The C_{60} Core: A Versatile Tecton for Dendrimer Chemistry

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Abstract: The synthesis, complete characterization and molecular dynamics simulations of dendrimers **4**–**8** involving [60]-fullerene as core tecton and first- to third-generation benzyl-ether-based dendrons as branches is described. In dendrimer **7** a core branching multiplicity of 12, the highest known to date, is realized for the first time with a T_h-symmetrical C_{60} core having an octahedral addition pattern. This unique structural type of core building block is only possible on the base of C_{60} and has no precedent in organic chemistry. NMR investigations as well as molecular modelling studies show that, owing to high core branching multiplicity, dendrimer **7** and to a minor extent the mixed adduct **8** already represent globular and densely packed macromolecules, although only first-generation dendrons are involved in their construction.

Keywords
conformation · dendrimers · fullerenes · molecular dynamics

Introduction

The field of dendrimer research[1] is attracting the attention of an increasingly broad cross-section of chemists. Dendrimers combine typical characteristics of *small* organic molecules like defined composition and monodispersivity with those of polymers, especially their high molecular weight, with the resulting multitude of physical properties. A similar combination of characteristics is realized in biopolymers like enzymes. Dendrimers consist of one or several cascade-like branches connected to a central core, which can be an atom or an achiral or chiral molecule. Either *similar* or *dissimilar* branches can be attached to a multifunctional core, for example, in convergent synthetic approaches. As cores, as well as methane-, amine-, or benzene-type systems, larger molecules like derivatives of adamantane,[2] cyclophane[3] or porphyrins[4, 5] have been used. With porphyrins as central building blocks, core branching multiplicities of up to eight have been realized.[5]

When we reported on regioselective formations of highly symmetric oligoadducts of C_{60} like the T_h-symmetrical hexamalonic acid $C_{66}(COOH)_{12}$ with an octahedral addition pattern, we stated that the spherical fullerene framework would be an ideal core tecton for dendrimers.[6] The following characteristics of C_{60} are appealing with respect to use as a dendrimer core: 1) the almost perfect spherical shape leading to globular systems even with low-generation dendrons, 2) the possibility of easily realizing variable degrees of addition within the fullerene core, especially mono- up to hexaadducts obtained by cycloadditions, 3) the possibility of realizing variable addition patterns for adducts (regioisomers) with a given degree of addition, 4) the possibility of addition patterns leading to inherent chirality of the fullerene core regardless of the nature of the addend and 5) the possibility of the addition of both similar and dissimilar addends in a stereochemically controlled way to permit combinations of different dendrons and also of dendrons and other addends with selected functionalities. No other building block in organic chemistry offers such great versatility. Hence, the establishment of C_{60} as a tecton in dendrimer chemistry opens up new and unprecedented opportunities for the design of new molecular architectures (Figure 1).

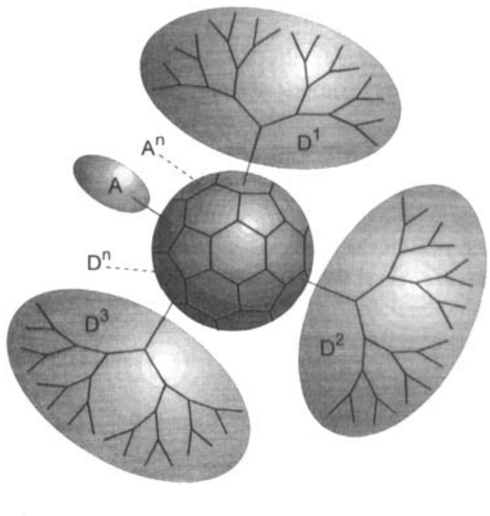

Figure 1. Schematic representation of possible dendrimer architectures with the C_{60} tecton as central core. D_1, D_2, D_3 … D_n denote identical or dissimilar dendrons attached to the fullerene framework. The A moieties are additional addends, which may also be attached to the core. The addends may have specific properties like electro-, photo- or catalytic properties or they may be just positional blockers, which enable the easy construction of a given addition pattern within the fullerene core or influence the conformational and steric expression of the dendrimer.

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The realization of selected degrees of addition and addition patterns (Figure 2) within regioisomeric fullerene derivatives containing identical or different addends has been achieved with several techniques, including tether-directed remote functionalization[7], template-mediated activation[6, 8] and topochemically controlled solid-state reactions.[9] As well as the preferred addition patterns of C_{60} with the addends bound in octahedral sites, adducts with other highly symmetrical addition patterns like the chiral core in adducts of type **VIII** (Figure 2) can be synthesized regioselectively in comparatively high relative yields.[10] These and other addition patterns are accessible in principle for the synthesis of dendrimers involving C_{60} as core unit. The attachment of dendrons could be achieved either by direct addition to [6,6] or [5,6] bonds of C_{60} or by coupling to anchor groups within preformed core blocks having the desired addition pattern.[10] Variable core branching multiplicities can be imagined, for example ranging from one for monoadducts to twelve for hexaadducts (two branches at each addition site).

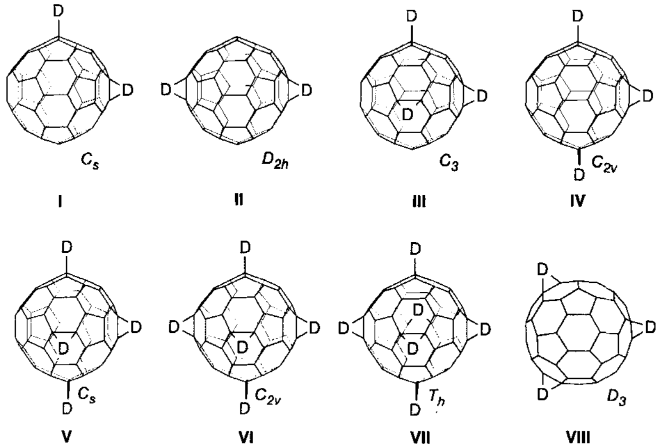
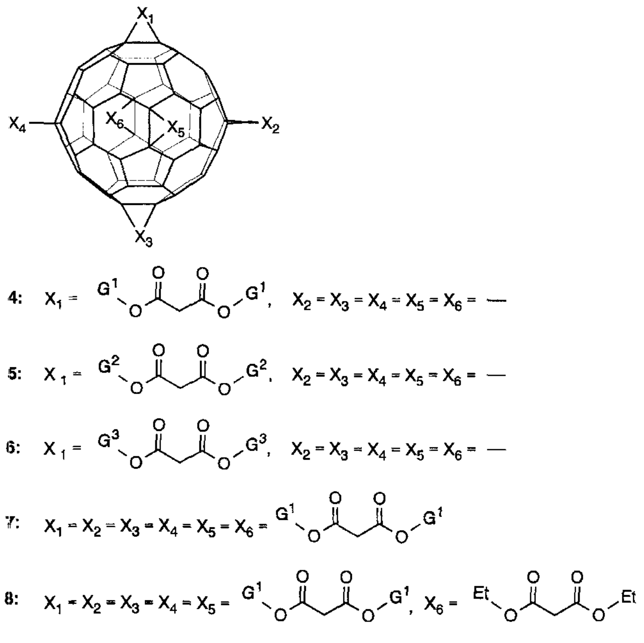


