# 26. Multiple Adducts of $C_{60}$ by Tether-Directed Remote Functionalization and Synthesis of Soluble Derivatives of New Carbon Allotropes $C_{n(60+5)}$

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A comprehensive series of multiple adducts of $C_{60}$ was prepared by tether-directed remote functionalization. When the tether-reactive-group conjugates **2** and **10** were attached to methano[60]fullerenecarboxylic acid (= cyclopropafullerene-$C_{60}$-$I_h$-carboxylic acid) and $C_{60}$, respectively, the *e*-bis-adducts **4** and **9** (*Schemes 1* and *2*) were obtained with complete regioselectivity as predicted by semi-empirical PM3 calculations (*Fig. 2*). Attachment of the anchor-tether-reactive-group conjugate **13** to $C_{60}$ by *Bingel* reaction, followed by double intramolecular *Diels-Alder* cycloaddition afforded the tris-adduct **12** (*Scheme 3*). Starting from **12**, a series of selective *e*-additions led to the tetrakis-adducts **16** and **19** (*Scheme 4*), pentakis-adducts **20–23** (*Scheme 5*), and, ultimately, to hexakis-adducts **24** and **25** (*Scheme 6*), and **29** and **30** (*Scheme 7*) with a pseudo-octahedral addition pattern on the fullerene core. Oxidative cyclization of diethynylmethanofullerene **30** under *Eglinton-Glaser* conditions afforded the trimeric and tetrameric acetylenic macrocycles **26**, with three, and **27**, with four appended $C_{60}$ moieties, respectively (*Scheme 8*). These multinanometer-sized compounds are the first soluble derivatives of $C_{195}$ and $C_{260}$, two members of a new class of fullerene-acetylene hybrid C-allotropes with the general formula $C_{n(60+5)}$. The matrix-assisted laser-desorption time-of-flight mass spectra of **26** and **27** showed a remarkable fragmentation; the sequential loss of fullerene spheres led to the formation of ions corresponding to mono-fullerene adducts of the cyclocarbons *cyclo*-$C_{15}$ and *cyclo*-$C_{20}$ (*Fig. 4*). Large solvent effects were observed in the *Bingel* addition of 2-bromomalonates to higher adducts of $C_{60}$, with the use of polar solvents enhancing the reaction rate without loss of regioselectivity. Experimental evidence for the enhanced reactivity of $e_{face}$ over $e_{edge}$ bonds was obtained, which had previously been predicted in computational studies. The correlated series of mono- to hexakis-adducts of $C_{60}$ allowed identification of the changes in reactivity and physical properties that occur, when the conjugated $\pi$-electron chromophore of the fullerene is reduced as a result of increasing functionalization; this analysis is the subject of the directly following paper.

**1. Introduction.** – A rich variety of methods for the preparation of covalent mono-adducts of buckminsterfullerene $C_{60}$ was developed in many laboratories worldwide [1–4] after the seminal discovery of a bulk fullerene preparation method by *Krätschmer, Huffman*, and coworkers in 1990 [5]. Subsequently, the regiospecific formation of covalent poly-adducts became the frontier in the exploration of the chemistry of the new molecular allotrope of carbon. Monofunctionalized $C_{60}$ possesses nine different 6-6 bonds (bonds at the junction between two six-membered rings) that can react in a second addition, and a widely accepted nomenclature to describe the various sites of second attack was introduced by *Hirsch* and coworkers [6] (*Fig. 1*). Similar problems of isomer formation arise in the attack by a third addend to a purified bis-adduct as well as in the formation of more highly functionalized fullerenes.

Multiple regioisomer formation is reduced in reversible reactions with transition metal complexes [7] or halogens [8], which yield the thermodynamically most stable isomer or an isomer that crystallizes from the reaction mixture. Alternatively, mixtures

of many possible multiple adducts were produced by successive, irreversible reactions at the $C_{60}$ sphere, and purification was subsequently accomplished by often tedious chromatographic separations or by recrystallization, if possible [6] [9].

