A Highly Regioselective Approach to Multiple Adducts of C_{60} Governed by Strain Minimization of Macrocyclic Malonate Addends

Uwe Reuther, Torsten Brandmüller, Wolfgang Donaubauer, Frank Hampel, and Andreas Hirsch*[a]

Abstract: New macrocyclic malonates **2**–**5** have been prepared by reaction of malonyl dichloride with alkanediols. Reactions of these *cyclo*-[*n*]-alkylmalonates with C_{60} are highly regioselective. The macrocycles containing identical alkyl spacers selectively form bis- and trisadducts of C_{60} with rotational symmetry. The addition pattern of the regioselectively formed oligoadducts is determined by the size of the alkyl spacer within the macrocyclic malonate. A variety of bis-, tris-, tetra-, and hexaadducts have been synthesized to show the scope of this approach. "Exotic" addition patterns such as *trans*-4,*trans*-4,*trans*-4, which has been synthesized and completely characterized for the first time, are also accessible by this method. The regioselectivity is ruled by the even distribution of the strain within the macrocyclic malonates containing spacer alkane chains of identical lengths: addition patterns with rotational symmetry provide exactly identical distances of the malonate oxygen atoms and are thus exclusively formed by this method. In contrast, when macrocycles with two different alkyl spacer lengths are used, such as **9** and **10**, the reaction exclusively yields C_s-symmetric bisadducts.

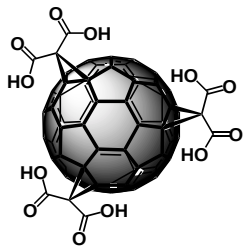
Keywords: diastereoselectivity · fullerenes · macrocycles · semiempirical calculations · topochemistry

Introduction

The high-yield synthesis of fullerene multiadducts with a defined addition pattern by means of the Bingel route[1] is mainly hampered by the fact that the regioselectivity of this reaction is quite low. In fact, the second addition of diethyl malonate to a monoadduct of C_{60} leads to a mixture of seven out of eight possible regioisomers.[2] Although the reaction favors the equatorial and *trans*-3 addition pattern with 15.5% and 12.0% yield, respectively, the product mixture has to be purified by a tedious chromatographic separation. The regioselectivity of further additions to bisadducts is higher; however, the separation of the reaction products remains difficult.

Consequently, the search for alternatives to this stepwise procedure has been a challenge ever since the development of fullerene chemistry began. One way to achieve a high degree of control of the regiochemistry of additions to fullerenes is the use of tethered addend systems, for example, malonates which are connected by a more or less rigid spacer.[3] The tether method proved to be a major breakthrough and provides relatively facile access to otherwise strongly disfavored addition patterns, such as *trans*-1.[4] The complex regiochemistry of C_{70} can also be controlled, as demonstrated by a recent contribution by the group of Diederich et al.[5], [6]

The selectivity of the known tether methods can be very high and may lead to quite unusual addition patterns.[7] However, the tethers are sometimes difficult to synthesize and up to now no facile building-block principle is available which enables a fast and reliable access to the whole variety of fullerene multiadducts with high regioselectivity. In addition to the synthesis of bisadducts, examples for tether-directed synthesis of trisadducts directly from C_{60} are also very rare. In fact, the only reaction published to date which achieves this goal was worked out by the Diederich group.[8] This approach, which uses a cyclotriveratrylene tether, allows the synthesis of a roughly 1:1 mixture of *trans*-3,*trans*-3,*trans*-3 and *e*,*e*,*e*-trisadducts. The overall yield is about 20%. Although the synthesis of the tether system is not too difficult, it does require a multistep sequence.[9] Despite these important improvements, the regioselective high-yield synthesis of fullerene trisadducts still remains an important goal in fullerene chemistry. For example, facile access to the *e*,*e*,*e*-hexaacid **1**[10] is most desirable, because it exhibits a high



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solubility in water and is a very potent antioxidant compound, much stronger indeed than vitamin E.[11] It has thus attracted much attention for possible use as a drug, since it is also likely that **1** or similar compounds will find use as therapeutics against neurodegenerative diseases.[12]

Furthermore, one-step tether-directed syntheses of tetra- or higher adducts are completely unknown to date. Here we introduce a new concept of a tether approach, which allows us to develop an easy to use "construction kit" for fullerene multiadducts. The tether system exhibits the following characteristics: a) facile synthesis from cheap starting materials; b) facile adaptation to a wide diversity of steric requirements; c) possibility to attach external functionalities; d) high yield and regioselectivity for the direct addition to C_{60}.

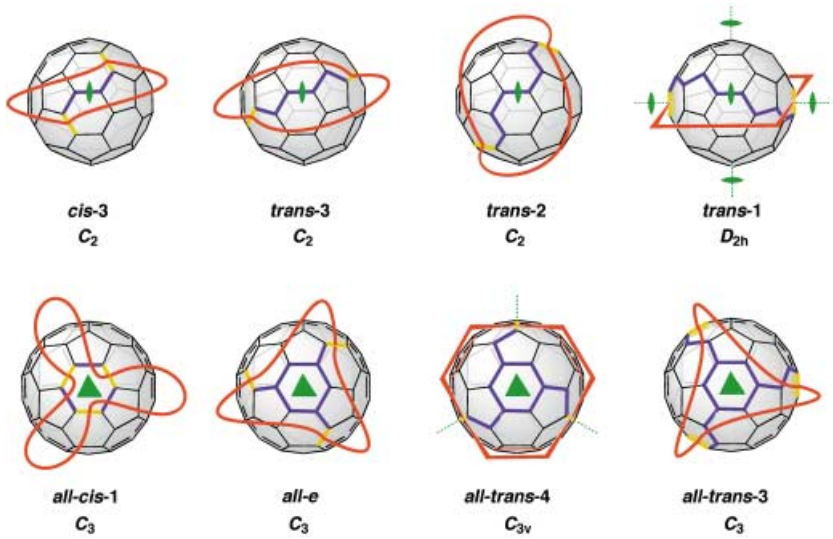

Figure 1. Possible bis- and trisadducts of C_{60} containing rotational axes. All distances between adjacent addend positions are identical. The yellow bonds denote the positions of the addends, such as malonates.

Results and Discussion

The concept: The direct synthesis of C_{60} multiadducts is basically possible by two different approaches: the first one, which has been used exclusively up to now, is the reaction with a specifically designed tether, which bears, for example, malonates in a preformed and quite rigid steric arrangement. This can be accomplished quite easily for several bisadduct patterns. However, if tris- and higher adducts are the target of the synthesis, the design of a suitable steric arrangement becomes an increasingly difficult, if not impossible task. A loss in regioselectivity and/or total yield is the consequence of insufficient preorganization of the malonates.

This is where the second alternative comes into play: the solution is to completely abandon the concept of rigid spacers and substitute them by the most flexible and simplest system at hand, which would be an alkyl chain. Of course, almost all regioselectivity would be lost, if this system were open-chained. To compensate for this, we incorporate the malonates into a macrocyclic ring.[13] This way, the regioselectivity is not based on steric preorganization, but on the avoidance of unequal strain in the alkyl chains. This has consequences for the symmetry of the addition pattern of the products: macrocycles with two and three malonate units are forced to form adducts with rotational symmetry, that is C_2 for bisadducts and C_3 for trisadducts. All other regioisomers are excluded a priori, since they would result in different distances between the ester functions and thus introduce strain. Figure 1 shows the addition patterns of bis- and trisadducts that fulfill these restrictions. The *cis*-1,*cis*-1,*cis*-1 isomer will not be formed because of steric crowding.[2]

The *trans*-1 bisadduct and the *trans*-4,*trans*-4,*trans*-4 trisadduct are special cases since they contain additional symmetry elements (i.e., mirror planes). However, this should not influence the selectivity. It is reasonable to assume that the selectivity can be adjusted by varying the length of the alkyl chain, which accounts for the high versatility of this method.

When mixed macrocycles with two alkyl spacers of different length are used, this selection rule can be reversed because now C_2-symmetric bisadducts would exhibit different strain in the alkyl chains. The consequence is the selective formation of bisadducts with a C_s-symmetrical addition pattern, as outlined in Figure 2. Again, the *cis*-1 isomer is sterically unfavorable.

In this paper, we present our concept for the highly regioselective synthesis of several examples of bis- to tetraadducts with rotational symmetry or with C_s symmetry.

Abstract in German: *Durch Reaktion von Malonyldichlorid mit Alkandiolen wurden neue makrozyklische Malonate wie* ***2*** *–* ***5*** *hergestellt. Reaktionen dieser cyclo-[n]-Alkylmalonate mit C_{60} sind hoch regioselektiv. Die Makrozyklen mit identischen Alkylspacern bilden mit C_{60} selektiv drehsymmetrische Bis- und Trisaddukte. Das Additionsmuster eines regioselektiv gebildeten Mehrfachadduktes ist durch die Länge des Alkylspacers innerhalb des makrozyklischen Malonates festgelegt. Zur Demonstration der Leistungsfähigkeit dieses Ansatzes wurden eine Auswahl von Bis-, Tris-, Tetra- und Hexaaddukten synthetisiert. Auch "exotische" Additionsmuster wie trans-4,trans-4,trans-4, das erstmalig synthetisiert und vollständig charakterisiert wurde, sind durch diese Methode zugänglich. Die Regioselektivität wird von der gleichmäßigen Spannungsverteilung in den makrozyklischen Malonaten mit Spacer-Alkanen identischer Länge bestimmt: Additionsmuster mit Rotationssymmetrie weisen exakt identische Abstände der Malonatsauerstoffatome auf und werden daher durch diese Methode ausschließlich gebildet. Wenn andererseits Makrozyklen mit zwei verschiedenen Alkyl-Spacerlängen, wie* ***9*** *und* ***10****, verwendet werden, führt die Reaktion ausschließlich zu C_s symmetrischen Additionsmustern.*

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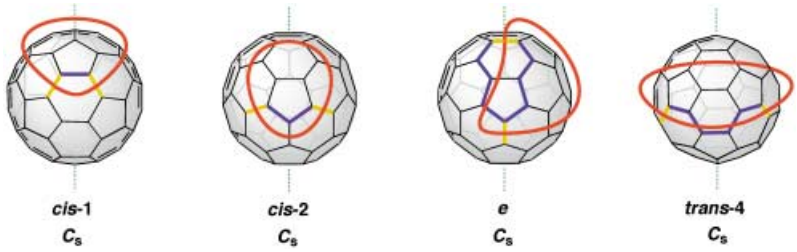


Figure 2. Bisadducts of C_{60} with C_s symmetry. The two possible distances between adjacent addend positions are different. The yellow bonds denote the positions of the addends such as malonates.

Synthesis of the macrocycles: Scheme 1 shows the quite simple synthesis of macrocycles obtained from the condensation of octanediol and malonyl dichloride. The reaction is best carried out at a concentration of ≈ 30 mmol L^{-1} diol. Further dilution only leads to a small increase in the total yield. Since the systematic names of the macrocycles are impractical, we use a simple nomenclature. We call these macrocycles "*cyclo*-[*n*]-alkylmalonates". The number in brackets represents the number of repetition units. Compound **2** is therefore named "*cyclo*-[2]-octylmalonate".

Compounds **2**–**5** can all be obtained in a pure form by separation with flash chromatography on silica gel. The elution sequence correlates with the number of repetition units; the smaller rings elute first. In principle, the larger macrocycles can also be obtained, but they have not been isolated here, since they are not important in this context. Macrocycles with up to nine repetition units can be detected in the FAB mass spectrum.

The synthesis of macrocycles with other chain lengths is also straightforward, and we produced a series of *cyclo*-[*n*]-propylmalonates with $n = 2-6$. In addition, we synthesized *cyclo*-[2]-dodecylmalonate (**6**), *cyclo*-[2]-hexadecylmalonate (**7**), and *cyclo*-[3]-tetradecylmalonate (**8**) to study the influence of the chain length on the bis- and trisaddition patterns. To test the selectivity of the formation of C_s-symmetric addition patterns, the mixed macrocycles *cyclo*-[2]-butyl-octylmalonate (**9**) and *cyclo*-[2]-octyl-tetradecylmalonate (**10**) were prepared by a statistic reaction of a 1:1 mixture of the corresponding diols and malonyl dichloride. To enable a clean separation of the product mixture, the chain lengths of the two diols should differ by at least four methylene units.