Figure 2. Selection of addition patterns of [6,6]-oligo adducts of C_{60} which can serve as core units for dendrimers. >D denotes the position of an addend, for example a dendron. Structures **III** and **VIII** represent chiral core tectons regardless of the geometrical nature of D.

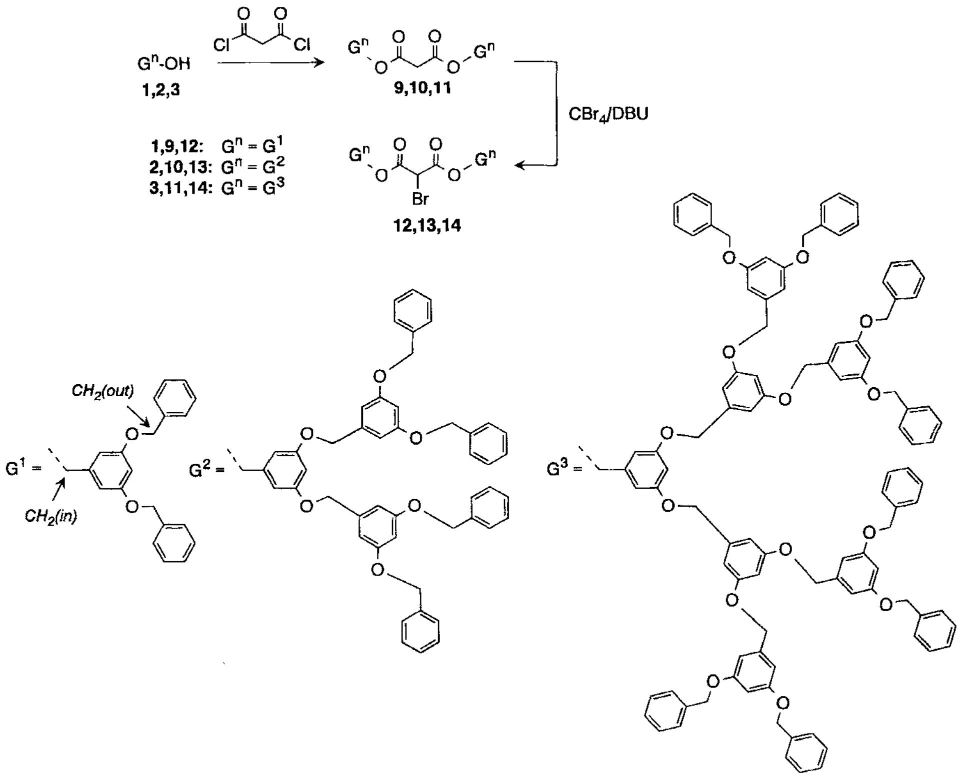
The convergent attachment of dendrons to C_{60} resulting in fullerene dendrimers as monoadducts has been reported by Fréchet et al.[11] In this paper we report on our progress on direct convergent additions of dendrons to the fullerene core. We present for the first time the regioselective synthesis, complete characterization and molecular dynamics simulations of stereochemically defined fullerene-based dendrimers with multiple branches. Within the very compact hexakisadduct **7**, a branching multiplicity of 12 is realized, which is the highest known to date.

Results and Discussion

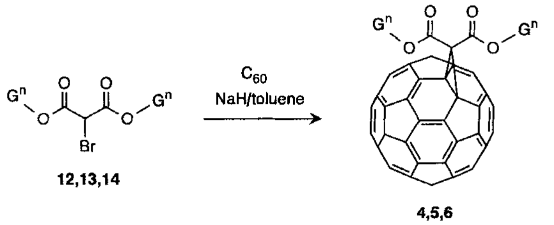
In this study we used the benzyl-ether-based dendrons G^1-OH (**1**), G^2-OH (**2**) and G^3-OH (**3**) introduced by Fréchet et al. as building blocks for the convergent synthesis of dendrimers **4**–**8** with C_{60} as core unit.[12] These branches had first to be transferred into a form suitable for undergoing coupling reactions with C_{60}. As coupling reaction for the direct binding of such dendritic branches we chose the nucleophilic cyclopropanation of C_{60} by treatment of the fullerene with bromomalonates in the presence of base.[13] These addition reactions are among the most elegant and reliable reactions in fullerene chemistry, since they proceed in fairly high yields, lead exclusively to closed [6,6]-bridged adducts and work with a large variety of malonates and related systems. For conversion into the malonates **9**–**11** we treated **1**–**3** with malonyl dichloride in the presence of pyridine (Scheme 1). The subsequent bromination to **12**–**14** was carried out by the reaction of the malonates **9**–**11** with CBr_4 in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Scheme 1). For this purpose we modified the procedure used by Diederich et al. to prepare related bromomalonates.[14]



