Dendritic Mixed Hexakisadducts of C_{60} with a T_h Symmetrical Addition Pattern

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Keywords: Dendrimers / Fullerenes / Macromolecular chemistry / Template synthesis

The synthesis and complete characterization of dendritic hexakisadducts **8–13** of C_{60} with a mixed (1:5, 2:4, 3:3 and 4:2) T_h symmetrical addition pattern is described. Pentakis-, tetrakis-, tris- and bisadducts **4–7** of C_{60} with diethyl malonate addends arranged in an incomplete octahedral addition pattern served as core building blocks. Completion of the pseudo-octahedral architecture was achieved by exhaustive cyclopropanation with first- to third-generation bromomalonate dendra **1–3** consisting of the corresponding Fréchet-type 3,5-dihydroxybenzyl alcohol subunits. This concept allows for the convergent synthesis of globular dendrimers with a variable number of dendritic malonates **(1–4)** and a high dendron density in good yields. The ^{1}H and ^{13}C NMR spectra reflect the T_h symmetrical addition pattern of the products and reveal spatial interactions of inner dendron branches.

Introduction

The spherical framework of C_{60} represents an excellent core tecton for dendrimer chemistry.[1−7] In contrast to many other core systems, the perfect spherical shape of C_{60} allows for the facile formation of globular dendrimers even if low generation dendra are used as addends. Moreover, exohedral addition chemistry of C_{60} offers the advantage that the degree of addition and the symmetry of addition patterns can be varied over a wide range.[8−10] Many addition patterns are inherently chiral regardless of the nature of the addends.[11−13] Of special interest are the hexakisadducts of C_{60} with a T_h symmetrical octahedral addition pattern.[8−10,14−16] This motif is unique in organic chemistry (Figure 1). Fullerene adducts of this type are not only aesthetically pleasing but are also easily accessible in good yields, since the regioselectivity of subsequent additions to the required equatorial [6,6] double bonds increases with an increasing number of addends already bound.[9] Nucleophilic cyclopropanations[17] with bromomalonates are especially suitable for the synthesis of such hexakisadducts, since a broad variety of functional groups and building blocks can be introduced under mild and selective conditions. In particular template-mediated cyclopropanation techniques[9][15] or tether-directed functionalization[10][16] allow for a straightforward production of such hexaadducts in large quantities. As examples for macromolecular architectures based on the T_h symmetric motif of the hexaaddition pattern, we recently synthesized fullerene dendrimers where six Fréchet type dendra (6:0 adduct), or a combination of five Fréchet type dendra and one small methylene addend as positional blocker (5:1 adduct), are bound to the C_{60} core.[3] Moreover, we prepared a series of functional dendrimers with one porphyrin and five dendritic addends.[7]

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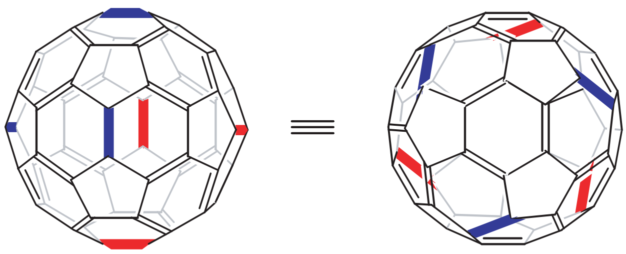

Figure 1. Two different views on the T_h symmetrical octahedral addition pattern of a hexakisadduct of C_{60} (the front sites of the hexaaddition are marked in blue and the rear sites in red)

Starting from precursor adducts with an incomplete octahedral addition pattern, like C_{2v}-symmetrical pentakisadducts, C_s-symmetrical tetrakisadducts, C_3-symmetrical *e,e,e*-trisadducts or C_s-symmetrical *e*-bisadducts, with all addends bound in octahedral sites, the regioselective formation of further mixed hexaaddition patterns can be expected.[9] In order to demonstrate the value of this concept for dendrimer chemistry we report here on the synthesis and characterization of a whole series of mixed dendritic 1:5-, 2:4-, 3:3- and 4:2-hexaadducts containing one, two, three or four Fréchet type[3][18] dendritic branches of first to third generation, respectively.

Results and Discussion

The bromomalonates **1**, **2** and **3** of the first (G1), second (G2) and third generation (G3) that we synthesized previously[3] were chosen as dendra to be attached to a C_{60}-based core tecton by nucleophilic cyclopropanation. They are easily accessible by the condensation of Fréchet's benzyl ether dendra with malonyl dichloride and subsequent bromination. As suitable dendrimer cores the C_{2v}-symmetrical pentakisadduct **4**, the corresponding C_s-symmetrical tetrakisadduct **5**, the C_3-symmetrical *e,e,e*-trisadduct **6** and the *e*-bisadduct **7** were taken.[11][14] These compounds represent

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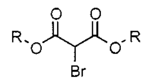
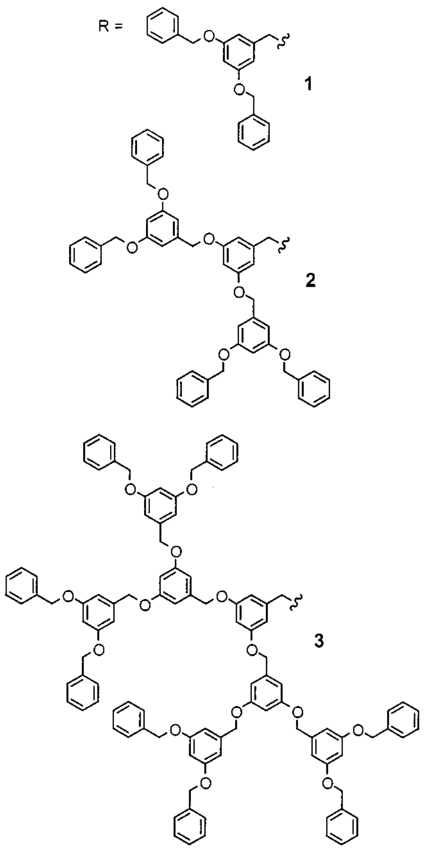
C_{60} tectons with an incomplete octahedral hexaaddition pattern. All the malonates are bound in octahedral sites.



