Full Paper
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Sequential Tether-Directed Synthesis of New [3:2:1] Hexakis-Adducts of C_{60} with a Mixed Octahedral Addition Pattern

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In memory of François Diederich

Abstract: A new concept for the regioselective synthesis of [3:2:1] hexakis-adducts of fullerene C_{60} was developed. Based on sequential tether-directed remote functionalizations, chiral [3:2] pentakis-adducts with an incomplete octahedral addition pattern were synthesized *via* stepwise cyclopropanation of C_{60} with suitable macrocyclic tri- and bifunctional cyclomalonate tethers. The four resulting stereoisomers were isolated using chiral HPLC. The corresponding pairs of enantiomers show mirror image behavior in their CD-spectra. The pentakis-adducts served as suitable building blocks for the spatially controlled synthesis of mixed hexakis-adducts. Implementation of functional group-bearing monomalonates afforded octahedral [3:2:1] hexakis-adducts suitable for the construction of larger molecular and supramolecular fullerene architectures in excellent yield.

Introduction

To date the exohedral functionalization of fullerene C_{60} is the most commonly applied method for chemical modifications of this fullerene core. The thirty [6,6] double bonds on the spherical surface of C_{60} facilitate a variety of functionalizations *via* single or multiple addition and cycloaddition reactions.[1] However, the first attempts of synthesizing fullerene bis-adducts without further control of regioselectivity resulted in seven of eight theoretical regioisomers.[2] Therefore, special concepts needed to be developed, which operate under high regioselectivity control, allowing for the selective synthesis of polyfunctional C_{60} derivatives with a defined addition pattern. For this purpose, the concept of tether-directed remote functionalization has been introduced by Diederich and co-workers,[3] which allows for the selective synthesis of otherwise thermodynamically or kinetically unfavored regioisomers of fullerene oligo-adducts, mostly bis-adducts.[4] This concept was further extended by our group. Cyclopropanation reactions with flexible cyclo-*[n]*-alkyl malonate macrocycles as tether-directing agents resulted in a variety of oligo-adducts with rotational symmetry, such as C_{3v}-symmetrical *e,e,e*-tris-adduct **1** (Figure 1) with a semioctahedral addition pattern.[5] Recently, the sequential addition of a trifunctional and a bifunctional tether to C_{60} provided access to four stereoisomers of [3:2] pentakis-adduct **2** in excellent regioselectivity.[6] However, isolation of the stereoisomers was reported to be difficult and only the two diastereomers of **2**, which differ in the orientation of the bis(β-keto ester) addend (Figure 1), could be separated.[6]

Such [3:2] pentakis-adducts with an incomplete octahedral addition pattern represent a highly attractive class of compounds. The sixth addition to the fullerene core of pentakis-adducts generally proceeds with high regioselectivity, due to

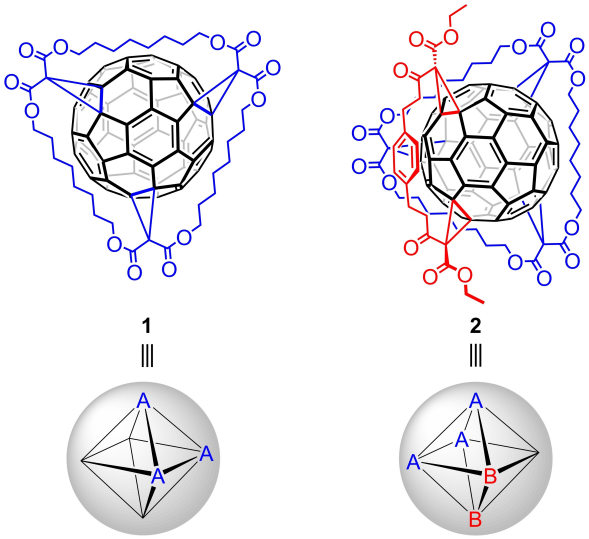

Figure 1. One enantiomer of a C_{3v}-symmetrical tris-adduct 1 (left) and a [3:2] pentakis-adduct 2 (right) with a schematic representation of the semi-octahedral and incomplete octahedral addition pattern at the fullerene core.

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This article belongs to a Joint Special Collection dedicated to François Diederich.

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the formation of stabilized supercyclophane substructures of the remaining π-system.[7]

Therefore, further functionalization of **2** is expected to yield [3:2:1] hexakis-adducts with an octahedral addition pattern (Figure 2) in high regioselectivity. Hexakis-adducts with three different types of addends are still exceedingly rare compounds and so far only a few synthetic approaches by Diederich and Rubin and their coworkers have been reported.[8]

In this work we have developed an efficient strategy for the synthesis of mixed octahedral [3:2:1] hexakis-adducts of C_{60} with a local T_h-symmetrical addition pattern. By applying the sequential tether-directed remote functionalization strategy, a novel all-*e* configurated [3:2] pentakis-adduct **6** was synthesized. For the first time all four stereoisomers of a [3:2] pentakis-adduct, which derive from the inherently chiral addition pattern at the fullerene core and the addend orientation,[9,10] could be separated by using a chiral HPLC column and were characterized by CD-, NMR-, UV/VIS-spectroscopy and MALDI-TOF. The separated isomers of **6** were further used as a precursor for the implementation of functional group-containing monomalonates with the aim of synthesizing

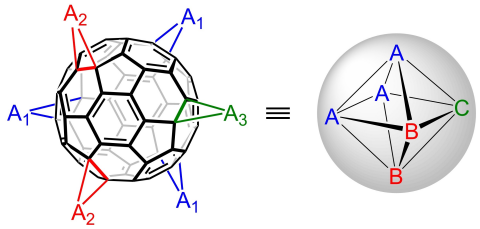


Figure 2. Schematic representation of a [3:2:1] hexakis-adduct with an octahedral addition pattern at the fullerene core.

[3:2:1] hexakis-adducts suitable for the construction of larger molecular and supramolecular fullerene architectures *via* click chemistry and hydrogen bonding. The corresponding hexakis-adduct stereoisomers were also separated by HPLC and fully characterized.

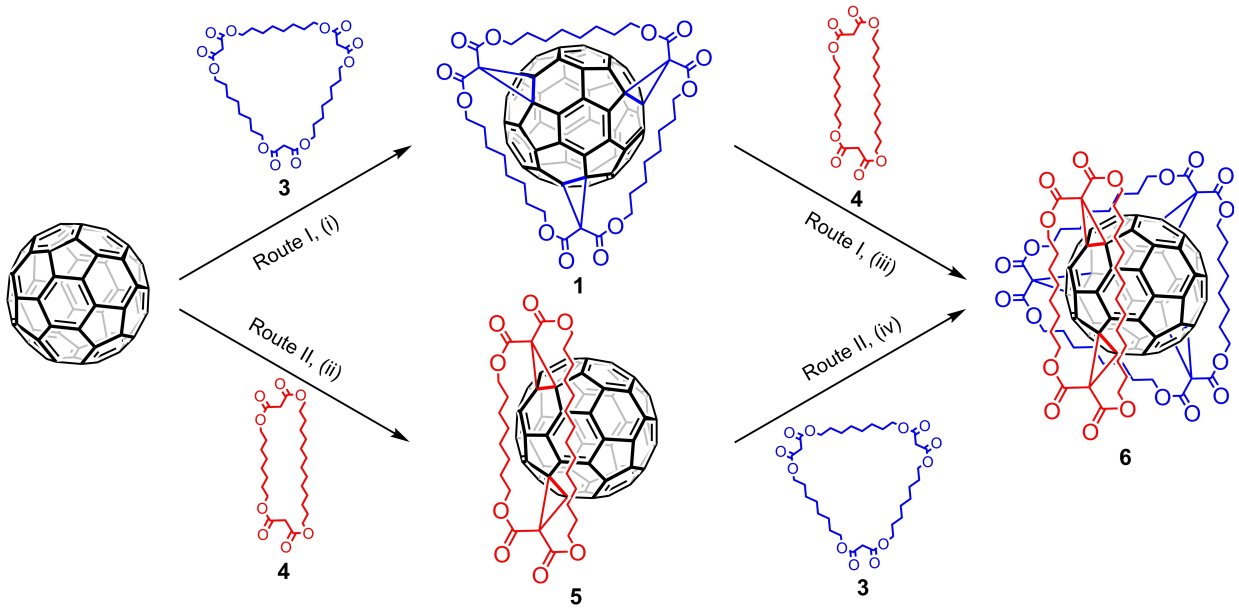
Results and Discussion

Synthesis of [3:2]-pentakis-adducts (±)-6a and (±)-6b

The trifunctional and bifunctional malonate macrocycles **3** and **4** were chosen as suitable precursors for the targeted synthesis of [3:2] pentakis-adduct **6** *via* sequential additions to the fullerene core under the mild reaction conditions of the Bingel-Hirsch reaction[11] (Scheme 1). It was previously shown by our group that functionalization of pristine C_{60} with **3** and **4** provides access to the *e,e,e*-tris-adduct **1** and the *e,e*-bis-adduct **5** in high regioselectivity.[5] Due to the inherent chirality of the all-*e*-trisaddition pattern of **1** (Figure 3) and different orientations of both malonate tethers relative to each other, the resulting [3:2] pentakis-adduct **6** was expected to yield a mixture of four stereoisomers (Figure 4).