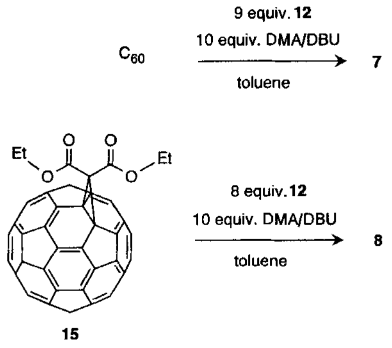
The syntheses of the dendrimers **4**–**6** with two dendrons in the side chains in up to 52% isolated yields were accomplished by treatment of C_{60} with the bromomalonates **12**–**14** in toluene in the presence of NaH (Scheme 2). Whereas isolation of **4** from unreacted C_{60} and bisaddition products was possible with flash chromatography on silica gel with toluene as eluent, size exclusion chromatography on a polystyrene GPC column attached to a preparative HPLC system was necessary to isolate the second- and third-generation analogues **5** and **6**. For the synthesis of the dendrimers **7** and **8** with ten and twelve dendritic branches attached to the fullerene core we used our efficient template activation method, which takes advantage of the activation of [6,6] double bonds in octahedral sites relative to the addends already bound resulting from reversible binding of 9,10-dimethylanthracene (DMA).[6, 8] This procedure guarantees the regioselective formation of oligoadducts of C_{60}, especially that of hexakisadducts with an octahedral addition pattern, in comparatively high yields. Also in the case of the synthesis of dendrimers **7** and **8**, despite the steric bulk of the dendrons to be attached to the core, this one-pot method worked satisfactorily (Scheme 3). Isolation of **7** and **8** from the reaction mixture was possible by flash chromatography followed by preparative HPLC on silica gel with mixtures of toluene and ethyl acetate as eluent.



Scheme 1. Conversion of benzyl-ether-based dendrons **1–3** into the malonates **9–11**.



Scheme 2. The syntheses of the dendrimers **4–6** by treatment of C_{60} with the bromomalonates **12–14**.



Scheme 3. Synthesis of dendrimers **7** and **8** by the template activation method.

The complete spectroscopic characterization of the dendrons **9–12** and the dendrimers **4–8** is straightforward and was achieved by NMR, UV/Vis, FT-IR and mass spectrometry. The NMR and UV/Vis spectra of the dendrimers **4–6** are those of typical [6,6] monoadducts of C_{60}. This is reflected, for example, in their ^{13}C NMR spectra by 16 signals between $\delta = 139$ and 145 and one signal at $\delta = 71$ for the 16 different types of sp^2 C atoms and the two equivalent sp^3 C atoms of the fullerene core, respectively; this reveals C_{2v} symmetry. All expected signals for the C atoms of the dendritic branches within **4–6** appear clearly resolved at about the same positions as those of the corresponding dendrons **9–11**. For higher generations, the ^{1}H NMR spectra of **4–6** reveal increasing line broadening for the signals of the H atoms within the branches compared with that observed in the dendrons **9–11**. In each electronic absorption spectrum of the red solutions of **4–6** the characteristic peak for closed [6,6]-bridged monoadducts of C_{60} appears at 425 nm.[10] In the FAB-MS spectra of the **4–6** the M^+ peak appears together with several fragmentation signals. The UV/Vis spectra of the yellow solutions of the dendritic hexakisadducts **7** and **8** show the characteristic features associated with the electronic core structure resulting from this octahedral addition pattern, which are, for example, the addend-independent absorptions at 280 nm and the typical double absorption at 320 and 340 nm.[8] In this case FAB mass spectrometry is also a suitable method for the detection of molecular ions and clearly proves the expected composition of **7** and **8** with the M^+ peak at 4961 for **7** and with the $(M+\mathrm{Na})^+$ peak at 4435 for **8** as base peaks. The local symmetries of the fullerene cores within the spherical dendrimers **7** and **8** and hence, since a convergent approach was applied, their monodispersivity, are impressively reflected by the ^{13}C NMR spectra. For example, in **7** only three signals at $\delta = 145.97$, 141.29 and 69.42 appear for the three types of magnetically inequivalent fullerene C atoms, which is only possible for an adduct with local T_h symmetry (Figure 3). The ^{13}C NMR spectrum of **8** exhibits 15 resolved signals for the quaternary C atoms of the fullerene core in the ranges between $\delta = 139$–145 (sp^2 C atoms) and $\delta = 67$–70 (sp^3 C atoms). This, together with the four resonances for the four magnetically inequivalent methylene bridges, clearly proves the expected C_{2v}

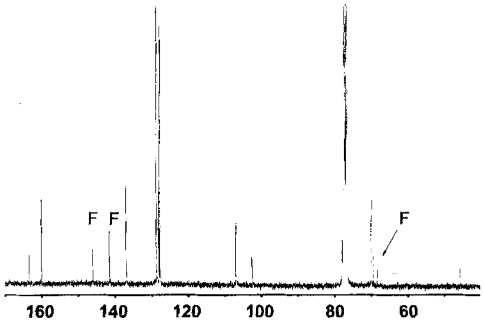


Figure 3. ^{13}C NMR spectrum (100 MHz, 31 °C, CDCl$_3$) of **7**. F denotes the signals of three magnetically different C atoms of the fullerene core.

symmetry. The T_h symmetry of **7** is also nicely reflected by its ^{1}H NMR spectrum, since, for example, in analogy to the monoadduct **4** only one singlet for each of the different types of methylene protons CH_2*(in)* and CH_2*(out)* appears at $\delta = 4.98$ and 4.78, respectively (Figure 4). Compared with the corresponding signals of monoadduct **4**, which appear at $\delta = 5.43$ and 4.95, significant highfield shifts of $\delta = 0.45$ for the CH_2*(in)* protons and $\delta = 0.17$ for the CH_2*(out)* protons are observed. These highfield shifts are caused by the influence of diatropic ring currents of the proximate aromatic rings within neighbouring dendrons. Monoadducts **5** and **6** do not give rise to similar effects. Obviously, the packing of the dendrons in **7** is much more dense than in the monoadducts **4–6**, since the extent of highfield shift for protons located above an aromatic plane greatly decreases with increasing distance. A highfield shift of more than 0.1 ppm is also observed for the protons of the inner aromatic rings, whereas that for the protons of the outer aromatic ring is less pronounced. In the ^{1}H NMR spectrum of **8** the expected number of signals for the corresponding groups within the branches is found, for example, four signals each for the four magnetically different CH_2*(in)* and CH_2*(out)* protons with the right intensity ratio of 1:1:1:2 (Figure 4). As was the case for **7** considerable highfield shifts are observed compared with the monoadduct **4**, especially for the signals of the CH_2*(in)* protons within **8**. However, since the shift of the centre of gravity for the various signals of **8** is somewhat less pronounced compared with the singlets of **7** (Figure 4), less dense packing of the dendrons is revealed. Especially for those dendrons that are located next to the diethylmalonate addend at the equator, a more sterically relaxed situation can be expected.

