaction mixture was filtered and evaporated. The crude product was then purified as outlined in the following text.

Diol 13. This compound was prepared from **12** and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) to give **13** (88%) as a colorless glassy product. ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.94 (t, J = 1.5 Hz, 1 H), 6.91 (d, J = 1.5 Hz, 2 H), 6.59 (d, J = 2 Hz, 1 H), 6.43 (t, J = 2 Hz, 2 H), 5.02 (s, 2 H), 4.66 (d, J = 5.5 Hz, 2 H), 4.11 (m, 4 H), 3.83 (m, 4 H), 3.50−3.75 (m, 16 H), 3.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 159.5, 158.3, 142.7, 139.0, 117.1, 111.1, 105.5, 100.4, 71.3, 70.2, 70.1, 70.0, 69.1, 66.9, 63.9, 58.5. Anal. Calcd for $C_{29}H_{44}O_{11}$: C, 61.25; H, 7.80. Found: C, 61.01; H, 7.99.

Diol 18. This compound was prepared from **17** and purified by column chromatography (SiO_2, acetone/CH_2Cl_2 7:3) to give **18** (89%) as a colorless glassy product. ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.95 (broad s, 1 H), 6.82 (broad s, 2 H), 6.59 (broad s, 2 H), 6.55 (d, J = 1.5 Hz, 4 H), 6.54 (broad s, 1 H), 6.43 (t, J = 1.5 Hz, 2 H), 5.03 (s, 2 H), 4.97 (s, 4 H), 4.64 (d, J = 6 Hz, 2 H), 4.13 (m, 8 H), 3.82 (m, 8 H), 3.75−3.50 (m, 32 H), 3.38 (s, 12 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 159.7, 159.6, 158.5, 142.8, 139.2, 138.8, 117.2, 111.6, 105.7, 105.6, 101.2, 100.7, 71.5, 70.4, 70.2, 70.1, 69.5, 69.3, 67.1, 64.2, 62.0, 58.6. Anal. Calcd for $C_{57}H_{84}O_{21}$: C, 61.94; H, 7.66. Found: C, 61.61; H, 7.83.

Diol 23. This compound was prepared from **22** and purified by column chromatography (SiO_2, acetone/CH_2Cl_2 7:3) to give **23** (91%) as a colorless glassy product. ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.95 (s, 1 H), 6.88 (s, 2 H), 6.65 (broad s, 4 H), 6.57 (broad s, 13 H), 6.44 (broad s, 4 H), 4.97 (s, 14 H), 4.63 (d, 4 H), 4.10 (m, 16 H), 3.83 (m, 16 H), 3.75−3.50 (m, 64 H), 3.37 (s, 24 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 159.4, 159.3, 158.3, 142.7, 139.0, 138.7, 138.5, 116.9, 111.1, 105.7, 105.3, 100.9, 100.4, 71.2, 70.9, 70.1, 69.9, 69.8, 69.2, 69.0, 66.8, 63.7, 58.3. Anal. Calcd for $C_{113}H_{164}O_{41}\cdot H_2O$: C, 61.79; H, 7.62. Found: C, 61.52; H, 7.89.

General Procedure for the Synthesis of Diacids 14, 19, and 24. A mixture of Meldrum's acid (2 equiv) and the appropriate diol (1 equiv) was heated at 120 °C for 4 h. Cooling and drying afforded the corresponding diacid which was used in the next step as received. Compounds **14**, **19**, and **24** have been characterized by ^1H NMR spectroscopy; the spectra being typically broad, they are not described here.

General Procedure for the Synthesis of Bis-Malonates 8, 10, 15, 20, and 25. DCC (2.2 equiv) was added to a stirred solution of **6** (2 equiv), the appropriate diacid (1 equiv), HOBt (0.1 equiv), and DMAP (0.5 equiv) in CH_2Cl_2 at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 24 h, filtered, and evaporated. The crude product was then purified as outlined in the following text.