The *cyclo*-[*n*]-octylmalonates show pronounced differences in their crystallizability: those with even *n* crystallize quite readily (melting points are 98.8 °C and 117.3 °C of **2** and **6**, respectively), whereas those with odd *n* exhibit a strong crystallization inhibition and are usually isolated as highly viscous oils. The X-ray structures of compounds **2**, **6**, and **10** are shown in Figure 3 along with representations of the unit cells.[14]

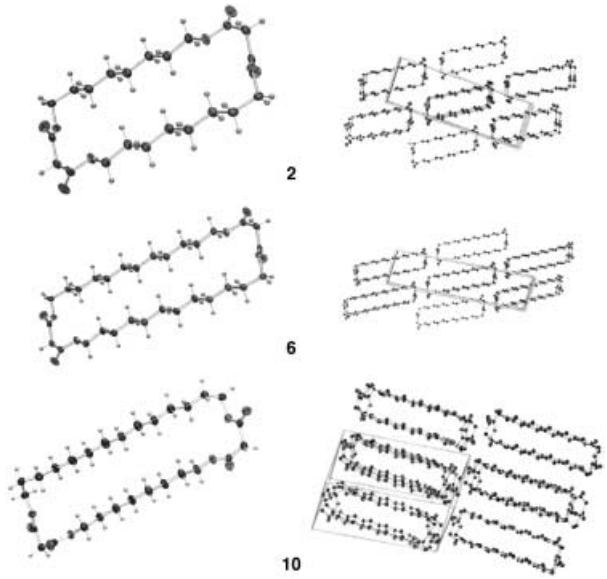
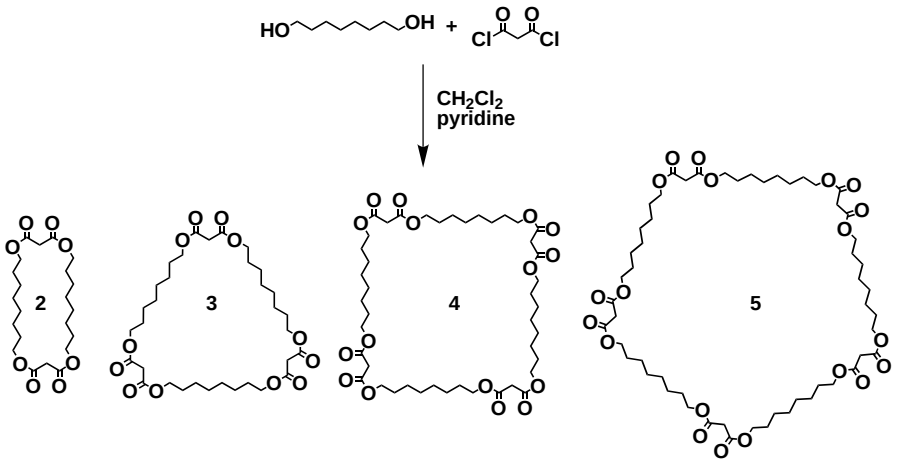


Figure 3. X-ray crystal structures of **2**, **6**, and **10** together with representations of the unit cells.

These structures are very remarkable for two reasons: firstly, the macrocycles crystallize in a perfectly rectangular shape. Secondly, the molecules arrange into columnar structures with a channel in the middle of each column (Figure 4). In the case of **2** and **6**, this channel is not really hollow because the hydrogen atoms fill it up almost completely. In the case of **3**–**5**, however, this channel should be big enough to serve as a kind of "pore" in the crystal structure, which could promote transport processes of guest molecules through the crystal.



Scheme 1. Synthesis of the *cyclo*-[*n*]-octylmalonates **2**–**5**.

Bisadducts: As already stated above, reactions of *cyclo*-[2]-alkylmalonates with two identi-

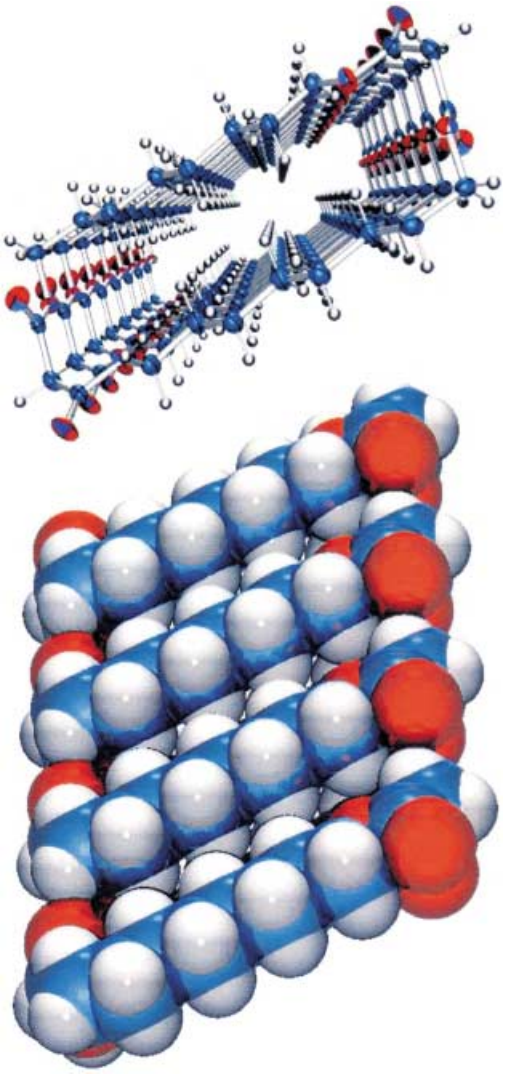
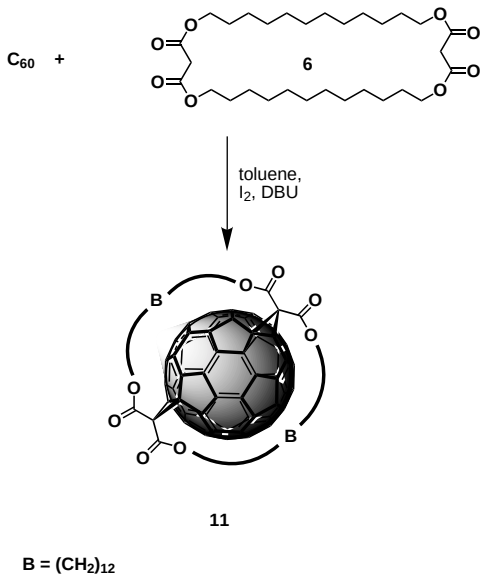


Figure 4. View of the "molecular channels" in the X-ray structure of **2**.

cal alkyl chains with C_{60} are expected to give selectively bisadducts with rotational symmetry. Indeed, we were able to prove this with the formation of the *trans*-3 and *trans*-1 adducts. The other two patterns (*cis*-3 and *trans*-2) represent special cases: because of the steric arrangement of the malonate bridges, both isomers would require quite long alkyl spacers. However, if the chain is of sufficient length, the formation of *trans*-3 and *trans*-1, respectively, is also possible and is actually preferred by the system. Introduction of a defined rigid bend (e.g., an *ortho*-disubstituted benzene ring) into the alkyl spacer may change the selectivity to *cis*-3 and *trans*-2. Experiments in this direction are currently underway. The bisadducts have been synthesized by the iodine variant of the Bingel reaction originally described by Bingel[15] and used extensively by the group of Diederich[16] and ourselves.[17] In the case of macrocyclization reactions this method seems to be superior to the usual CBr_4/DBU sequence (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).[18]

When *cyclo*-[2]-dodecylmalonate **6** is treated with C_{60} under the Bingel conditions, the *trans*-3 bisadduct **11** was obtained almost exclusively with a yield of 56% (Scheme 2). Traces of oligomeric side products can be removed by simple flash



Scheme 2. Synthesis of the *trans*-3 bisadduct **11**.

chromatography. If, on the other hand, *cyclo*-[2]-octylmalonate **2** is used under the same conditions, a complex mixture of several adducts as well as polymeric material is formed, which could not be separated even by HPLC. The polymeric material does not move on silica gel. Evidently, this macrocycle **2** is not suitable for the formation of a strain-free bisadduct with rotational symmetry because of the specific length of its spacer units. Nevertheless, this clearly demonstrates the high selectivity of our approach. In all of the further reactions described below, suitable macrocycles were used that allow the selective formation of oligoadducts. In almost every case, the only side products are intermolecular addition adducts (oligomers and polymers) that do not move on silica gel.

The structure of **11** was ascertained by comparison of its UV spectrum with that of the known *trans*-3 bisadduct.[19] The NMR spectra are also in accordance with the proposed structure. Figure 5 shows the calculated structure of **11** as a space-filling model.

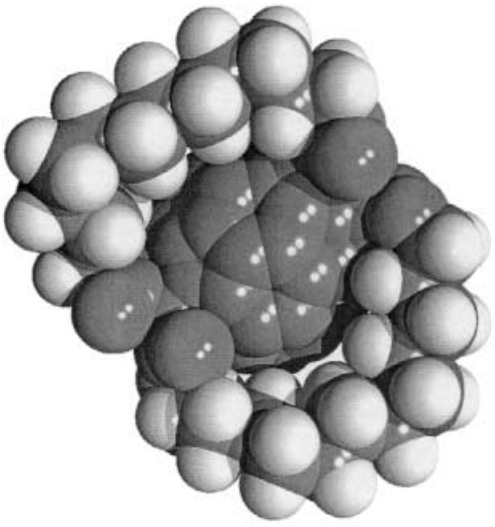


Figure 5. PM3 calculated structure of the *trans*-3 bisadduct **11**.

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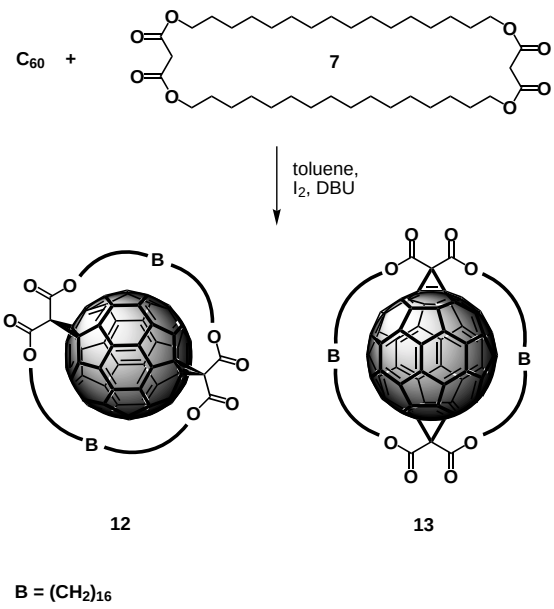
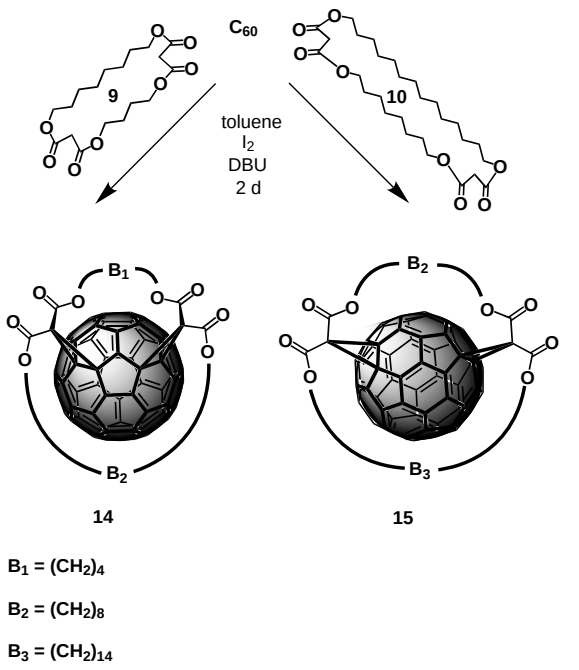
Although the formation of the *trans*-2 and *trans*-1 addition patterns should be conceptually possible, it is apparently necessary to use even longer chains to disfavor the *trans*-3 addition pattern. Consequently, we used *cyclo*-[2]-hexadecylmalonate **7** and were able to isolate a 55:45 mixture of the *trans*-3- and *trans*-1-bisadducts **12** and **13** (Scheme 3). It is reasonable to assume that the relative yield of the *trans*-1 bisadduct can be further increased by the use of even longer alkyl chains.



Scheme 3. Synthesis of the *trans*-3- and *trans*-1-bisadducts **12** and **13**.