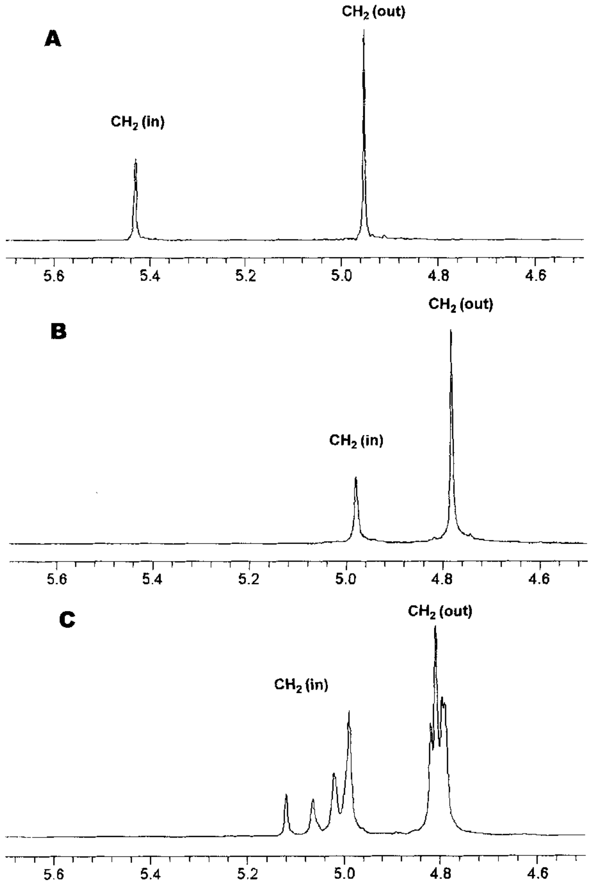


Figure 4. ^{1}H NMR spectra (400 MHz, 31 °C, $CDCl_3$) in the range of the methylene protons of **A**) **4**, **B**) **7** and **C**) **8**.

It was impossible to synthesize the second-generation analogue of **7**. Not even traces of a corresponding hexakisadduct could be detected by various MS techniques including MALDI-TOF and ESI. Similar observations are reported by Fréchet et al.,[11b] who did not detect the formation of adducts higher than bisadducts of C_{60} with fourth-generation dendrons, even if an excess of the dendritic coupling component was used. Obviously, the dendrimer **7** is already a remarkably compact system, although it is built up of only first-generation branches. The core branching multiplicity in **7** is 12, which is by far the highest realized to date. To our knowledge **7** is the smallest spherical organic system which exhibits such a dense structure.

For a computational determination of minimum energy structures at 0 K of dendrimers **4–8** we carried out MD simulations with the MM^+ forcefield implemented in the package HYPERCHEM.[15] The structures obtained from these simulations are represented in Figure 5. Of interest is the dense packing of the branches around the core in all the dendrimers. For the monoadducts **4–6** face-to-face arrangements of the fullerene core with several aromatic rings of the branches indicate favourable π–π stacking interactions, which leads to a very pronounced wrapping of the branches around the fullerene sphere (Figure 5). Such favourable π–π interactions are a well-known phenomenon in fullerene chemistry, which is clearly reflected by the enhanced solubility of fullerenes in polycyclic or electron-rich aromatics, for example,[10] as well as by the analysis of a variety of single crystal structures of C_{60} derivatives with aromatics in the side chain.[9, 16] These solid-state structures nicely reveal the face-to-face arrangements between the fullerene core and the aromatic groups in the side chain. Within the dendrimers **7** and **8** several stacking arrangements between phenyl rings of the branches are present in the calculated structures. The dendrons are densely packed and in the case of **7** are partially interpenetrating. More space is available in the region of the sterically less demanding di(ethoxycarbonyl)methylene addend of **8** (Figure 5). Of course, since solvent effects are neglected and 0 K structures are considered, these modelling investigations reflect only partially the driving forces that are responsible for the geometrical expression of the structures of **4–8** under the actual experimental conditions. In solutions at higher temperatures, the crystallinity of branch packing around the core is certainly substantially removed. However, it is reasonable to assume that the steric constraints associated with the core branching multiplicity of 12 in **7** as well as the possibility of conformations with energetically favourable π–π interactions also account for a comparatively dense structure in solution at room temperature.

Summary and Conclusion

With the synthesis, complete characterization and molecular dynamics simulations of dendrimers **4–8** we present our first results in the field of dendrimer chemistry involving C_{60} as core tecton. We report a dendrimer (**7**) with the core branching multiplicity of 12, the highest yet reached, which is realized by