According to synthesis route I (Scheme 1) the functionalization of the fullerene core with the malonate macrocycle **3** (blue) leads to a racemic mixture of clockwise (^fC) and anticlockwise (^fA) configurated tris-adduct enantiomers.[10,12,13] Both, the clockwise (^fC) and anticlockwise (^fA) orientation of an *e,e,e*-tris-adduct with a semioctahedral addition pattern, like **1**, are depicted by the corresponding Schlegel diagrams in Figure 3.[13]

The subsequent addition of the asymmetric bifunctional tether **4** to an enantiomeric mixture of tris-adduct **1** results in



Scheme 1. Synthesis route I and II towards [3:2] pentakis-adduct **6** with an incomplete octahedral addition pattern *via* sequential additions of the malonate macrocycles **3** and **4** (Note that there is only one possible stereoisomer shown for each fullerene adduct). Reagents and conditions: (i) I_2, DBU, toluene, 3 h, rt (**1**: 55%); (ii) I_2, DBU, toluene, 30 min, rt (**5**: 51%); (iii) CBr_4, P_1-*t*-Bu, CH_2Cl_2, 12 min, rt (**6**: 20%); (iv) CBr_4, P_1-*t*-Bu, CH_2Cl_2, 15 min, rt (**6**: 22%).

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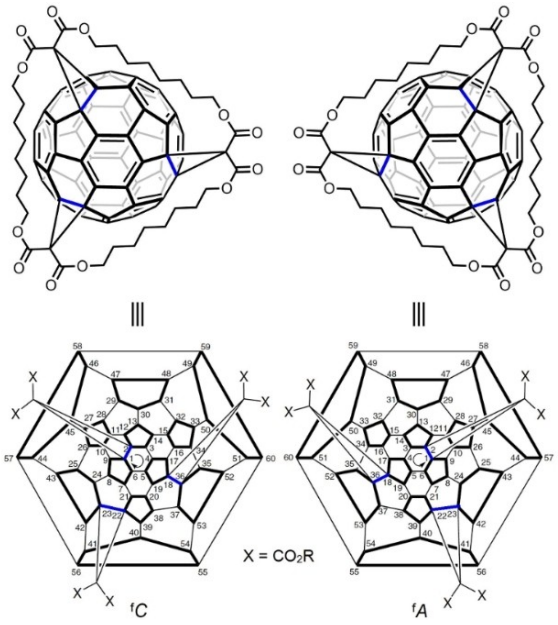

Figure 3. Schematic representation of both clockwise *fC* (left) and anticlockwise *fA* (right) enantiomers of fullerene tris-adduct **1** with a semioctahedral addition pattern at the fullerene core and the corresponding Schlegel diagrams for clarification of the helicity.[13]

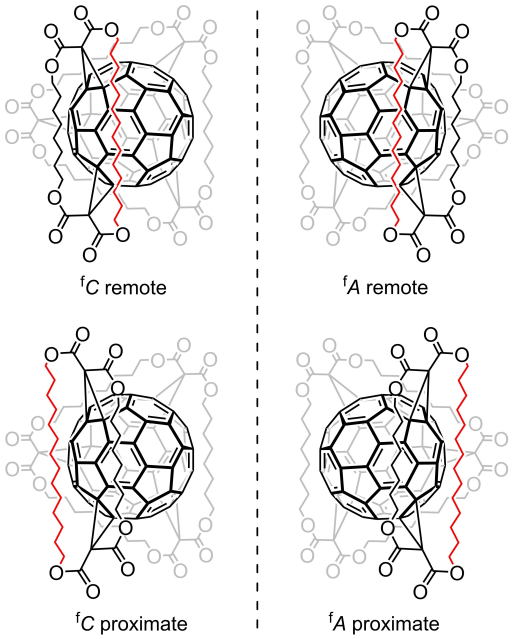

Figure 4. Schematic representation of both diastereoisomeric pairs of [3:2] pentakis-adduct **6** with the tetradecyl chain (red) remote or proximate to the tris-malonate addend.

two diastereoisomeric pairs of [3:2] pentakis-adduct. The diastereomers differ in the orientation of the octyl- and tetradecyl spacer of the bifunctional tether relative to the tris-malonate addend of **1**.[14] The tetradecyl chain (red) of **4** can be oriented either proximate or remote to the already attached cyclo-[3]-octylmalonyl framework (Figure 4). The formation of two diastereoisomeric pairs of pentakis-adducts is also expected for synthesis route II (Scheme 1), where the bifunctional tether **4** is added first, followed by functionalization of bis-adduct **5** with trifunctional tether **3**.

The PM3 level of theory calculated molecular models of all four pentakis-adduct stereoisomers are shown in Figure 5. For simplification, the *fC* remote/*fA* remote and *fC* proximate/*fA* proximate isomers of **6** will henceforth be labelled as (±)-**6a** and (±)-**6b**.

The [3:2] pentakis-adducts of **6** were synthesized under Bingel-Hirsch reaction conditions employing two reaction routes (Scheme 1). Tris-adduct **1** and bis-adduct **5** were prepared following a synthetic procedure established in our group.[5] For further functionalization stoichiometric amounts of fullerene adduct and the corresponding malonate tether were reacted with tetrabromomethane (4 Eq.) as an *in-situ* brominating agent and DBU (5 Eq.) or Schwesinger phosphazene base P_1-*t*-Bu (5 Eq.). Synthetic attempts using Schwesinger phosphazene base P_1-*t*-Bu generally resulted in higher selectivity, shorter reaction times and better yields of the desired products. After purification *via* column chromatography, a mixture of diastereoisomeric pairs of [3:2] pentakis-adduct was obtained for both reaction routes. For the separation of all four stereoisomers (+)-**6a**, (−)-**6a**, (+)-**6b** and (−)-**6b** of [3:2] pentakis-adduct, the mixture obtained from column chromatography was dissolved in *n*-hexane/DCM/*i*-PrOH 60:30:10 and transferred to a chiral CHIRALPAK-IB HPLC column with *n*-hexane/*i*-PrOH 55:45 as an eluent. The elugram revealed four peaks in a 1:2:1:2 ratio, indicating towards a diastereomeric ratio of 2:1 and an enantiomeric ratio of 1:1.

The four stereoisomers were characterized by CD-, NMR-, UV/VIS-spectroscopy and MALDI-TOF. The CD spectra of the [3:2] pentakis-adducts (+)-**6a**, (−)-**6a**, (+)-**6b** and (−)-**6b** are

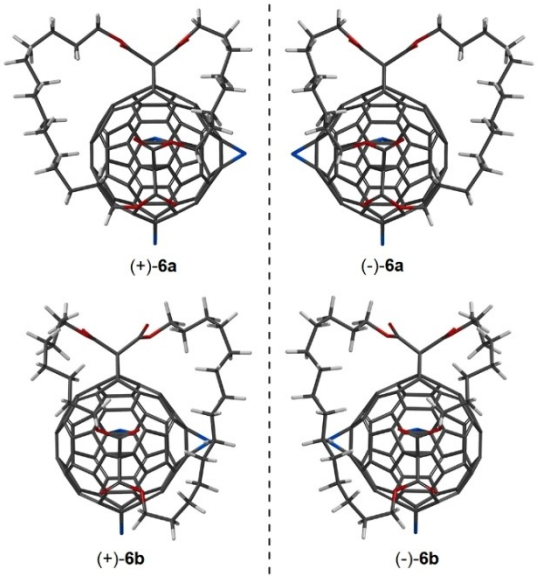

Figure 5. Semi-empirical calculations (PM3 level of theory) of the stereoisomers of [3:2] pentakis-adduct **6**. For visual clarity, the cyclo-[3]-octylmalonate addend was simplified and is only presented by the three cyclopropanated rings (blue) attached to the fullerene core.

