Fullerene Dendrimers and Lipofullerenes with an Inherently Chiral Hexaaddition Pattern

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The facile synthesis of enantiomerically pure C_3-symmetrical fullerene dendrimers *all-R-*^{f}*A*-**7**, *all-S-*^{f}*C*-**8**, *all-R-*^{f}*C*-**9**, and *all-S-*^{f}*A*-**10**, as well as lipofullerenes *all-S-*^{f}*A*-**11** and *all-S-*^{f}*C*-**12** involving an octahedral [3:3] addition pattern is described. The C_3 symmetrical tris[bis(4-phenyl-2-oxazoline)methano]-fullerenes **1**, **2**, **3**, and **4** with known absolute configuration were used as precursors. The completion of the octahedral addition pattern was achieved by a threefold cyclopropanation with the dendritic 3,5-dihydroxybenzylic bromomalonate **5** and the lipophilic dioctadecyl bromomalonate **6**. The absolute configurations of the precursor trisadducts were retained in the inherently chiral C_3-symmetrical hexakisadducts **7–12**. The structure and the isomeric purity of all hexakisadducts **7–12** were unambiguously proven by NMR spectroscopy and other techniques. Preliminary experiments with the dendritic hexakisadducts *all-S-*^{f}*C* **8** and *all-S-*^{f}*A* **10** revealed that these macromolecular ligands posess catalytic properties with respect to stereoselective cyclopropanations of styrene with ethyl diazoacetate.

Introduction

Buckminsterfullerene C_{60} can be used as a spherical building block for the facile construction of globular dendrimers[1–3] and lipofullerenes[4–6] with an octahedral addition pattern (Figure 1). The concept of using C_{60} as the central core involving this unique structural motif is very versatile since it allows not only for the synthesis of adducts with T_h symmetry,[7] but also of those with C_{2v}, C_s, and C_3 symmetry. In these adducts of lower symmetry, two types of addends, instead of one, are bound in a [5:1]-, [4:2]- and [3:3]-fashion. We have recently shown,[1–6] that the synthesis of such mixed dendritic hexakisadducts is straightforward, and can be achieved by applying template mediated cyclopropanations[7,8] starting, for example, from pentakis-, tetrakis- and trisadducts with C_{2v}, C_s, and C_3 symmetry, respectively.[3] Of special interest are C_3 symmetrical dendritic hexakisadducts containing two different types of addends, since their addition pattern is inherently chiral. Using achiral addends only, we succeeded in isolating several examples of dendrimers with such a chiral core motif as racemic mixtures. In this contribution we report on the synthesis and isolation of enantiomerically pure C_3-symmetrical C_{60} dendrimers and lipofullerenes involving an octahedral [3:3] addition pattern. This concept is based on the use of enantiomerically pure *e,e,e* bisoxazoline trisadducts with known absolute configuration that we described previously.[9] The chiral dendrimers presented here can serve as chiral catalysts (*dendrizymes*) for stereoselective syntheses, and the chiral lipofullerenes have potential as intercalation components for lipid membranes.

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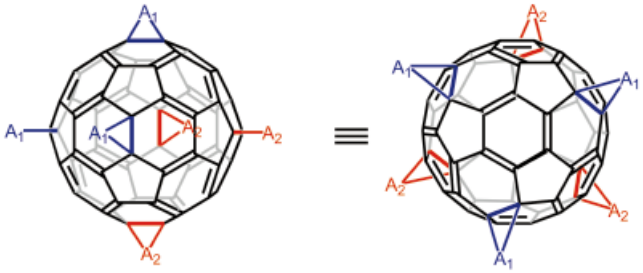

Figure 1. Two different views on the C_3-symmetrical addition pattern of a [3:3]-hexakisadduct of C_{60} (the front sites of the [3:3] adduct are marked in blue and the rear sites in red); A_1, A_2 represent methylene addends introduced by nucleophilic cyclopropanation

Results and Discussion

The tris[bis(4-phenyl-2-oxazoline)methylene] adducts *all-R-*^{f}*C*-(+)-**1**, *all-S-*^{f}*A*-(–)-**2**, *all-R-*^{f}*A*-(+)-**3**, and *all-S-*^{f}*C*-(–)-**4**[9] were used as precursors for the synthesis of the chiral dendrimers and lipofullerenes. These precursors were obtained by stepwise cyclopropanation of C_{60} with bis(4*R*)- or bis[(4*S*)-4-phenyloxazoline]methane in the presence of DBU and CBr_4. The absolute configuration of these C_3-symmetrical trisadducts with an inherently chiral addition pattern were determined by the comparison of their calculated and experimental CD spectra.[9b] Adducts **1** and **2**, as well as **3** and **4**, represent pairs of enantiomers. The other combinations are diastereomers. Three more [6,6] double bonds in equatorial sites are available for subsequent nucleophilic cyclopropanations in order to complete the octahedral addition pattern. For the introduction of the dendritic and lipophilic addends, 2nd generation 3,5-dihydroxybenzylic bromomalonate **5**[1] (Frechét-type dendrimer) and lipophilic dioctadecyl bromomalonate **6**[8] were used. Although the sense of configuration of the trisadducts is retained in the

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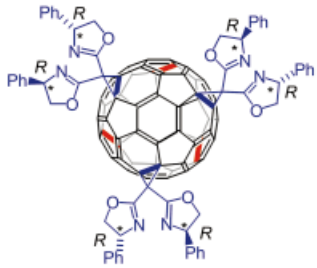
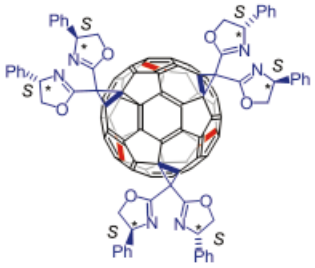
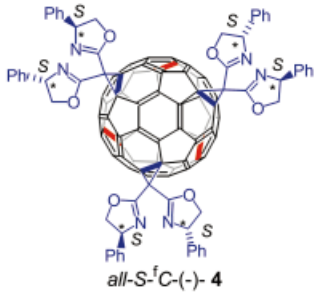
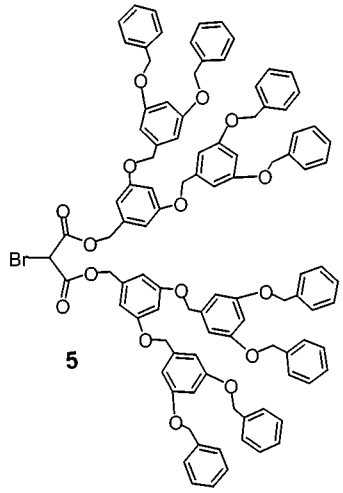
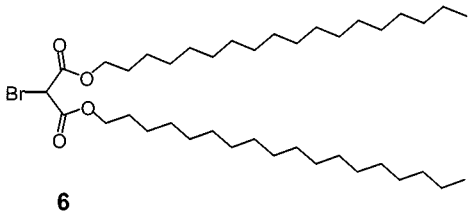