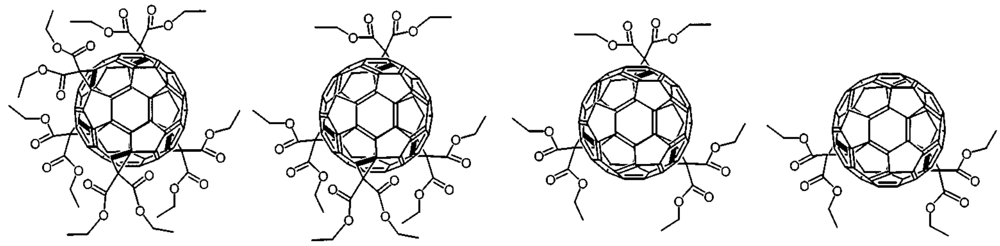
1, 2, 3



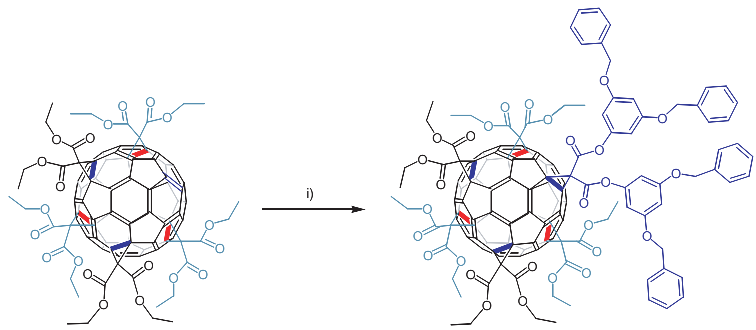
For the synthesis of mixed 1:5 dendrimers, the pentakisadduct **4** served as the precursor core. It can be readily obtained from a [6,6] monoadduct with methyl azidoacetate. Subsequent template-mediated exhaustive cyclopropanation of this triazolinofullerene and final thermal decomposition leads to **4** in good overall yields.[19] In this reaction sequence, the azido addend serves as a protective group of the [6,6] double bond, which can be removed upon thermal cycloreversion. Nucleophilic cyclopropanation of **4** with the first generation Fréchet-type bromomalonate dendron $CHBr(COOG1)_2$ **(1)** (Scheme 1) afforded the mixed 1:5 hexaadduct $C_{66}(COOEt)_{10}(COOG1)_2$ **(8)** in 69% yield as a yellow solid. The newly attached dendron addend reduced the polarity relative to the precursor pentakisadduct **4**, hence the hexakisadduct product **8** eluted before the starting material on silica gel with toluene/ethyl acetate as eluent. With the same procedure, the second and third generation dendrimers $C_{66}(COOEt)_{10}(COOG2)_2$ **(9)** (Scheme 2) and $C_{66}(COOEt)_{10}(COOG3)_2$ **(10)** (Scheme 3) were obtained in yields of 72 and 95%, respectively, as yellow solids by the reaction of **4** with the second (G2) and third generation (G3) dendra **2** and **3**.

The dendrimers **8**, **9** and **10** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, UV/VIS and IR spectroscopy and mass spectrometry. In Figure 2 the ^{1}H NMR spectra of the three related dendrimers are compared. With increasing generation number (G1−**8** → G3−**10**) the multiplets of the ethyl protons at $\delta = 1.3$ and 4.3 undergo a successive broadening reflecting increasing interactions between the ethyl malonate groups and the different dendritic addends. Considerable line broadening is also observed for the proton signals of the dendra themselves as the generation number increases. The multiplets for the protons of the peripheral phenyl rings appear at $\delta = 7.3$ whereas the corresponding signals of the inner phenyl rings are located at $\delta = 6.48-6.52$ (first generation, **8**), 6.42−6.63 (second generation, **9**) and 6.27−6.68 (third generation, **10**). The benzylic proton signals are found in the region $\delta = 4.55-5.30$. With increasing generation number additional benzylic signals appear. The low intensity signals found in this part of the spectrum of **10** cannot be explained by impurities (integration corresponds exactly to 60 H-atoms), but must be assigned to the diastereotopic and magnetically different inner benzylic CH_2-groups. In addition, due to steric crowding, free rotations of individual inner segments are hindered.

Figure 3 shows the comparative ^{13}C NMR spectra of dendrimers **8**, **9** and **10**. Only nine (**8**), six (**9**) and seven signals (**10**) of the expected twelve lines of the sp^2 carbons of these C_{2v}-symmetrical hexakisadducts are resolved in the range $\delta = 140-150$. These signals are located in two groups at $\delta = 141$ and 146. These are the chemical shifts usually found for the two sp^2 signals of T_h-symmetrical hexakisadducts.[14] This clearly reflects the high local T_h symmetry of the addition pattern. The same grouping of signals of C_{2v}-symmetrical mixed hexakisadducts with a T_h-symmetrical addition pattern has previously been observed.[3,7,18] The signals of the sp^3 fullerene carbons are located at $\delta = 69$ and the signal for the methylene bridges at $\delta = 45$. With increasing generation number, the signals of the fullenere C atoms and the signals of the diethyl malonate addends at $\delta = 164$, 63 and 14, respectively, become less intense relative to the signals of the dendron C atoms.

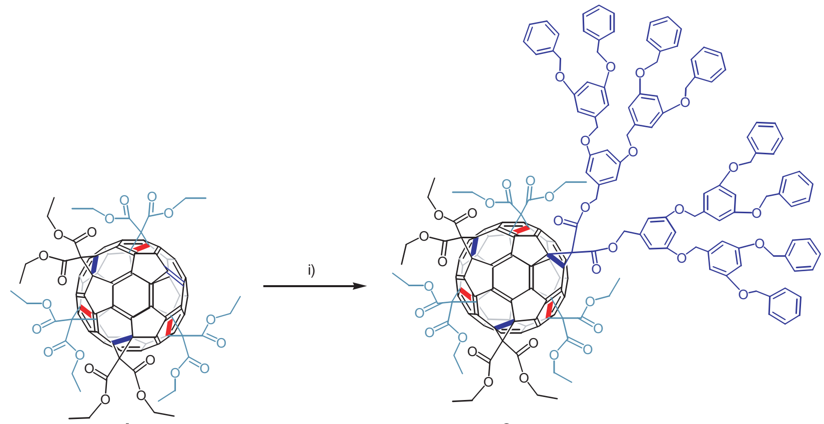


4 **5** **6** **7**



4 8

Scheme 1. Synthesis of **8** by nucleophilic cyclopropanation of **4** with bromomalonate **1**; i) CHBr(COOG1) **1**, DBU, toluene/CH_2Cl_2, 3d, room temp.



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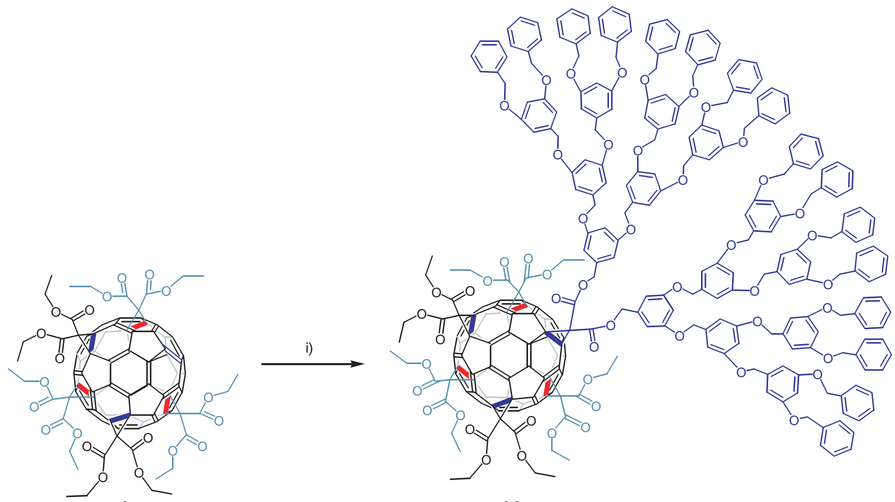
Scheme 2. Synthesis of **9**; i) CHBr(COOG2) **2**, DBU, toluene/CH_2Cl_2, 24 h, room temp.



4 10

Scheme 3. Synthesis of **10**; i) CHBr(COOG3) **3**, DBU, toluene/CH_2Cl_2, 24 h, room temp.

The tetrakisadduct **5**, obtained from fourfold cyclopropanation of C_{60}[14] served as the core building block for the synthesis of the third generation 2:4-hexakisadduct $C_{66}(COOEt)_8(COOG3)_4$ (**11**). Twofold cyclopropanation of this precursor core with the third generation dendron **3** in the presence of DBU afforded C_s-symmetrical **11** in 75% yield as a yellow powder (Scheme 4). Compound **11** is less polar than the starting material **5** and can be easily isolated from the reaction mixture by flash chromatography.