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shown in Figure 6. The 1st and 3rd as well as the 2nd and 4th eluted isomer obtained from HPLC separation exhibit mirror image CD curves with characteristic band shapes between 245 and 600 nm.

The ^{13}C-NMR spectra show all the expected signals of the corresponding [3:2] pentakis addition pattern. The underlying C_1 symmetry is nicely displayed in each signal section (Figure 7).

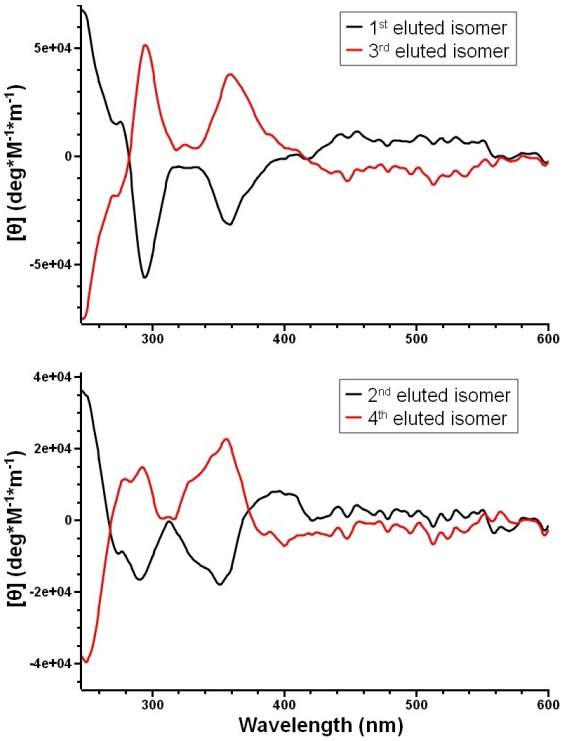

Figure 6. CD spectra of the 1st, 2nd, 3rd and 4th eluted stereoisomer of [3:2] pentakis-adduct **6** in CH_2Cl_2 at rt.

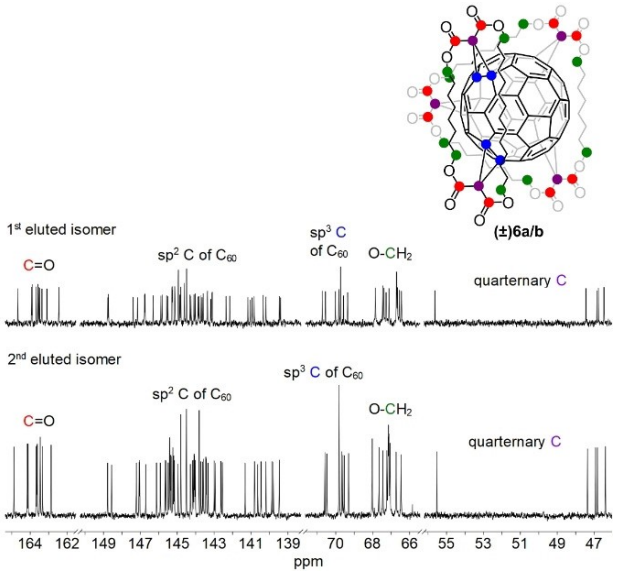

Figure 7. Characteristic signal sections of the ^{13}C-NMR spectra (151 MHz, $CDCl_3$) of 1st and 2nd eluted isomer of **6**.

The spectra of 1st and 3rd as well as 2nd and 4th eluted isomer are identical demonstrating that they are enantiomers. This is in perfect accordance with the results of CD-spectroscopy (Figure 6).

The incomplete octahedral addition pattern was confirmed by UV/VIS-spectroscopy (Figure 8). The absorption spectra of all four isomers display similar absorption behaviour between 280 and 570 nm. In comparison with literature, this absorption pattern shows all features of the expected fivefold incomplete octahedral functionalization motif of the fullerene core.[15]

Unfortunately, the spectroscopical data does not allow for an assignment of the pentakis-adduct diastereomers **6a** and **6b** to the eluted fractions 1–4. Therefore, our efforts are currently focused on growing single crystals suitable for X-ray diffraction, which would unambiguously determine the structure of the stereoisomers. However, due to the high degrees of freedom introduced by the alkyl chains, crystallization of **6** seems to be quite challenging.

Synthesis of [3:2:1]-hexakis-adducts

After the regioselective synthesis and separation of four [3:2] pentakis-adduct isomers of **6**, the octahedral addition pattern was completed by a final cyclopropanation reaction. Therefore, a variety of symmetrical and unsymmetrical monomalonate addends were prepared and used with one isolated isomer of **6** (1st, 2nd, 3rd or 4th eluted isomer from HPLC) for the synthesis of novel [3:2:1] hexakis-adducts. The corresponding hexakis-adducts were expected to be formed isomerically pure for symmetrical monomalonates or as a mixture of two diastereoisomers for unsymmetrical monomalonates. The diastereomers differ in the orientation of the malonate tails (Scheme 2).[16] Each synthetic attempt was carried out with either 1st, 2nd, 3rd or 4th eluted isomer of [3:2] pentakis-adduct of **6** (1 Eq.) (see Experimental Section for the exact isomer) and an excess of the corresponding malonate addend (2 Eq.) under Bingel-Hirsch reaction conditions with tetrabromomethane as an *in-situ* brominating agent and Schwesinger phosphazene base P_1-*t*-Bu.

In a first test reaction [3:2:1] hexakis-adduct **7** was synthesized with commercially available diethylmalonate and

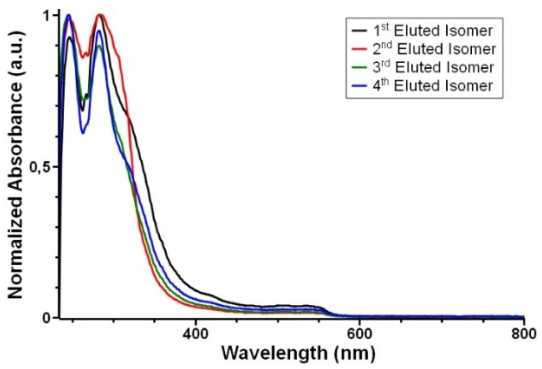

Figure 8. UV/VIS spectra of all four stereoisomers of [3:2] pentakis-adduct **6** in CH_2Cl_2 at rt.

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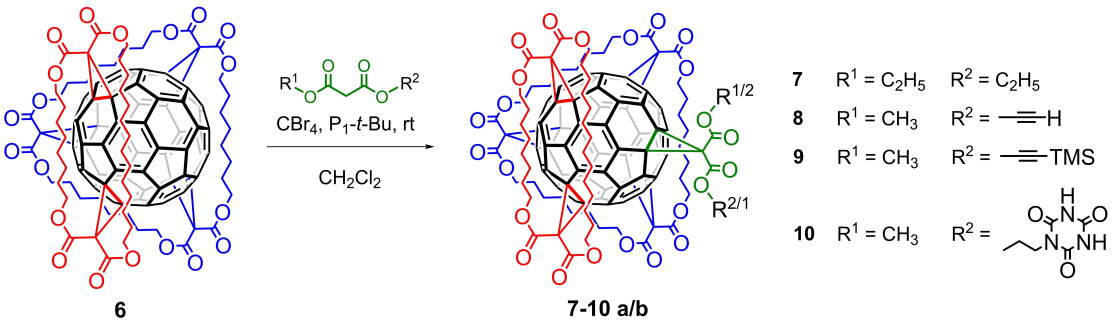

Scheme 2. Synthesis of [3:2:1] hexakis-adducts **7**–**10** with a T_h-symmetrical octahedral addition pattern *via* additions of the corresponding monomalonate addends to one isolated isomer of [3:2] pentakis-adduct **6** (Note that there is only one possible stereoisomer shown for each fullerene adduct).