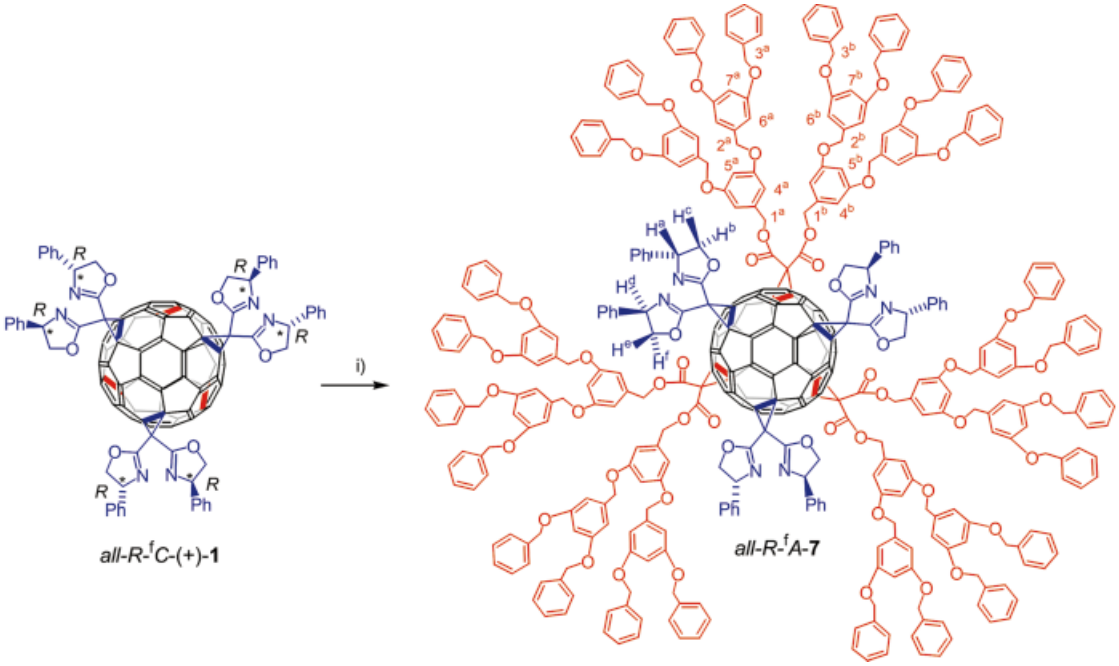




hexakisadducts, because of the higher priority of the malonate compared to the bisoxazoline addends (CIP rules), the assignment of the configuration is changed from ^{f}C to ^{f}A and vice versa, in going from the tris- to the hexakisadducts.

Fullerene Dendrimers with an Inherently Chiral C_3-Symmetrical Hexaaddition Pattern

For the preparation of the hexakisadduct **7** with *all-R*-^{f}A-configuration, *all-R*-^{f}C-(+)-**1** was treated for three hours

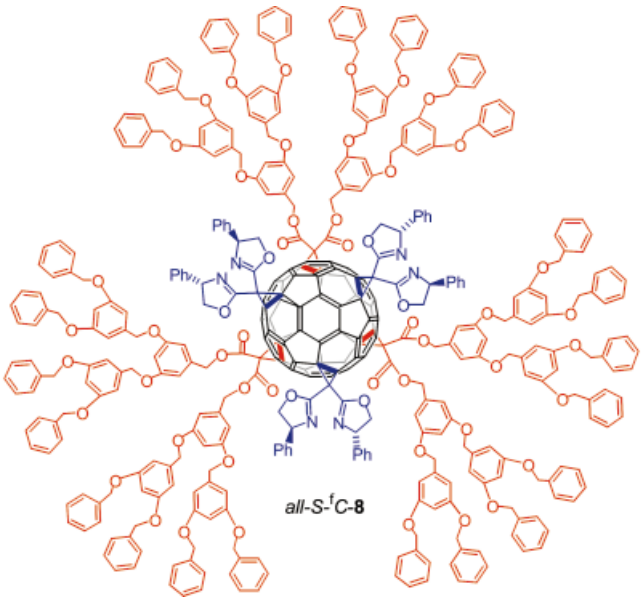


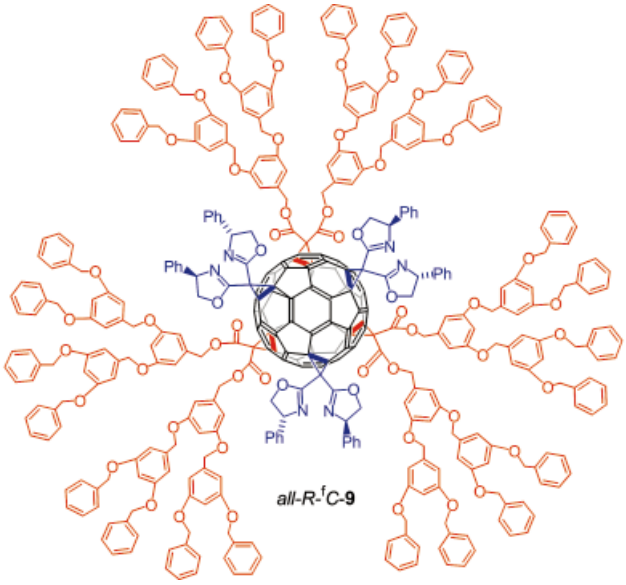
Scheme 1. Synthesis of *all-R*-^{f}A-**7** by nucleophilic cyclopropanation of *all-R*-^{f}C-(+)-**1** with bromomalonate **5**: i) DMA, 3 h, 5, DBU, 48 h, toluene (the numbers and assignments of H atoms refer to the NMR spectra in Figure 2)

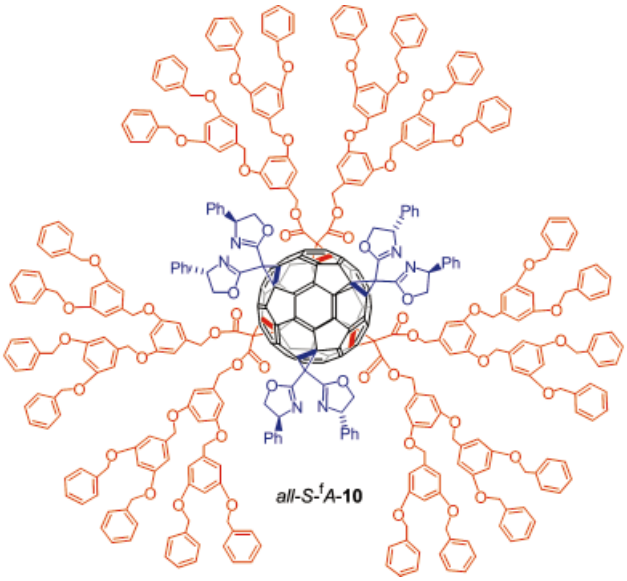
with DMA, and subsequently cyclopropanated with the dendritic bromomalonate **5** in the presence of DBU. This template mediation technique guarantees a high regioselectivity (Scheme 1).[7,8] After a period of 48 hours the reaction was stopped. The product was purified by flash chromatography (toluene/ethyl acetate = 94:6), where it eluted as the least-polar orange-colored fraction. This fraction still contained a small amount of the more polar pentakisadducts. After a final purification step by preparative HPLC on Nucleosil (toluene/ethyl acetate = 95:5), pure **7** was obtained as yellow solid in 70% yield.