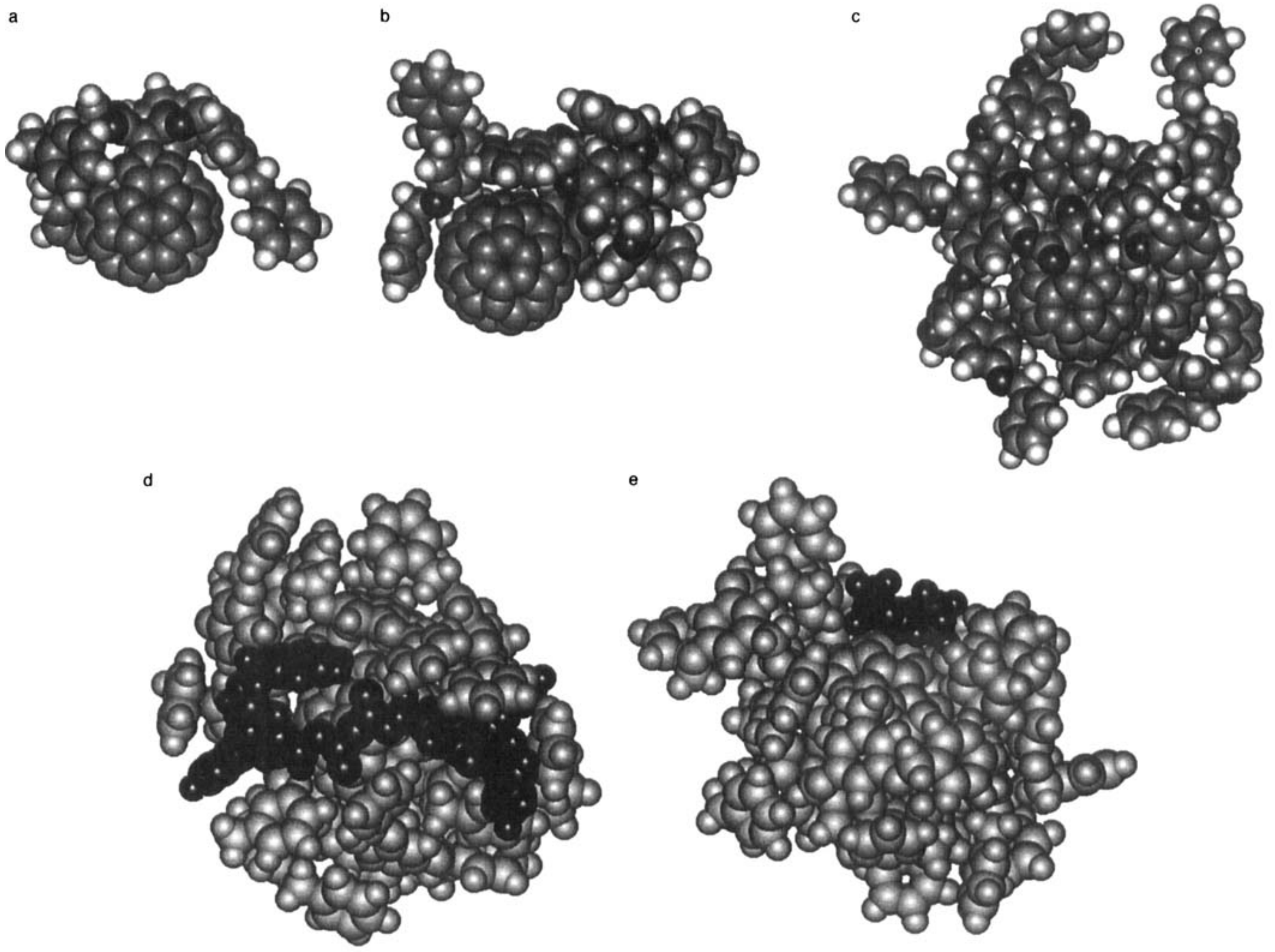


Figure 5. Minimum energy structures at 0 K of the dendrimers a) **4**, b) **5**, c) **6**, d) **7** and e) **8** after molecular dynamics (MD) simulation [15]. All structures were preminimized with the MM$^+$ forcefield implemented in HYPERCHEM [15] prior to the MD simulation. During the MD simulations the structures were heated to 1000 K and kept at this temperature for equilibration before they were allowed to cool to 0 K to establish the minimum energy structure. Conditions for the simulated annealing: heat time: 5 ps, run time: 15 ps, cool time: 50 ps, step size: 0.001 ps, starting temperature: 0 K, simulation temperature: 1000 K, final temperature: 0 K, in vacuo, data collection period: 1 time step. The black segment in the structure of **7** (d) is one of the six double branches, highlighted to reveal its interpenetration with other branches. The black segment in the structure of **8** (e) is the di(ethoxycarbonyl)methylene addend.

means of a T_h-symmetrical C_{60} core with an octahedral addition pattern. This unique structure type of a core building block is only possible on the basis of C_{60} and has no precedent in organic chemistry. Because of the high core branching multiplicity within **7** the dendrons are densely packed; this is implied, for example, by molecular dynamics simulations and by ^1H NMR spectroscopy. Dendrons with longer spacers between the aromatic subunits will probably lead to less densely packed systems and may also provide access to higher-generation dendrimers of the construction type. The synthesis of very compact and small dendrimers, on the other hand, could be of importance for the design of fullerene-based architectures with a uniform and conformationally completely restricted structure. Compounds like this would have properties resembling those typical for biopolymers like enzymes. The general building principle (Figures 1 and 2) of dendrimers based on C_{60} as probably the most versatile core tecton creates countless possibilities for structure variation by systematic change in the degree and pattern of addition to C_{60}, by the use of different dendrons and by the possibility of combining them with additional *functional molecules*, for example, electroactive species like porphyrins. We will report on the synthesis as well as the determination of the properties of further new fullerene dendrimer architectures in due course.

Experimental Section

^1H NMR and ^{13}C NMR: JEOL PMX 60 and JEOL JNM GX 400; MS: Varian MAT 311 A (EI) and Finnigan MAT 900 (FAB); FT-IR: Bruker Vector 22; UV/Vis: Shimadzu UV 3102 PC; HPLC preparative: Shimadzu SIL 10A, SPD 10A, CBM 10A, LC 8A, FRC 10A (Grom-Sil 100 Si, NP1, 5 µm, 25 × 2.0 cm and Nucleogel GFC 500-10); TLC: Macherey–Nagel, Alugram SIL G/UV$_{254}$. Reagents used were commercially available reagent grade and were prepared according to common procedures. HPLC solvents were from SDS. CH_2Cl_2, THF and toluene used for the reactions were dried according to the usual procedures. All reactions were carried out under a positive pressure of argon. Products were isolated where possible by flash column chromatography (silica gel 60, particle size 0.04–0.063 nm, Merck).