1st eluted isomer of [3:2] pentakis-adduct **6**. After 20 min the former orange coloured solution had turned pale yellow, which is indicating towards the formation of a hexakis-adduct.

Reaction control by TLC and HPLC revealed that only one hexakis-adduct and no by-products had formed during the reaction, which is in accordance with our expectations using a symmetrical monomalonate and underlines the high stereo- and regioselectivity of the final addition to the fullerene core. Purification of hexakis-adduct **7** was achieved by simple plug filtration.

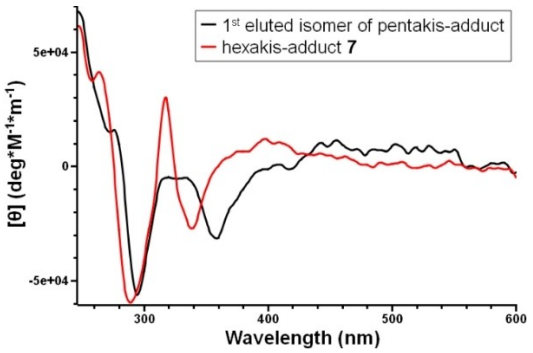

Figure 9. CD spectra of hexakis-adduct **7** and the corresponding pentakis-adduct isomer precursor in CH_2Cl_2 at rt.

The CD spectra of hexakis-adduct **7** and the corresponding pentakis-adduct precursor are shown in Figure 9. In comparison to 1st eluted isomer of **6**, the spectrum of **7** is shifted towards lower wavelengths with an intense positive cotton effect at 317 nm.

The ^{13}C-NMR spectrum of **7** is depicted in Figure 10. The C_1-symmetric hexakis-adduct shows "clustering" of the sp^2-hybridized carbon atom signals of the fullerene core. The expected 48 signals are split equally into two signal sections and appear at 147–144 ppm and 143–140 ppm, which is characteristic for hexakis-adducts with a T_h-symmetrical octahedral addition pattern.[17] The splitting in the other signal areas is also in accordance with the low symmetry of **7**. Further structural confirmation came from MALDI-TOF mass spectrometry and UV/VIS-spectroscopy. The corresponding absorption spectrum (Figure 11) reveals a distinct band at 249 nm, a double peak at 277 and 284 nm and two shoulders at 315 and 335 nm, which are characteristic features for hexakis-adducts with an octahedral addition pattern at the fullerene core.[15]

Hexakis-adducts **8** and **9** with a triple bond functionalization were synthesized according to the procedure used for the synthesis of **7** (Scheme 2). Instead of diethylmalonate, the unsymmetrical methylmalonates with an unprotected respec-

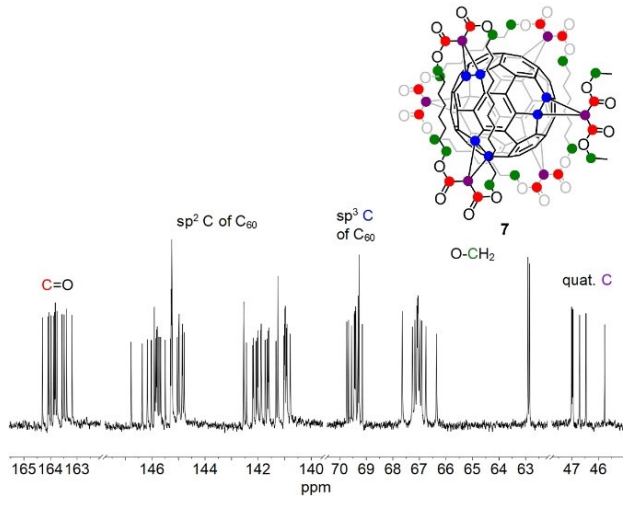

Figure 10. Characteristic signal sections of the ^{13}C-NMR spectrum (151 MHz, $CDCl_3$) of [3:2:1] hexakis-adduct **7**.

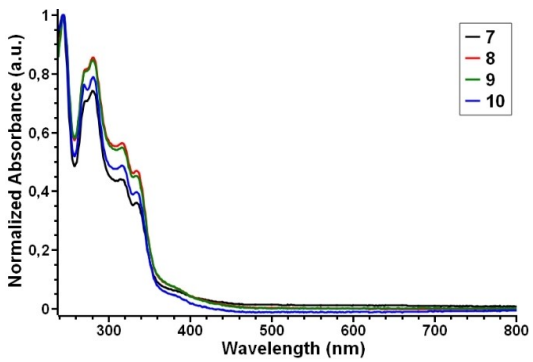

Figure 11. UV/VIS spectra of [3:2:1] hexakis-adducts **7**–**10** in CH_2Cl_2 at rt.

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tively TMS-protected triple bond were used for the addition to one isolated isomer of [3:2] pentakis-adduct of **6**. The reaction progress of hexakis-adducts **8** and **9** could easily be followed by the progressing colour change of the reaction mixture from orange to pale yellow. Reaction control of **8** and **9** by TLC and HPLC revealed the formation of two diastereomers of hexakis-adducts, which is in accordance with our expectations using an unsymmetrical monomalonate and isomerically pure pentakis-adduct for the final addition to the fullerene core.

Hexakis-adduct **10** was synthesized by Bingel-Hirsch cyclopropanation using an unsymmetrical methylmalonate with a cyanurate functionalization and a flexible propyl spacer (Scheme 2). According to literature most cyanurate functionalized fullerene-adducts, mostly monoadducts, were synthesized by cyclopropanation with a bromomalonate derivative followed by an S_N2 substitution of bromide with cyanuric acid.[18] However, the yields of the final S_N2 substitution are usually quite low and therefore insufficient for isomerically pure [3:2] pentakis-adduct **6** as a precursor. Therefore, the S_N2 substitution of bromide was carried out before the final Bingel-Hirsch cyclopropanation. In comparison with the hexakis-adducts **8** and **9**, the synthesis of **10** required slightly longer reaction times and additional phosphazene base (15 Eq.). Contrary to the synthetic attempts of hexakis-adducts **7**–**9**, **10** could not be afforded by using DBU as a base instead of phosphazene base P_1-*t*-Bu. Analogously to **8** and **9**, reaction control of **10** by TLC and HPLC revealed the formation of two diastereomers of hexakis-adduct. Purification and separation of the resulting [3:2:1] hexakis-adduct diastereomers of **8**–**10** was achieved by analytical HPLC using a non-chiral Nucleosil column (based on unmodified silica) and toluene/ethyl acetate mixtures as an eluent. The resulting diastereomers of **8**–**10** were obtained in good yield and characterized by CD, NMR, UV/VIS and MALDI-TOF.

The CD spectra of both diastereoisomers of hexakis-adducts **8**–**10** and the corresponding pentakis-adduct precursors are shown in Figure 12. Analogously to hexakis-adduct **7**, the spectra of **8**–**10** are shifted towards lower wavelengths with an intense cotton effect at 317 nm. The sign of the molar circular dichroism is clearly depending on the corresponding pentakis-adduct isomer used for synthesis and the spectra of 1st and 2nd eluted diastereomer of each hexakis-adduct are almost identical. The hexakis-adduct diastereomers of **8** and **9** as well as **7** and **10** exhibit very similar CD curves, which is reasonable for using pentakis-adduct isomers with similar optical activity. Therefore, the obtained CD curves are strongly dependent on the fullerene chromophore and its addition pattern. The nature and orientation of the final malonate addend has only minor influence on the resulting optical activity.