In 1993, we became interested in developing a more rational approach to the production of a single, desired regioisomer in multiple-functionalization reactions. Our ultimate objective was to provide selective access to tailor-made multiple adducts of $C_{60}$ with any desirable functionalization pattern for potential future use as novel three-dimensional building blocks in the construction of advanced materials and in biomedical applications. Furthermore, we hoped to identify the changes in reactivity and physical properties which occur when the conjugated $\pi$-electron chromophore of the fullerene is reduced as a result of increasing functionalization. To achieve regioselective multiple additions, we applied the concept of tether-directed remote functionalization (*Fig. 1*), which had been developed by *Breslow* [10] for the regioselective derivatization of steroids and long-chain alkanes. A great variety of fullerene multiple adducts has now been prepared in our group by this methodology which is described in detail in this paper [11–14].

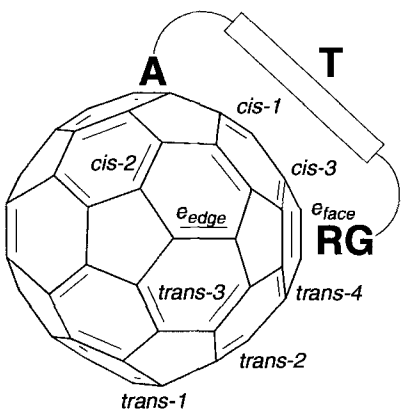



Fig. 1. *Naming of the bis-addition patterns, relative to the 'anchor' mono-adduct, according to* Hirsch *and coworkers* [6] *and schematic representation of the tether-directed remote bis-functionalization of* $C_{60}$. A = anchor, T = tether, RG = reactive group. The $e_{face}$ bond sees the face of the anchor A whereas the $e_{edge}$ bond sees its edge.

Several other protocols, some of which also rely on tether control [15], have in the meanwhile been applied to the regioselective multiple functionalization of $C_{60}$. We recently described a new tether-controlled remote functionalization which, upon application of chiral tethers, permitted the enantioselective preparation of optically active bis-adducts whose chirality resulted exclusively from the addition pattern [16]. Various groups reported the regioselective formation of 'diazafulleroids' with N-atoms bridging two adjacent open 6-5 bonds (at the junction of a six- and a five-membered ring) of the carbon sphere [17]. An elegant, topochemically controlled solid-state reaction provided access to a *trans-1* bis-adduct of $C_{60}$ [18]. Hexakis-adducts of $C_{60}$, with a pseudo-octahedral addition pattern (see below), were prepared directly from $C_{60}$ or from mono-adducts with [19] [20] or without [21] assistance by a reversible template. A reversible template was also used to control the regiochemistry of bis-additions [22].

In this paper, we give a full account on our versatile, tether-directed remote functionalization method which allowed for the first time the regioselective formation of a

complete series of bis- to hexakis-adducts of $C_{60}$ [11–13]. All compounds were isolated in pure form without the application of HPLC methods. Subsequently, we describe the formation of soluble derivatives of $C_{195}$ and $C_{260}$, two members of a new class of fullerene-acetylene hybrid carbon allotropes [20] [23] with the general molecular formula $C_{n(60+5)}$. The directly following paper [24] reports an important extension of the new methodology which allows removal of the tether-reactive-group conjugate under formation of another series of multiple adducts that are not accessible by stepwise additions. The second paper also provides an in-depth analysis of the changes in chemical reactivity and physical properties that occur when the conjugated fullerene $\pi$-chromophore is reduced in a specific way as a result of increasing functionalization.

**2. Results and Discussion.** – 2.1. *Design of the Anchor/Tether-Reactive-Group Conjugate.* We first targeted the selective formation of an equatorial bis-adduct of $C_{60}$ starting from methano[60]fullerenecarboxylic acid (= cyclopropafullerene-$C_{60}$-$I_h$-carboxylic acid; **1**) [25] as the anchor (see below, *Scheme 1*). As the reactive group, we chose a 2-substituted buta-1,3-diene known to undergo irreversible *Diels-Alder* reactions with $C_{60}$ at 6-6 bonds [26] [27]. The selection of the correct tether between anchor and reactive group was critical for the regioselectivity of the intramolecular *Diels-Alder* addition. It should favor attack at the $e_{face}$ bond (*Fig. 1*) over attack at the second equatorial $e_{edge}$ or the *cis-3* and *trans-4* bonds near the equator. We selected the 4-substituted benzyl alcohol **2** as tether reactive-group conjugate since molecular-model examinations suggested that mono-adduct **3**, in which conjugate **2** had been attached to anchor **1**, would readily differentiate between the desired position of attack ($e_{face}$) and the $e_{edge}$ and *trans-4* bonds. A PM3 computational study [28] finally predicted that **3** would also lead to a large preference for the targeted $e_{face}$ bis-adduct **4** over the *cis-3* regioisomer **5** (*Fig. 2*). The heat of formation of **4** was calculated to be 6.5 kcal mol$^{-1}$ lower than that of the lowest-energy conformer of **5**. A closer examination of the calculated geometry of **5** showed that the tether was