Bis-Malonate 8. This compound was prepared from **7** and purified by column chromatography (SiO_2, CH_2Cl_2/hexane 2:1) to give **8** (76%) as a colorless glassy compound. IR (CH_2Cl_2, cm^{-1}): 1748 (C═O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 7.29 (m, 4 H), 6.66 (broad s, 8 H), 6.55 (broad s, 26 H), 6.40 (broad s, 8 H), 5.16 (s, 4 H), 5.10 (s, 4 H), 4.95 (broad s, 24 H), 3.93 (t, J = 6.5 Hz, 32 H), 3.47 (s, 4 H), 1.77−1.73 (m, 32 H), 1.50−1.20 (m, 288 H), 0.90−0.87 (t, J = 6.5 Hz, 48 H). Anal. Calcd for $C_{304}H_{478}O_{36}$: C, 77.47; H, 10.31. Found: C, 77.51; H, 10.60.

Bis-Malonate 10. This compound was prepared from **9** and purified by column chromatography (SiO_2, acetone/CH_2Cl_2 3:2) to give **10** (70%) as a colorless glassy compound. IR (CH_2Cl_2, cm^{-1}): 1749 (C═O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.86 (broad s, 3 H), 6.66 (broad s, 8 H), 6.54 (broad s, 26 H), 6.39 (broad s, 8 H), 5.11 (broad s, 8 H), 4.93 (broad s, 24 H), 4.11 (m, 2 H), 3.91 (t, 32 H, J = 6.5 Hz), 3.85 (m, 2 H), 3.60−3.40 (m, 8 H), 3.37 (s, 3 H), 3.34 (s, 4 H), 1.75 (m, 32 H), 1.50−1.20 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). Anal. Calcd for $C_{311}H_{496}O_{40}$: C, 76.62; H, 10.25. Found: C, 76.18; H, 10.51.

Bis-Malonate 15. This compound was prepared from **14** and purified by column chromatography (SiO_2, CH_2Cl_2/acetone 97:3) to give **15** (53%) as a colorless glassy product. IR (CH_2Cl_2, cm^{-1}): 1748 (C═O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.90 (broad s, 3 H), 6.66 (broad s, 8 H), 6.54 (broad s, 28 H), 6.40 (broad s, 9 H), 5.11 (broad s, 8 H), 4.93 (broad s, 26 H), 4.11 (m, 4 H), 3.92 (t, J = 6.5 Hz, 32 H), 3.78 (m, 4 H), 3.75−3.50 (m, 16 H), 3.38 (s, 6 H), 3.32 (s, 4 H), 1.76 (m, 32 H), 1.50−1.20 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). Anal. Calcd for $C_{325}H_{516}O_{45}$: C, 75.89; H, 10.11. Found: C, 75.68; H, 10.39.

Bis-Malonate 20. This compound was prepared from **19** and purified by column chromatography (SiO_2, CH_2Cl_2/acetone 5:1) to give **20** (41%) as a colorless glassy product. IR (CH_2Cl_2, cm^{-1}): 1748 (C═O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.90 (broad s, 3 H), 6.66 (broad s, 8 H), 6.54 (broad s, 34 H), 6.39 (broad s, 9 H), 5.11 (broad s, 8 H), 4.93 (broad s, 30 H), 4.10 (m, 8 H), 3.92 (t, J = 6.5 Hz, 32 H), 3.80 (m, 8 H), 3.75−3.50 (m, 32 H), 3.36 (s, 12 H), 3.32 (s, 4 H), 1.76 (m, 32 H), 1.50−1.20 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). Anal. Calcd for $C_{353}H_{552}O_{55}$: C, 74.70; H, 9.80. Found: C, 74.58; H, 10.05.

Bis-Malonate 25. This compound was prepared from **24** and purified by column chromatography (SiO_2, CH_2Cl_2/acetone 5:1) to give **25** (35%) as a colorless glassy product. IR (CH_2Cl_2, cm^{-1}): 1748 (C=O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 6.90 (broad s, 3 H), 6.66−6.38 (m, 63 H), 5.14 (broad s, 8 H), 4.91 (broad s, 38 H), 4.09 (m, 16 H), 3.92 (t, J = 6.5 Hz, 32 H), 3.81 (m, 16 H), 3.75−3.50 (m, 64 H), 3.36 (s, 24 H), 3.32 (s, 4 H), 1.75 (m, 32 H), 1.50−1.20 (m, 288 H), 0.87 (t, J = 6.5 Hz, 48 H). Anal. Calcd for $C_{353}H_{552}O_{55}$: C, 72.74; H, 9.49. Found: C, 72.40; H, 9.78.