Similarly, dendrimer **8**, which is the enantiomer of **7**, was synthesized starting from the trisadduct *all-S-*^{f}*A*-(–)-**2** by the corresponding treatment with the second generation dendron **5**. After work-up using the same conditions, *all-S-*^{f}*C*-**8** was isolated in 64% yield. As expected, enantiomer **8** shows the same properties as **7** when it was subjected to ^{1}H, ^{13}C NMR, FT-IR, UV/Vis spectroscopy and mass spectrometry. In the same way, *all-R-*^{f}*C*-**9** and *all-S-*^{f}*A*-**10** were synthesized in an enantiomerically pure form using the trisadducts *all-R-*^{f}*A*-(+)-**3** and *all-S-*^{f}*C*-(–)-**4**, respectively. The two dendrimers **9** and **10** are diastereomers of the hexakisadducts **7** and **8**. Because of their enantiomeric relationship *all-R-*^{f}*C*-**9** and *all-S-*^{f}*A*-**10** reveal identical spectroscopic data.

The C_3-symmetry of the products **7**, **8**, **9**, and **10** can be unambiguously deduced from their NMR spectra. Since the two oxazoline units from one bisoxazoline addend are unequivalent ("*exo*" and "*endo*" positions), the six oxazolines can be separated into two groups, and as a result reveal two different sets of ^{1}H signals (Figure 2). The exact assignment of signals was carried out by COSY, ROESY, and NOE difference spectroscopy of the starting materials **1**–**4**. As expected, the two topologically different dendra of each dendritic malonate addend next to the bisoxazoline addends also give rise to two sets of signals for the corresponding magnetically unequivalent protons (Figure 2).







Fourteen out of the sixteen resonances expected for the sp^2 C atoms of a C_3-symmetrical hexakisadduct are resolved in the ^{13}C NMR spectra of *all-R-*^{f}*A*-**7** and *all-R-*^{f}*C*-**9** (Figure 3). They are distributed in two groups of signals centred around δ = 142 and 146. This behaviour is very typical for mixed hexakisadducts with an octahedral addition pattern. The fullerene sp^3-carbons resonate at δ = 70. The three identical C atoms of the methylene bridges carrying the bisoxazoline addends resonate at δ = 35.17. The corresponding methylene C atoms of the dendritic addends appear at δ = 45.30 (Figure 3). The two unequivalent oxazoline subunits lead to two signals for the O–*C*=N C atoms at δ = 163.2 and 163.4. While the two carbonyl carbon signals of the dendra in *all-R-*^{f}*A*-**7** addends appear at δ = 160.50 and 160.80, those of *all-R-*^{f}*C*-**9** are overlapping and give rise to one peak at δ = 160.70.

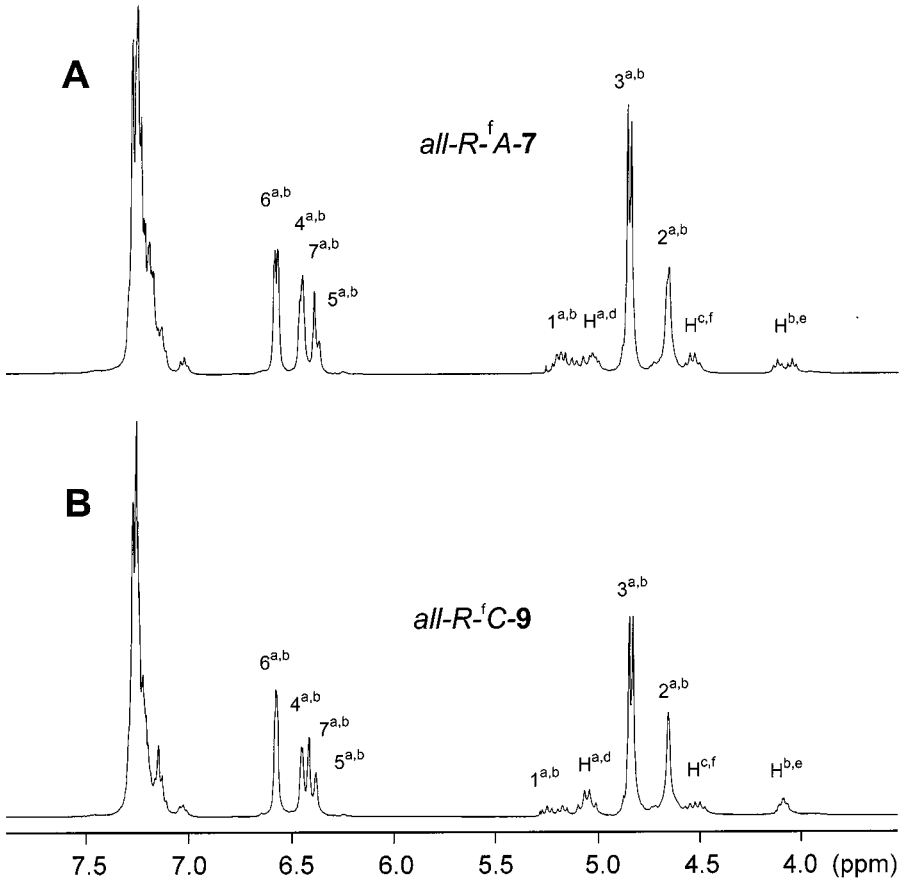


Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of the dendrimeric hexakisadducts **A**) *all-R-*^{f}*A*-**7** and **B**) *all-R-*^{f}*C*-**9**; for the assignment of H atoms see Scheme 1