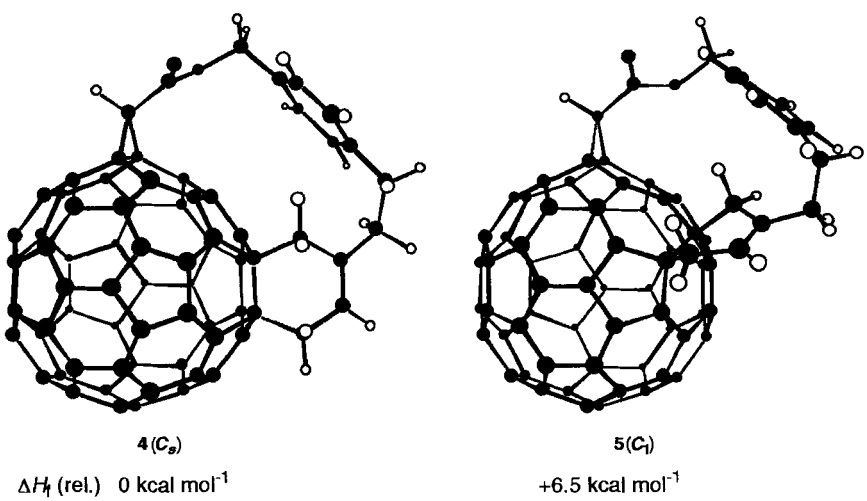
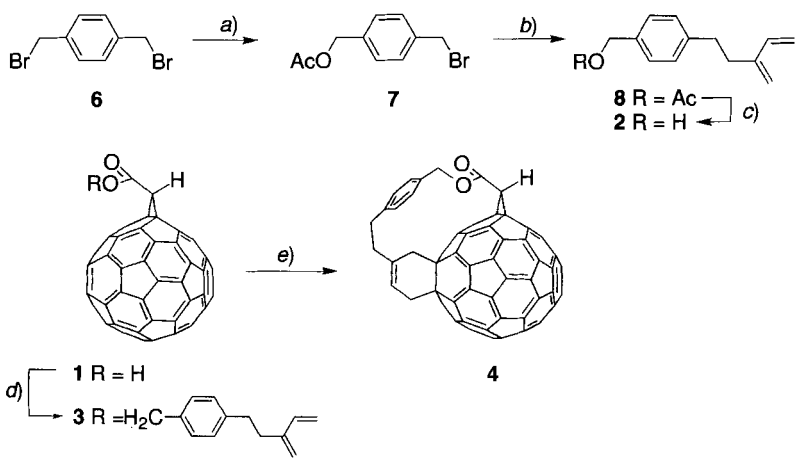



Fig. 2. *PM3-Calculated structures and heats of formation for the two possible regioisomeric bis-adducts* **4** *and* **5**

too short in the conformer shown and too long in the higher-energy conformer in which the double bond of the cyclohexene boat is oriented towards the anchor. This mismatch of the tether length in **5** leads to distortions in the bridging benzene ring and also to skewing of the ester group, which both increase the heat of formation. Experimentally, the different symmetries of **4** ($C_s$) and **5** ($C_1$) were expected to allow facile identification of the bis-adduct formed by $^{13}$C-NMR spectroscopy.