The C_3-symmetrical *eee*-trisadduct **6**,[11,13,21] served as starting material for the synthesis of mixed 3:3-hexakisadducts. For the completion of the octahedral addition pat-

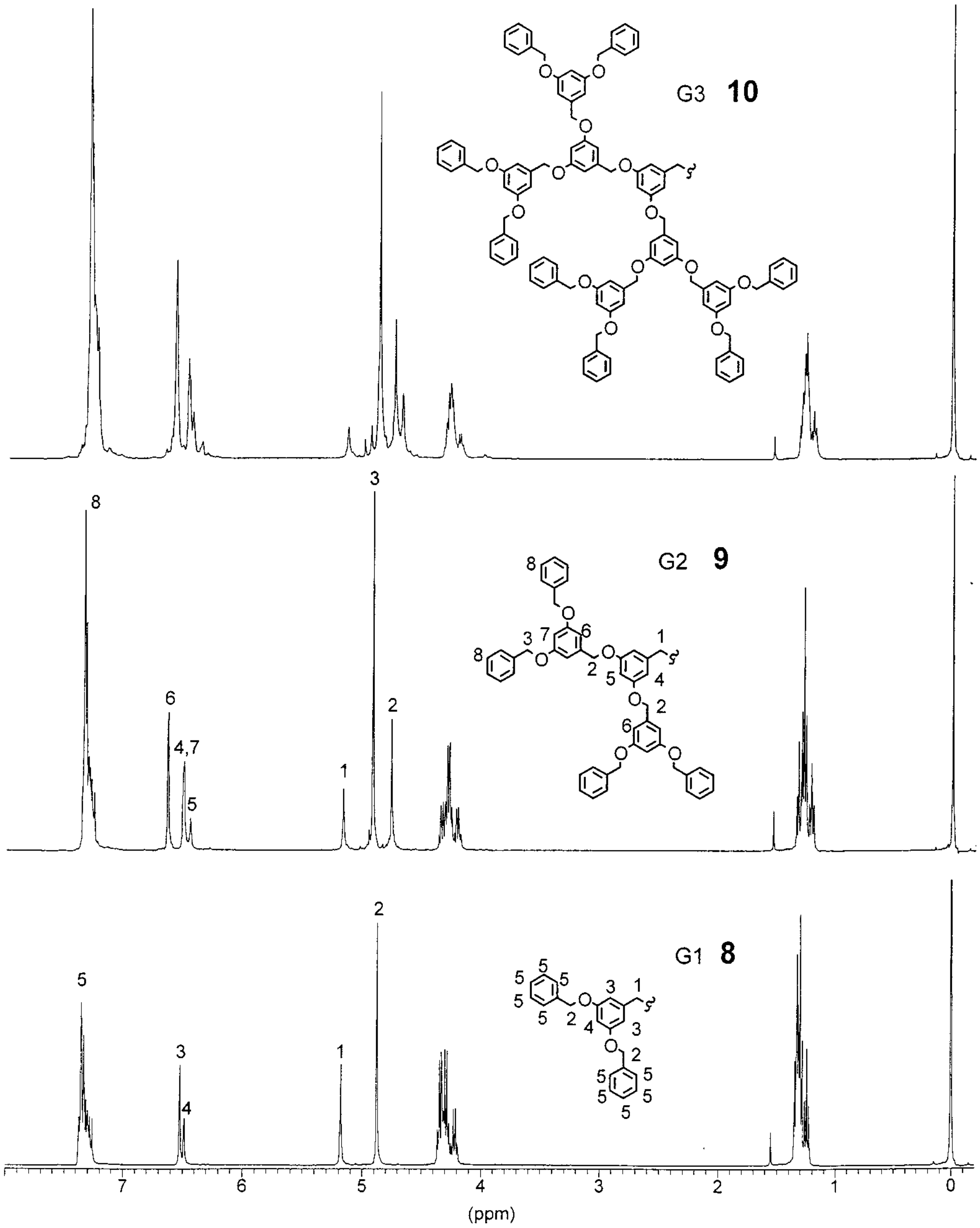


Figure 2. ^{1}H NMR spectra of $C_{66}(COOEt)_{10}(COOG1)_2$ **8** (bottom), $C_{66}(COOEt)_{10}(COOG2)_2$ **9** (middle) and $C_{66}(COOEt)_{10}(COOG3)_2$ **10** (top) ($CDCl_3$, 25°C, 400 MHz)

tern, DMA template-mediated cyclopropanation[15] of **6** with the second and third generation bromomalonates $BrCH(COOG2)_2$ **(2)** and $BrCH(COOG3)_2$ **(3)** gave the mixed 3:3 dendrimers $C_{66}(COOEt)_6(COOG2)_6$ **(12)** and $C_{66}(COOEt)_6(COOG3)_6$ **(13)** in 44 and 28% yields, respectively, as yellow powders (Scheme 5, 6). Both chiral compounds have C_3 symmetry and were obtained as racemic mixtures from the racemic starting trisadduct **6**. The two dendrimeric compounds are good examples of the appearance of chirality due to the addition pattern of the adduct only.[11–13] Finally, to obtain a mixed 4:2-hexaadduct dendrimer, the *e*-bisadduct **7**[11] was successively cyclopropanated by template activation with DMA with the G2 dendron **2** to give $C_{66}(COOEt)_4(COOG2)_8$ **(14)** in 73% yield as a yellow powder (Scheme 7).

A comparison of the ^{1}H NMR spectra of the dendrimers **10**, **11** and **13**, containing dendra of the same generation with different degrees of dendron addition, shows considerable broadening of the signals of both the protons of the ethyl malonate addends and those of the dendritic branches as the degree of dendron addition increases. The ^{13}C NMR spectra of **10**, **11** and **13** (Figure 4) impressively demonstrate the strong influence of the high local symmetry. In each spectrum three groups of signals appear for the fullerene C atoms reminescent of those of the three magnetically inequivalent fullerene C atoms of the hexakisadduct carry-