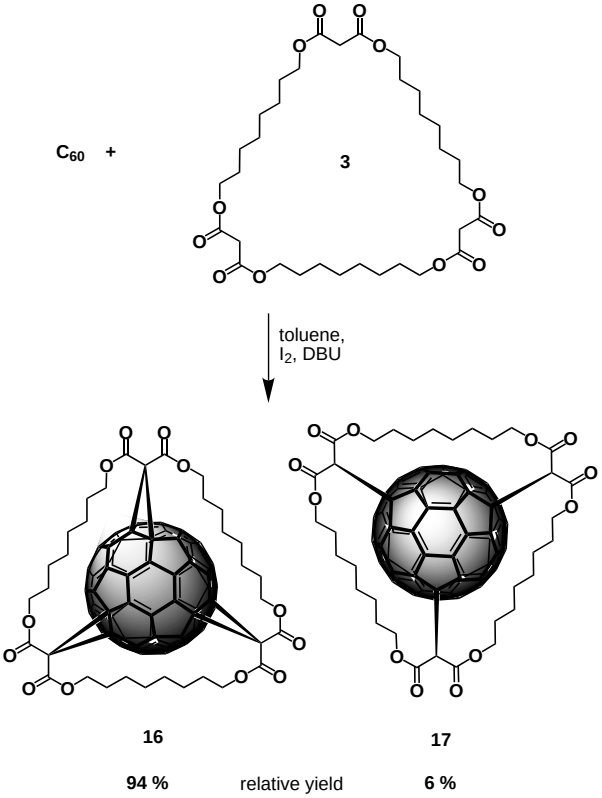
When C_{60} was treated with *cyclo*-[2]-butyl-octylmalonate (**9**) or *cyclo*-[2]-octyl-tetradecylmalonate (**10**), the exclusive formation of adducts that have a C_s-symmetric bisaddition pattern was observed, as expected. In the former case, the *cis*-2 bisadduct **14** was isolated and in the latter the *e*-bisadduct **15** (Scheme 4). The isolated yields of **14** and **15** were 39.5 % and 51.1 %, respectively. Their isolation was achieved by simple flash chromatography and thus use of tedious HPLC separation was not necessary.



Scheme 4. Synthesis of the C_s symmetric *cis*-2 and *e*-bisadducts **14** and **15**.

Trisadducts: The reaction of *cyclo*-[3]-octylmalonate (**3**) with C_{60} can theoretically lead to the four isomers shown in Figure 1, namely *cis*-1,*cis*-1,*cis*-1, *e*,*e*,*e*, *trans*-4,*trans*-4,*trans*-4, and *trans*-3,*trans*-3,*trans*-3. From these, the *cis*-1,*cis*-1,*cis*-1 isomer is sterically impossible with malonate addends. Other trisadducts should not be formed, since they do not possess threefold rotational symmetry.

When the reaction is carried out, it leads to the *e*,*e*,*e* isomer **16**, which is formed in 94 % relative and 42 % isolated yield (Scheme 5). The raw product of the reaction contains 59 % of **16** (HPLC); this indicates that a substantial amount is lost during work-up. As a less polar byproduct, the hitherto unknown *trans*-4,*trans*-4,*trans*-4 trisadduct **17**[20] was formed. The solutions of the trisadduct **17** exhibit an olive-green color. Both isomers can be isolated in a pure form by preparative HPLC on Nucleosil; the *trans*-3,*trans*-3,*trans*-3 trisadduct could not be detected at all.



Scheme 5. Synthesis of the *e*,*e*,*e*- (**16**) and *trans*-4,*trans*-4,*trans*-4- (**17**) trisadducts.

This result was corroborated by semiempirical calculations (PM3)[21] of the three possible isomers. The *trans*-3,*trans*-3,*trans*-3 isomer is noticeably higher in energy than **16** and **17** (Figure 6). Because of the considerable conformational free-

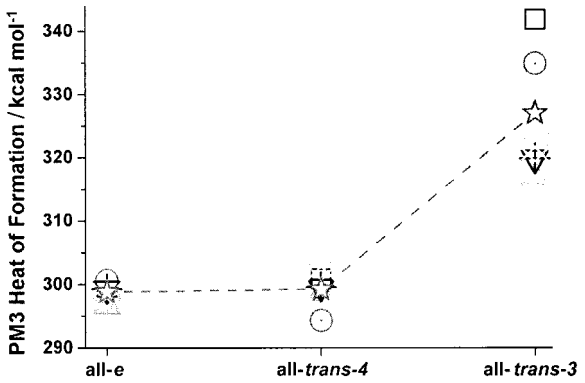


Figure 6. Relative PM3 heats of formation of the three possible C_{60} trisadducts with rotational symmetry (excluding *all-cis*-1). The dashed line shows the median value from the five molecular dynamics calculations.

dom of the alkyl chains, the calculations were carried out on five different geometries for each isomer that were generated by consecutive molecular dynamics calculations followed by a force-field minimization. The median values of the calculations are connected by the dashed line in Figure 6 and show a small increase in energy in going from the all-*e* (298.8 kcal mol^{-1}) to the *all-trans*-4 isomer (299.3 kcal mol^{-1}), which accounts for the observed product distribution. The value for the all-*trans*-3 isomer (327.1 kcal mol^{-1}) is considerably higher, which is in good agreement with the experimental observations.

The ^{13}C NMR spectra of **16** and **17** are in complete accordance with the proposed structures and are shown in direct comparison in Figure 7. For the trisadduct **16** the expected 18 signals for the sp^2 carbon atoms of the fullerene

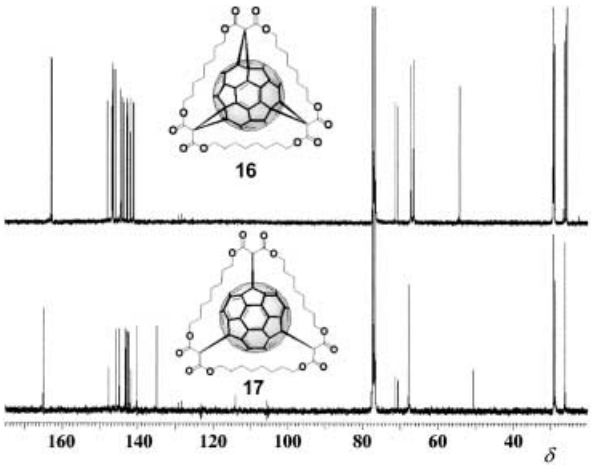


Figure 7. ^{13}C NMR spectra of the trisadducts **16** and **17**.

cage are found in the range of $\delta = 148-140$. In agreement with the higher symmetry, **17** shows only the expected ten signals in this region. Furthermore, in contrast to **16**, compound **17** has only one resonance for the carbon atoms of the carbonyl group. The signal set for the carbon atoms of the alkyl tether also contains only four resonances at $\delta =$ 67.74, 29.13, 28.79 and 26.14, which accounts for the C_{3v} symmetry of **17**.

The UV spectrum of **17** (Figure 8) is mainly characterized by a series of three distinct bands in the region $\lambda = 550-700$ nm.[22]

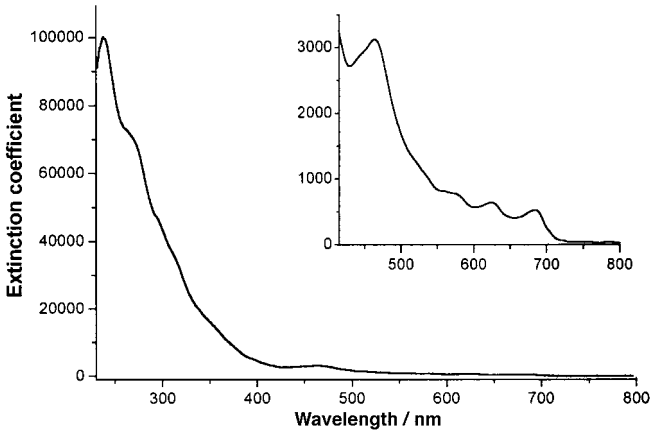


Figure 8. UV/Vis spectrum of the *all-trans*-4 trisadduct **17**.

The trisadduct **16** can be saponified to the corresponding *e*,*e*,*e*-hexaacid **1** by the standard procedure described above.[23] Therefore, this reaction sequence provides a valuable tool for the large-scale production of water-soluble **1**. When the *cyclo*-[3]-tetradecylmalonate **8** was treated with C_{60} under the same conditions, the *trans*-3,*trans*-3,*trans*-3 trisadduct **18** was isolated as the only trisadduct in 29.9% yield. The work-up required flash chromatography only and further purification by HPLC was not necessary. This is an impressive example for the almost complete change of regioselectivity from *e*,*e*,*e* to *trans*-3,*trans*-3,*trans*-3 effected by a simple change of the tether length from eight to fourteen methylene groups.

Tetraadducts: When *cyclo*-[4]-octylmalonate (**4**) is used as the tether component in the reaction with C_{60}, it is evident that no highly symmetric adducts can result, since tetraadducts of C_{60} with a C_4-symmetric addition pattern are not possible. The only alternative would be the D_{2h}-symmetric *trans*-1,*e*′,*e*′ addition pattern described by the group of Diederich.[24] However, this addition pattern is thermodynamically disfavored,[25] and is thus unlikely to be formed with a flexible tether system, such as **4**. The main product from the reaction is the *trans*-1,*e*′,*e*″-tetraadduct **19** together with a less polar byproduct **20** in a 86:14 ratio, as determined by HPLC. Both products can be obtained in a pure form by HPLC. Tetraadduct **19** was identified as the *trans*-1,*e*′,*e*″ isomer by comparison of its UV spectrum with that of the corresponding octaethyl ester.[25] Corroboration of this assignment by ^{13}C NMR spectroscopy is not possible as the molecule is C_1-symmetric because of the arrangement of the tether arms. However, the reaction of **19** with an excess of diethylmalonate under Bingel conditions leads to a hexaadduct with a tetrahedral addition pattern, as will be shown in the next section, thus further corroborating this assignment.

The ^{13}C NMR spectrum of **20** (Figure 9) reveals pure C_2 symmetry: the expected number of 26 signals with equal intensity appears in the sp^2 region, four carbonyl signals can be found from $\delta = 164.80$ to 163.32. Furthermore, four

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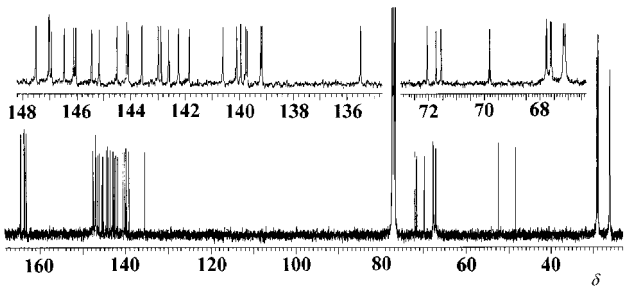

Figure 9. ^{13}C NMR spectrum of the tetraadduct **20**.

fullerene sp^3 peaks ($\delta = 72.04 - 69.81$), two signals for the bridgehead carbons ($\delta = 52.43$ and 48.46), four signals for the $-O-CH_2$ groups of the tether, and 11 of the 12 expected signals for the remaining methylene groups of the tether ($\delta = 29.20 - 26.03$, one with double intensity) are present in the spectrum.

To obtain a sensible structure suggestion for tetraadduct **20**, a systematic overview of all possible C_{60} tetraadducts with pure C_2 symmetry is given in Table 1. It can be shown that a C_2-symmetric tetraadduct pattern can always be split into two bisadduct patterns which also have C_2 symmetry. There are only three such patterns, namely *cis*-3, *trans*-3, and *trans*-2. The D_{2h}-symmetric *trans*-1 pattern, however, must also be considered, since it contains three C_2 axes. A combination of these patterns leads to the ten possible C_2-symmetric tetraadducts shown in Table 1. Three setup possibilities exist for the *trans*-1 pattern, corresponding to the three C_2 axes. These are marked with (1), (2), and (3) in Table 1. It has to be noted that the combination of two identical patterns, for example, *cis*-3/*cis*-3 leads to patterns with a symmetry higher than C_2. Therefore, such combinations do not appear in the table.

It is unlikely that the tetraadduct **20** contains *cis* relationships in its structure because such structures would result in a very uneven distribution of the addends over the cage. The only pattern without a *cis* relationship is the *trans*-4,*trans*-3,*e* isomer 6. Since this is also the isomer with a minimum of strain difference in the alkane chain, we postulate that this is the correct structure for **20**. The structures of **19** and **20** are shown in Figure 10.