The ^{13}C-NMR spectra, which are presented in the Supporting Information, show all the expected signals of the corresponding [3:2:1] hexakis-adducts. Analogously to **7** all spectra reveal an equal split of the 48 sp^2-hybridized carbon atom signals of the fullerene core in two signal sections between 147–144 ppm and 143–140 ppm. The UV/VIS spectra (Figure 8) of hexakis-adducts **7**–**10** are very similar, confirming the strong dependency of the absorption behavior on the fullerene chromophore and its

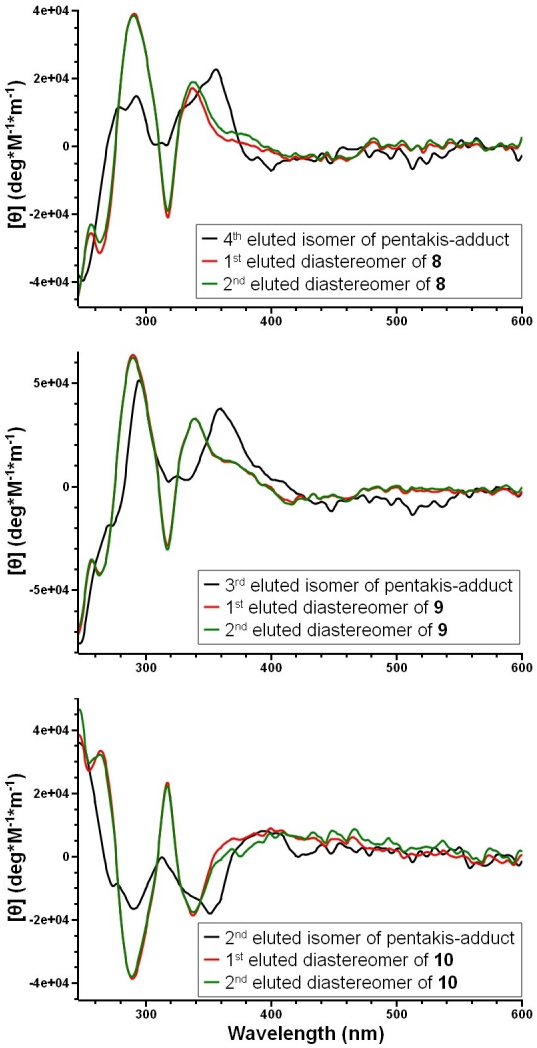

Figure 12. CD spectra of the isolated isomers of hexakis-adducts **8**–**10** and the corresponding pentakis-adduct isomer precursors in CH_2Cl_2 at rt.

addition pattern. The nature of the non-chromophoric addends has no observable influence on the resulting absorption features.

1st eluted diastereomer of [3:2:1] hexakis-adduct **8** containing a terminal triple bond was investigated as a precursor for click chemistry (Scheme 3). In a test reaction under classic click conditions with commercially available phenyl azide, the corresponding fullerene triazole derivative **11** was obtained after workup in good yield. [3:2:1] Hexakisadduct **11** was characterized by NMR, UV/VIS and MALDI-TOF and showed to be isomerically pure. Therefore, **8** was proven to be a useful precursor for click chemistry, which opens an easy access route towards a variety of molecular [3:2:1] hexakis-adduct-containing fullerene architectures in the future.

The supramolecular complexation of both separated cyanurate functionalized hexakis-adduct diastereoisomers of **10** and a Hamilton-Receptor containing counterpart *via* hydrogen bonding (Figure 13) was investigated by NMR-titration. First experiments for a 1:1 complexation showed similar results when

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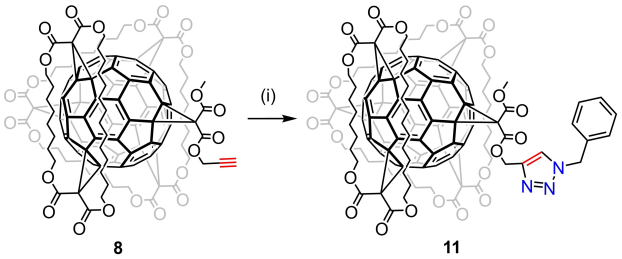

Scheme 3. Synthesis of [3:2:1] fullerene triazole derivative **11** (Note that the stereochemistry of starting material **8** and product **11** are unknown). Reagents and conditions: benzyl azide, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, DCM/water 1:1, 22 h, rt (**11**: 72%).

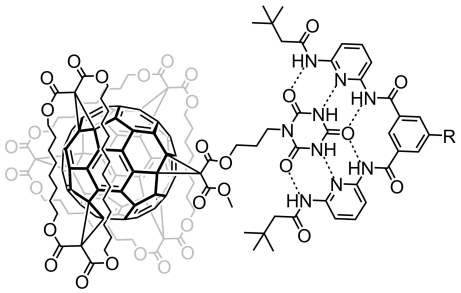

Figure 13. Complexation of cyanurate functionalized hexakis-adduct isomers of **10** and Hamilton receptor containing counterparts *via* hydrogen bonding.

compared to cyanurate functionalized fullerene monoadducts reported by our group.[19] However, further titration experiments need to be carried out to verify the results. After successful verification, the diastereomers of **10** could be used as a versatile precursor for the construction of a variety of novel supramolecular [3:2:1] hexakis-adduct-containing fullerene architectures in the future.

Conclusion

We have introduced a new concept for the synthesis of [3:2:1] hexakis-adducts of C_{60} with a T_h-symmetrical addition pattern. In the first step of the reaction sequence, novel all-*e* configurated [3:2] pentakis-adducts **6** with an incomplete octahedral addition pattern were synthesized by sequential additions of cyclo-[3]-octylmalonate and cyclo-[2]-octyl-tetradecylmalonate to C_{60}. The four [3:2] pentakis-adduct stereoisomers of **6**, which were separated by chiral HPLC, showed excellent regioselectivity for the final addition to the fullerene core and were used as versatile building blocks for the synthesis of a series of [3:2:1] hexakis-adducts with local T_h symmetry at the fullerene core. Hexakis-adducts with a terminal triple bond and a cyanurate functionalization were prepared, which could be used as suitable precursors for the construction of larger molecular and supramolecular fullerene architectures *via* click chemistry and hydrogen bonding in the future.

Experimental Section

Materials and chemicals: All reagents and solvents were purchased from commercial suppliers. Chemicals were used without further purification and solvents were distilled prior to use. Column chromatography was performed on silica gel (Macherey-Nagel, M–N Silica Gel 60 M, deactivated, 0.04–0.063 mm, 230–400 mesh).

Technical equipment: NMR spectra were acquired with Bruker Ascend 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and referenced to residual solvent signals. UV/VIS-spectroscopy was carried out with a Varian Cary 5000 UV/VIS-NIR spectrophotometer. HRMS spectra were recorded with a Bruker Daltonics UltrafleXtreme TOF/TOF spectrometer. For MALDI-TOF mass spectrometry *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malono-nitrile (DCTB) was used as a matrix. The fullerene pentakis- and hexakis-adduct isomers were separated by a SHIMADZU LC-20AT prominence liquid chromatograph. A Daicel Chiralpak IB N-5 (250×10 mm) chiral HPLC column and a Macherey-Nagel Nucleosil (based on unmodified silica) (250×10 mm) HPLC column were used. The PM3 semiempirical calculations were conducted with the software SPARTAN by WAVEFUNCTION. The models were modified by using the software Mercury 3.0.

Synthesis of [3:2] pentakis-adducts (±)-6a and (±)-6b: Route I: Under N_2-atmosphere *e*,*e*,*e*-trisadduct **1** (95.0 mg, 70.0 μmol), cyclo-[2]-octyl-tetradecyl-malonate **4** (35.9 mg, 70.0 μmol) and tetrabromomethane (92.9 mg, 280 μmol) were dissolved in dry DCM (70 mL). The mixture was degassed by introducing N_2 for 10 min before phosphazene base P_1-*t*-Bu (82.0 mg, 89.2 μL, 350 μmol) was added dropwise under stirring. After stirring for 12 min under light exclusion, the reaction mixture was subjected directly to a silica plug (DCM/EtOAc 98:2). Further purification *via* column chromatography (SiO_2, DCM, R_f = 0.37) afforded a mixture of four stereoisomers of [3:2] pentakis-adduct **6** as an orange-red solid (26.7 mg, 14.3 μmol, 20%).