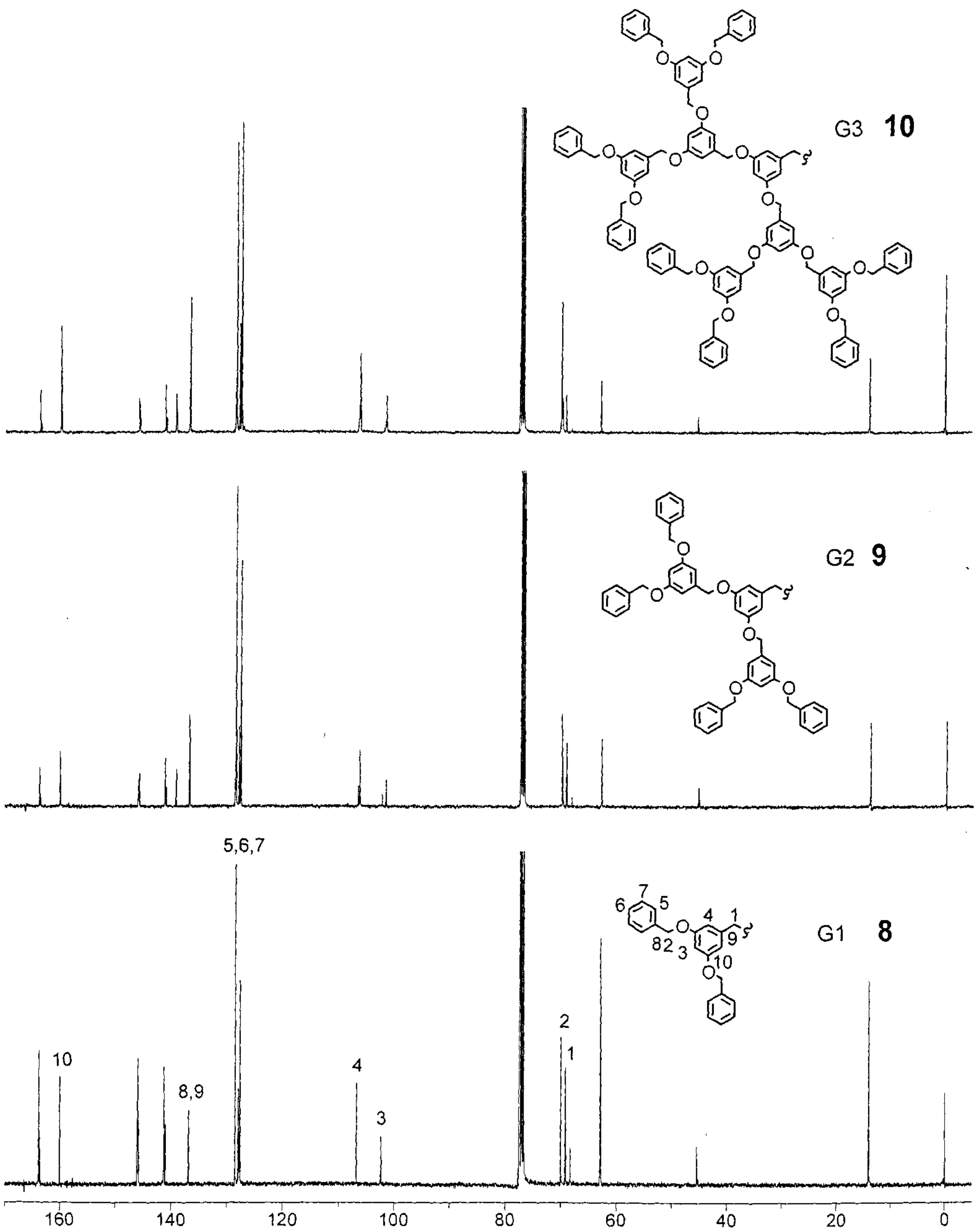
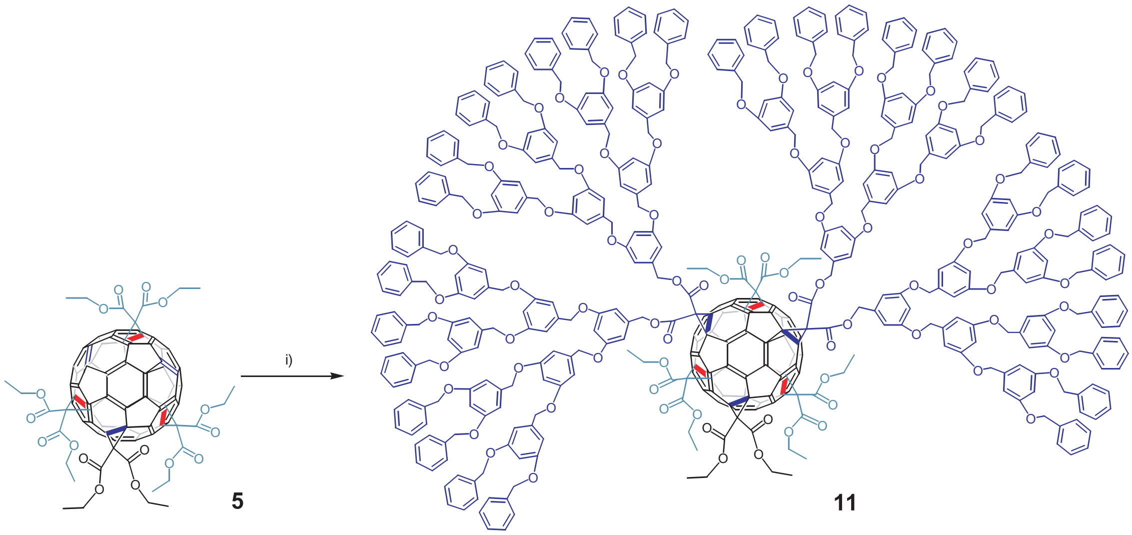


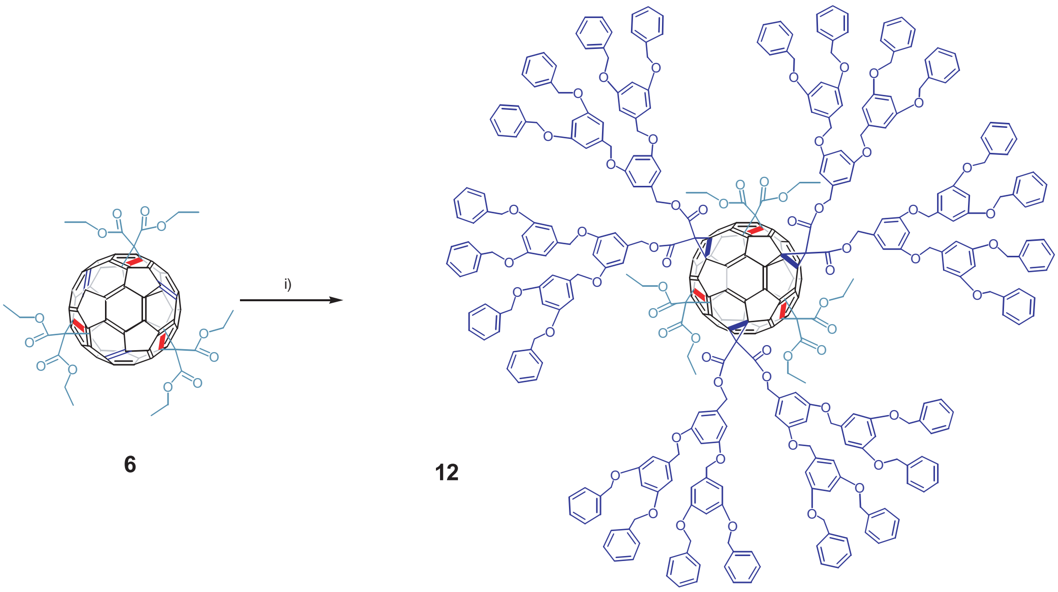
Figure 3. ^{13}C NMR spectra of $C_{66}(COOEt)_{10}(COOG1)_2$ **8** (bottom), $C_{66}(COOEt)_{10}(COOG2)_2$ **9** (middle) and $C_{66}(COOEt)_{10}(COOG3)_2$ **10** (top) ($CDCl_3$, 25°C, 100 MHz)

ing just one type of addend (overall T_h symmetry). No influence of the overall symmetry of **10**, **11** and **13** which is C_{2v}, C_s or C_3 respectively can be deduced. With increasing dendron density (G3−**10** → G3−**11** → G3−**13**) the three signal groups of the fullerene sp^2 and sp^3 C atoms at δ = 146, 141 and δ = 69 become less intensive relative to those of the C atoms of the dendra.

The UV/Vis spectra of all the synthesized fullerene dendrimers reveal the characteristics of hexakisadducts, i.e. two doublet absorption bands at 271 and 281, and at 315 and 335 nm, respectively.[3,7,11,14,15,20] Going from lower to higher generations causes the short wavelength doublet band to broaden until the twin peak maximum collapses to a single, broad absorption peak. Furthermore, the absorption maximum at λ = 244 nm disappears and becomes superimposed by the phenylic group absorptions. Mass spectra were recorded using FAB, ESI and MALDI-TOF ionization. For all the substances, except for **13**, the corresponding molecular ion peaks or quasi-molecular ion peaks could be observed.



Scheme 4. Synthesis of **11** by nucleophilic cyclopropanation of **5** with **3**; i) CHBr(COOG3) **3**, DBU, toluene/CH_2Cl_2, 3d, room temp.