When two equivalents of *cyclo*-[2]-dodecylmalonate **6** are treated with C_{60}, the formation of a C_2-symmetric tetraadduct containing two macrocycle addends is observed. As **6** leads to

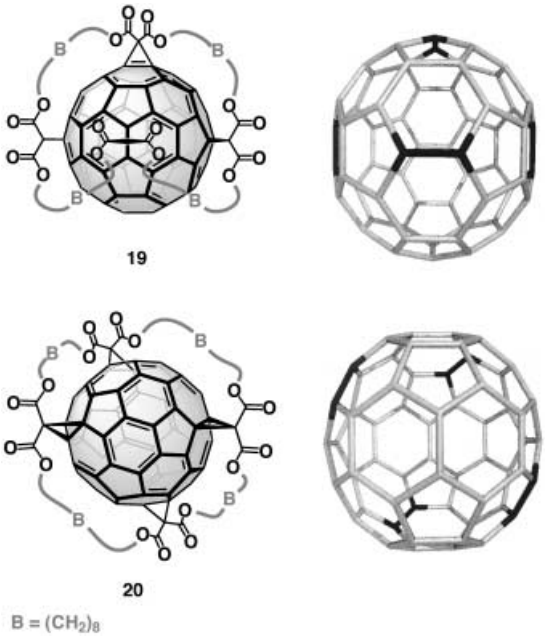

Figure 10. Structures of the *trans*-1,*e*′,*e*″- (**19**) and *trans*-4,*trans*-3,*e*- (**20**) tetraadducts.

the completely regioselective formation of *trans*-3 patterns (see bisadduct **11**), it seems reasonable to assume that the addition pattern of the tetraadduct **21** contains two such relationships. The only C_2-symmetric structure which meets this requirement is the *cis*-3,*trans*-3,*trans*-2 isomer shown in Figure 11. This adduct contains a subaddition pattern of a hexaadduct recently synthesized by Diederich et al.[7]

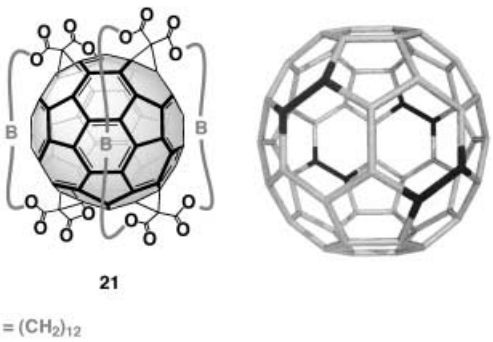

Figure 11. Structure of the *cis*-3,*trans*-3,*trans*-2-tetraadduct **21**.

Table 1. All possible C_{60} tetraadducts with C_2 symmetry.

	Isomer No.	Addition pattern (short nomenclature)	Absolute addend positions	Addition pattern (complete nomenclature)	Constituting addition patterns
cis-**3**	1	*cis*-**2**, *cis*-**3**, *e*	1,2/8,24/28,29/31,32	I, III^2, IV^4, *e*II^2	*cis*-**3**, *trans*-**2**
	2	*cis*-**3**, *trans*-**2**, *e*	1,2/18,36/28,29/56,57	I, IV^4, *e*I^1, II*^{3}	*cis*-**3**, *trans*-**3**
	3	*cis*-**1**, *cis*-**1**, *trans*-**1**	1,2/3,4/9,10/55,60	I, II^1, II^3, I*	*cis*-**3**, *trans*-**1** (1)
	4	*cis*-**2**, *cis*-**3**, *trans*-**3**	1,2/8,24/16,17/33,50	I, III^2, IV^1, III*^{1}	*cis*-**3**, *trans*-**1** (2)
	5	*cis*-**3**, *trans*-**4**, *trans*-**1**	1,2/16,17/28,29/37,38	I, IV^1, IV^4, IV*^{2}	*cis*-**3**, *trans*-**1** (3)
trans-**3**	6	*trans*-**4**, *tra*ns-**3**, *e*	1,2/18,36/43,44/48,49	I, *e*I^1, IV*^{3}, III*^{4}	*trans*-**3**, *trans*-**2**
	7	*cis*-**1**, *trans*-**2**, *trans*-**1**	1,2/3,4/53,54/55,60	I, II^1, II*^{2}, I*	*trans*-**3**, *trans*-**1** (1)
	8	*cis*-**2**, *cis*-**2**, *trans*-**1**	1,2/7,21/13,30/55,60	I, III^1, III^3, I*	*trans*-**3**, *trans*-**1** (2)
	9	*cis*-**3**, *trans*-**4**, *trans*-**1**	1,2/19,20/33,50/46,47	I, IV^2, III*^{1}, IV*^{4}	*trans*-**3**, *trans*-**1** (3)
trans-**2**	10	*cis*-**2**, *trans*-**3**, *trans*-**1**	1,2/7,21/33,50/55,60	I, III^1, III*^{1}, I*	*trans*-**2**, *trans*-**1**

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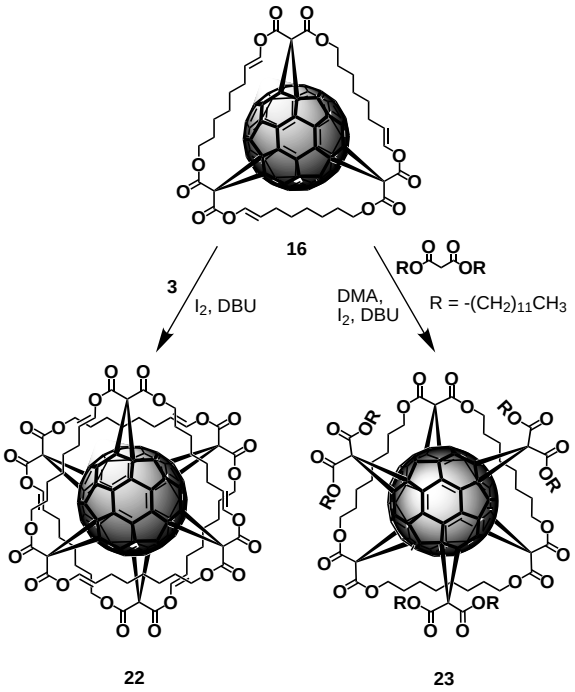
Hexaadducts: The adducts produced by the reaction of C_{60} with one macrocycle unit can be further derivatized either by reaction with other macrocycles or untethered malonates. For example, the trisadduct **16** can be treated with another equivalent of *cyclo*-[3]-octylmalonate **3** as well as with an excess of didodecylmalonate under template activation conditions with 9,10-dimethylanthracene (DMA)[26] to produce the two hexaadducts **22** and **23** (Scheme 6).



Scheme 6. Synthesis of the hexaadducts **22** and **23**.

The ^{13}C NMR spectra of **22** and **23** are depicted in Figure 12. The C_3-symmetric hexaadduct **23** shows 15 signals, one with double intensity, for the 16 different sp^2 carbons of the fullerene cage. The number of all the other signals is also in accordance with this symmetry.

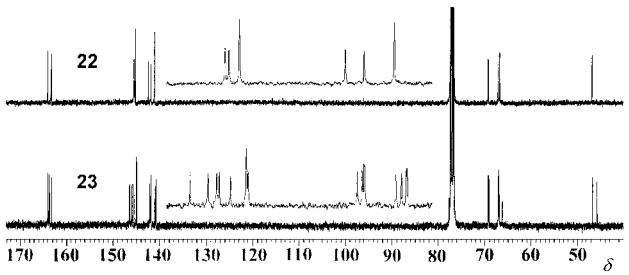


Figure 12. Comparison of the ^{13}C NMR spectra of the hexaadducts **22** and **23**.

The UV spectrum of **23** is identical to that of normal T_h-symmetric hexaadducts.[27] The same is true of the hexaadduct **22**, but instead of two signals in the sp^2 region of the ^{13}C NMR spectrum, six signals are observed, two of them with double intensity. The reason for this effect is the symmetry lowering from T_h to C_{3i} caused by the tether chains. For a hexaadduct of this point group, eight signals of the same intensity are expected in the sp^2 region (Figure 13): all symmetry-equivalent carbon atoms are shown in the same color. The signals are divided into two groups, one consists of the signals for the carbons α to the sp^3 carbons (sets 1, 4, 5, and 7) and the other one of the signals for the β carbons (sets 2, 3, 6, and 8). The same principle holds true for the sp^2 signals of **23**, the only difference is the double signal set as consequence of the lower symmetry.

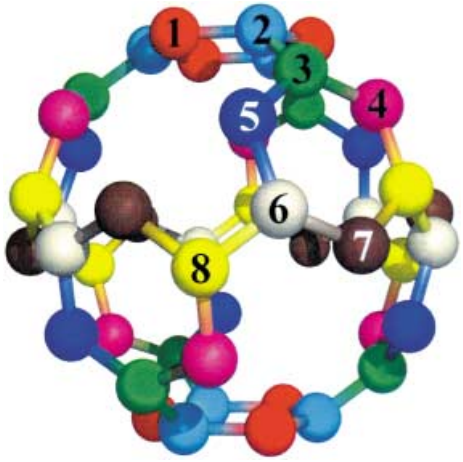
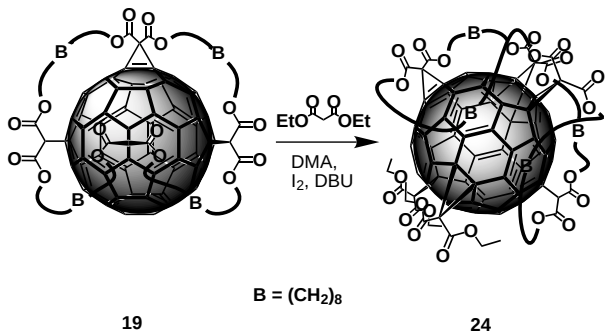


Figure 13. Sets of symmetry-equivalent sp^2 carbon atoms in the hexaadduct **22**.

To prove the structure of the *trans*-1,*e*′,*e*″ tetraadduct **19** unambiguously, compound **19** was treated with an excess of diethylbromomalonate and DBU under template activation conditions to yield the hexaadduct **24** (Scheme 7). The reaction proceeds very smoothly and the product can be isolated in pure form by simple flash chromatography.



Scheme 7. Synthesis of the mixed hexaadduct **24**.

Although the ^{13}C NMR spectrum of **24** still shows C_1 symmetry, a "clustering" of the sp^2 carbon signals into two groups at $\delta \approx 141$ and 146 (the signal positions of a normal T_h-symmetric hexaadduct) as in the spectra of **22** and **23** takes place, indicating the formation of an octahedral hexaaddition pattern (Figure 14). For a C_1-symmetric addition pattern, 48 signals are expected in the sp^2 region. In the cluster around $\delta = 146$, 19 signals are found, three of them with double and one with threefold intensity, which corresponds to 24 carbon

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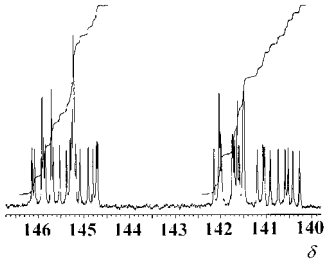

Figure 14. The sp^2 region of the ^{13}C NMR spectrum of **24**.

atoms. The cluster around $\delta = 141$ contains 21 resolved signals with three of double intensity, and thus also corresponding to 24 carbons. Figure 14 also shows the integral curves of both clusters, which have exactly the same height. The UV spectrum of **24** is characteristic for a hexaadduct containing a local T_h-symmetrical addition pattern and therefore unambiguously corroborates the structure assignment.[27]

Conclusion

With the *cyclo*-[*n*]-octylmalonates **2**–**5** we have introduced a new concept for the tether-directed multifunctionalization of C_{60}. As a result of the identical spacer lengths in these macrocycles, only bis- and trisadducts with rotational symmetry are formed. Reactions with these tether systems usually proceed with a very high degree of regioselectivity and very good yields, which has been demonstrated by several examples ranging from bis- to tetraadducts. In many cases, the only byproduct is some polymeric material that does not move on silica gel. Furthermore, this approach is highly flexible and allows a very exact fine tuning of the addend system, so that it is possible to address alternative addition patterns by simple variation of the macrocyclic ring size. The very regioselective formation of adducts with C_s-symmetric addition patterns is also possible by this method, when mixed *cyclo*-[*n*]-alkylmalonates with different spacer lengths are used, as has been demonstrated by the isolation of the *cis*-2- and *e*-bisadducts. The use of *cyclo*-[*n*]-alkylmalonates with additional anchor groups on the alkyl chain, which provide an facile access to highly functionalized fullerene architectures, as well as of chiral macrocyclic malonates allowing for the diastereoselective synthesis of dissymmetric addition patterns, is currently under investigation.