2.2. *Synthesis of Bis-adducts of $C_{60}$*. The synthesis of the tether-reactive-group conjugate **2** (*Scheme 1*) started from α,α′-dibromo-*p*-xylene (**6**) which was transformed into the acetoxy derivative **7**. Formation of the benzylic zinc organometallic [29], followed by transmetallation to the cyanocuprate and reaction with 2-(bromomethyl)buta-1,3-diene [30] gave **8** which was deprotected to yield **2**. Coupling of **2** to anchor **1** *via* esterification proceeded smoothly in the presence of dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), and 4-(dimethylamino)pyridine (DMAP) and afforded the intermediate wine-red methanofullerene **3** which was purified by flash chromatography ($SiO_2$, PhMe/hexane 2:1). Characterization of **3** was limited to UV/VIS spectroscopy which showed the two diagnostic absorption bands of a mono-adduct at $\lambda_{max}$ 429 and 692 nm [31 a]. Further characterization was not attempted due to rapid polymerization of **3** upon evaporation to dryness, presumably through intermolecular *Diels-Alder* reaction.

Scheme 1. *Synthesis of Bis-adduct* **4**




*a*) KOAc, [18]crown-6, MeCN, r.t.; 47%. *b*) Zn, THF, 5°; then CuCN, LiCl, THF, −75°; then 2-(bromomethyl) buta-1,3-diene, −75 → 20°; 61%. *c*) $K_2CO_3$, MeOH, r.t.; 96%. *d*) DCC, HOBt, DMAP, PhBr, r.t. *e*) PhMe, 80°, 44 h; 23%.

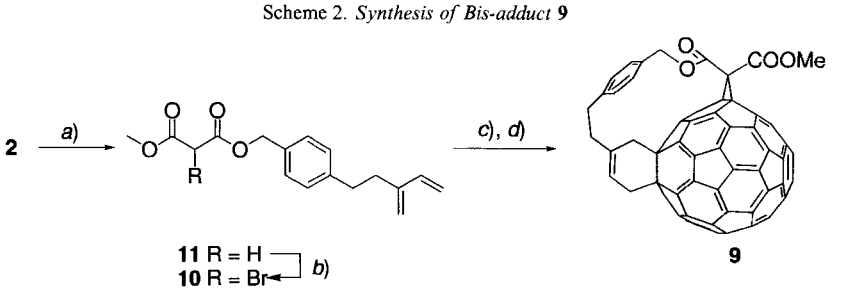
When a *ca.* 0.1M solution of **3** in PhMe was heated for 44 h to 80°, a color change from wine-red to orange-brown occurred, and subsequent flash chromatographic workup and recrystallization gave bis-adduct **4** in 23% yield. The compound was poorly soluble in PhMe or $CHCl_3$, but sufficient solubility in $CS_2$ allowed its complete spectroscopic characterization. Unambiguous evidence for formation of $C_s$-symmetrical **4** was obtained by $^1$H- and $^{13}$C-NMR spectroscopy. The $^1$H-NMR spectrum did not show any diastereotopic methylene protons which strongly suggested molecular $C_s$-symmetry on

the NMR time scale with the two boat forms of the cyclohexene ring [26a] [31] and the rotamers formed by rotation about the ester group rapidly interconverting. The presence of 32 resonances for the fullerene C-atoms demonstrated conclusively that the intramolecular *Diels-Alder* reaction had occurred at the $e_{face}$-6-6 bond to give $C_s$-symmetrical **4**.

Cyclohexene rings fused to $C_{60}$ such as those formed by *Diels-Alder* cycloaddition were shown by *Rubin* and coworkers [32] to rapidly undergo a $^1O_2$-ene reaction in the presence of light and $O_2$, with the fullerene derivative acting as a photosensitizer for the formation of $^1O_2$ [9d] [33]. This reaction also caused rapid decomposition of **4** as well as of most of the other higher adducts described in the following and, therefore, these compounds must be handled with extreme caution with exclusion of light and air. In the solid state under Ar at 0° in the dark, however, **4** is stable for extended periods of time. One other fullerene product (*ca.* 5% yield) was also present in the reaction mixture, but matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) showed it to be a by-product due to oxidation of **4** rather than a regioisomeric bis-adduct. The isomeric bis-adduct **5** was not detected in the reaction mixture. The rather low isolated yield of **4** is a reflection of the difficulties encountered with its chromatographic separation from its oxidation product.