Di(3,5-dibenzyloxybenzyl)propanedionate (**9**): To a solution of **1** (3.11 g, 9.72 mmol) in dry CH_2Cl_2 (20 mL), pyridine (0.78 mL, 9.64 mmol) was added under argon. The mixture was cooled with an ice bath and after that propanedioyl dichloride (0.47 mL, 4.83 mmol) were added dropwise over 10 min. After 2 h the ice bath was removed and the solution was stirred at room temperature overnight. The solution was extracted with water and the organic layer was dried over Na_2SO_4. Flash chromatography on silica gel with CH_2Cl_2 as eluent gave 3.00 g of malonic diester **9**. Yield: 87.6%. ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 3.47$ (s, 2H, CH_2), 4.97 (s, 8H, $ArCH_2O$), 5.11 (s, 4H, CH_2O_2C), 6.55 (t, 2H, $J = 2$ Hz, Ar*H*), 6.58 (d, 4H, $J = 2$ Hz, Ar*H*), 7.28–7.40 (m, 20H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 41.38$ (CH_2), 66.97 (CH_2O_2C), 70.01 ($ArCH_2O$), 101.91 (arom. *CH*), 106.93 (arom. *CH*), 127.55 (Ph *CH*), 128.03 (Ph *CH*), 128.60 (Ph *CH*), 137.60 (Ph *C*), 137.53 (arom. *C*), 160.14 (arom. *C*), 166.22 (C=O); MS (EI): $m/z = 708$ (M^+), 617 ($M - PhCH_2^+$).

Bromobis(3,5-dibenzyloxybenzyl)propanedionate (12): A mixture of **9** (2.81 g, 3.96 mmol) and DBU (0.59 mL, 3.96 mmol) in dry THF (20 mL) was cooled to −78 °C under argon. Then a solution of CBr_4 (1.31 g, 3.96 mmol) in THF (5 mL) was added and the mixture stirred for 2 h. The reaction was quenched with HCl (50 mL, 0.1 M) and the cooling bath was removed. Subsequently Et_2O (50 mL) was added, the organic layer was extracted with sat. aq. $NaHCO_3$ (to ca. pH 6) and sat. aq. NaCl solutions and dried over Na_2SO_4. Purification by flash chromatography (SiO_2, hexane/CH_2Cl_2 2:1) gave 2.23 g of **11** as a yellow oil; 165 mg of **9** were recovered. Yield: 71.5%. ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 4.91$ (s, 1H, $CHBr$), 4.97 (s, 8H, $ArCH_2O$), 5.16 (s, 4H, CH_2O_2C), 6.55–6.57 (m, 6H, Ar*H*), 7.29–7.40 (m, 20H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 42.00$ ($CHBr$), 68.39 (CH_2O_2C), 70.04 ($ArCH_2O$), 102.17 (arom. *CH*), 106.86 (arom. *CH*), 127.56 (Ph *CH*), 128.07 (Ph *CH*), 128.63 (Ph *CH*), 136.66 (Ph *C*), 136.81 (arom. *C*), 160.17 (arom. *C*), 164.30 (C=O); MS (EI): $m/z = 789$ (M^+), 787 (M^+), 708 ($M - Br^+$).

Compound 4: To a solution of C_{60} (100 mg, 0.139 mmol) in toluene (50 mL), the bromomalonate **12** (165 mg, 0.209 mmol) in toluene (10 mL) and sodium hydride (35 mg, 1.46 mmol) were added. After 72 h stirring at room temperature the excess sodium hydride was destroyed with 2 N sulfuric acid. The organic layer was dried over magnesium sulfate and the solvent evaporated under reduced pressure. Purification with flash chromatography (SiO_2/toluene) afforded 103 mg (52.0%) of **4** and 62 mg (21.9%) of a mixture of bisadducts. UV/Vis (CH_2Cl_2): $\lambda_{max} = 271.0$, 327.0, 426.50 nm; ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 4.95$ (s, 8H, $ArCH_2O$), 5.43 (s, 4H, CH_2O_2C), 6.56 (t, 2H, $J = 2.5$ Hz, Ar*H*), 6.70 (d, 4H, $J = 2.5$ Hz, Ar*H*), 7.28–7.39 (m, 20H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 51.76$ (methano bridge), 68.66 (CH_2O_2C), 70.08 ($ArCH_2O$), 71.36 (C_{60} sp^3 *C*), 102.28 (arom. *CH*), 107.53 (arom. *CH*), 127.60 (Ph *CH*), 128.10 (Ph *CH*), 128.63 (Ph *CH*), 136.59 (Ph *C*), 136.90 (arom. *C*), 139.07, 140.92, 141.86, 142.20, 142.98, 143.01, 143.05, 143.10, 143.85, 144.56, 144.68, 144.89, 144.98, 145.11, 145.17, 145.24 (C_{60} sp^2 *C*), 160.23 (arom. *C*), 163.39 (*C*=O); MS (FAB): $m/z = 1427.5$ (M^+), 719.9 (C_{60}^+); IR (KBr): $\tilde{\nu} = 3060.9$ cm^{-1}, 3028.4, 2923.5, 2857.5, 1745.3, 1594.4, 1450.9, 1372.1, 1226.5, 1157.7, 1057.9, 831.3, 753.2, 695.5, 526.3.

Compound 7: A mixture of C_{60} (170 mg, 0.236 mmol) and 9,10-dimethylanthracene (DMA) (487 mg, 2.36 mmol) in toluene (50 mL) was stirred at room temperature for 2 h. Then the bromomalonate **12** (1.65 g, 2.10 mmol) in toluene (20 mL) and DBU (360 mg, 2.36 mmol) were added. After 96 h the solvent was evaporated under reduced pressure and the crude mixture separated by flash chromatography (SiO_2, toluene/AcOEt 98:2) followed by preparative HPLC (Grom-Sil 100 Si, NP1, 5 µm) with the same eluent, and preparative HPLC (Nucleogel GFC 500-10) with toluene as eluent, to give 63 mg of the hexaadduct **7**. Yield: 5.4%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 282.5$, 319.0, 338.0, 384.0 nm; ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 4.78$ (s, 48H, $ArCH_2O$), 4.98 (s, 24H, CH_2O_2C), 6.42 (br s, 36H, Ar*H*), 7.19–7.32 (m, 120H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 45.44$ (methano bridge), 68.13 (C_{60} sp^3 *C*), 69.25 (CH_2O_2C), 69.83 ($ArCH_2O$), 102.27 (arom. *CH*), 106.73 (arom. *CH*), 127.60 (Ph *CH*), 127.90 (Ph *CH*), 128.52 (Ph *CH*), 136.82 (Ph *C*), 136.85 (arom. *C*), 141.30 (C_{60} sp^2 *C*), 145.98 (C_{60} sp^2 *C*), 160.02 (arom. *C*), 163.37 (*C*=O); MS (FAB): $m/z = 4961$ (M^+), 4254.1 (penta$^+$), 3547.5 (tetra$^+$), 2840.3 (tris$^+$); IR (film): $\tilde{\nu} = 3091.5$ cm^{-1}, 3067.3, 3034.5, 2925.9, 2872.6, 1747.0, 1598.2, 1454.9, 1375.0, 1341.3, 1294.5, 1264.8, 1212.4, 1160.5, 1061.4, 933.1.