Experimental Section

General: ^1H NMR and ^{13}C NMR: Jeol JNM EX 400 and Jeol JNM GX 400. MS: Finnigan MAT 900 (FAB). FT IR: Bruker Vector 22. UV/VIS: Shimadzu UV 3102 PC. Analytical HPLC: Shimadzu SIL 10 A, SPD M 10 A, CBM 10 A, LC 10 AT. Preparative HPLC: Shimadzu SIL 10 A, SPD 10 A, CBM 10 A, LC 8 A, FRC 10 A. TLC: Macherey-Nagel, Alugram Sil G/UV 254. Reagents used were commercially available reagent grade and were purified according to standard procedures.

***cyclo*-[*n*]-Octylmalonates 2–5**: In a dry 2 L round-bottomed flask equipped with a gas inlet, 500 mL dropping funnel, and magnetic stirrer, octanediol (2.00 g, 13.7 mmol, 1.00 equiv) was dissolved under argon in dry dichloromethane (1 L). Pyridine (2.16 g, 27.3 mmol, 2.22 mL, 2.00 equiv) was added to this solution. Subsequently, a solution of malonyl dichloride (3.85 g, 27.3 mmol, 2.66 mL, 2.00 equiv) in dry dichloromethane (500 mL) was added dropwise over a period of 8 h. After stirring for 2 d at room temperature, the mixture was concentrated with a rotary evaporator and filtered over a silica plug (6 × 6 cm) with CH_2Cl_2/EtOAc 90:10 to remove polymeric material and pyridine salts. The solution was evaporated, and the resulting slightly yellow crude product separated by flash chromatography on silica gel (6 × 35 cm, CH_2Cl_2/EtOAc 90:10). The order of elution was **2**, **3**, **4**, and **5**. The product fractions were evaporated to dryness to give colorless solids (**2** and **4**) or oils (**3** and **5**). Total yield of macrocycles: 30.3 %. Crystals of **2** suitable for X-ray analysis were grown from CH_2Cl_2/pentane.

Compound ***2***: Yield: 462 mg (1.08 mmol), 15.8 %; m.p. 99 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.11$ (t, $^3J(H,H) = 6.7$ Hz, 8 H), 3.33 (s, 4 H), 1.61 (tt, $^3J(H,H) = 6.7$ Hz, 8 H), 1.29 (m, 16 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 166.44, 65.49, 42.18, 29.26, 28.49, 25.83; IR (KBr): $\tilde{\nu} = 2960$, 2921, 2854, 1746, 1325, 1264, 1253, 1217, 1137, 1064, 1028, 1003, 891, 724, 675, 616, 583, 478, 469 cm^{-1}; elemental analysis calcd (%) for $(C_{11}H_{18}O_4)_n$ ((214.26)$_n$): C 61.66, H 8.47; found C 61.71, H 8.57; MS (FAB/NBA): *m*/*z*: 429 [M^+].

Compound ***3***: Yield: 251 mg (0.390 mmol), 8.6 %; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.11$ (t, $^3J(H,H) = 6.6$ Hz, 12 H), 3.33 (s, 6 H), 1.60 (tt, $^3J(H,H) = 7.2$ Hz, 12 H), 1.29 (m, 24 H); ^{13}C NMR ($CDCl_3$, 100.4 MHz): $\delta =$ 166.55, 65.43, 41.74, 28.90, 28.34, 25.57; IR (film): $\tilde{\nu} = 2933$, 2858, 1735, 1466, 1413, 1388, 1330, 1272, 1152, 1013, 666 cm^{-1}; MS (FAB, NBA): *m*/*z*: 643 [M^+].

Compound ***4***: Yield: 114 mg (0.133 mmol), 3.9 %; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.11$ (t, $^3J = 6.7$ Hz, 16 H), 3.34 (s, 8 H), 1.61 (tt, $^3J = 7.2$ Hz, 16 H), 1.30 (m, 32 H); ^{13}C NMR ($CDCl_3$, 100.4 MHz): $\delta = 166.63$, 65.51, 41.71, 29.01, 28.40, 25.67; IR (film): $\tilde{\nu} = 2932$, 2853, 1747, 1730, 1466, 1406, 1346, 1315, 1273, 1227, 1194, 1165, 1063, 1026, 956, 666 cm^{-1}; MS (FAB, NBA): *m*/*z*: 857 [M^+].

Compound ***5***: Yield: 59.1 mg (0.0552 mmol), 2.0 %; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.08$ (t, $^3J = 6.7$ Hz, 20 H), 3.32 (s, 10 H), 1.59 (tt, $^3J = 7.1$ Hz, 20 H), 1.27 (m, 40 H); ^{13}C NMR ($CDCl_3$, 100.4 MHz): $\delta = 166.55$, 65.43, 41.60, 28.93, 28.34, 25.59; IR (film): $\tilde{\nu} = 2933$, 2858, 1731, 1466, 1412, 1388, 1331, 1273, 1151, 1013, 879, 725, 666 cm^{-1}; MS (FAB, NBA): *m*/*z*: 1071 [M^+].

***cyclo*-[2]-Dodecylmalonate (6)**: Synthesis and separation were analogous to those of the *cyclo*-[2]-octylmalonate. Yield: 640 mg (1.12 mmol, 8 %). Colorless solid; m.p. 117 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.11$ (t, $^3J(H,H) = 6.6$ Hz, 8 H), 3.33 (s, 4 H), 1.61 (tt, $^3J(H,H) = 6.6$ Hz, 8 H), 1.29 (m, 32 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 166.53$, 65.60, 42.11, 29.65, 29.62, 29,31, 28.51, 25.87; IR (KBr): $\tilde{\nu} = 2959$, 2917, 2851, 1743, 1477, 1326, 1263, 1234, 1216, 1138, 1066, 1050, 1035, 1022, 1007, 984, 892, 718, 616, 583, 419 cm^{-1}; MS (FAB/NBA): *m*/*z*: 541 [M^+];elemental analysis calcd (%) for $C_{30}H_{52}O_8$ (540.73): C 66.64, H 9.69; found C 66.17, H 9.53.

***cyclo*-[2]-Hexadecylmalonate (7)**: Synthesis and separation were analogous to those of the cyclo-[2]-octylmalonate. Yield: 73.4 mg (0.075 mmol, 6 %). Colorless solid; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.08$ (t, $^3J(H,H) =$ 6.4 Hz, 8 H), 3.21 (s, 4 H), 1.57 (tt, $^3J(H,H) = 6.8$ Hz, 8 H), 1.29 (m, 48 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.02$, 66.44, 36.90, 30.40, 30.37, 30.33, 30.28, 30.05, 29.93, 26.51; IR (KBr): $\tilde{\nu} = 2961$, 2920, 2853, 1744, 1477, 1332, 1263, 1217, 1138, 1099, 1022, 975, 910, 892, 852, 802, 720. 676, 616, 584, 470 cm^{-1}; MS (FAB/NBA): *m*/*z*: 653 [M^+].

***cyclo*-[3]-Tetradecylmalonate (8)**: Synthesis and separation were analogous to those of the cyclo-[2]-octylmalonate. Yield: 52.3 mg (0.06 mmol, 8 %). Colorless solid; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.14$ (t, $^3J(H,H) =$ 6.8 Hz, 12 H), 3.36 (s, 6 H), 1.63 (tt, $^3J(H,H) = 6.8$ Hz, 12 H), 1.37–1.24 (m, 60 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 166.56$, 65.61, 42.08, 29.72, 29.66, 29.60, 29.30, 28.51, 25.87; IR (KBr): $\tilde{\nu} = 2959$, 2917, 2851, 1740, 1479, 1326, 1263, 1216, 1137, 1066, 1053, 1035, 1020, 1007, 984, 892, 718, 616, 585 cm^{-1}; MS (FAB/NBA): *m*/*z*: 896 [M^+].

***cyclo*-[2]-Octyl-tetradecylmalonate (10)**: In a dry 2 L round-bottomed flask equipped with a gas inlet, 500 mL dropping funnel, and magnetic stirrer, octanediol (322 mg, 2.2 mmol, 1.00 equiv) and tetradecanediol (500 mg, 2.2 mmol, 1.00 equiv) were dissolved under argon in dry dichloromethane (1 L). Pyridine (418 mg, 5.2 mmol, 0.43 mL, 2.40 equiv) was added to this solution. Subsequently, a solution of malonyl dichloride (744 mg, 5.3 mmol, 0.51 mL, 2.40 equiv) in dry dichloromethane (500 mL) was added dropwise over a period of 8 h. After stirring for 2 d at room temperature, the mixture was concentrated with a rotary evaporator and

filtered over a silica plug (6 × 6 cm) with CH_2Cl_2/EtOAc 95:5 to remove polymeric material and pyridine salts. The solution was evaporated, and the resulting slightly yellow crude product separated by flash chromatography on silica gel (6 × 35 cm, CH_2Cl_2/EtOAc 95:5). The product eluted as the third fraction with the other fractions being *cyclo*-[2]-octylmalonate (**2**) and *cyclo*-[2]-tetradecylmalonate (**8**). The product was evaporated to dryness to give a colorless solid. Yield: 112.7 mg (0.22 mmol, 10%). Crystals of **10** suitable for X-ray analysis were grown from CH_2Cl_2/pentane. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.14$ (m, 8H), 3.35 (s, 4H), 1.62 (m, 8H), 1.31–1.25 (m, 28H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 166.51$, 166.48, 65.53, 65.47, 41.95, 29.38, 29.30, 29.28, 29.10, 29.02, 28.46, 28.43, 28.38, 25.78, 25.72; IR (KBr): $\tilde{\nu} = 2994$, 2952, 2914, 2851, 1754, 1733, 1476, 1412, 1319, 1287, 1217, 1164, 1080, 1049, 1030, 982, 954, 889, 861, 833, 790, 774, 718, 689, 607, 585, 571, 491, 455, 424 cm^{-1}; MS (FAB/NBA): m/z: 513 [M^+].

***cyclo*-[2]-Butyl-octylmalonate (9)**: Synthesis and separation were analogous to those of compound **10**. Yield: 48.0 mg (0.13 mmol/3.3%). Highly viscous oil; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.17$ (m, 8H), 3.37 (s, 4H), 1.74 (m, 4H), 1.64 (m, 4H), 1.32 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 166.44$, 166.39, 65.38, 65.00, 42.00, 28.59, 28.25, 25.48, 25.21; IR (KBr): $\tilde{\nu} = 2996$, 2950, 2911, 2848, 1757, 1728, 1476, 1411, 1320, 1287, 1219, 1160, 1081, 1049, 1035, 980, 955, 889, 863, 831, 790, 771, 719, 689, 605, 587, 573, 493, 455, 422 cm^{-1}; MS (FAB/NBA): m/z: 373 [M^+].

***trans*-3-(*cyclo*-[2]-Dodecylmalonyl)tetrahydro[60]fullerene (11)**: In a dry 100 mL three-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (50 mg, 0.069 mmol, 1.1 equiv) was dissolved under argon in dry toluene (50 mL). Subsequently, the macrocycle **6** (34 mg, 0.063 mmol, 1.0 equiv) and iodine (32 mg, 0.13 mmol, 2.0 equiv) were added to the solution followed by the dropwise addition of a solution of DBU (38 mg, 0.25 mmol, 4.0 equiv, 38 μL) in dry toluene (20 mL) over a period of 1.5 h. After additional stirring at room temperature for ≈10 min, the raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). The bisadduct **11** was eluted with toluene. Precipitation from CH_2Cl_2/pentane yielded 44.4 mg (0.0353 mmol, 56%) of **11**. Brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.76$ (m, 2H), 4.54 (m, 2H), 4.31 (m, 4H), 1.80–0.90 (m, 40H); ^{13}C NMR ($CDCl_3$, 400 MHz): $\delta = 164.42$ (2C, C=O), 163.40 (2C, C=O), 147.26 (2C), 147.05 (2C), 147.01 (2C), 146.75 (2C), 146.67 (2C), 146.47 (2C), 146.33 (2C), 146.26 (4C), 145.45 (2C), 145.23 (2C), 145.09 (2C), 144.61 (2C), 144.23 (2C), 144.09 (2C), 143.83 (2C), 143.45 (4C), 143.29 (2C), 142.76 (2C), 142.41 (2C), 141.83 (2C), 141.54 (2C), 141.41 (2C), 141.35 (2C), 140.20 (2C), 139.02 (2C), 138.37 (2C), 71.71 (2C, sp^3), 71.63 (2C, sp^3), 67.94 (2C, O-*C*H$_2$), 67.74 (2C, O-*C*H$_2$), 53.22 (2C, quart), 30.16 (2C, alkyl), 30.03 (2C, alkyl), 29.64 (2C, alkyl), 29.54 (2C, alkyl), 29.42 (2C, alkyl), 29.39 (2C, alkyl), 28.86 (2C, alkyl), 28.84 (2C, alkyl), 27.40 (2C, alkyl), 26.85 (2C, alkyl); IR (KBr): $\tilde{\nu} = 2924$, 2851, 1753, 1729, 1462, 1430, 1388, 1231, 1213, 1176, 1104, 1064, 709, 529, 522 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 249 (110000), 297 (45000), 411 (3900), 422 (3200), 485 nm (2900 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): m/z: 1257 [M^+], 720 [C_{60}^+].