Route II: Under N_2-atmosphere *e*,*e*-bisadduct **5** (31.1 mg, 25.3 μmol), cyclo-[3]-octylmalonate **3** (16.3 mg, 25.3 μmol) and tetrabromomethane (33.5 mg, 101 μmol) were dissolved in dry DCM (50 mL). The mixture was degassed by introducing N_2 for 10 min before phosphazene base P_1-*t*-Bu (29.8 mg, 32.0 μL, 127 μmol) was added dropwise under stirring. After stirring for 15 min under light exclusion, the reaction mixture was subjected directly to a silica plug (DCM/EtOAc 98:2). Further purification *via* column chromatography (SiO_2, DCM, R_f = 0.37) afforded a mixture of four stereoisomers of [3:2] pentakis-adduct **6** as an orange-red solid (10.6 mg, 5.68 μmol, 22%).

For isomer separation, the mixture of stereoisomers was dissolved in *n*-hexane/DCM/*i*-PrOH 60:30:10 and transferred to a chiral CHIRALPAK-IB HPLC column with *n*-hexane/*i*-PrOH 55:45 as an eluent.

1st and 3rd eluted isomer: $[\alpha]_D^{20}$ (c = 0.048 g/100 mL) = +110° and $[\alpha]_D^{20}$ (c = 0.065 g/100 mL) = −106°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.83–3.88 (*m*, 20H), 1.73–1.15 (*m*, 72H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.7, 163.9, 163.9, 163.7, 163.6, 163.5, 163.5, 163.3, 163.1, 162.4, 148.8, 148.7, 147.4, 147.1, 146.8, 146.7, 146.3, 145.9, 145.8, 145.6, 145.5, 145.3, 145.3, 145.2, 145.1, 145.1, 144.9, 144.9, 144.8, 144.8, 144.8, 144.6, 144.5, 144.3, 144.2, 144.1, 144.0, 143.9, 143.8, 143.7, 143.6, 143.6, 143.4, 143.3, 143.2, 143.1, 143.1, 142.3, 142.1, 141.1, 141.0, 140.9, 140.8, 140.3, 140.2, 139.5, 139.4, 70.7, 70.6, 70.0, 69.8, 69.8, 69.7, 69.7, 69.6, 69.3, 67.8, 67.5, 67.4, 67.3, 67.1, 66.7, 66.7, 66.5, 66.4, 55.6, 47.4, 46.9, 46.8, 46.5, 32.1, 30.9, 30.5, 29.8, 29.8, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.1, 29.0, 29.0, 28.9, 28.9, 28.8, 28.3, 27.2, 27.1, 26.6, 26.6, 26.4, 26.3, 26.3, 25.9, 25.8 ppm; UV/VIS (DCM, rt): λ_{max} = 245, 267, 282, 317, 416, 509,

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536 nm; MALDI HRMS (dctb): m/z calculated for $C_{121}H_{92}O_{20}^{+}$ $[M]^{+}$: m/z = 1864.6182, found m/z = 1864.6179.

2nd and 4th eluted isomer: $[\alpha]_D^{20}$ (c = 0.21 g/100 mL) = +4.32° and $[\alpha]_D^{20}$ (c = 0.27 g/100 mL) = −7.67°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.87–3.94 (*m*, 20H), 1.75–1.17 (*m*, 72H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.9, 164.1, 164.1, 163.7, 163.6, 163.6, 163.5, 163.4, 163.3, 162.9, 148.8, 148.6, 147.2, 147.1, 147.0, 146.7, 146.1, 145.9, 145.6, 145.6, 145.5, 145.4, 145.3, 145.3, 145.2, 145.2, 145.2, 145.1, 144.9, 144.8, 144.5, 144.3, 144.2, 144.1, 144.1, 144.1, 144.0, 143.8, 143.7, 143.6, 143.6, 143.4, 143.4, 143.3, 143.0, 142.9, 142.6, 142.5, 141.3, 140.8, 140.6, 140.4, 140.2, 139.9, 139.8, 139.5, 70.6, 70.5, 69.8, 69.8, 69.8, 69.7, 69.6, 69.5, 69.3, 68.0, 67.7, 67.5, 67.2, 67.2, 67.1, 67.1, 67.1, 66.7, 66.5, 55.5, 47.4, 46.9, 46.8, 46.4, 32.1, 30.9, 30.6, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 29.2, 29.2, 29.1, 29.0, 29.0, 29.0, 28.8, 28.8, 28.6, 28.5, 28.4, 27.6, 27.4, 26.8, 26.6, 26.6, 26.6, 26.5, 26.1, 26.0, 25.9, 25.7 ppm; UV/VIS (DCM, rt): λ_{max} = 245, 267, 282, 317, 416, 509, 536 nm; MALDI HRMS (dctb): m/z calculated for $C_{121}H_{92}O_{20}^{+}$ $[M]^{+}$: m/z = 1864.6182, found m/z = 1864.6176.

Synthesis of hexakis-adduct 7: Under N_2-atmosphere 1st eluted isomer of [3:2] pentakis-adduct **6** (10.7 mg, 5.73 μmol), diethyl malonate (1.84 mg, 1.75 μL, 11.5 μmol) and tetrabromomethane (7.59 mg, 23.0 μmol) were dissolved in dry DCM (15 mL). The mixture was degassed by introducing N_2 for 10 min before phosphazene base P_1-*t*-Bu (6.72 mg, 7.31 μL, 28.7 μmol) was added dropwise under stirring. After stirring for 25 min under light exclusion, the colour of the former orange reaction mixture had turned pale yellow. Purification *via* plug filtration (SiO_2, toluene/EtOAc 96:4, R_f = 0.31) afforded **7** as a yellow solid (11.1 mg, 5.48 μmol, 96%). $[\alpha]_D^{20}$ (c = 0.11 g/100 mL) = +40.9°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.72–3.99 (m, 24H), 1.82–0.94 (m, 78H); ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.3, 163.9, 163.9, 163.8, 163.7, 163.7, 163.7, 163.6, 163.4, 163.3, 163.2, 163.2, 146.8, 146.2, 146.0, 145.9, 145.7, 145.7, 145.7, 145.7, 145.6, 145.6, 145.5, 145.3, 145.1, 145.1, 145.1, 145.1, 144.9, 144.8, 144.8, 144.8, 144.8, 144.8, 144.8, 142.5, 142.4, 142.0, 142.0, 141.9, 141.9, 141.8, 141.7, 141.7, 141.6, 141.5, 141.5, 141.4, 141.2, 141.1, 140.9, 140.8, 140.8, 140.8, 140.8, 140.8, 140.8, 69.9, 69.5, 69.4, 69.3, 69.3, 69.3, 69.2, 69.2, 69.2, 69.2, 67.6, 67.5, 67.1, 67.0, 66.9, 66.9, 66.9, 66.8, 66.8, 66.6, 66.2, 62.8, 62.7, 47.0, 46.8, 46.8, 46.6, 46.3, 45.8, 30.8, 30.5, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 29.2, 29.0, 29.0, 29.0, 28.9, 28.9, 28.9, 28.8, 28.8, 28.7, 28.6, 28.4, 28.1, 27.8, 27.2, 27.0, 26.7, 26.5, 26.4, 26.3, 26.0, 25.9, 25.8, 25.8, 25.6, 14.2, 14.2 ppm; UV/VIS (DCM, rt): λ_{max} = 249, 277, 284, 315, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{128}H_{102}O_{24}^{+}$ $[M]^{+}$: m/z = 2022.6761, found m/z = 2022.6756.

Synthesis of hexakis-adducts with a terminal triple bond 8 a/b: Under N_2-atmosphere 4th eluted isomer of [3:2] pentakis-adduct **6** (15.5 mg, 8.31 μmol), 2-propynyl methyl malonate (2.59 mg, 16.6 μmol) and tetrabromomethane (11.0 mg, 33.2 μmol) were dissolved in dry DCM (25 mL). The mixture was degassed by introducing N_2 for 10 min before phosphazene base P_1-*t*-Bu (9.75 mg, 10.6 μL, 41.6 μmol) was added dropwise under stirring. After stirring for 30 min under light exclusion, the reaction mixture was subjected directly to a silica plug (Tol/EtOAc 96:4, R_f = 0.28). Further purification *via* analytical HPLC (Nucleosil, rt, Tol/EtOAc 96:4) afforded two diastereomers of hexakis-adduct **8** as yellow solids in 36% and 35% yield.