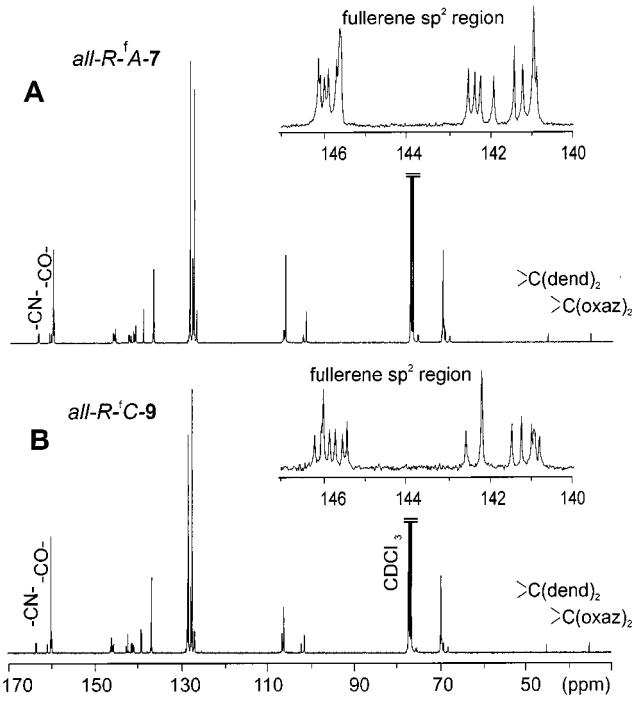


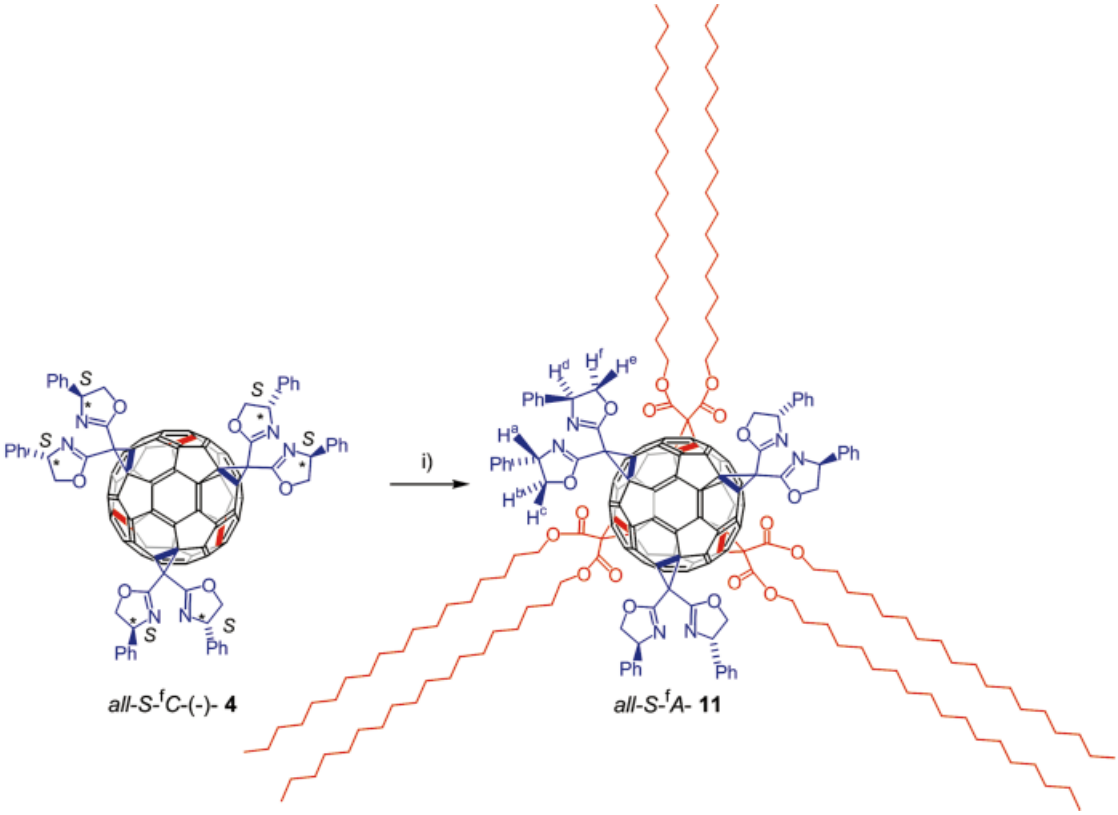
Figure 3. ^{13}C NMR spectra (100 MHz, $CDCl_3$, 25 °C) of **A**) *all-R-*^{f}*A*-**7** and **B**) *all-R-*^{f}*C*-**9**; the offset shows the fullerene-sp^2 region; for the assignment of H atoms see Scheme

Lipofullerenes with an Inherently Chiral C_3-Symmetrical Hexaaddition Pattern

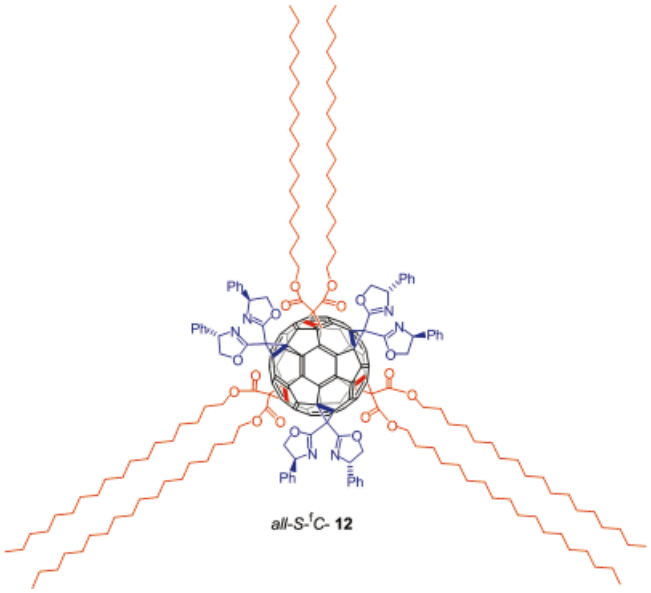
For the synthesis of the chiral lipofullerenes, the two diastereomeric precursor trisadducts *all-S-*^{f}*C*-**4** and *all-S-*^{f}*A*-**2** were cyclopropanated with dioctadecyl bromomalonate **6** using the template mediation method (Scheme 2).[7] The C_3-symmetrical lipofullerenes *all-S-*^{f}*A*-**11** and *all-S-*^{f}*C*-**12** were obtained in 60 and 66% yield, respectively. Like their precursor trisadducts *all-S-*^{f}*C*-**4** and *all-S-*^{f}*A*-**2**, lipofullerenes *all-S-*^{f}*A*-**11** and *all-S-*^{f}*C*-**12** represent a pair of diastereomers.

The ^{1}H NMR spectra of diastereomers **11** and **12** (Figure 4) are very similar. The sets of signals for the protons of the three identical *exo*- and the three *endo*-oxazoline subunits have similar chemical shifts, and collapse to give four multiplets at δ = 4.27, 4.78, 5.42 and 7.30. The signal δ = 4.27 is superimposed by the absorptions of the twelve –CH_2–O protons from the octadecyl chains. The other alkyl protons resonate at δ = 0.87 (18 CH_3), 1.25 (180 H, CH_2) and 1.68 (12 H, OCH_2CH_2).

In analogy to the ^{13}C NMR spectra of the fullerene dendrimers **7–10**, the sp^2 C atoms of *all-S-*^{f}*A*-**11** and *all-S-*^{f}*C*-**12** are distributed in two groups of signals centred at δ = 141 and 146, which is the typical location for the two mag-



Scheme 2. Synthesis of *all-S-*^{f}*A*-**11** by nucleophilic cyclopropanation of *all-S-*^{f}*C*-(–)-**4** with bromomalonate **6**: i) DMA, 3 h, **6**, DBU, 48 h, toluene toluene (the assignments of H atoms refer to the NMR spectra in Figure 4)



netically different sp^2 C atoms of a T_h symmetrical hexakis-adduct.[1–7] In the ^{13}C NMR spectrum of *all-S-*^{f}*A*-**11** eleven of the sixteen expected signals of fullerene sp^2 C atoms are clearly resolved. Similarly, in the spectrum of *all-S-*^{f}*C*-**12** fourteen of the sixteen expected signals are resolved. Since some of the signals are closely overlapping, peaks with double or fourfold intensity are observed. As expected for the C_3 symmetry of **11** an **12**, only one signal appears for the three malonate cyclopropane C atoms at δ = 45.31, and one for the three corresponding bisoxazoline C atoms at δ = 34.93. The two ^{13}C signals of the two unequivalent C=N oxazoline C atoms are located at δ = 163.60 and 164.10. The C atoms of the C=O carbonyl units give rise to two signals for *all-S-*^{f}*A*-**11**, or one signal with double intensity for *all-S-*^{f}*C*-**12** at δ = 160. All twelve of the fullerene sp^3 C atoms appear as three or four signals, respectively, at δ = 69.59 (3 C), 69.80 (3C) and 70.18 (6 C) for *all-S-*^{f}*A*-**11,** and at δ = 69.28, 69.68, 70.12 and 70.19 for *all-S-*^{f}*C*-**12**, each representing three C atoms. The lipofullerenes *all-S-*^{f}*A*-**11** and *all-S-*^{f}*C*-**12** consist of a polar and a nonpolar hemisphere because of the two different sets of addends. Nevertheless, both compounds reveal no pronounced overall polarity. This is demonstrated by the fact that they elute as the very first chromatographic fraction on silica gel using toluene/ethyl acetate (97:3) as eluent. The mixed hexakisadducts **11** and **12** exhibit a low melting temperature. The melting process was recorded by differential scanning calorimetry. The melting range (46–78 °C) of both lipofullerenes is very broad. In both cases the minimum of the endothermic phase transition is located at 60 °C. The specific transition enthalpy was determined to be 20.70 J/g. No second phase transition or liquid-crystalline properties were found.