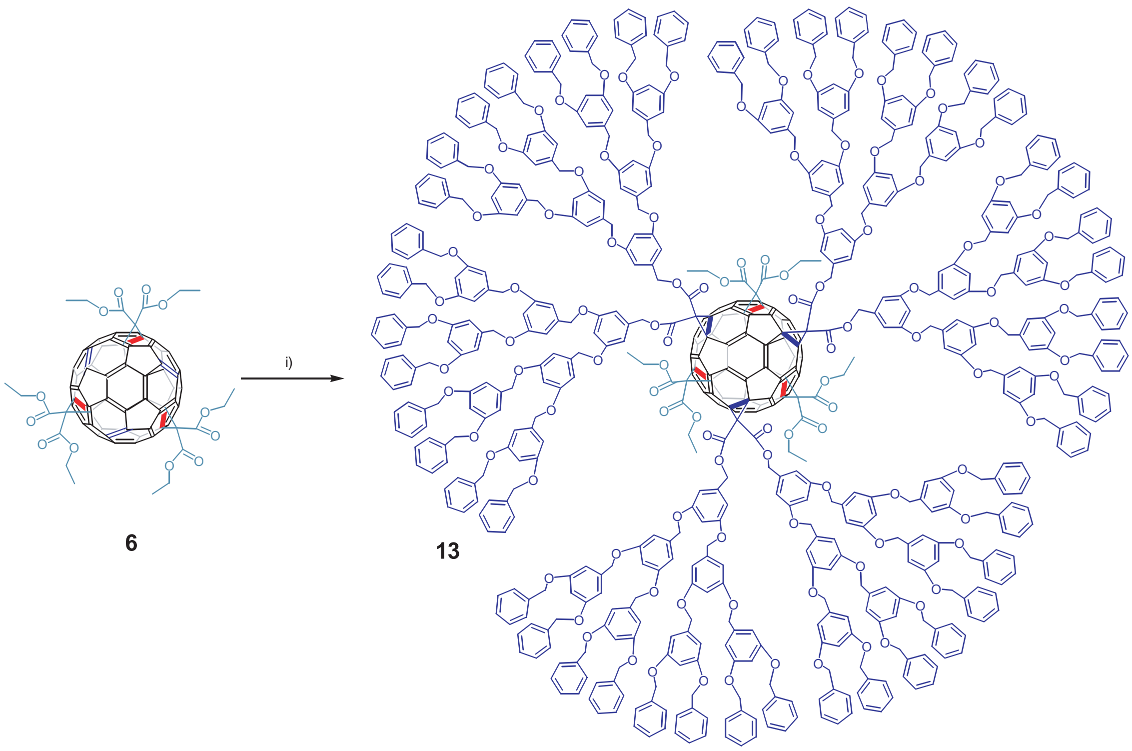
Scheme 5. Synthesis of **12** by DMA-template mediated cyclopropanation of **6** with **2**; i) DMA, CHBr(COOG2) **2**, DBU, toluene, 2d, room temp.

Conclusion

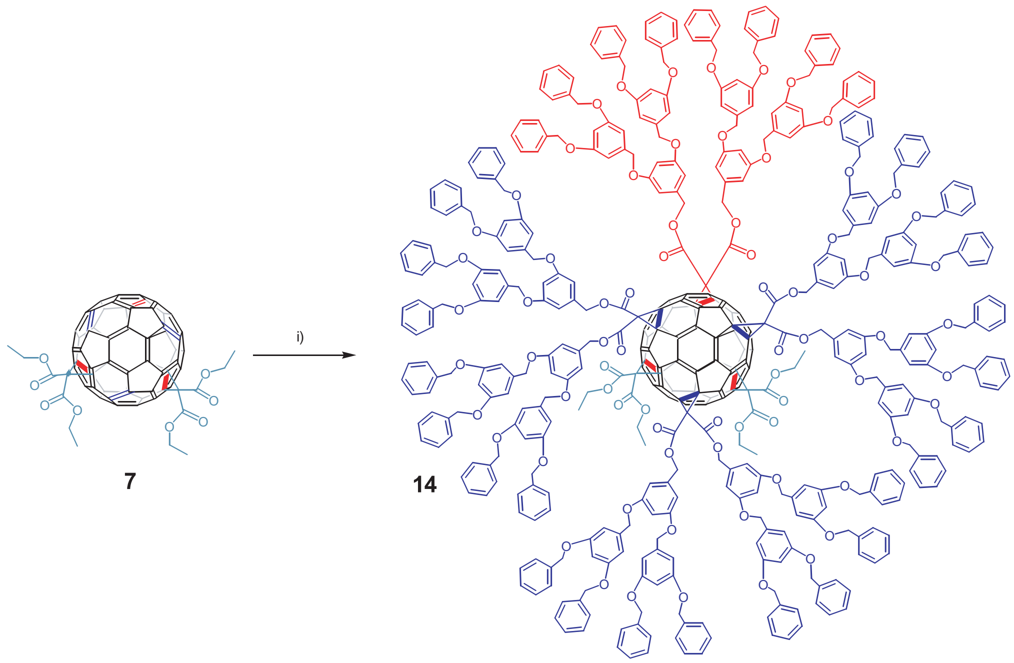
With this contribution we have demonstrated that dendritic hexakisadducts of C_{60} with a mixed octahedral T_h-symmetrical addition pattern are easily accessible. Dendrimers based on C_{60} as core building block, with variable combinations of one to four dendritic malonates, and with five to two diethyl malonates as positional blockers have been synthesized in good yields. The success of this concept is based on the regioselectivity of attacks at the [6,6]-double bonds located in the equatorial position to the addends already bound. The spectroscopic characterization of such dendrimers is facilitated by the high symmetry of the addition pattern leading to characteristic fingerprints, for example in their NMR and electronic absorption spectra. Conceptually, some of those dendrimers, like the C_3-symmetrical compounds **12** and **13** are inherently chiral due to the nature of the addition pattern. In a forthcoming contribution we will report on the synthesis, isolation and characterization of enantiomerically pure systems containing chiral C_3-symmetrical fullerene cores with known absolute configuration.

Experimental Section

General Remarks: ^1H NMR and ^{13}C NMR: Jeol Alpha 500, Jeol JNM EX 400 and Jeol JNM GX 400; MS: Varian MAT 311A (EI),



Scheme 6. Synthesis of **13** by nucleophilic cyclopropanation of **6** with **3**; i) CHBr(COOG3) **3**, DBU, toluene, 2d, room temp.



Scheme 7. Synthesis of **14** by template mediated cyclopropanation of **7** with **2**; i) DMA, CHBr(COOG2) **2**, DBU, toluene/CH_2Cl_2, 3d, room temp.

Micromass Zabspec (FAB/EI), Micromass Tofspec (MALDI); IR: Bruker FT-IR IFS 88 and FT-IR Vector 22; UV/Vis: Shimadzu UV 3102 PC; HPLC: Shimadzu Class-LC10 and DAD detector SPD M10A, analytical (Grom-Sil 100Si, 5µ, 200 × 4, and Buckyclutcher, 1.5 mL/min) and preparative (20 mL/min, Grom-Sil 100Si, NP1, 5µ, 250 × 20). The Fréchet type bromomalonate dendra of first, second and third generation G1−**1**, G2−**2** and G3−**3** were obtained by treating the corresponding benzyl ethers of 3,5-dihydroxybenzyl alcohol subunits with malonyl dichloride and subsequent bromination with CBr_4 in the presence of base according to ref.[3] The starting fullerene pentaadduct **4** was prepared according to ref.[19] The other fullerene starting materials **5**, **6** and **7** were obtained by successive cyclopropanation of C_{60} with diethyl bromomalonate according to ref.[15] C_{60} "gold grade" was obtained