General Procedure for the Synthesis of Fullerodendrimers 1−5. DBU (4 equiv) was added to a stirred solution of C_{60} (1 equiv), I_2 (3 equiv), and the appropriate bis-malonate (1 equiv) in toluene (2 mL/mg of C_{60}). The resulting solution was stirred for 24 h, then filtered through a short plug of SiO_2, and eluted first with toluene (to remove unreacted C_{60}) and then with CH_2Cl_2/8% MeOH. The crude product was then purified as outlined in the following text.

Fullerodendrimer 1. This compound was prepared from **8** and purified by column chromatography (SiO_2, toluene/hexane 2:1) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **1** (44%) as a dark-orange glassy product. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 437 (2000), 382 (sh, 8200), 323 (sh, 23 600), 263 (85 600). IR (CH_2Cl_2, cm^{-1}): 1751 (C=O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 7.40 (m, 4 H), 6.69 (broad s, 8 H), 6.52 (broad s, 26 H), 6.41 (broad s, 8 H), 5.84 (d, J = 14 Hz, 2 H), 5.20 (AB, J = 14 Hz, 4 H), 5.06 (d, J = 14 Hz, 2 H), 4.93−4.86 (m, 24 H), 3.92 (t, J = 6.5 Hz, 32 H), 1.76 (m, 32 H), 1.50−1.22 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 162.6, 162.0, 160.4, 160.1, 159.9, 145.9, 145.8, 145.6, 145.5, 145.4, 145.1, 145.0, 144.9, 144.7, 144.6, 144.4, 144.1, 144.0, 143.9, 143.8, 143.6, 143.4, 143.0, 142.5, 142.2, 141.0, 140.8, 139.9, 138.8, 138.7, 137.8, 136.8, 136.5, 135.8, 135.5, 134.26, 128.8, 126.7, 123.6, 107.6, 106.4, 105.6, 102.3, 101.6, 100.7, 70.6, 70.1, 70.0, 68.4, 67.9, 67.3, 66.8, 49.1, 31.8, 29.6, 29.6, 29.55, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6, 14.0. MALDI-TOF-MS (m/z): $[M + H]^+$ calcd for $C_{364}H_{479}O_{36}$, 5430.8; found, 5430.5. Anal. Calcd for $C_{364}H_{478}O_{36}\cdot CH_2Cl_2$: C, 79.50; H, 8.77. Found: C, 79.35; H, 8.80.

Fullerodendrimer 2. This compound was prepared from **10** and purified by column chromatography (SiO_2, CH_2Cl_2) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **2** (42%) as a dark-orange glassy product. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 438 (2560), 381 (sh, 8750), 326 (sh, 24 100), 262 (87 200). IR (CH_2Cl_2, cm^{-1}): 1751 (C=O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 7.10 (broad s, 1 H), 6.77 (broad s, 2 H), 6.63 (broad s, 8 H), 6.54 (broad s, 26 H), 6.39 (broad s, 8 H), 5.75 (d, J = 14 Hz, 2 H), 5.25 (AB, J = 14 Hz, 4 H), 5.04 (d, J = 14 Hz, 2 H), 4.91 (broad s, 24 H), 4.09 (m, 2 H), 3.91 (t, 32 H, J = 6.5 Hz), 3.80 (m, 2 H), 3.70−3.40 (m, 8 H), 3.37 (s, 3 H), 1.75 (m, 32 H), 1.50−1.20 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 162.6, 162.5, 160.5, 160.1, 160.0, 158.8, 148.6, 147.3, 147.3, 147.2, 146.0, 145.9, 145.7, 145.6, 145.5, 145.2, 145.1, 145.0, 144.8, 144.4, 144.2, 144.1, 143.9, 143.7, 143.5, 143.1, 142.6, 142.3, 141.1, 140.9, 140.0, 138.8, 138.1, 137.1, 136.9, 135.9, 135.5, 134.1, 115.1, 112.5, 107.7, 106.5, 105.7, 102.4, 101.7, 100.8, 71.9, 70.8, 70.6, 70.5, 70.2, 70.1, 69.6, 68.5, 68.0, 67.5, 67.3, 66.8, 59.0, 49.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1. MALDI-TOF-MS (m/z): $[M + H]^+$ calcd for $C_{371}H_{493}O_{40}$, 5593.0; found, 5593. Anal. Calcd for $C_{371}H_{492}O_{40}\cdot CH_2Cl_2$: C, 78.71; H, 8.77. Found: C, 78.83; H, 8.65.