Since bis-adduct **4** was too insoluble for electrochemical studies in $CH_2Cl_2$ [13], we prepared the more soluble derivative **9** by tether-directed remote functionalization. For the synthesis of the anchor/tether-reactive-group conjugate **10**, benzyl alcohol **2** was esterified with 'methyl malonyl chloride' ($MeO_2CCH_2COCl$) to give **11**, followed by bromination (*Scheme 2*). Attachment of **10** to $C_{60}$ in a *Bingel* reaction [34], followed by heating the wine-red mono-adduct in refluxing PhMe for 39 h to complete the intramolecular *Diels-Alder* addition, afforded **9** in 50% yield as a $CH_2Cl_2$-soluble brown solid which was isolated by flash chromatography. The spectral data for **9** were almost identical to those recorded for **4**, which supported the proposed $C_s$-symmetrical structure.

Scheme 2. *Synthesis of Bis-adduct* **9**

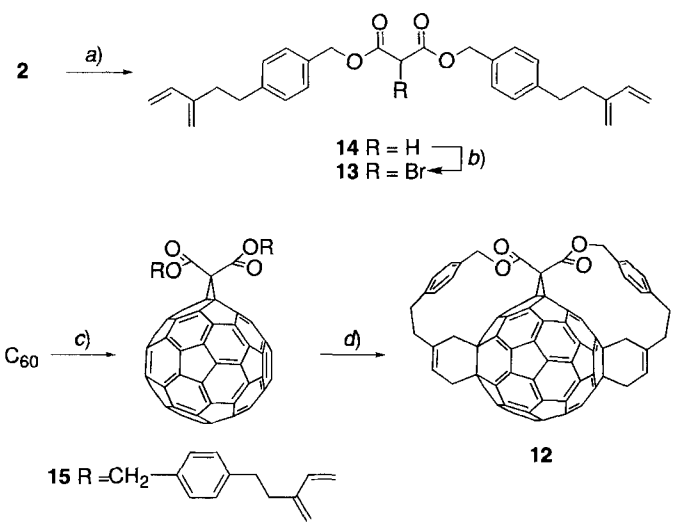



*a*) $MeO_2CCH_2COCl$, $C_5H_5N$, $CH_2Cl_2$ −5°; 81%. *b*) $CBr_4$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), THF, −78°; 68%. *c*) $C_{60}$, DBU, PhMe, r.t. *d*) PhMe, 110°, 39 h; 50%.

2.3. *Synthesis of Tris-adduct* **12**. For the regiospecific formation of tris-adduct **12**, resulting from double *Diels-Alder* addition to the two $e_{face}$-6-6 bonds in relation to the anchor, the doubly tethered precursor **13** was prepared by reacting malonyl dichloride with **2** (2 equiv.) to give **14**, followed by bromination (*Scheme 3*). *Bingel* addition of **13** to $C_{60}$ afforded the wine-red methanofullerene **15** which was separated by flash chro-

matography from excess $C_{60}$. The identity of **15** was established by $^1$H-NMR and UV/VIS spectroscopy. The $^1$H-NMR spectrum showed all expected resonances for tether and reactive groups, and the electronic absorption spectrum displayed the two diagnostic mono-adduct bands [31 a] at $\lambda_{max}$ 429 and 690 nm. Heating a solution of **15** (*ca.* 0.6 mM) in PhMe to 110° for 36 h resulted in a color change from wine-red to brown-orange, and subsequent flash chromatography provided $C_{2v}$-symmetrical **12** in 60% yield (based on conjugate **13**). By this method, gram-quantities of tris-adduct became readily accessible in single runs.

Scheme 3. *Synthesis of Tris-adduct* **12**




*a*) $ClCOCH_2COCl$, $C_5H_5N$, $CH_2Cl_2$, 0°; 80%. *b*) $CBr_4$, DBU, THF, −78°; 79%. *c*) **13**, DBU, PhMe, r.t. *d*) PhMe, 110°, 39 h; 60%.