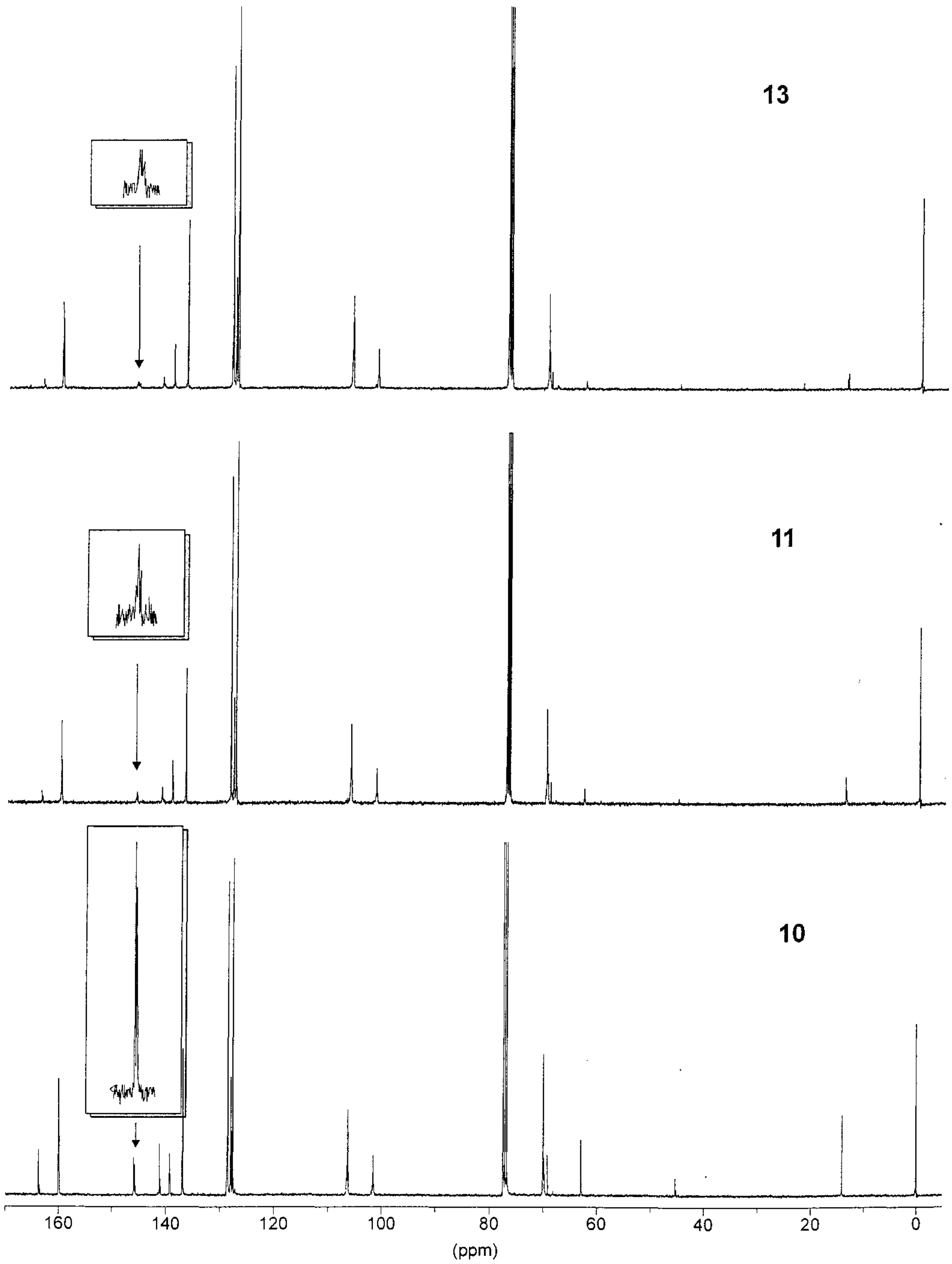


Figure 4. ^{13}C NMR spectra of 1:5 adduct $C_{66}(COOEt)_{10}(COOG3)_2$ **10** (bottom), 2:4 adduct $C_{66}(COOEt)_8(COOG3)_4$ **11** (middle), and $C_{66}(COOEt)_6(COOG3)_6$ **13** (top) ($CDCl_3$, 25°C, 400 MHz)

from Hoechst AG, Frankfurt (Germany). Materials and solvents were obtained from commercial suppliers and were dried and purified according to known procedures. Products were isolated by flash column chromatography (silica gel 60, particle size 0.04−0.063 nm, Merck) or by preparative TLC (silica gel, particle size 0.04−0.063 nm, Merck).

1,2-Bis[(3′,5′-dibenzyloxy)benzyloxycarbonyl]methano-18,36:22,23:27,45:31,32:55,56-pentakis-[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodecahydro[60]fullerene $C_{66}(COOEt)_{10}$-$(COOG1)_2$ (8): Under an atmosphere of nitrogen, three equivalents of bromomalonate $CHBr(COOG1)_2$ **(1)** (39 mg, 50 μmol) and 2.5 equivalents DBU (6 μL, 41 μmol) were added to a solution of pentakisadduct **4** (25 mg, 17 μmol) in 20 mL toluene and 5 mL dichloromethane. The mixture was stirred for three days at room temperature and the dendrimeric product **5** separated from the starting material by flash chromatography (silica gel) using a mixture of toluene/ethyl acetate (95:5, R_f = 0.39 and 0.33 for **8** and **4**, respectively). The eluents were removed in vacuum and the product dissolved in dichloromethane and precipitated with pentane (yield: 25 mg, 69%, yellowish solid, melting range 106−110°C).

8: ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.32 (m, 20 H, Ph), 6.52 (s, 4 H, C*H* arom.), 6.48 (s, 2 H, C*H* arom.), 5.18 (s, 4 H, CH_2), 4.88 (s, 8 H, CH_2), 4.28 (m, 20 H, CH_2), 1.29 (m, 30 H, CH_3). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.81 (*C*O), 163.78 (*C*O), 163.70 (*C*O), 163.56 (*C*O), 159.99 (4 C, quat. arom.), 145.90, 145.83, 145.76, 145.72, 145.67, 141.21, 141.17, 141.10, 141.92, 136.79 (4 C, quat. Ph), 128.47 (8 C, tert. Ph), 127.87 (4 C, tert. Ph), 127.61 (8 C, tert. Ph), 106.77 (4 C, tert. arom.), 102.33 (2 C, tert. arom.), 69.91 (4 C, *C*H$_2$ Bz), 69.09 (2 C, *C*H$_2$ Bz), 69.03 (sp^3 fullerene), 68.23 (sp^3 fullerene), 62.82 (*C*H$_2$ Et), 45.39 (methylene), 45.35 (methylene), 45.32(methylene), 45.19 (methylene), 14.03 (*C*H$_3$), 13.96 (*C*H$_3$). − IR (KBr): ṽ = 2980, 2930, 2859, 1745, 1598, 1454, 1369, 1265, 1220, 1159, 1079, 1044, 1018, 856, 737, 715, 529 cm^{-1}. − UV/VIS (CH_2Cl_2): λ_{max} (ε) = 244 (103000), 271 (79000), 281 (87000), 315 (51000), 335 (42000), 381 nm (5000). − MS (FAB, NBA): *m/z* (%) = 2350 (M + Cs$^+$), 2217 (M$^+$), 720 (C_{60}^+). − MS (ESI): *m/z* = 2218 (M$^+$).

1,2-Bis(G2dendryloxycarbonyl)methano-18,36:22,23:27,45:31,32:55,56-pentakis-[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodecahydro-[60]fullerene $C_{66}(COOEt)_{10}(COOG2)_2$ (9): As for **8** with pentakisadduct **4** (20 mg, 13 µmol), two equivalents of bromomalonate CHBr(COOG2)$_2$ **(2)** (43 mg, 26 µmol) and 1.5 equivalents DBU (3 µL, 20 µmol) in toluene/dichloromethane. After stirring for 24 h the dendrimer was separated by flash chromatography (silica gel) using a mixture of toluene/ethyl acetate (96:4, R_f = 0.21 and 0.14 for **9** and **4**, respectively). The eluent was removed in vacuo and the product dissolved in dichloromethane and precipitated with pentane (yield: 29 mg, 72%, light yellow solid, melting range 83−90°C).