1st eluted diastereomer (6.0 mg, 2.97 μmol, 36%): $[\alpha]_D^{20}$ (c = 0.050 g/100 mL) = −10.3°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.85–3.98 (*m*, 22H), 3.87 (*s*, 3H), 2.55 (t, ^4J = 2.4 Hz, 1H), 1.80–1.12 (*m*, 72H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.3, 164.1, 164.0, 164.0, 163.8, 163.8, 163.8, 163.7, 163.5, 163.4, 163.3, 163.2, 146.7, 146.4, 146.3, 146.1, 146.0, 145.9, 145.9, 145.9, 145.7, 145.7, 145.6, 145.5, 145.4, 145.4, 145.3, 145.3, 145.2, 145.1, 145.1, 145.0, 145.0, 144.9, 144.9, 144.8, 142.6, 142.5, 142.4, 142.2, 142.1, 142.0, 142.0, 141.9, 141.7, 141.6, 141.4, 141.3, 141.3, 141.0, 141.0, 141.0, 141.0, 140.8, 140.8, 140.6, 76.5, 76.3, 69.8, 69.5, 69.5, 69.4, 69.4, 69.4, 69.4, 69.3, 69.3, 69.3, 69.2, 69.0, 67.7, 67.3, 67.2, 67.2, 67.1, 67.1, 67.0, 67.0, 66.8, 66.5, 54.2, 53.7, 47.1, 47.0, 47.0, 46.7, 46.5, 44.9, 32.1, 30.8, 30.6, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 29.4, 29.2, 29.1, 29.1, 29.0, 29.0, 29.0, 28.9, 28.8, 28.7, 28.6, 28.3, 28.0, 27.3, 27.1, 26.8, 26.6, 26.5, 26.4, 26.2, 26.1, 25.9, 25.9, 25.8 ppm; UV/VIS (DCM, rt): λ_{max} = 245, 272, 281, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{128}H_{98}O_{24}^{+}$ $[M]^{+}$: m/z = 2018.6448, found m/z = 2018.6454.

2nd eluted diastereomer (5.8 mg, 2.87 μmol, 35%): $[\alpha]_D^{20}$ (c = 0.050 g/100 mL) = −6.20°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.89–3.99 (*m*, 22H), 3.88 (*s*, 3H), 2.55 (t, ^4J = 2.4 Hz, 1H), 1.80–1.12 (*m*, 72H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.2, 164.1, 164.0, 164.0, 163.8, 163.4, 163.4, 163.2, 162.9, 146.8, 146.4, 146.2, 146.1, 146.0, 146.0, 145.8, 145.8, 145.7, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.2, 145.1, 145.0, 144.8, 144.8, 144.8, 142.5, 142.5, 142.3, 142.2, 142.1, 142.0, 142.0, 141.9, 141.7, 141.6, 141.4, 141.3, 141.3, 141.2, 141.1, 141.0, 140.9, 140.9, 140.7, 76.6, 76.3, 69.8, 69.5, 69.5, 69.4, 69.4, 69.4, 69.4, 69.3, 69.3, 69.2, 69.0, 67.7, 67.3, 67.2, 67.1, 67.1, 67.1, 66.9, 66.8, 66.6, 54.0, 53.8, 47.0, 47.0, 47.0, 46.7, 46.5, 45.0, 32.1, 30.8, 30.6, 30.0, 29.8, 29.8, 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 29.1, 29.1, 29.0, 29.0, 29.0, 28.9, 28.8, 28.8, 28.6, 28.2, 27.9, 27.4, 27.2, 26.8, 26.6, 26.5, 26.5, 26.2, 26.0, 25.9, 25.8, 25.8 ppm; UV/VIS (DCM, rt): λ_{max} = 245, 272, 281, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{128}H_{98}O_{24}^{+}$ $[M]^{+}$: m/z = 2018.6448, found m/z = 2018.6443.

Synthesis of hexakis-adducts with a TMS-protected triple bond 9 a/b: Under N_2-atmosphere 3rd eluted isomer of [3:2] pentakis-adduct **6** (10.0 mg, 5.36 μmol), 3-(trimethylsilyl)-2-propynyl methyl malonate (2.44 mg, 10.7 μmol) and tetrabromomethane (7.10 mg, 21.4 μmol) were dissolved in dry DCM (15 mL). The mixture was degassed by introducing N_2 for 10 min before phosphazene base P_1-*t*-Bu (6.28 mg, 6.83 μL, 26.8 μmol) was added dropwise under stirring. After stirring for 35 min under light exclusion, the reaction mixture was subjected directly to a silica plug (DCM, R_f = 0.33). Further purification *via* analytical HPLC (Nucleosil, rt, Tol/EtOAc 96:4) afforded two diastereomers of hexakis-adduct **9** as yellow solids in 24% and 24% yield.

1st eluted diastereomer (2.70 mg, 1.29 μmol, 24%): $[\alpha]_D^{20}$ (c = 0.10 g/100 mL) = −20.0°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.45–3.64 (*m*, 22H), 3.36 (*s*, 3H), 1.80–1.14 (*m*, 72H), 0.11 (*s*, 9H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.9, 164.1, 164.0, 164.0, 163.8, 163.6, 163.5, 163.5, 163.5, 163.4, 162.8, 147.4, 147.1, 146.9, 146.8, 146.8, 146.7, 146.7, 146.6, 146.5, 146.5, 146.4, 146.3, 146.3, 146.2, 146.1, 146.0, 145.9, 145.9, 145.8, 145.7, 145.7, 145.6, 145.1, 145.1, 144.2, 144.0, 143.6, 143.5, 143.2, 143.0, 142.9, 142.8, 142.7, 142.6, 142.5, 142.5, 142.4, 142.3, 142.3, 142.2, 142.0, 142.0, 142.0, 141.8, 141.6, 141.5, 141.4, 98.9, 92.8, 70.5, 70.4, 70.4, 70.4, 70.3, 70.3, 70.2, 70.1, 69.8, 67.8, 67.6, 67.0, 66.9, 66.9, 66.9, 66.6, 66.5, 66.4, 66.4, 54.6, 53.1, 48.3, 48.2, 48.1, 47.6, 46.1, 45.5, 33.4, 32.4, 31.5, 30.9, 30.9, 30.6, 30.5, 30.2, 30.2 30.1, 29.9, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 28.9, 28.3, 27.6, 27.3, 27.2, 26.4, 26.0, 25.1, −0.3 ppm; UV/VIS (DCM, rt): λ_{max} = 245, 272, 281, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{131}H_{106}O_{24}Si^{+}$ $[M]^{+}$: m/z = 2090.6843, found m/z = 2090.6849.

2nd eluted diastereomer (2.7 mg, 1.29 μmol, 24%): $[\alpha]_D^{20}$ (c = 0.093 g/100 mL) = −40.2°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 4.86–3.77 (*m*, 22H), 3.15 (*s*, 3H), 1.71–1.17 (*m*, 72H), 0.11 (*s*, 9H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.3, 164.1, 164.1, 164.0, 163.9, 163.9, 163.8, 163.7, 163.5, 163.5, 163.2, 162.7, 147.6, 147.0, 147.0, 146.6, 146.6, 146.6, 146.5, 146.5, 146.4, 146.3, 146.3, 146.2, 146.1, 146.1, 146.1, 146.0, 145.9, 145.5, 145.3, 145.3, 145.0, 143.6, 143.5, 143.5, 143.4, 143.2, 143.1, 143.1, 143.1, 142.8, 142.7, 142.7, 142.4, 142.4, 142.3, 142.2, 142.2, 142.1, 142.0, 141.9, 141.7, 141.7, 141.6, 98.9, 92.8, 70.5, 70.5, 70.4, 70.4, 70.3, 70.3, 70.2, 70.1, 70.1, 70.1, 70.0, 67.6, 67.4, 67.3, 66.9, 66.9, 66.8, 66.8, 66.7, 66.6, 66.5, 54.5, 53.1, 48.2, 48.1, 48.0, 47.9,

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47.5, 46.3, 32.4, 30.6, 30.5, 30.2, 30.2, 30.1, 30.0, 29.9, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 28.9, 27.7, 26.6, 26.4, 25.7, 25.1, −0.3 ppm; UV/VIS (DCM, rt): λ_{max} = 245, 272, 281, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{131}H_{106}O_{24}Si^+$ $[M]^+$: m/z = 2090.6843, found m/z = 2090.6838.