Reaction of C_{60} with macrocycle 7 to give *trans*-3-(*cyclo*-[2]-hexadecylmalonyl)tetrahydro[60]fullerene (12) and *trans*-1-(*cyclo*-[2]-hexadecylmalonyl)tetrahydro[60]fullerene (13): In a dry 100 mL two-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (43.2 mg, 0.06 mmol, 1.0 equiv) was dissolved in toluene (50 mL) under argon. Subsequently, the macrocycle **7** (39.2 mg, 0.06 mmol, 1.0 equiv) and iodine (38.0 mg, 0.15 mmol, 2.5 equiv) were added followed by the dropwise addition of a solution of DBU (36.5 mg, 0.24 mmol, 35.9 μL, 4 equiv) in dry toluene (20 mL) over a period of 1 h. The solution was stirred at room temperature for 2 d. The raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). The bisadducts were eluted with toluene. Precipitation from CS_2/pentane yielded 10.6 mg (0.0083 mmol, 12.9%) of **12** and 7.5 mg (0.0059 mmol, 9.1%) of **13** as brown and olive-green solids, respectively.

*Compound **12***: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.78$ (m, 2H), 4.52 (m, 2H), 4.40 (m, 4H), 1.84–0.88 (m, 56H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 164.02 (2C, C=O), 163.73 (2C, C=O), 147.08 (2C), 146.98 (2C), 146.90 (2C), 146.61 (2C), 146.42 (2C), 146.33 (4C), 146.20 (2C), 145.59 (2C), 145.35 (2C), 144.56 (2C), 144.38 (2C), 144.14 (2C), 143.87 (2C), 143.57 (2C), 143.51 (4C), 143.38 (2C), 143.06 (4C), 142.51 (2C), 142.35 (2C), 142.31 (2C), 141.86 (2C), 141.58 (2C), 140.43 (2C), 138.29 (2C), 137.47 (2C), 71.91 (2C, sp^3), 71.54 (2C, sp^3), 67.43 (2C, O-*C*H$_2$), 66.83, (2C, O-*C*H$_2$), 52.95, (2C, quart), 29.61, 29.50, 29.43, 29.28, 29.25, 29.18, 28.84, 28.66, 28.60, 28.39, 26.10, 25.76; IR (KBr): $\tilde{\nu} = 2924$, 2851, 1753, 1729, 1462, 1430, 1388, 1231, 1213, 1176, 1104, 1064, 709, 529, 522 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 248 (85000), 275 (49000), 317 (28000), 377 (7500), 412 (3000), 423 (2500), 485 nm (2000 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): m/z: 1369 [M^+], 720 [C_{60}^+].

*Compound **13***: ^{1}H NMR (CS_2/$CDCl_3$, 400 MHz): $\delta = 4.59$ (t, ^3J(H,H) = 5.5 Hz, 8H), 1.86 (tt, ^3J(H,H) = 4.9 Hz, 8H), 1.49 (tt, ^3J(H,H) = 7.7 Hz, 8H), 1.30–1.13 (m, 36H), 0.90 (t, ^3J(H,H) = 7.2 Hz, 4H); ^{13}C NMR (CS_2/$CDCl_3$, 100 MHz): $\delta = 163.48$ (4C, C=O), 145.02 (4C), 144.93 (8C), 144.50 (8C), 143.86 (8C), 143.35 (4C), 143.17 (8C), 141.00 (8C), 138.23 (8C), 69.99 (4C, sp^3), 67.16 (4C, O-*C*H$_2$), 35.39 (2C, quart), 30.55 (4C, alkyl), 30.28 (4C, alkyl), 30.20 (4C, alkyl), 30.01 (4C, alkyl), 29.90 (4C, alkyl), 29.19 (4C, alkyl), 27.17 (4C, alkyl); IR (KBr): $\tilde{\nu} = 2923$, 2852, 1743, 1637, 1457, 1384, 1232, 1209, 1093, 1061, 1032, 864, 810, 738, 702, 672, 573, 544, 524 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 237 (92500), 254 (75500), 318 (4100), 442 (3300), 472 nm (3900 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): m/z: 1369 [M^+], 720 [C_{60}^+].

***cis*-2-(*cyclo*-[2]-Butyl-octylmalonyl)tetrahydro[60]fullerene (14)**: In a dry 100 mL two-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (94.0 mg, 0.13 mmol, 1.0 equiv) was dissolved in toluene (50 mL) under argon. Subsequently, the macrocycle **9** (48.0 mg, 0.13 mmol, 1.0 equiv) and iodine (66.0 mg, 0.26 mmol, 2 equiv) were added followed by the dropwise addition of a solution of DBU (79.0 mg, 0.52 mmol, 78.0 μL, 4 equiv) in dry toluene (20 mL) over a period of 1 h. The solution was stirred at room temperature for 2 d. The raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). The bisadduct was eluted with toluene. Precipitation from toluene/pentane yielded 55.1 mg (0.0505 mmol, 39%) of **14** as a dark red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.68$ (m, 2H), 4.41 (m, 6H), 2.09–1.26 (m, 16H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 163.65$ (2C, C=O), 163.50 (2C, C=O), 149.3 (2C), 147.4 (2C), 147.4 (2C), 147.3 (2C), 146.8 (2C), 146.2 (2C), 145.9 (2C), 145.8 (2C), 145.3 (2C), 145.3 (2C), 145.0 (2C), 145.0 (2C), 144.7 (2C), 144.5 (2C), 144.4 (2C), 144.3 (2C), 144.1 (2C), 143.7 (2C), 143.6 (2C), 143.4 (2C), 142.5 (2C), 142.4 (2C), 141.2 (2C), 141.0 (2C), 139.1 (2C), 137.5 (2C), 136.2 (2C), 136.1 (2C), 70.69 (4C, sp^3), 67.49 (1C, O-*C*H$_2$), 67.43 (1C, O-*C*H$_2$), 66.60 (2C, O-*C*H$_2$), 50.90 (2C, quart), 28.27 (2C, alkyl), 27.69 (2C, alkyl), 26.71 (2C, alkyl), 24.74 (2C, alkyl); IR (KBr): $\tilde{\nu} = 923$, 2853, 2334, 1944, 1749, 1731, 1458, 1389, 1262, 1230, 1210, 1174, 1099, 1059, 1019, 953, 905, 807, 730, 704, 646, 580, 551, 526 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (86000), 273 (57000), 322 (25000), 346 (14000), 371 (9000), 382 (8000), 438 (2300), 465 nm (1900 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): m/z: 1089 [M^+], 720 [C_{60}^+].

***e*-(*cyclo*-[2]-Octyl-tetradecylmalonyl)tetrahydro[60]fullerene (15)**: In a dry 100 mL two-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (86.5 mg, 0.12 mmol, 1.0 equiv) was dissolved in toluene (50 mL) under argon. Subsequently, the macrocycle **10** (60.0 mg, 0.12 mmol, 1.0 equiv) and iodine (60.9 mg, 0.24 mmol, 2 equiv) were added followed by the dropwise addition of a solution of DBU (73.1 mg, 0.48 mmol, 72.1 μL, 4 equiv) in dry toluene (20 mL) over a period of 1 h. The solution was stirred at room temperature for 2 d. The raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). The bisadduct was eluted with toluene. Precipitation from toluene/pentane yielded 75.2 mg (0.0612 mmol, 51.1%) of **15** as a dark red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.82$ (m, 1H), 4.73 (m, 1H), 4.64 (m, 1H), 4.56 (m, 1H), 4.36 (m, 1H), 4.29 (m, 1H), 4.23 (m, 1H), 4.18 (m, 1H), 1.77–1.10 (m, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 164.35$ (1C, C=O), 163.23 (1C, C=O), 163.12 (1C, C=O), 163.00 (1C, C=O), 148.8 (1C), 147.9 (1C), 147.1 (1C), 146.4 (1C), 146.3 (1C), 146.3 (1C), 146.1 (1C), 146.0 (1C), 145.9 (1C), 145.5 (3C), 145.2 (3C), 145.1 (1C), 145.0 (1C), 145.0 (1C), 144.9 (1C), 144.7 (3C), 144.6 (3C), 144.5 (1C), 144.3 (1C), 144.2 (1C), 144.1 (1C), 144.0 (1C), 143.9 (1C), 143.8 (1C), 143.7 (1C), 143.6 (1C), 143.6 (1C), 143.5 (1C), 143.4 (1C), 143.3 (1C), 143.3 (1C), 143.2 (1C), 143.0 (1C), 143.0 (1C), 141.9 (1C), 141.9 (1C), 141.8 (1C), 141.7 (1C), 141.6 (1C), 141.6 (1C), 141.4 (1C), 140.9 (1C), 139.4 (1C), 139.3 (1C), 138.7 (1C), 138.4 (1C), 71.95 (2C, sp^3), 71.84 (2C, sp^3), 67.94 (1C, O-*C*H$_2$), 67.88 (1C, O-*C*H$_2$), 67.09 (1C, O-*C*H$_2$), 66.50 (1C, O-*C*H$_2$), 54.22 (1C, quart), 52.51 (1C, quart), 30.64, 30.33, 29.70, 29.48, 29.36, 29.23, 29.04, 28.82, 28.45, 27.60, 27.31, 26.57, 26.40, 25.90; IR (KBr): $\tilde{\nu} = 2994$, 2952, 2914, 2851, 1754, 1733, 1476, 1412, 1319, 1287, 1217, 1164, 1080, 1049, 1030, 982, 954, 889, 861, 833, 790, 774, 718, 689, 607, 585, 571, 491, 455, 424 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 (85000), 282 (49000), 313 (32000), 360 (12000), 398 (3500), 421

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(2200), 475 nm (2600 $mol^{-1}dm^3cm^{-1}$); MS (FAB, NBA): *m/z*: 1229 [M^+], 720 [C_{60}^+].

Reaction of C_{60} with macrocycle 3 to give *e*,*e*,*e*-(*cyclo*-[3]-octylmalonyl)-hexahydro[60]fullerene (16) and *trans*-4,*trans*-4,*trans*-4-(*cyclo*-[3]-octylmalonyl)hexahydro[60]fullerene (17): In a dry 1 L three-necked flask equipped with a gas inlet, 250 mL dropping funnel, and magnetic stirrer, C_{60} (255 mg, 0.354 mmol, 1.0 equiv) was dissolved under argon in dry toluene (400 mL). Subsequently, the macrocycle **3** (205 mg, 0.319 mmol, 0.9 equiv) and iodine (243 mg, 0.956 mmol, 2.7 equiv) were added to the solution followed by the dropwise addition of a solution of DBU (404 mg, 2.65 mmol, 7.5 equiv, 397 μL) in dry toluene (160 mL) over a period of 3 h. The color of the solution turned to deep orange. After additional stirring at room temperature for about 10 min, the raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). Traces of C_{60} and other impurities were eluted with toluene, then the eluent was changed to toluene/ethyl acetate 98:2 and the trisadducts **16** and **17** were eluted together as a bright orange band. Compounds **16** and **17** were separated by preparative HPLC on Nucleosil (toluene/ethyl acetate 98:2). Precipitation from CH_2Cl_2/pentane yielded 174.0 mg (0.128 mmol, 40.2 %) of **16** (orange solid) and 8.8 mg (0.0065 mmol, 2.0 %) of **17** (olive-green solid).

*Compound **16***: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.71$ (m, 6H), 4.12 (m, 3H), 4.01 (m, 3H), 1.78 (m, 3H), 1.56 (m, 12H), 1.37 (m, 3H), 1.19 (m, 18H), 0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 162.87$ (3C, C=O), 162.63 (3C, C=O), 147.94 (3C), 146.69 (3C), 146.60 (3C), 146.56 (3C), 146.39 (3C), 146.37 (3C), 146.33 (3C), 145.61 (3C), 145.59 (3C), 144.49 (3C), 144.45 (3C), 143.83 (3C), 143.66 (3C), 142.76 (3C), 142.56 (3C), 141.79 (3C), 141.08 (3C), 140.95 (3C), 71.30 (3C, sp^3), 70.62 (3C, sp^3), 67.16 (3C, O-*C*H_2), 66.41 (3C, O-*C*H_2), 54.28 (3C, quart), 29.36 (3C, alkyl), 29.19 (3C, alkyl), 29.03, (3C, alkyl), 28.94 (3C, alkyl), 26.35 (3C, alkyl), 25.71 (3C, alkyl); IR (KBr): $\tilde{\nu} = 2928$, 2855, 1747, 1458, 1384, 1273, 1254, 1233, 1214, 1178, 1104, 1065, 741, 714, 704, 528, 522 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 251 (82000), 281 (60000), 305 (44000), 380 (5900), 481 (4000), 565 nm (1300 $mol^{-1}dm^3cm^{-1}$); MS (FAB, NBA): *m/z*: 1357 [M^+], 720 [C_{60}^+].