9: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.30 (m, 40 H, Ph), 6.63 (m, 8 H, C*H* arom.), 6.50 (m, 8 H, C*H* arom.), 6.44 (s, 2 H, C*H* arom.), 5.17 (s, 4 H, CH_2 Bz), 4.92 (s, 16 H, CH_2 Bz), 4.77 (s, 8 H, CH_2 Bz), 4.27 (m, 20 H, CH_2 Et), 1.28 (m, 30 H, CH_3 Et). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.78 (*C*O), 163.74 (*C*O), 163.65 (*C*O), 163.54 (*C*O), 160.03 (quat. arom.), 159.90 (quat. arom.), 145.89, 145.83, 145.74, 145.69, 141.15, 140.93, 139.18 (quat. arom.), 136.81 (quat. Ph), 128.49 (tert. Ph), 127.87 (tert. Ph), 127.52 (tert. Ph), 106.64 (tert. arom.), 106.36 (tert. arom.),102.34 (tert. arom.), 101.59 (tert. arom.), 69.93 (*C*H$_2$ Bz), 69.80 (*C*H$_2$ Bz), 69.09 (sp^3 fullerene), 68.23 (*C*H$_2$ Bz), 62.82 (*C*H$_2$ Et), 45.35 (methylene), 45.21 (methylene), 14.03 (*C*H$_3$), 14.00 (*C*H$_3$), 13.94 (*C*H$_3$). − IR (KBr): ṽ = 2984, 2938, 2875, 1745, 1596, 1453, 1369, 1296, 1265, 1220, 1158, 1080, 1045, 1018, 829, 739, 715, 699, 529 cm^{-1}. − UV/VIS (CH_2Cl_2): λ_{max} (ε) = 244 (106000), 272 (80000), 282 (89000), 316 (47000), 224 (39000), 378 nm (6000). − MS (ESI): *m/z* = 3067 (M$^+$).

1,2-Bis(G2dendryloxycarbonyl)methano-18,36:22,23:27,45:31,32:55,56-pentakis-[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodecahydro-[60]fullerene $C_{66}(COOEt)_{10}(COOG3)_2$ (10): To a solution of pentakisadduct **4** (15 mg, 10 µmol) in 10 mL toluene and 2 mL dichloromethane were added 1.3 equivalents of bromomalonate CHBr(COOG3)$_2$ **(3)** (13 µmol, 42 mg) and 1.5 equivalents of DBU (15 µmol, 2,2 µL) under a nitrogen atmosphere at room temperature. After stirring for one day the product mixture was purified by flash chromatography (silica gel) with a mixture of toluene and ethyl acetate (95:5) as eluent. The hexakisadduct **10** is less polar and hence elutes prior to **4**. After removing the solvent, isolation of **10** was achieved by precipitation from dichloromethane with pentane (yield: 45 mg, 95%, light-yellow solid, melting range 78−88°C).

10: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.28 (m, 80 H, Ph), 6.36−6.58 (m, 42 H, C*H* arom.), 4.68−5.15 (m, 60 H, CH_2 Bz), 4.25 (m, 20 H, CH_2 Et), 1.26 (m, 30 H, CH_3 Et). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.72 (*C*O), 163.54 (*C*O), 160.01 (quat. arom.), 159.88 (quat. arom.), 159.83 (quat. arom.), 145.90, 145.85, 145.74, 145.67, 141.17, 141.10, 140.92, 139.24 (quat. arom.), 139.11 (quat. arom.), 136.75 (quat. Ph), 128.47 (tert. Ph), 127.87 (tert. Ph), 127.50 (tert. Ph), 106.45 (tert. arom.), 106.27 (tert. arom.), 101.65 (tert. arom.), 101.48 (tert. arom.), 70.06 (*C*H$_2$ Bz), 69.89 (*C*H$_2$ Bz), 69.76 (*C*H$_2$ Bz), 69.71 (*C*H$_2$ Bz), 69.07 (sp^3 fullerene), 68.08 (*C*H$_2$ Bz), 62.82 (*C*H$_2$ Et), 45.32 (methylene), 45.17 (methylene), 14.00 (*C*H$_3$), 13.94 (*C*H$_3$). − IR (KBr): ṽ = 3063, 3023, 2922, 2875, 1744, 1597, 1497, 1453, 1370, 1297, 1265, 1220, 1157, 1048, 833, 738, 715, 698, 529 cm^{-1}. − UV/VIS (CH_2Cl_2): λ_{max} (ε) = 271 (98000), 281 (113000), 315 (49000), 335 (40000), 376 nm (6000). − MS (ESI): *m/z* = 4787 (^{12}C304^{13}C4H232O52 + Na)$^+$.

1,2:18,36-Bis[bis(G2dendryloxycarbonyl)methano]-22,23:27,45:31,32:55,56-tetrakis-[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodecahydro[60]fullerene $C_{66}(COOEt)_8(COOG3)_4$ (11): To a solution of tetrakisadduct $C_{64}(COOEt)_8$ **(5)** (11 mg, 8 µmol) in 10 mL toluene were added two equivalents of bromomalonate CHBr(COOG3)$_2$ **(3)** (16 µmol, 54 mg) and 2.5 equivalents DBU (20 µmol, 3 µL) at room temperature under nitrogen protection. After 24 h the crude reaction mixture was purified by flash chromatography (silica gel) with toluene/ethyl acetate (95:5) as eluent. The hexakisadduct **11** is less polar than the starting material and the additionally formed mixed pentaadduct and hence elutes first (R_f = 0.48 **11**; R_f = 0.41 pentakisadduct; R_f = 0.30 tetrakisadduct). After removing the solvent, **11** was dissolved in dichloromethane and precipitated with pentane (yield: 48 mg, 75%, light-yellow solid, melting range 68−75°C).

11: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.27 (m, 160 H, Ph), 6.30−6.67 (m, 84 H, C*H* arom.), 4.65−5.17 (m, 120 H, CH_2 Bz), 4.18 (m, 20 H, CH_2 Et), 1.18 (m, 30 H, CH_3 Et). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.63 (*C*O), 163.45 (*C*O), 160.07 (quat. arom.), 159.96 (quat. arom.), 159.85 (quat. arom.), 146.09, 146.01, 145.92, 145.83, 145.74, 145.65, 141.24, 141.19, 141.04, 140.92, 139.20 (quat. arom.), 139.13 (quat. arom.), 139.09 (quat. arom.), 136.73 (quat. Ph), 128.45 (tert. Ph), 127.85 (tert. Ph), 127.49 (tert. Ph), 106.42 (tert. arom.), 106.24 (tert. arom.), 101.59 (tert. arom.), 101.43 (tert. arom.), 70.04 (*C*H$_2$ Bz), 69.97 (*C*H$_2$ Bz), 69.84 (*C*H$_2$ Bz), 69.65 (*C*H$_2$ Bz), 69.11 (sp^3 fullerene), 68.16 (*C*H$_2$ Bz), 62.82 (*C*H$_2$ Et), 45.35 (methylene), 45.22 (methylene), 13.94 (*C*H$_3$), 13.89 (*C*H$_3$). − IR (KBr): ṽ = 3055, 3444, 3031, 2930, 2871, 1743, 1596, 1497, 1452, 1373, 1321, 1296, 1265, 1217, 1157, 1054, 833, 737, 715, 697, 529 cm^{-1}. − UV/VIS (CH_2Cl_2): λ_{max} (ε) = 273 (119000), 282 (137000), 317 (45000), 334 (36000), 379 nm (5000). − MS (MALDI-TOF): *m/z* = 7883.9 (M + Na)$^+$.

1,2:18,36:22,23-Tris[bis(G2dendryloxycarbonyl)methano]-27,45:31,32:55,56-tris-[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodecahydro-[60]fullerene $C_{66}(COOEt)_6(COOG2)_6$ (12): To a solution of *eee*-$C_{63}(COOEt)_6$ **(6)** (20 mg, 17 µmol) in 20 mL toluene was added four equivalents of 9,10-dimethylanthracene (DMA) (14 mg, 67 µmol) under a nitrogen atmosphere. After stirring for 2 h at room temperature 4.5 equivalents of bromomalonate CHBr(COOG2)$_2$ **(2)** (123 mg, 75 µmol) and DBU (11 µL, 75 µmol) were added. After stirring for two days the 3:3-hexakisadduct **12** was separated by flash chromatography (silica gel) with a mixture of toluene/ethyl acetate (97:3)as eluent. The R_f value of the product **12** was 0.39 (toluene/ethyl acetate = 96:4), followed by pentaadducts (R_f = 0.36) and some tetraadducts (R_f = 0.32). For further purification the product fraction was chromatographed by thick layer chromatography. After removing the solvents the product was dissolved in dichloromethane and precipitated with pentane (yield: 43 mg, 44%, light-yellow solid, melting range 70−85°C).