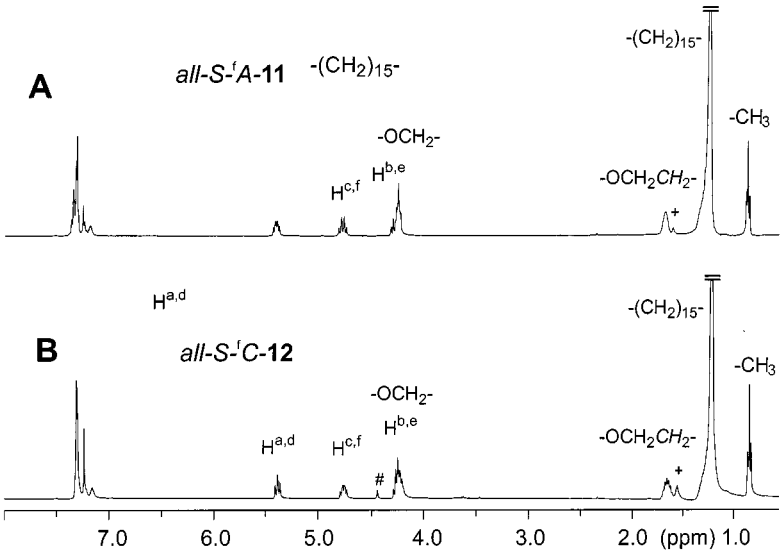


Figure 4. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of lipofullerenes **A**) *all-S-*^{f}*A*-**11** and **B**) *all-S-*^{f}*C*-**12**; $^{\#}$ = impurity, $^+$ = H_2O

Optical Measurements

The electronic absorption spectra of all the synthesized fullerene dendrimers **7–10** and lipofullerenes **11** and **12** exhibit the characteristic pattern of hexakisadducts with an octahedral addition pattern (Figure 5).[1–7] The yellow solutions only show weak absorptions in the visible region between 400 and 800 nm. The five characteristic absorption bands of octahedral hexakisadducts appear in the short wavelength region between 240 and 350 nm at 244, 271, 281, 315, and 335 nm. In contrast to the precursor trisadducts **1–4** which show very large Cotton effects and $[\alpha]_D$ values, the hexakisadducts **7–12** exhibit very weak chiroptical properties. In the CD spectra almost flat lines are observed between 300 and 800 nm (Figure 6). Due to the absorptions in the visible region, the small $[\alpha]_D$ values of **7–12** are very difficult to determine. Weak chiroptical properties of the hexakisadducts **7–12** were expected since the

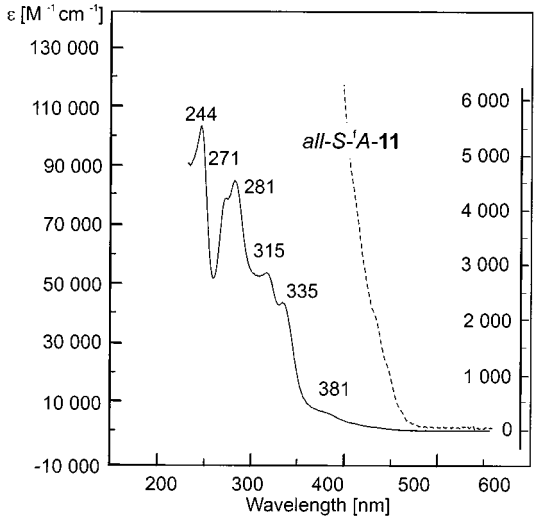


Figure 5. UV/Vis spectrum (CH_2Cl_2) of *all-S-*^{f}*A*-**11** lipofullerene

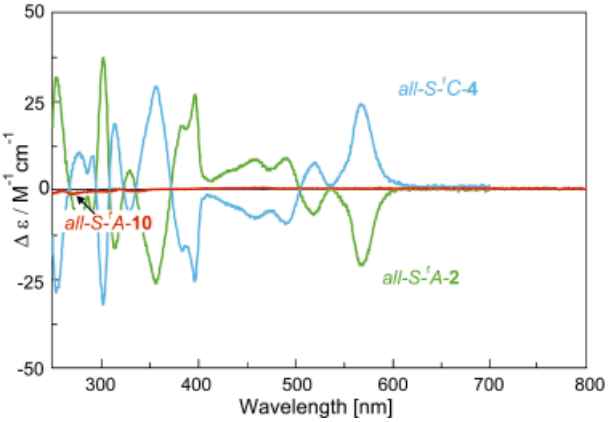


Figure 6. Comparison of CD spectra ($CHCl_3$, d = 1 cm, 25 °C) of *all-S-*^{f}*C*-**4** (blue) and *all-S-*^{f}*A*-**2** (green) trisadducts with that of dendrimeric hexaadduct *all-S-*^{f}*A*-**10** (red)

local symmetry of the fullerene core is close to T_h, which is an achiral point group. Like all octahedral hexakisadducts, the π-system of the chromophore in **7–12** represents an achiral T_h-symmetrical supercyclophane substructure with eight benzenoid rings. The overall C_3 symmetry of the mixed hexakisadducts **7–12** is just a consequence of the fact that two sets of different malonates are bound. Model calculations show that the introduction of two types of malonates causes only a negligible distortion of the conjugated π-system of the fullerene core. In the trisadducts **1–4**, however, the whole π-system of the chromophore has a C_3 symmetry no matter whether identical or different addends are bound. Like in helicenes, the chirality of the whole π-system is responsible for the pronounced Cotton effects.[5]

Catalytic Properties

The C_2-symmetrical bisoxazoline as a bidentate ligand is known to form complexes with metals such as Fe, Mg, and Cu. Such complexes can be used as catalysts for stereoselec-

tive syntheses.[10] Cu-bisoxazoline complexes, for example, served as catalysts for the cyclopropanation of styrene with ethyl diazoacetate.[11] This reaction leads to four stereoisomers, namely the two pairs of enantiomers ethyl *trans*-(1*S*,2*S*)-2-phenylcyclopropanecarboxylate and ethyl *trans*-(1*R*,2*R*)-2-phenylcyclopropanecarboxylate, as well as ethyl *cis*-(1*R*,2*S*)-2-phenylcyclopropanecarboxylate and ethyl *cis*-(1*S*,2*R*)-2-phenylcyclopropanecarboxylate. The efficiency of the catalysts is reflected in the *detrans:cis*, *eetrans* and *eecis* values. Preliminary test experiment with the dendritic hexakisadducts *all-S*-^{f}A **8** and *all-S*-^{f}C **10** indeed showed that these globular macromolecular ligands also exhibit catalytic properties.

However, the observed stereoselectivities caused by these first prototypes of fullerene based *dendrizymes* are very low compared to those obtained with other bisoxazoline catalysts. The *eetrans* values for the cyclopropanation of styrene using **8** and **10** in the presence of CuOTf as catalysts were determined to be 2 and 1, whereas the *eecis* values were found to be 9 and 7, respectively. Significantly, **10** showed a pronounced diastereoselectivity in favour of the formation of *trans* products, giving *de* = 95.