*Compound **17***: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.55$ (m, 6H), 4.35 (m, 6H), 1.68 (m, 12H), 1.20 (m, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 164.89 (6C, C=O), 147.67 (6C), 145.58 (6C), 144.74 (6C), 143.22 (6C), 142.95 (6C), 142.49 (6C), 142.22 (6C), 141.77 (3C), 140.08 (6C), 134.78 (6C), 71.29 (3C, sp^3), 70.54 (3C, sp^3), 67.73 (6C, O-*C*H_2), 50.48 (3C, quart), 29.12 (6C, alkyl), 28.79 (6C, alkyl), 26.13 (6C, alkyl); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (100000), 262 (73000), 294 (47000), 313 (35000), 349 (17000), 447 (2900), 463 (3100), 526 (1200), 564 (830), 624 (670), 690 nm (520 $mol^{-1}dm^3cm^{-1}$); MS (FAB, NBA): *m/z*: 1357 [M^+], 720 [C_{60}^+].

***trans*-3,*trans*-3,*trans*-3-(*cyclo*-[3]-Tetradecylmalonyl)hexahydro[60]fullerene (18)**: In a dry 100 mL two-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (44.7 mg, 0.06 mmol, 1.0 equiv) was dissolved in toluene (50 mL) under argon. Subsequently, the macrocycle **8** (50.0 mg, 0.06 mmol, 1.0 equiv) and iodine (42.5 mg, 0.17 mmol, 2.7 equiv) were added, followed by the dropwise addition of a solution of DBU (72.0 mg, 0.47 mmol, 69.5 μL, 7.5 equiv) in dry toluene (20 mL) over a period of 1 h. The solution was stirred at room temperature for 2 d. The raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). The trisadduct was eluted with toluene. Precipitation from CH_2Cl_2/pentane yielded 29.9 mg (0.0181 mmol, 29.9 %) of **18** as a red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.59$ (t, ^3J(H,H) = 5.5 Hz, 8H), 1.86 (tt, ^3J(H,H) = 4.9 Hz, 8H), 1.49 (tt, ^3J(H,H) = 7.7 Hz, 8H), 1.30–1.13 (m, 44H), 0.90 (t, ^3J(H,H) = 7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 163.48$ (4C, C=O), 145.02 (4H), 144.93 (8H), 144.50 (8H), 143.86 (8H), 143.35 (4H), 143.17 (8H), 141.00 (8H), 138.23 (8H), 69.99 (4C, sp^3), 67.16 (4C, O-CH_2), 35.39 (2C, quart), 30.55 (4C, alkyl), 30.28 (4C, alkyl), 30.20 (4C, alkyl), 30.01 (4C, alkyl), 29.90 (4C, alkyl), 29.19 (4C, alkyl), 27.17 (4C, alkyl); IR (KBr): $\tilde{\nu} = 2922$, 2850, 1742, 1637, 1457, 1432, 186, 1253, 1230, 1210, 1176, 1103, 1062, 1034, 813, 709, 671, 572, 544, 528 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 240 (78000), 295 (36000), 399 (3400), 473 (2600), 556 (1100), 630 nm (240 $mol^{-1}dm^3cm^{-1}$); MS (FAB, NBA): *m/z*: 1611 [M^+], 720 [C_{60}^+].

Reaction of C_{60} with macrocycle 4 to give *trans*-1,*e*′,*e*″-(*cyclo*-[4]-octylmalonyl)octahydro[60]fullerene (19) and *trans*-4,*trans*-3,*e*-(*cyclo*-[4]-octylmalonyl)octahydro[60]fullerene (20): In a dry 250 mL three-necked flask equipped with a gas inlet, 100 mL dropping funnel, and magnetic stirrer, C_{60} (119 mg, 0.164 mmol, 1.0 equiv) was dissolved under argon in dry toluene (400 mL). Subsequently, the macrocycle **4** (141 mg, 0.164 mmol, 1.0 equiv) and iodine (167 mg, 0.658 mmol, 4.0 equiv) were added to the solution, followed by the dropwise addition of a solution of DBU (250 mg, 1.64 mmol, 10 equiv, 246 μL) in dry toluene (50 mL) over a period of 1.5 h. After additional stirring at room temperature for 2 d, the raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). Traces of impurities were eluted with toluene, then the eluent was changed to toluene/ethyl acetate 95:5 and the tetraadducts **19** and **20** were eluted together as a bright orange band. Compounds **19** and **20** were separated by preparative HPLC on Nucleosil (toluene/ethyl acetate 98:2). Precipitation from CH_2Cl_2/pentane yielded 67.0 mg (0.0427 mmol, 26.0 %) of **19** and 14.9 mg (0.00949 mmol, 5.8 %) of **20** as bright orange (**19**) and olive-green (**20**) solids.

*Compound **19***: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.73$ (m, 4H), 4.44 (m, 4H), 4.33 (m, 1H), 4.17 (m, 6H), 3.98 (m, 1H), 1.85 (m, 1H), 1.71 (m, 8H), 1.57 (m, 8H), 1.44 (m, 1H), 1.23 (m, 28H), 0.97 (m, 1H), 0.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 164.69$ (1C, C=O), 163.88 (1C, C=O), 163.77 (1C, C=O), 163.71 (1C, C=O), 163.34 (1C, C=O), 163.31 (1C, C=O), 162.74 (1C, C=O), 162.55 (1C, C=O), 147.59 (1C), 147.50 (1C), 147.42 (1C), 147.38 (1C), 147.29 (1C), 147.25 (1C), 146.90 (1C), 146.87 (1C), 146.79 (1C), 146.61 (2C), 146.55 (1C), 146.47 (1C), 146.37 (1C), 146.08 (1C), 146.01 (1C), 145.86 (1C), 145.46 (1C), 145.41 (1C), 145.38 (2C), 145.29 (1C), 145.14 (1C), 145.02 (1C), 144.51 (1C), 144.49 (1C), 144.45 (1C), 144.42 (1C), 144.37 (1C), 144.09 (1C), 144.06 (1C), 143.84 (1C), 143.76 (1C), 143.68 (1C), 143.54 (1C), 143.30 (1C), 143.25 (2C), 143.03 (1C), 142.33 (1C), 142.30 (1C), 142.25 (1C), 142.19 (1C), 142.10 (1C), 142.05 (1C), 141.98 (1C), 141.61 (1C), 141.43 (1C), 139.97 (1C), 139.93 (1C), 139.77 (1C), 139.42 (1C), 70.95 (1C, sp^3), 70.79 (1C, sp^3), 70.69 (1C, sp^3), 70.44 (1C, sp^3), 69.77 (1C, sp^3), 69.51 (1C, sp^3), 69.24 (1C, sp^3), 68.76 (1C, sp^3), 67.44 (1C, O-*C*H_2), 67.21 (1C, O-*C*H_2), 67.15 (2C, O-*C*H_2), 67.07 (1C, O-*C*H_2), 67.00 (1C, O-*C*H_2), 66.91 (1C, O-*C*H_2), 66.43 (1C, O-*C*H_2), 55.36 (1C, quart), 54.01 (1C, quart), 46.72 (1C, quart), 46.61 (1C, quart), 29.24 (1C, alkyl), 29.22 (1C, alkyl), 29.18 (1C, alkyl), 29.03 (2C, alkyl), 29.00 (2C, alkyl), 28.79 (1C, alkyl), 28.70 (1C, alkyl), 28.62 (1C, alkyl), 28.53 (1C, alkyl), 28.50 (1C, alkyl), 28.47 (1C, alkyl), 28.36 (2C, alkyl), 28.08 (1C, alkyl), 26.28 (1C, alkyl), 26.18 (1C, alkyl), 26.15 (1C, alkyl), 26.07 (1C, alkyl), 26.03 (1C, alkyl), 25.92 (2C, alkyl), 25.72 (1C, alkyl); IR (KBr): $\tilde{\nu} =$ 2930, 2855, 1748, 1460, 1388, 1353, 1253, 1215, 1172, 1107, 1075, 1020, 993, 709, 667, 526 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (98000), 285 (73000), 346 (18000), 373 (7600), 423 (3800), 498 (3200), 543 nm (2000 $mol^{-1}dm^3cm^{-1}$); MS (FAB, NBA): *m/z*: 1570 [M^+], 720 [C_{60}^+].

*Compound **20***: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.74$ (m, 4H), 4.59 (m, 2H), 4.28 (m, 10H), 1.87 (m, 2H), 1.69 (m, 11H), 1.51 (m, 5H), 1.34 (m, 15H), 1.19 (m, 15H); ^{13}C ($CDCl_3$, 100 MHz): $\delta = 164.80$ (2C, C=O), 164.61 (2C, C=O), 163.75 (2C, C=O), 163.32 (2C, C=O), 147.51 (2C), 147.01 (2C), 146.99 (2C), 146.91 (2C), 146.46 (2C), 146.09 (2C), 146.03 (2C), 145.43 (2C), 145.16 (2C), 144.50 (2C), 144.14 (2C), 144.08 (2C), 143.58 (2C), 142.99 (2C), 142.87 (2C), 142.59 (2C), 142.23 (2C), 141.84 (2C), 140.59 (2C), 140.09 (2C), 139.93 (2C), 139.75 (2C), 139.69 (2C), 139.19 (2C), 139.15 (2C), 135.49 (2C), 72.04 (2C, sp^3), 71.72 (2C, sp^3), 71.54 (2C, sp^3), 69.81 (2C, sp^3), 67.77 (2C, O-*C*H_2), 67.62 (2C, O-*C*H_2), 67.15 (2C, O-*C*H_2), 67.10 (2C, O-*C*H_2), 52.43 (2C, quart), 48.46 (2C, quart), 29.20 (2C, alkyl), 29.17 (2C, alkyl), 29.13 (2C, alkyl), 29.04 (2C, alkyl), 28.87 (4C, alkyl), 28.83 (2C, alkyl), 28.76 (2C, alkyl), 26.28 (2C, alkyl), 26.12 (2C, alkyl), 26.08 (2C, alkyl), 26.04 (2C, alkyl); IR (KBr): $\tilde{\nu} = 2929$, 2855, 1749, 1726, 1460, 1389, 1294, 1273, 1225, 1174, 1114, 1073, 992, 705, 669, 548, 519 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (110000), 274 (70000), 287 (67000), 386 (7600), 412 (4300), 464 (4100), 599 (910), 673 nm (160 $mol^{-1}dm^3cm^{-1}$); MS (FAB, NBA): *m/z*: 1570 [M^+], 720 [C_{60}^+].