Compound 8: A mixture of $C_{61}(COOEt)_2$ (**15**) (240 mg, 0.273 mmol) and 9,10-dimethylanthracene (DMA) (563 mg, 2.729 mmol) in toluene (50 mL) was stirred at room temperature for 2 h. Then bromomalonate **12** (1.72 g, 2.184 mmol) in toluene (20 mL) and DBU (416 mg, 2.73 mmol) were added. After 96 h the solvent was evaporated under reduced pressure and the crude mixture separated by flash chromatography (SiO_2, toluene/AcOEt 98:2) followed by preparative HPLC (Grom-Sil 100 Si, NP1, 5 µm) with toluene/AcOEt 99:1 as eluent to give 184 mg of the mixed hexaadduct **8**. Yield: 15.3%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 282.0$, 319.0, 337.5, 384.5 nm; ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 1.17$ (t, 6H, $J = 6.8$ Hz, CH_3), 4.13 (q, 4H, $J = 6.8$ Hz, CH_2O_2C), 4.79 (s, 8H, $ArCH_2O$), 4.80 (s, 8H, $ArCH_2O$), 4.81 (s, 16H, $ArCH_2O$), 4.82 (s, 8H, $ArCH_2O$), 4.99 (s, 8H, CH_2O_2C), 5.02 (s, 4H, CH_2O_2C), 5.06 (s, 4H, CH_2O_2C), 5.12 (s, 4H, CH_2O_2C), 6.43–6.59 (m, 30H, Ar*H*), 7.21–7.40 (m, 100H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 13.87$ (CH_3), 41.43 (CH_2O_2C), 45.33 (methano bridge), 45.36 (methano bridge), 45.39 (methano bridge), 45.56 (methano bridge), 62.81 (CH_2O_2C), 67.03, 68.14 (br), 69.19, 69.21, 69.83, 70.04 (CH_2O_2C, $ArCH_2O$, C_{60} sp^3 *C*) 101.93 (arom. *CH*), 102.27 (arom. *CH*), 106.65 (arom. *CH*), 106.71 (arom. *CH*), 106.78 (arom. *CH*), 106.96 (arom. *CH*), 127.61 (arom. *CH*), 127.91 (arom. *CH*), 128.07 (arom. *CH*), 128.26 (arom. *CH*), 128.51 (arom. *CH*), 128.63 (arom. *CH*), 136.71, 136.80, 136.84, 136.88 (arom. *C*, Ph *C*), 141.20, 141.23, 141.30, 141.48, 145.84, 145.89, 145.97, 146.02, 146.06 (C_{60} sp^2 *C*), 163.40, 163.49, 163.63 (arom. *C*), 166.27 (*C*=O); MS (FAB): $m/z = 4435.12$ ($(M+Na)^+$); IR (film): $\tilde{\nu} = 3067.0$ cm^{-1}, 3034.4, 2935.3, 2873.2, 1746.9, 1597.9, 1498.0, 1453.7, 1374.7, 1343.1, 1320.5, 1294.2, 1264.6, 1209.5, 1160.7, 1080.2, 1061.9, 1029.6, 908.7.

Compound 10: Pyridine (1.29 mL, 15.95 mmol) was added to a solution of **2** (12.29 g, 16.50 mmol) in dry CH_2Cl_2 (75 mL) under argon. The mixture was cooled with an ice bath and after that propanedioyl dichloride (0.80 mL, 8.22 mmol) was added dropwise over 10 min. After 2 h the ice bath was removed and the solution was stirred at room temperature overnight. The solution was extracted with water, and the organic layer dried over Na_2SO_4. Purification by flash chromatography (SiO_2, hexane/AcOEt 4:1, gradually increasing to hexane/AcOEt 1:1) gave 10.5 g of the malonic diester **10**. Yield: 82.1%. ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 3.48$ (s, 2H, CH_2), 4.89 (s, 8H, $ArCH_2O$), 4.99 (s, 16H, $PhCH_2O$), 5.10 (s, 4H, $ArCH_2OCO$), 6.50 (t, 2H, $J = 2.4$ Hz, Ar*H*), 6.55 (t, 4H, $J = 2.4$ Hz, Ar*H*), 6.64 (d, 8H, $J = 2.4$ Hz, Ar*H*), 6.65 (d, 4H, $J = 2.4$ Hz, Ar*H*), 7.26–7.4 (m, 40H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 41.45$ (CH_2), 67.00 (CH_2O_2C), 69.90 ($ArCH_2O$), 70.04 ($PhCH_2O$), 101.56 (arom. *CH*), 101.95 (arom. *CH*), 106.37 (arom. *CH*), 106.95 (arom. *CH*), 127.60 (Ph *CH*), 128.03 (Ph *CH*), 128.61 (Ph *CH*), 136.79 (Ph *C*), 137.53 (arom. *C*), 139.15 (arom. *C*), 160.05 (arom. *C*), 160.21 (arom. *C*), 166.27 (*C*=O).

Compound 13: A mixture of malonate **10** (9.50 g, 6.1 mmol) and DBU (0.91 mL, 6.1 mmol) in THF (70 mL) was treated with a solution of CBr_4 (2.02 g, 6.1 mmol) in THF (15 mL) in the same way as compound **9**. After the work-up an inseparable mixture of **13**, the corresponding dibromomalonate and **10** was obtained with a yield of **13** higher than 60% (^{1}H NMR). Since the dibromomalonate **13**-Br and **10** are inert under the conditions for the base-catalysed coupling to fullerenes[13] this mixture was used for the subsequent reaction with C_{60}.