Conclusion

With the synthesis of the fullerene dendrimers **7–10** and lipofullerenes **11** and **12** we provide the first series of functional fullerene macromolecules involving an inherently chiral C_3-symmetrical addition pattern with a defined absolute configuration. Conceptually, this mixed octahedral addition motif is derived from that of hexakisadducts with a T_h-symmetrical addition pattern by changing three addends in one hemisphere. For a facile access to enantiomerically pure isomers we used the trisadducts **1–4** as precursor molecules, whose absolute configurations were determined by the comparison of their calculated and experimental CD spectra. Using our template mediation method, the mixed hexakisadducts **7–12** were obtained in good yields due to the preferred regioselectivity of attack onto equatorial sites of addends already bound. The structure and the isomeric purity of all hexakisadducts **7–12** were unambiguously determined by NMR spectroscopy and other techniques. Due to the fact that in a first approximation the local symmetry of the fullerene core is T_h, and the overall C_3 symmetry is only due to the special arrangement of the two different sets of addends, all chiral hexakisadducts **7–12** exhibit only very weak optical rotations. This is in contrast to their trisadduct precursors **1–4**, where the conjugated π-system has a C_3 symmetry regardless of the nature of the addends, causing pronounced Cotton effects similar to those of helicenes. First experiments using the chiral dendrimers **8** and **10** as catalysts for stereoselective cyclopropanations of styrene reveal low *ee* values, but a comparatively high *de* value for **10**. In order to improve the catalytic properties of such new types of *dendrizymes* we are currently systematically investigating variations of the addition pattern, of the nature of the dendra, as well as of the substituent on the oxazoline subunits. The results will be reported in due course.

Experimental Section

General Remarks: Due to the identity of the spectroscopic date of the pairs of enantiomers **7** and **8** as well as **9** and **10**, only one set of data is listed for each pair of isolated enantiomers. ^{1}H NMR and ^{13}C NMR: Bruker ARX250, Bruker AMX 400, Jeol JNM EX 400 and Jeol JNM GX 400; MS: Varian MAT 311A (EI), Micromass Zabspec (FAB/EI), Micromass Tofspec (MALDI); IR: Bruker FT-IR IFS 88 and FT-IR Vector 22; UV/Vis: Shimadzu UV 3102 PC; CD: Jasco J 720, *d* = 1 cm, 25 °C. HPLC: Shimadzu Class-LC10, analytical (DAD detector SPD M10A; Grom-Sil 100 Si, 5μ, 200 × 4 ID, 1.5 mL/min; Macherey–Nagel ET 200/4, Nucleosil, 1.5 mL/min; Macherey–Nagel ET 250/8/4, Nucleosil 5 NO_2, 1.5 mL/min; Grom-Sil Amino, 5μ, 250 × 4.6 ID, 1.5 mL/min; Regis Rexchrom Buckyclutcher Semiprep. 250 × 10 ID, 5μ, 4.5 mL/min; ICN Alumina, 9μ, 250 × 4 ID, 1.5 mL/min) and preparative (20 mL/min; UV/Vis detector SPD-10A und fraction collector FRC-10 A; Grom-Sil 100 Si, NP1, 5μ, 250 × 20 ID; Nucleosil 100 Si, 5μ, 250 × 20 ID; Macherey–Nagel Nucleosil 100–5 NO_2, Varioprep ET 250/21; Grom-Sil Amino, 5μ, 250 × 20 ID; Regis Rexchrom Buckyclutcher 250 × 20 ID, 5μ; ICN Alumina, 5μ, 250 × 20 ID). Retention behaviour of the products is expressed by the capacity factor k′, C_{60} served as internal standard. TLC was performed with silica gel F_{254} (Riedel-de Haen), alumina N/UV_{254} (Machery-Nagel) and UV detection; column LC with silica gel 60 (230–400 mesh, 0.04–0.063 nm, Merck) and alumina (neutral, Brockmann I, STD grade, 150 mesh, 58Å, Aldrich). Products were isolated by flash column chromatography (silica gel 60, particle size 0.04–0.063 nm, Merck) and by preparative TLC (silica gel, particle size 0.04–0.063 nm, Merck).

The precursor trisadducts *all-R*-^{f}C-(+)-**1**, *all-S*-^{f}A-(–)-**2**, *all-R*-^{f}A-(+)-**3**, and *all-S*-^{f}C-(–)-**4** were prepared by stepwise cyclopropanation of C_{60} with either bis(4*R*)- or bis[(4*S*)-4-phenyloxazoline]methane, in the presence of DBU and CBr_4 according to reference.[7] The Fréchet type second generation bromomalonates **5** 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 reference.[1] Dioctadecyl bromomalonate **6** was obtained by esterification of malonyl dichloride with stearyl alcohol, and subsequent bromination.[8] Materials and solvents were obtained from commercial suppliers and were dried and purified according to known procedures.

General Procedure for the Synthesis of the Dendrimers 7–10: To a solution of the corresponding bisoxazolidine trisadducts **1**, **2**, **3**, or **4** (20 mg, 12 μmol) in 20 mL toluene, four equivalents dimethylanthracene [DMA] (10 mg, 48 μmol) were added under N_2. After stirring the reaction mixture for 3 h, four equivalents of bromomalonate **5** (80 mg, 48 μmol) and four equivalents DBU (7.2 μL, 48 μmol) were successively added. After stirring for 48 h the reaction mixture was separated from starting materials by flash chromatography on silica gel using toluene/ethyl acetate (94:6) as eluent. The hexakisadducts **7–10**, comprising the most nonpolar fraction, were eluted first prior to lower adducts and starting materials. The crude orange coloured product fraction was still contaminated with pentakisadducts. The final purification was achieved by preparative HPLC on Nucleosil using toluene/ethyl acetate = 95:5 as eluent. Dendrimers **7–10** were obtained as yellow solids after evaporation of the solvent.

27,45:-31,32:55,60-Tris{bis[3,5-bis(3′,5′-dibenzyloxy)benzyloxy]-benzyloxycarbonyl}methano-1,2:18,36:22,23-tris{di[(4*R*)-4-phenyl-