Fullerodendrimer 3. This compound was prepared from **15** and purified by column chromatography (SiO_2, CH_2Cl_2/acetone 97:3) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **3** (33%) as an orange glassy compound. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 439 (2850), 380 (sh, 9430), 327 (sh, 25 650), 261 (89 200). IR (CH_2Cl_2, cm^{-1}): 1748 (C=O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 7.15 (broad s, 1 H), 6.77 (broad s, 2 H), 6.63 (broad s, 8 H), 6.54 (broad s, 28 H), 6.39 (broad s, 9 H), 5.74 (d, J = 14 Hz, 2 H), 5.25 (AB, J = 14 Hz, 4 H), 5.05 (d, J = 14 Hz, 2 H), 4.90 (broad s, 26 H), 4.12 (m, 4 H), 3.91 (t, J = 6.5 Hz, 32 H), 3.85−3.50 (m, 20 H), 3.38 (s, 6 H), 1.75 (m, 32 H), 1.50−1.20 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 162.5, 160.4, 160.1, 160.0, 158.8, 148.6, 147.3, 146.0, 145.7, 145.5, 145.3, 145.1, 144.8, 144.5, 144.2, 144.1, 143.9, 143.7, 143.5, 143.1, 142.6, 141.1, 140.9, 140.0, 138.8, 138.6, 138.1, 137.9, 136.9, 135.6, 112.7, 107.7, 106.6, 106.5, 105.8, 102.4, 101.7, 100.8, 77.2, 71.9, 70.8, 70.6, 70.5, 70.1, 69.6, 68.0, 67.5, 66.8, 59.0, 49.2, 31.9, 31.6, 29.4, 29.3, 26.1, 21.8, 14.1. MALDI-TOF-MS (m/z): $[M + H]^+$ calcd for $C_{385}H_{512}O_{45}$, 5861.3; found, 5862. Anal. Calcd for $C_{385}H_{512}O_{45}$: C, 78.91; H, 8.81. Found: C, 78.32; H, 8.51.

Fullerodendrimer 4. This compound was prepared from **15** and purified by column chromatography (SiO_2, CH_2Cl_2/acetone 9:1) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **4** (30%) as an orange glassy compound. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 437 (2950), 380 (sh, 9750), 327 (sh, 27 450), 263 (91 500). IR (CH_2Cl_2, cm^{-1}): 1749 (C=O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 7.10 (broad s, 1 H), 6.79 (broad s, 2 H), 6.63 (broad s, 8 H), 6.54 (broad s, 34 H), 6.39 (broad s, 9 H), 5.74 (d, J = 14 Hz, 2 H), 5.24 (AB, J = 14 Hz, 4 H), 5.03 (d, J = 14 Hz, 2 H), 4.90 (broad s, 30 H), 4.11 (m, 8 H), 3.91 (t, J = 6.5 Hz, 32 H), 3.85−3.50 (m, 40 H), 3.37 (s, 12 H), 1.75 (m, 32 H), 1.50−1.20 (m, 288 H), 0.88 (t, J = 6.5 Hz, 48 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 162.6, 160.5, 160.1, 160.0, 159.9, 158.8, 148.6, 147.3, 147.2, 146.0, 145.9, 145.7, 145.5, 145.2, 145.1, 144.9, 144.8, 144.5, 144.2, 144.1, 144.0, 143.9, 143.7, 143.5, 143.1, 142.6, 142.3, 141.1, 140.9, 140.0, 139.0, 138.8, 138.2, 137.9, 136.9, 135.8, 135.5, 134.3, 112.5, 107.7, 106.5, 106.1, 105.8, 102.4, 101.7, 101.1, 100.8, 77.2, 75.2, 71.9, 70.8, 70.6, 70.5, 70.1, 69.9, 69.7, 68.0, 67.5, 66.8, 59.0, 49.1, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.1, 23.0, 14.1. MALDI-TOF-MS (m/z): $[M + H]^+$ calcd for $C_{413}H_{553}O_{55}$, 6397.9; found, 6399. Anal. Calcd for $C_{413}H_{552}O_{55}$: C, 77.55; H, 8.70. Found: C, 77.46; H, 8.49.