12: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.27 (m, 120 H, Ph), 6.39−6.65 (m, 54 H, C*H* arom.), 4.67−5.10 (m, 84 H, CH_2 Bz), 4.19 (m, 20 H, CH_2 Et), 1.20 (m, 30 H, CH_3 Et). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.63 (*C*O), 163.56 (*C*O), 163.43 (*C*O), 163.35 (*C*O), 160.12 (quat. arom.), 159.99 (quat. arom.), 159.83 (quat. arom.), 146.00, 145.83, 145.70, 141.30, 141.14, 141.08, 140.97, 139.14 (quat. arom.), 136.79 (quat. Ph), 128.45 (tert. Ph), 127.85 (tert. Ph), 127.50 (tert. Ph), 106.66 (tert. arom.), 106.56 (tert. arom.), 106.33 (tert. arom.), 102.29 (tert. arom.), 101.54 (tert. arom.), 70.04 (*C*H_2 Bz), 69.87 (*C*H_2 Bz), 69.73 (*C*H_2 Bz), 69.20 (sp^3 fullerene), 68.21 (*C*H_2 Bz), 62.82 (*C*H_2 Et), 45.43 (methylene), 45.32 (methylene), 14.09 (*C*H_3), 14.03 (*C*H_3), 13.96 (*C*H_3), 13.91 (*C*H_3). − IR (KBr): $\tilde{\nu}$ = 3063, 3031, 2926, 2875, 1744, 1597, 1497, 1453, 1373, 1296, 1265, 1214, 1158, 1057, 833, 738, 716, 698, 529 cm^{-1}. − UV/VIS (CH_2Cl_2): λ_{max} (ε) = 272 (111000), 282 (130000), 317 (53000), 336 (43000), 385 nm (6000). − MS (FAB, NBA): *m*/*z* = 5992 (^{12}C381^{13}C3H288O60 + Cs)$^+$, 720 (C_{60}^+).

1,2:18,36:22,23-Tris[bis(G2dendryloxycarbonyl)methano]-27,45:31,32:55,56-tris-[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodecahydro-[60]fullerene $C_{66}(COOEt)_6$-$(COOG3)_6$ (13): To a solution of trisadduct *eee*-$C_{63}(COOEt)_6$ **(6)** (15 mg, 13 µmol) in 10 mL toluene were added 4.5 equivalents of bromomalonate $CHBr(COOG3)_2$ **(3)** (56 µmol, 188 mg) and 4.5 equivalents of DBU (56 µmol, 8,4 µL) at room temperature under an atmosphere of nitrogen. After two days the mixture was purified by flash chromatography (silica gel) with a mixture of toluene/ethyl acetate (97:3) as eluent. The hexakisadduct **13** is less polar than the starting material and the also formed mixed tetra- and pentaadducts and hence elutes first (**13**: R_f = 0.58, pentakisadduct: R_f = 0.52, tetrakisadduct: R_f = 0.44, and trisadduct: R_f = 0.39, with toluene/ethyl acetate = 96:4). For further purification the product fraction was repeatedly chromatogaphed by preparative thick layer chromatography. After removal of solvents the product was precipitated from dichloromethane with pentane (yield: 39 mg, 28%, light-yellow solid, melting range 60−75°C).

13: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.24 (m, 240 H, Ph), 6.41−6.62 (m, 126 H, C*H* arom.), 4.61−5.06 (m, 180 H, CH_2 Bz), 4.03 (m, 20 H, CH_2 Et), 1.20 (m, 30 H, CH_3 Et). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.48 (*C*O), 163.34 (*C*O), 160.10 (quat. arom.), 159.97 (quat. arom.), 159.86 (quat. arom.), 159.81 (quat. arom.), 146.23, 146.05, 145.90, 145.79, 145.65, 141.37, 141.24, 141.08, 140.95, 139.24 (quat. arom.), 139.13 (quat. arom.), 136.77 (quat. Ph), 128.53 (tert. Ph), 128.44 (tert. Ph), 127.94 (tert. Ph), 127.83 (tert. Ph), 127.47 (tert. Ph), 106.42 (tert. arom.), 106.35 (tert. arom.), 106.27 (tert. arom.), 101.61 (tert. arom.), 101.47 (tert. arom.), 70.00 (*C*H_2 Bz), 69.84 (*C*H_2 Bz), 69.67 (*C*H_2 Bz), 69.22 (sp^3 fullerene), 68.16 (*C*H_2 Bz), 62.86 (*C*H_2 Et), 62.78 (*C*H_2 Et), 45.43 (methylene), 45.37 (methylene), 14.03 (*C*H_3), 13.89 (*C*H_3), 13.83 (*C*H_3). − IR (KBr): $\tilde{\nu}$ = 3441, 3063, 3032, 2928, 2872, 1744, 1597, 1497, 1452, 1374, 1321, 1296, 1265, 1214, 1157, 1055, 833, 738, 697, 529 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 281 (183000), 317 (51000), 335 (41000), 379 nm (6000).

1,2:18,36:22,23:27,45-Tetra[bis(G2dendryloxycarbonyl)methano]-31,32:55,56-bis[bis(ethoxycarbonyl)methano]-1,2,18,36,22,23,27,45,31,32,55,56-dodeca-hydro[60]fullerene $C_{66}(COOEt)_4(COOG2)_8$ (14): To a solution of *e*-$C_{62}(COOEt)_4$ **(7)** (20 mg, 19 µmol) in 20 mL toluene was added six equivalents DMA under an atmosphere of nitrogen and the mixture stirred for 2 h at room temperature. Subsequently, seven equivalents of bromomalonate $CHBr(COOG2)_2$ **(2)** (221 mg, 135 µmol) and six equivalents DBU (17 µL, 116 µmol) were added. After stirring for four days the product was purified by flash chromatography. Final purification by successive precipitation from dichloromethane with pentane gave the title compound (yield: 102 mg, 73%, orange-yellow solid, melting range 63−70°C).

14: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.26 (m, 160 H, Ph), 6.43−6.64 (m, 72 H, C*H* arom.), 4.67−5.10 (m, 112 H, CH_2 Bz), 4.15 (m, 20 H, CH_2 Et), 1.16 (m, 30 H, CH_3 Et). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 163.47 (*C*O), 163.36 (*C*O), 163.30 (*C*O), 160.10 (quat. arom.), 159.96 (quat. arom.), 159.81 (quat. arom.), 145.98, 145.92, 145.83, 141.37, 141.32, 141.26, 141.18, 141.14, 141.03, 139.15 (quat. arom.), 139.07 (quat. arom.), 136.77 (quat. Ph), 136.71 (quat. Ph), 128.52 (tert. Ph), 128.42 (tert. Ph), 127.95 (tert. Ph), 127.79 (tert. Ph), 127.46 (tert. Ph), 106.89 (tert. arom.), 106.63 (tert. arom.), 106.33 (tert. arom.), 102.28 (tert. arom.), 101.91 (tert. arom.), 101.53 (tert. arom.), 70.02 (*C*H_2 Bz), 69.82 (*C*H_2 Bz), 69.71 (*C*H_2 Bz), 69.23 (sp^3 fullerene), 68.18 (*C*H_2 Bz), 62.81 (*C*H_2 Et), 45.38 (methylene), 45.33 (methylene), 14.03 (*C*H_3), 13.86 (*C*H_3). − IR (KBr): $\tilde{\nu}$ = 3062, 3031, 2926, 2875, 1745, 1602, 1597, 1498, 1452, 1374, 1342, 1320, 1296, 1265, 1214, 1158, 835, 738, 697, 529 cm^{-1}. − UV/VIS (CH_2Cl_2): λ_{max} (ε) = 272 (141000), 282 (163000), 317 (56000), 336 (43000), 381 nm (8000). − MS (ESI): *m*/*z* = 7283 (M^++ Na)$^+$.

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