2-oxazoline]methano}-1,2:18,36:22,23:27,45:31,32:55,60-dodecahydro-[60]fullerene [*all-R-*^{f}*A*-7]: From 20 mg (12 μmol) *all-R-*^{f}*C*-**1** and 80 mg (48 μmol) bromomalonate dendron **5**. Yield: 70%, yellow solid, m.p. 60.4 °C determined by DSC. *k′*(Nucleosil, toluene/ethyl acetate 95:5): 5.08. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.04 (dd, *J*(H,H) = 8.28 Hz, *J*(H,H) = 8.28 Hz, 3 H, oxaz–CH_2), 4.11 (dd, *J*(H,H) = 8.28 Hz, *J*(H,H) = 8.28 Hz, 3 H, oxaz–CH_2), 4.54 (m, 6 H, oxaz–CH_2), 4.65 (br s, 24 H, CH_2-bnz), 4.83 (s, 24 H, CH_2-bnz), 4.85 (s, 24 H, CH_2-bnz), 5.02 (m, 12 H, CH_2-bnz), 5.18 (m, 6 H, oxaz–C*H*), 6.36 (br s, 6 H, C*H*–arom), 6.39 (br s, 12 H, C*H*–arom), 6.45 (m, 12 H, C*H*–arom), 6.58 (m, 24 H, C*H*–arom), 7.0–7.3 (m, 150 H, Ph–*H*). – ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 35.14 (3 C, dend-cycloprop–*C*), 45.27 (3 C, oxaz-cycloprop–*C*), 68.16 (3 C, oxaz–*C*H_2), 68.24 (3 C, oxaz–*C*H_2), 69.31 (3 C, sp^3–*C*), 69.60 (3 C, sp^3–*C*), 69.66 (3 C, sp^3–*C*), 69.71 (3 C, sp^3–*C*), 69.86 (36 C, *C*H_2-bnz), 69.95 (3 C, *C*H_2-bnz), 70.09 (3 C, *C*H_2-bnz), 75.42 (3 C, oxaz–*C*H), 75.61 (3 C, oxaz–*C*H), 101.54 (12 C, dend-*tert* arom), 102.18 (3 C, dend-*tert* arom), 102.24 (3 C, dend-*tert* arom), 106.28 (24 C, dend-*tert* arom), 106.60 (6 C, dend-*tert* arom), 106.78 (6 C, dend-*tert* arom), 126.82 (6 C, oxaz-*tert* arom), 126.89 (6 C, oxaz-*tert* arom), 127.44 (48 C, dend-*tert* arom), 127.77 (12 C, dend-*tert* arom and 3 C, oxaz-*tert* arom), 127.83 (12 C, dend-*tert* arom and 3 C, oxaz-*tert* arom), 128.41 (24 C, dend-*tert* arom), 128.44 (24 C, dend-*tert* arom), 128.65 (12 C, oxaz-*tert* arom), 136.75 (12 C, *C*H–bnz), 136.79 (24 C, *C*H–bnz), 139.16 (6 C, *C*H–bnz und 6 C, oxaz-*tert* arom), 140.91, 140.98, 141.25, 141.45, 141.94, 142.26, 142.39, 145.54, 145.57, 145.61, 145.67, 145.96, 146.07, 146.11, 159.82 (12 C, dend-quart arom), 159.97 (24 C, dend-quart arom), 160.49 (3 C, *C*O), 160.82 (3 C, *C*O), 163.19 (3 C, *C*N), 163.42 (3 C, *C*N). – IR (KBr): $\tilde{\nu}$ = 3087, 3062, 3030, 2928, 2872, 1745 (CO), 1664 (CN), 1596 (Ph–*H*), 1496, 1451, 1373, 1295, 1208, 1156 (ether), 1055, 832, 737, 697, 527 cm^{-1}. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 272 (110 000), 282 (117 000), 317 (48 000), 336 (38 700), 380 nm (5 400).

27,45:-31,32:55,60-Tris{bis[3,5-bis(3′,5′-dibenzyloxy)benzyloxy]-benzyloxycarbonyl}methano-1,2:18,36:22,23-tris{di[(4*S*)-4-phenyl-2-oxazoline]methano}-1,2:18,36:22,23:27,45:31,32:55,60-dodecahydro-[60]fullerene [*all-S-*^{f}*C*-8]: From 20 mg (12 μmol) *all-S-*^{f}*A*-**2** and 80 mg (48 μmol) bromomalonate dendron **5**. Yield: 64%, yellow solid, m.p. 60.4 °C determined by DSC. k′(Nucleosil, toluene/ethyl acetate 95 : 5): 5.08; spectral data identical with those of *all-R-*^{f}*A*-**7**.

27,45:31,32:55,60-Tris{bis[3,5-bis(3′,5′-dibenzyloxy)benzyloxy]-benzyloxycarbonyl}methano-1,2:18,36:22,23-tris{di[(4*S*)-4-phenyl-2-oxazoline]methano}-1,2:18,36:22,23:27,45:31,32:55,60-dodecahydro-[60]fullerene [*all-R-*^{f}*C*-9]: From *all-R-*^{f}*A*-**2** and and 80 mg (48 μmol) bromomalonate dendron. Yield: 62%, yellow solid. k′(Nucleosil, toluene/ethyl acetate 95 : 5): 5.08. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.09 (m, 6 H, oxaz–CH_2), 4.52 (m, 6 H, oxaz–CH_2), 4.66 (br s, 24 H, CH_2-bnz), 4.83 (s, 24 H, CH_2-bnz), 4.85 (s, 24 H, CH_2-bnz), 5.05 (m, 12 H, CH_2-bnz), 5.18 (dd, *J*(H,H) = 9.28 Hz, *J*(H,H) = 9.76 Hz, 3 H, oxaz–C*H*), 5.25 (dd, *J*(H,H) = 9.76 Hz, *J*(H,H) = 9.76 Hz, 3 H, oxaz–C*H*), 6.38 (br s, 6 H, C*H*–arom), 6.42 (br s, 12 H, C*H*–arom), 6.45 (br d, 12 H, C*H*–arom), 6.58 (m, 24 H, C*H*–arom), 7.0–7.3 (m, 150 H, Ph–*H*). – ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 35.16 (3 C, dend-cycloprop–*C*), 45.27 (3 C, oxaz-cycloprop–*C*), 68.16 (6 C, oxaz–*C*H_2), 69.22 (3 C, sp^3–*C*), 69.34 (3 C, sp^3–*C*), 69.59 (3 C, sp^3–*C*), 69.69 (3 C, sp^3–*C*), 69.86 (42 C, *C*H_2-bnz), 75.36 (3 C, oxaz–*C*H), 75.76 (3 C, oxaz–*C*H), 101.50 (6 C, dend-*tert* arom), 101.57 (6 C, dend-*tert* arom), 102.24 (6 C, dend-*tert* arom), 106.28 (12 C, dend-*tert* arom), 106.31 (12 C, dend-*tert* arom), 106.67 (12 C, dend-*tert* arom), 126.82 (6 C, oxaz-*tert* arom), 126.98 (6 C, oxaz-*tert* arom), 127.47 (48 C, dend-*tert* arom), 127.80 (24 C, dend-*tert* arom and 6 C, oxaz-*tert* arom), 128.44 (48 C, dend-*tert* arom), 128.53 (6 C, oxaz-*tert* arom), 128.64 (6 C, oxaz-*tert* arom), 136.76 (36 C, *C*H–bnz), 139.11 (6 C, *C*H–bnz), 139.24 (6 C, oxaz-*tert* arom), 140.83, 140.97 (2 C), 141.03, 141.27, 141.50, 142.23 (2 C), 142.59, 145.41, 145.52, 145.69, 145.82, 145.98 (2 C), 146.19, 159.79 (6 C, dend-quart arom), 159.85 (6 C, dend-quart arom), 159.99 (24 C, dend-quart arom), 160.72 (3 C, *C*O), 160.76 (3 C, *C*O), 163.19 (3 C, *C*N), 163.46 (3 C, *C*N). – IR (KBr): $\tilde{\nu}$ = 3087, 3062, 3030, 2927, 2872, 1745 (CO), 1664 (CN), 1596 (Ph–H), 1496, 1451, 1373, 1295, 1269, 1208, 1156 (ether), 1055, 832, 736, 697, 527 cm^{-1}. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 272 (122 000), 282 (143 000), 317 (58 000), 336 (47 800), 380 nm (6 600).

27,45:31,32:55,60-Tris{bis[3,5-bis(3′,5′-dibenzyloxy)benzyloxy]-benzyloxycarbonyl}methano-1,2:18,36:22,23-tris{di[(4*S*)-4-phenyl-2-oxazoline]methano}-1,2:18,36:22,23:27,45:31,32:55,60-dodecahydro-[60]fullerene [*all-S-*^{f}*A*-10]: From *all-S-*^{f}*C*-**4** and 80 mg (48 μmol) bromomalonate dendron **5**. Yield: 68%, yellow solid. *k′*(Nucleosil, toluene/ethyl acetate 95:5): 5.08. Spectral data are identical with those of *all-R-*^{f}*C*-**9**.