Synthesis of cyanurate functionalized hexakis-adducts 10 a/b: Under N_2-atmosphere 2nd eluted isomer of [3:2] pentakis-adduct **6** (10.0 mg, 5.36 μmol), 3-(2,4,6-trioxo-1,3,5-triazi-nan-1-yl)propyl methyl malonate (3.07 mg, 10.7 μmol) and tetrabromomethane (7.10 mg, 21.4 μmol) were dissolved in dry DCM (30 mL). The mixture was degassed by introducing N_2 for 10 min before phosphazene base P_1-*t*-Bu (6.25 mg, 6.80 μL, 26.6 μmol) was added dropwise under stirring. After stirring for 2 h under light exclusion, more phosphazene base P_1-*t*-Bu (18.8 mg, 20.4 μL, 80 μmol) was added. The reaction mixture was stirred for another 3 h and subjected directly to a silica plug (DCM→MeOH). Further purification *via* analytical HPLC (Nucleosil, rt, Tol/EtOAc 3:1) afforded two diastereomers of **10** as yellow solids in 32% and 42% yield.

1st eluted diastereomer (3.70 mg, 1.72 μmol, 32%): $[\alpha]_D^{20}$ (c = 0.050 g/100 mL) = +12.3°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 8.26 (*s*, 2H), 4.72–3.95 (*m*, 22H), 3.89 (*s*, 3H), 2.09–2.02 (*m*, 2H), 1.79–1.13 (*m*, 74H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.3, 164.3, 164.2, 164.2, 164.1, 164.0, 163.8, 163.8, 163.4, 163.3, 162.9, 148.7, 146.7, 146.5, 146.3, 146.1, 146.0, 146.0, 145.9, 145.9, 145.8, 145.7, 145.6, 145.6, 145.5, 145.5, 145.3, 145.3, 145.2, 145.2, 145.2, 145.1, 144.9, 144.9, 144.8, 144.7, 142.5, 142.5, 142.4, 142.2, 142.1, 142.1, 142.0, 142.0, 142.0, 141.9, 141.5, 141.5, 141.4, 141.3, 141.2, 141.2, 141.1, 141.0, 141.0, 140.9, 140.9, 140.8, 140.6, 69.8, 69.6, 69.5, 69.4, 69.4, 69.4, 69.4, 69.3, 69.3, 69.3, 69.2, 69.0, 67.6, 67.6, 67.2, 67.1, 67.0, 66.8, 66.8, 66.7, 64.9, 54.0, 47.1, 47.0, 46.7, 46.5, 46.5, 45.5, 40.0, 32.1, 30.8, 30.6, 30.0, 29.8, 29.8, 29.8, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 29.0, 29.0, 28.9, 28.7, 28.5, 28.2, 28.0, 27.4, 27.0, 27.0, 26.8, 26.6, 26.5, 26.2, 26.1, 25.9, 25.8, 25.8 ppm; UV/VIS (DCM, rt): λ_{max} = 249, 272, 282, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{131}H_{103}N_3O_{27}^+$ $[M]^+$: m/z = 2149.6779, found m/z = 2149.6789.

2nd eluted diastereomer (4.8 mg, 2.23 μmol, 42%): $[\alpha]_D^{20}$ (c = 0.096 g/100 mL) = +14.6°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 8.21 (*s*, 2H), 4.71–3.93 (*m*, 22H) ppm, 3.88 (*s*, 3H), 2.07–1.99 (*m*, 2H), 1.83–1.10 (*m*, 74H); ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.7, 164.5, 164.0, 163.9, 163.9, 163.8, 163.8, 163.7, 163.6, 163.5, 163.3, 148.7, 146.8, 146.5, 146.4, 146.2, 146.1, 146.1, 145.9, 145.9, 145.7, 145.6, 145.5, 145.5, 145.4, 145.3, 145.3, 145.2, 145.2, 145.1, 145.1, 145.0, 145.0, 144.7, 142.7, 142.4, 142.4, 142.1, 142.0, 142.0, 142.0, 142.0, 141.6, 141.5, 141.5, 141.4, 141.3, 141.2, 141.2, 141.0, 141.0, 140.9, 140.8, 140.8, 140.7, 69.8, 69.6, 69.5, 69.5, 69.4, 69.4, 69.4, 69.3, 69.3, 69.2, 69.1, 69.0, 67.6, 67.4, 67.3, 67.3, 67.2, 67.0, 67.0, 67.0, 66.8, 66.7, 64.9, 53.8, 47.1, 47.0, 46.6, 46.6, 46.4, 45.6, 39.9, 32.1, 30.8, 30.6, 30.0, 29.8, 29.8, 29.5, 29.4, 29.4, 29.2, 29.2, 29.1, 29.1, 29.0, 29.0, 28.9, 28.9, 28.9, 28.8, 28.6, 28.5, 28.2, 28.0, 27.4, 27.2, 27.1, 26.8, 26.6, 26.5, 26.4, 26.2, 26.1, 25.9, 25.8 ppm; UV/VIS (DCM, rt): λ_{max} = 249, 272, 282, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{131}H_{103}N_3O_{27}^+$ $[M]^+$: m/z = 2149.6779, found m/z = 2149.6773.

Synthesis of fullerene triazole derivative 11: Copper sulfate pentahydrate (0.090 mg, 0.35 μmol) and sodium ascorbate (0.21 mg, 1.04 μmol) were added to a solution of 1st eluted diastereomer of hexakis-adduct **8** (7.0 mg, 3.47 μmol) and benzyl azide (0.92 mg, 6.94 μmol) in DCM/water (1:1, 2 mL). After stirring for 22 h, DCM (30 mL) and water (20 mL) were added. The organic phase was washed with water (3×10 mL), separated and the solvent was evaporated under reduced pressure. Further purification of the crude product by column chromatography (SiO_2, DCM/EtOAc 98:2, R_f = 0.31) afforded fullerene triazole derivative **11** (5.40 mg, 2.51 μmol) in 72% yield. $[\alpha]_D^{20}$ (c = 0.025 g/100 mL) = -8.67°; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 7.57 (*s*, 1H), 7.40–7.28 (*m*, 5H), 5.56 (*s*, 2H), 5.42–5.33 (*m*, 2H), 4.68–3.98 (*m*, 20H), 3.67 (*s*, 3H), 1.81–1.59 (*m*, 12H), 1.50–1.05 (*m*, 60H) ppm; ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 164.1, 163.9, 163.8, 163.8, 163.8, 163.7, 163.7, 163.6, 163.6, 163.3, 163.2, 163.1, 146.6, 146.2, 146.1, 145.9, 145.8, 145.8, 145.6, 145.6, 145.5, 145.3, 145.2, 145.1, 145.1, 145.1, 145.0, 145.0, 145.0, 144.9, 144.7, 144.6, 142.4, 142.3, 142.2, 142.1, 142.1, 142.0, 141.9, 141.9, 141.8, 141.8, 141.8, 141.5, 141.5, 141.4, 141.2, 141.1, 141.0, 141.0, 140.9, 140.9, 140.8, 140.7, 140.6, 134.6, 129.1, 128.8, 128.2, 124.2, 69.6, 69.4, 69.3, 69.3, 69.3, 69.2, 69.1, 69.0, 68.9, 67.5, 67.1, 67.0, 67.0, 67.0, 66.9, 66.9, 66.8, 66.7, 66.6, 59.9, 54.2, 53.5, 46.9, 46.8, 46.8, 46.6, 46.3, 45.0, 31.9, 30.6, 30.4, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 29.2, 29.0, 29.0, 29.0, 28.9, 28.9, 28.9, 28.8, 28.8, 28.7, 28.6, 28.4, 28.1, 27.8, 27.1, 26.9, 26.6, 26.4, 26.4, 26.3, 26.0, 25.9, 25.8, 25.7, 25.6 ppm; UV/VIS (DCM, rt): λ_{max} = 251, 272, 282, 317, 335 nm; MALDI HRMS (dctb): m/z calculated for $C_{135}H_{105}N_3NaO_{24}^+$ $[M+Na]^+$: m/z = 2174.6980, found m/z = 2174.6971.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cyclopropanation · exohedral functionalization · fullerenes · functional organic materials · regioselectivity

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