Compound 5: The reaction was performed as described for **4**, with C_{60} (100 mg, 0.139 mmol), the 60:40 mixture of **13**, **13**-Br and **10** (340 mg) and NaH (50 mg, 2 mmol). After purification by flash chromatography (SiO_2, toluene gradually increasing to toluene/ethyl acetate 9:1), followed by preparative HPLC (Nucleogel GFC 500-10) with toluene as eluent, 63 mg of **5** were obtained. Yield: 19.9%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 258.5$, 320.0, 420.5 nm; ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 4.80$–4.93 (m, 28H, CH_2O), 6.49–6.65 (m, 18H, Ar*H*), 7.20–7.38 (m, 40H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 48.59$ (methano bridge), 70.05 (br), 70.55 (CH_2O), 71.32 (C_{60} sp^3 *C*), 101.64 (arom. *CH*), 102.42 (arom. *CH*), 106.49 (arom. *CH*), 106.75 (arom. *CH*), 127.60 (Ph *CH*), 128.03 (Ph *CH*), 128.61 (Ph *CH*), 136.77 (Ph *C*), 136.91 (arom. *C*), 139.02, 140.92, 141.85, 142.18, 142.98, 143.04, 143.85, 144.52, 144.54, 144.67, 144.90, 144.95, 145.08, 145.11, 145.17, 145.22 (C_{60} sp^2 *C*), 160.14 (arom. *C*), 160.21 (arom. *C*), 163.41 (*C*=O); MS (FAB): $m/z = 2276.7$ (M^+), 1556.8 ($M - C_{60}^+$); IR (film): $\tilde{\nu} = 3066.3$ cm^{-1}, 3033.6, 2926.2, 2855.0, 1745.8, 1647.9, 1596.8, 1497.5, 1452.8, 1374.2, 1343.7, 1322.9, 1295.7, 1269.1, 1211.0, 1159.0, 1058.1, 1029.6.

Compound 11: Pyridine (0.265 mL, 3.27 mmol) was added to a solution of **3** (5.264 g, 3.30 mmol) in dry CH_2Cl_2 (60 mL) under argon. The mixture was cooled with an ice bath and after that propanedioyl dichloride (0.16 mL, 1.64 mmol) was added dropwise over 10 min. After 2 h the ice bath was removed and the solution was stirred at room temperature overnight. The solution was extracted with water, and the organic layer was dried over Na_2SO_4. Purification by flash chromatography (SiO_2, hexane/CH_2Cl_2 1:1, gradually increasing to 100% CH_2Cl_2) gave 3.53 g of the malonic diester **11**. Yield: 65.9%. ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 3.44$ (s, 2H, CH_2), 4.82 (s, 8H, ArCH_2O), 4.86 (s, 16H, ArCH_2O), 4.94 (s, 32H, PhCH_2O), 5.06 (s, 4H, CH_2O_2C), 6.49 (t, 4H, $J = 2.4$ Hz, Ar*H*), 6.52 (m, 10H, Ar*H*), 6.60 (d, 8H, $J = 2.4$ Hz, Ar*H*), 6.63 (m, 20H, Ar*H*), 7.20–7.53 (m, 80H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 41.38$ (CH_2), 66.78 (CH_2O), 68.17 (ArCH_2O), 69.76 (ArCH_2O), 69.88 (PhCH_2O), 101.48 (arom. *CH*), 101.78 (arom. *CH*), 101.98 (arom. *CH*), 106.30 (arom. *CH*), 106.58 (arom. CH), 106.69 (arom. CH), 127.48 (Ph *CH*), 127.90 (Ph *CH*), 128.48 (Ph *CH*), 136.74 (Ph *C*), 139.08 (arom. *CH*), 139.11 (arom. C), 139.19 (arom. *C*), 159.96 (arom. C), 160.00 (arom. C), 160.10 (arom. C), 166.13 (*C*=O).

Compound 14: A mixture of malonate **11** (3.28 g, 1.01 mmol) and DBU (0.15 mL, 1.005 mmol) in THF (50 mL) was treated with a solution of CBr_4 (0.34 g, 1.01 mmol) in THF (5 mL) in the same way as compound **9**. After the work-up an inseparable mixture of **14**, the corresponding dibromomalonate and **11** was obtained with a yield of **14** higher than 60% (^{1}H NMR). Since the dibromomalonate **14**-Br and **11** are inert under the conditions for the base-catalysed coupling to fullerenes[13] this mixture was used for the subsequent reaction with C_{60}.

Compound 6: The reaction was performed as described for **4** with C_{60} (200 mg, 0.277 mmol), the 60:40 mixture of **14** and **14**-Br (1.73 g) and NaH (100 mg, 4.17 mmol). After purification by flash chromatography (SiO_2, toluene/ethyl acetate 98:2) followed by preparative HPLC (Nucleogel GFC 500-10) with toluene as eluent gave 473 mg of **6**. Yield: 42.9%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 426.0$, 327.0, 269.0 nm; ^{1}H NMR (400 MHz, 31 °C, $CDCl_3$): $\delta = 4.80$–4.93 (m, 60H, CH_2O), 6.49–6.65 (m, 42H, Ar*H*), 7.20–7.38 (m, 80H, Ph*H*); ^{13}C NMR (100 MHz, 31 °C, $CDCl_3$): $\delta = 51.73$ (methano bridge), 69.77 (br), 69.88 (br) (CH_2O), 71.29 (C_{60} sp^3 *C*), 101.48 (arom. *CH*), 101.61 (arom. *CH*), 106.34 (arom. *CH*), 106.42 (arom. *CH*), 127.50 (Ph *CH*), 127.91 (Ph *CH*), 128.49 (Ph *CH*), 136.73, 136.92 (Ph *CH*, arom. *CH*), 139.15, 140.76, 141.68, 142.00, 142.79, 143.67, 144.37, 144.40, 144.48, 144.69, 144.83, 144.92, 144.96, 145.05 (C_{60} sp^2 *C*), 160.03 (arom. *C*), 160.11 (arom. *C*), 163.23 (*C*=O); MS (FAB): $m/z = 3974.5$ (M^+); IR (film): $\tilde{\nu} = 3066.3$ cm^{-1}, 3033.5, 2928.6, 2871.8, 1748.7, 1596.6, 1497.6, 1453.1, 1374.1, 1341.6, 1320.7, 1296.1, 1159.0, 1056.0, 908.8.

Acknowledgements: This work was supported by the BMBF and Hoechst AG.

Received: September 3, 1996 [F472]

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