Fullerodendrimer 5. This compound was prepared from **24** and purified by column chromatography (SiO_2, CH_2Cl_2/acetone 8:2) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **5** (36%) as an orange glassy compound. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 438 (3000), 382 (sh, 9800), 327 (sh, 28 100), 263 (92 500). IR (CH_2Cl_2, cm^{-1}): 1748 (C=O). ^1H NMR ($CDCl_3$, 200 MHz, δ): 7.15 (broad s, 1 H), 6.76 (broad s, 2 H), 6.70−6.35 (m, 63 H), 5.73 (d, J = 14 Hz, 2H), 5.22 (AB, J = 14 Hz, 4 H), 5.02 (d, J = 14 Hz, 2H), 4.90 (m, 38 H), 4.10 (m, 16 H), 3.89 (t, J = 6.5 Hz, 32 H), 3.83 (m, 16 H), 3.75−3.50 (m, 64 H), 3.36 (s, 24 H), 1.74 (m, 32 H), 1.50−1.20 (m, 288 H), 0.87 (t, J = 6.5 Hz, 48 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 162.6, 162.5, 160.4, 160.0, 159.9, 158.8, 148.6, 147.3, 145.9, 145.8, 145.6, 145.5, 145.4, 145.2, 145.0, 144.9, 144.7, 144.4, 144.2, 144.1, 144.0, 143.9, 143.6, 143.4, 143.0, 142.7, 142.5, 142.2, 142.0, 141.7, 141.0, 140.9, 140.0, 139.0, 138.9, 138.8, 138.2, 137.8, 136.8, 135.7, 135.4, 134.2, 112.4, 107.7, 106.5, 106.0, 105.7, 102.4, 101.6, 101.1, 100.7, 77.2, 71.8, 70.7, 70.6, 70.5, 70.0, 69.6, 68.0, 67.4, 66.7, 58.9, 49.2, 31.8, 31.5, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6, 14.0. MALDI-TOF-MS (m/z): $[M + H]^+$ calcd for $C_{469}H_{633}O_{75}$, 7471.1; found, 7471. Anal. Calcd for $C_{469}H_{632}O_{75}$: C, 75.41; H, 8.53. Found: C, 75.57; H, 8.52.

Langmuir and Langmuir−Blodgett Films. The setup for the Langmuir and LB experiments is described in ref 5. Solutions at ≈1 mg·mL^{-1} concentration were prepared using chloroform (Analysis Grade). Usually, 50 μL of these solutions was spread on the water surface using a microsyringe. Films were left to equilibrate for 15 min before any measurement was started. The monolayers were compressed at typical speeds of 40 Å^2·molecule^{-1}·min^{-1}.

LB films were obtained by transfer on hydrophilic silicon wafers (111) at surface pressures of 9, 25, 35, and 35 mN·m^{-1} for **2**, **3**, **4**, and **5**, respectively. Transfers started from below the surface, with a typical emersion speed of 1 mm/min. The

silicon wafers were rendered hydrophilic by treatment with an oxidizing mixture of H_2SO_4/H_2O_2 (1:1 v/v), followed by several rinses in water. All treatments were done in an ultrasonic bath.

Acknowledgment. This research was supported by the CNRS and the French Ministry of Research (ACI Jeunes Chercheurs). S.Z. and Y.R. thank the Direction de la Recherche of the French Ministry of Research and F.C. thanks the Région Alsace for their fellowships. We further thank L. Oswald for technical help and J.-M. Strub for the MALDI-TOF-MS measurements.

JO035040A