***cis*-3,*trans*-3,*trans*-2-Bis(*cyclo*-[2]-dodecylmalonyl)octahydro[60]fullerene (21)**: In a dry 100 mL three-necked flask equipped with a gas inlet, 100 mL dropping funnel, and magnetic stirrer, C_{60} (43.2 mg, 0.06 mmol, 1.0 equiv) was dissolved in toluene (50 mL) under argon. Subsequently, the macrocycle **6** (38.9 mg, 0.07 mmol, 1.2 equiv) and iodine (38.0 mg, 0.15 mmol, 2.5 equiv) were added, followed by the dropwise addition of a solution of DBU (36.5 mg, 0.24 mmol, 35.9 μL, 4 equiv) in dry toluene (20 mL) over a period of 1 h. The solution was stirred at room temperature for 2 d. The raw mixture was subjected to flash chromatography on silica gel (6 × 25 cm). Two fractions were obtained. The first consisted of the fullerene **11**, whereas the second was the fullerene **21**. Further purification by HPLC on Nucleosil was necessary (toluene/EtOAc 97:3). Precipitation from toluene/pentane yielded 5.0 mg (0.0028 mmol, 4.7 %) of **21** as a dark red solid.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.40$ (m, 16H), 1.58 (m, 32H), 1.27 (m, 48H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 165.85$ (2C, C=O), 164.59 (2C, C=O), 163.56 (2C, C=O), 163.47 (2C, C=O), 148.72 (4C), 148.52 (6C), 147.60 (6C), 147.48 (4C), 147.12 (4C), 146.46 (4C), 145.57 (4C), 144.30 (4C), 143.21 (4C), 143.02 (4C), 142.30 (4C), 141.83 (4C), 141.01 (4C), 71.88 (1C, sp^3), 71.65 (1C, sp^3), 71.55 (2C, sp^3), 67.97 (2C, O-CH_2), 67.89 (2C, O-CH_2), 67.62 (2C, O-CH_2), 67.30 (2C, O-CH_2), 53.41 (2C, quart), 52.53 (2C, quart), 30.16 (2C, alkyl), 30.01 (2C, alkyl), 29.84 (2C, alkyl), 29.75 (2C, alkyl), 29.73 (2C, alkyl), 29.67 (2C, alkyl), 29.62 (2C, alkyl), 29.59 (2C, alkyl), 29.51 (2C, alkyl), 29.46 (2C, alkyl), 29.41 (2C, alkyl), 29.38 (2C, alkyl), 29.31 (2C, alkyl), 29.28 (2C, alkyl), 29.25 (2C, alkyl), 29.21 (2C, alkyl), 28.83 (2C, alkyl), 28.69 (2C, alkyl), 28.60 (1C, alkyl), 28.43 (1C, alkyl), 28.40 (2C, alkyl), 27.43 (2C, alkyl), 26.72 (2C, alkyl), 26.05 (2C, alkyl), 25.82 (2C, alkyl), 25.78 (2C, alkyl); IR (KBr): $\tilde{\nu} = 2923$, 2852, 2055, 1741, 1637, 1460, 1432, 1384, 1225, 1178, 1108, 1062, 805, 723, 709, 529 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 241 (93500), 295 (45300), 401 (3900), 473 (3400), 559 (1500), 606 nm (500 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): *m/z*: 1793 [M^+], 720 [C_{60}^+].

***e,e,e,e,e,e,e*-Bis(*cyclo*-[3]-octylmalonyl)dodecahydro[60]fullerene (22)**: In a dry 100m L three-necked flask equipped with a gas inlet, 100 mL dropping funnel, and a magnetic stirrer, the trisadduct **16** (50.0 mg, 0.0368 mmol, 1.0 equiv) was dissolved under argon in dry toluene (50 mL). Subsequently, the macrocycle **3** (23.7 mg, 0.0368 mmol, 1.0 equiv) and iodine (28.0 mg, 0.110 mmol, 3.0 equiv) were added to the solution, followed by the dropwise addition of a solution of DBU (42 mg, 0.276 mmol, 7.5 equiv, 41.2 µL) in dry toluene (20 mL) over a period of 2 h. After additional stirring at room temperature for 5 d, the reaction mixture was quenched with HCl (200 µL, 2N), concentrated, and subjected to flash chromatography on silica gel (4 × 25 cm) with toluene/ethyl acetate 95:5 as the eluent. The column was equipped with an UV/Vis detector set at $\lambda = 320$ nm to provide a better detection of the pale yellow product band eluting after traces of the reactants. Precipitation from CH_2Cl_2/pentane yielded 10.4 mg (0.00522 mmol, 14%) of **22** as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.58$ (m, 12H), 4.17 (m, 6H), 4.06 (m, 6H), 1.75 (m, 8H), 1.59 (m, 12H), 1.35 (m, 8H), 1.21 (m, 36H), 1.01 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 163.94$ (6C, C=O), 163.25 (6C, C=O), 145.48 (6C), 145.38 (6C), 145.09 (12C), 142.31 (6C), 141.80 (6C), 141.02 (12C), 69.34 (6C, sp^3), 69.23 (6C, sp^3), 67.07 (6C, O-CH_2), 66.75 (6C, O-CH_2), 46.86 (6C, quart), 29.33 (6C, alkyl), 28.89 (6C, alkyl), 28.84 (6C, alkyl), 28.54 (6C, alkyl), 26.46 (6C, alkyl), 25.70 (6C, alkyl); IR (KBr): $\tilde{\nu} = 2931$, 2857, 1748, 1461, 1384, 1356, 1264, 1219, 1171, 1082, 994, 759, 714, 540, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 245 (94000), 272 (72000), 281 (76000), 316 (47000), 335 (38000), 383 nm (5500 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): *m/z*: 1993 [M^+].

***e,e,e,e,e,e,e*-(*cyclo*-[3]-Octylmalonyl)tris[di(dodecyloxycarbonyl)methano]-dodecahydro[60]fullerene (23)**: In a dry 100 mL three-necked flask equipped with a gas inlet, 100 mL dropping funnel, and magnetic stirrer, the trisadduct **16** (34.5 mg, 0.0254 mmol, 1.0 equiv) and dimethylanthracene (26.2 mg, 0.127 mmol, 5.0 equiv) were dissolved under argon in dry toluene (50 mL) and stirred for 2 h at room temperature. Subsequently, didodecylmalonate (33.6 mg, 0.0763 mmol, 3.0 equiv) and iodine (19.4 mg, 0.0763 mmol, 3.0 equiv) were added to the solution, followed by the dropwise addition of a solution of DBU (29.0 mg , 0.191 mmol, 7.5 equiv, 28.5 µL) in dry toluene (20 mL) over a period of 1 h. After additional stirring at room temperature for 7 d, the reaction mixture was subjected to flash chromatography on silica gel (4 × 20 cm). DMA and byproducts were eluted with toluene, the product fraction with toluene/ethyl acetate 95:5. The hexaadduct **23** was obtained in pure form by preparative HPLC on Nucleosil with toluene/ethyl acetate 99:1 as the eluent. Precipitation from CH_2Cl_2/pentane yielded 12.0 mg (0.00449 mmol, 18%) of **23** as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.64$ (m, 6H), 4.18 (m, 15H), 3.99 (m, 3H), 1.62 (m, 26H), 1.23 (m, 130H), 0.86 (t, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 163.86$ (3C, C=O), 163.71 (3C, C=O), 163.64 (3C, C=O), 163.16 (3C, C=O), 146.39 (3C), 145.91 (3C), 145.69 (3C), 145.61 (3C), 145.32 (3C), 144.90 (6C), 144.86 (3C), 141.98 (3C), 141.85 (3C), 141.80 (3C), 141.78 (3C), 140.82 (3C), 140.68 (3C), 140.66 (3C), 69.27 (3C, sp^3), 69.26 (3C, sp^3), 69.21 (3C, sp^3), 69.11 (3C, sp^3), 67.05 (3C, O-CH_2), 66.95 (6C, O-CH_2), 66.23 (3C, O-CH_2), 46.67 (3C, quart), 45.63 (3C, quart), 31.92 (6C, alkyl), 29.66 (21 C, alkyl), 29.57 (6C, alkyl), 29.37 (6C, alkyl), 29.27 (6C, alkyl), 29.19 (3C, alkyl), 28.85 (3C, alkyl), 28.80 (3C, alkyl), 28.45 (3C, alkyl), 28.41 (3C, alkyl), 26.37 (3C, alkyl), 25.85 (6C, alkyl), 25.61 (3C, alkyl), 22.69 (6C, alkyl), 14.12 (6C, alkyl); IR (KBr): $\tilde{\nu} = 2925$, 2854, 1748, 1634, 1464, 1380, 1353, 1263, 1217, 1081, 994, 760, 715, 540, 528 cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda_{max} = 245$, 272, 282, 317, 335, 378 nm; MS (FAB, NBA): *m/z*: 2673 [M^+], 720 [C_{60}^+].

***e,e,e,e,e,e,e*-(*cyclo*-[4]-Octylmalonyl)bis[di(ethoxycarbonyl)methano]-dodecahydro[60]fullerene (24)**: In a dry 100 mL three-necked flask equipped with a gas inlet and magnetic stirrer, the tetraadduct **19** (60.0 mg, 0.0382 mmol, 1.0 equiv) and dimethylanthracene (31.5 mg, 0.153 mmol, 4.0 equiv) were dissolved under argon in dry toluene (50 mL) and stirred for 2 h at room temperature. Subsequently, diethylbromomalonate (36.6 mg, 0.153 mmol, 4.0 equiv, 25.7 µL) and DBU (46.6 mg, 0.306 mmol, 8.0 equiv, 45.6 µL) were added to the solution. After additional stirring at room temperature for 1 d, the color of the reaction mixture had changed from orange to yellow. The reaction mixture was subjected to flash chromatography on silica gel (4 × 15 cm). DMA and byproducts were eluted with toluene, the hexaadduct **24** with toluene/ethyl acetate 95:5 (the column was equipped with an UV/Vis detector set at $\lambda =$ 320 nm to provide a better detection of the pale yellow product band). Precipitation from CH_2Cl_2/pentane yielded 45.9 mg (0.0244 mmol, 64%) of **24** as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.59$ (m, 4H), 4.30 (m, 14H), 4.07 (m , 6H), 1.60 (m, 16H), 1.30 (m, 12H), 1.19 (m, 27H), 0.99 (m, 4H), 0.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 164.72$ (1C, C=O), 164.54 (1C, C=O), 164.40 (1C, C=O), 163.78 (1C, C=O), 163.76 (1C, C=O), 163.65 (1C, C=O), 163.63 (1C, C=O), 163.54 (1C, C=O), 163.43 (1C, C=O), 163.38 (1C, C=O), 163.36 (1C, C=O), 163.10 (1 , C=O), 146.13 (1C), 146.07 (1C), 145.91 (2C), 145.87 (1C), 145.84 (1C), 145.71 (2C), 145.67 (1C), 145.52 (1C), 145.37 (1C), 145.30 (1C), 145.26 (1C), 145.23 (3C), 145.21 (2C), 145.17 (1C), 145.08 (1C), 144.90 (1C), 144.80 (1C), 144.72 (1C), 144.70 (1C), 142.15 (1C), 142.03 (2C), 142.01 (1C), 141.98 (1C), 141.74 (1C), 141.72 (1C), 141.69 (1C), 141.64 (2C), 141.60 (1C), 141.51 (1C), 141.50 (2C), 141.48 (1C), 141.19 (1C), 141.07 (1C), 141.03 (1C), 140.92 (1C), 140.74 (1C), 140.59 (1C), 140.53 (1C), 140.42 (1C), 140.26 (1C), 69.42 (1C, sp^3), 69.30 (1C, sp^3), 69.27 (2C, sp^3), 69.20 (1C, sp^3), 69.18 (1C, sp^3), 69.13 (1C, sp^3), 69.11 (2C, sp^3), 69.06 (1C, sp^3), 68.81 (1C, sp^3), 68.74 (1C, sp^3), 67.16 (1C, O-CH_2), 67.09 (1C, O-CH_2), 67.00 (1C, O-CH_2), 66.98 (1C, O-CH_2), 66.91 (1C, O-CH_2), 66.82 (1C, O-CH_2), 66.72 (1C, O-CH_2), 66.19 (1C, O-CH_2), 62.97 (1C, O-CH_2-CH_3), 62.93 (1C, O-CH_2-CH_3), 62.70 (1C, O-CH_2-CH_3), 62.65 (1C, O-CH_2-CH_3), 46.81 (1C, quart), 46.50 (1C, quart), 46.48 (1C, quart), 46.40 (1C, quart), 45.66 (1C, quart), 45.43 (1C, quart), 29.30 (1C, alkyl), 29.12 (2C, alkyl), 28.97 (1C, alkyl), 28.95 (1C, alkyl), 28.84 (1C, alkyl), 28.77 (1C, alkyl), 28.73 (1C, alkyl), 28.66 (1C, alkyl), 28.54 (1C, alkyl), 28.49 (1C, alkyl), 28.35 (1C, alkyl), 28.31 (2C, alkyl), 28.25 (1C, alkyl), 28.08 (1C, alkyl), 26.25 (1C, alkyl), 26.20 (1C, alkyl), 26.15 (1C, alkyl), 26.02 (1C, alkyl), 25.99 (1C, alkyl), 25.88 (1C, alkyl), 25.81 (1C, alkyl), 25.51 (1C, alkyl), 14.06 (1C, CH_3), 14.05 (1C, CH_3), 14.03 (1C, CH_3), 14.01 (1C, CH_3); IR (KBr): $\tilde{\nu} = 2932$, 2857, 1748, 1635, 1462, 1388, 1368, 1265, 1220, 1172, 1081, 1045, 1018, 760, 714, 540, 528 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 245 (94000), 272 (73000), 282 (77000), 318 (48000), 335 (40000), 377 nm (6100 mol^{-1} dm^3 cm^{-1}); MS (FAB, NBA): *m/z*: 1885 [M^+].

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