General Procedure for the Synthesis of Lipofullerenes 11 and 12: To a solution of the corresponding bisoxazolidine trisadducts *all-S-*^{f}*C*-**4** and *all-S-*^{f}*A*-**2** (20 mg, 12 μmol) in 20 mL toluene, was added four equivalents dimethylanthracene [DMA] (10.1 mg, 49 μmol) under N_2, and the reaction mixture was stirred. After stirring for 3 h, four equivalents of dioctadecyl bromomalonate **6** (32 mg, 49 μmol) and 4 equivalents DBU (7.35 μL, 49 μmol) were added. After 48 h the reaction was stopped and the product purified by flash chromatography on silica gel using toluene/ethyl acetate (95:5) as mobile phase. The hexakisaddukts **11** and **12**, comprising the most nonpolar fraction, were eluted prior to lower adducts and starting materials as an orange coloured fraction. The crude product fraction was still contaminated with pentakisaddukts and had to be purified again by preparative HPLC on a Buckyclutcher stationary phase using toluene/ethyl acetate = 97:3 as eluent.

27,45:-31,32:55,60-Tris[bis(octadecyloxycarbonyl)methano]-1,2:18,36:22,23-tris{di[(4*S*)-4-phenyl-2-oxazoline]methano}-1,2:18,36:22,23:27,45:31,32:55,60-dodecahydro[60]fullerene [*all-S-*^{f}*A*-11]: From *all-S-*^{f}*C*-**4** and dioctadecyl bromomalonate **6**. Yield: 60% of a yellow solid. *k′*(Nucleosil, toluene/ethyl acetate 97:3): 2.65. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.87 (t, *J*(H,H) = 6.36 Hz, 18 H, CH_3,), 1.25 (m, 180 H, CH_2), 1.68 (m, 12 H, CH_2CH$_2$O), 4.26 (m, 6 H, oxaz–*CH*$_2$ and m, 12 H, CH_2O), 4.79 (m, 6 H, oxaz–*CH*$_2$), 5.41 (dd, *J*(H,H) = 9.28 Hz, *J*(H,H) = 9.76 Hz, 6 H, oxaz–C*H*), 7.1–7.4 (m, 30 H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.10 (6 C, *C*H$_3$), 22.67, 25.80, 25.85, 28.45, 29.29, 29.36, 29.58, 29.65, 29.71, 31.92 (*C*H$_2$), 34.91 (3 C, oxaz-cycloprop–*C*), 45.29 (3 C, chain-cycloprop–*C*), 66.96 (3 C, O*C*H$_2$), 69.08 (3 C, O*C*H$_2$), 69.32 (3 C, oxaz–*C*H$_2$), 69.59 (3 C, sp^3-full–*C*), 69.65 (3 C, oxaz–*C*H$_2$), 69.80 (3 C, sp^3-full–*C*), 70.18 (6 C, sp^3-full–*C*), 75.53 (3 C, oxaz–*C*H), 75.75 (3 C, oxaz–*C*H), 126.97 (6 C, Ph–*C*), 127.06 (6 C, Ph–*C*), 127.59 (6 C, Ph–*C*), 128.65 (6 C, Ph–*C*), 128.71 (6 C, Ph–*C*), 140.75 (3 C, Ph–*C*), 140.84 (3 C, Ph–*C*), 141.13, 141.26, 141.55, 141.59, 141.95, 142.04, 142.12, 142.17, 145.44, 145.64, 145.72, 145.81, 145.88, 160.90 (3 C, *C*O), 161.17 (3 C, *C*O), 163.66 (3 C, *C*N), 164.13 (3 C, *C*N). – IR (KBr): $\tilde{\nu}$ = 3061, 3029, 2922 (alkyl), 2852 (alkyl), 1754 (CO), 1665 (CN), 1606, 1533, 1494, 1466 (CH$_3$), 1455 (CH$_3$), 1354, 1268, 1211, 1123, 1072, 1030, 958, 928, 750, 714, 699, 540, 528 cm^{-1}. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (103 000), 271 (79 000), 281 (87 000), 315 (51 000), 335 (42 000), 381 nm (5 000). – MS (FAB/3-NBA): *m/z* = 3450 (M^+, 10%), 720 (C_{60}^+, 100%).

27,45:-31,32:55,60-Tris[bis(octadecyloxycarbonyl)methano]-1,2:18,36:22,23-tris{di[(4*S*)-4-phenyl-2-oxazoline]methano}-1,2:18,36:22,23:27,45:31,32:55,60-dodecahydro[60]fullerene [*all-S*-^{f}*C*-12]: From *all-S*-^{f}*A*-**2** and dioctadecyl bromomalonate **6**. Yield 66% of a yellow solid. *k'*(Nucleosil, toluene/ethyl acetate 95:5): 6.4. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.87 (t, *J*(H,H) = 6.84 Hz, 18 H,CH_3,), 1.25 (m, 180 H, CH_2), 1.68 (m, 12 H, CHCH_2O), 4.27 (m, 6 H, oxaz–CH_2 and m, 12 H, CH_2O), 4.78 (m, 6 H, oxaz–CH_2), 5.42 (m, 6 H, oxaz–CH), 7.1–7.4 (m, 30 H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.09 (6 C, *C*H_3), 22.65, 25.82, 28.43, 28.46, 29.24, 29.27, 29.33, 29.56, 29.63, 29.69, 31.89 (*C*H_2), 34.93 (3 C, oxaz-cycloprop–*C*), 45.31 (3 C, chain-cycloprop–*C*), 66.93 (3 C, O*C*H_2), 66.96 (3 C, O*C*H_2), 69.09 (3 C, oxaz–*C*H_2), 69.28 (3 C, sp^3-full–*C*), 69.51 (3 C, oxaz–*C*H_2), 69.68 (3 C, sp^3-full–*C*), 70.12 (3 C, sp^3-full–*C*), 70.19 (3 C, sp^3-full–*C*), 75.57 (3 C, oxaz–*C*H), 75.70 (3 C, oxaz–*C*H), 126.95 (6 C, Ph–*C*), 127.06 (6 C, Ph–*C*), 127.56 (6 C, Ph–*C*), 128.61 (6 C, Ph–*C*), 128.70 (6 C, Ph–*C*), 140.77 (3 C, Ph–*C*), 140.83 (3 C, Ph–*C*), 141.12, 141.22, 141.57, 141.82, 142.09, 142.23, 145.58, 145.63, 145.73, 145.85, 146.02, 146.07, 161.10 (6 C, *C*O), 163.63 (3 C, *C*N), 164.10 (3 C, *C*N). – IR (KBr): $\tilde{\nu}$ = 3061, 3029, 2922 (alkyl), 2852 (alkyl), 1746 (CO), 1665 (CN), 1494, 1466 (CH_3), 1455 (CH_3), 1356, 1211, 1123, 1073, 1031, 984, 928, 750, 714, 699, 589, 540 cm^{-1}. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (113 000), 271 (86 000), 281 (95 000), 315 (56 000), 335 (46 000), 381 nm (5 000). – MS (FAB/3-NBA): *m*/*z* = 3450 (M^+, 8%), 720 (C_{60}^+, 100%).

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