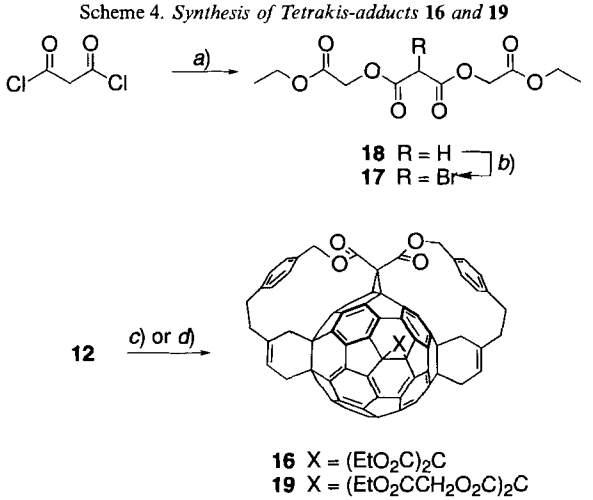
Tris-adduct **12** was poorly soluble in PhMe, $CS_2$, and $CHCl_3$, but reasonably soluble in $Cl_2CDCDCl_2$, which allowed its complete characterization. The $^1$H-NMR spectrum of **12** closely resembled that of **4**, minus the resonance for the proton of the methano moiety. The $^{13}$C-NMR spectrum showed the expected 17 resonances for the fullerene C-atoms in a $C_{2v}$-symmetrical molecule. Tris-adduct **12** appeared to be less sensitive to light and $O_2$ than bis-adduct **4** which could be due to a reduced ability of the higher adduct to photosensitize the formation of $^1O_2$; however, it was still necessary to work with as little exposure to light and air as possible.

2.4. *Synthesis of Tetrakis-adducts of* $C_{60}$. The regioselectivity observed by *Hirsch* and coworkers in the formation of an *e,e,e*-tris-adduct (all addends are in an equatorial relation to each other) starting from an *e*-bis-adduct [6] raised our optimism that further functionalization of **12** would lead to regioisomerically pure tetrakis- and even higher adducts. We first tested the reactivity of our tris-adduct in comparison to $C_{60}$. Upon treatment of **12** with an excess of anthracene (12 equiv.) in $Cl_2CHCHCl_2$ at 65°, no color change was noted within 19 h, whereas $C_{60}$ readily underwent a *Diels-Alder* addition under these conditions [9d] [35]. In a second test, a solution of **12** in PhCl was treated

with an excess of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (10 equiv.), which generates dimethoxycarbene at elevated temperatures [36]. Whereas $C_{60}$ readily formed 61,61-dimethoxymethano[60]fullerene under these conditions [37] [38], no reaction was observed with **12** (TLC). Clearly, threefold functionalization significantly reduces the chemical reactivity of **12** as compared to free $C_{60}$.

In contrast, the *Bingel* addition of diethyl 2-bromomalonate (5 equiv.) to **12** in PhCl at room temperature in the presence of DBU (5 equiv.) was successful and yielded tetrakis-adduct **16** as a bright-red solid in 72% yield (*Scheme 4*). The $C_s$-symmetrical structure, resulting from regioselective addition of the malonate to a 6-6 bond which is equatorial to all three previously introduced addends, was proven by $^1$H- and $^{13}$C-NMR spectroscopy. Specifically, the $^1$H-NMR spectrum showed two sets of signals for the diastereotopic $CH_2$ protons in the cyclohexene rings as well as two chemically nonequivalent ethyl groups. The $^{13}$C-NMR spectrum displayed 32 resonances for the fullerene core C-atoms, which conclusively established $C_s$ symmetry. Compound **16** is the only possible tetrakis-adduct with this symmetry that can be prepared starting from **12**; all other regioisomers are either $C_{2v}$- or $C_1$-symmetrical. The tetrakis-adduct is thermally robust and showed no sign of melting or decomposition below 270°; in contrast to its precursor molecules, it is highly soluble in $CHCl_3$.

Scheme 4. *Synthesis of Tetrakis-adducts* **16** *and* **19**




*a*) $HOCH_2COOEt$, $C_5H_5N$, $CH_2Cl_2$, 0°; 73%. *b*) $CBr_4$, DBU, THF, −70°; 75%. *c*) $(EtO_2C)_2CHBr$ (5 equiv.), DBU (5 equiv.), PhCl, r.t.; 72%. *d*) **17** (7.5 equiv.), DBU (7.5 equiv.), PhCl, r.t.; 70%. The two newly formed benzenoid ring substructures in **16** and **19** are highlighted in bold.

No isomeric tetrakis-adducts were detected by TLC or $^1$H-NMR spectroscopy. This high selectivity is in accord with the computational studies by *Hirsch* and coworkers [9e] who showed that the orbital coefficients in the LUMO, which apparently control kinetic-product formation, are enhanced at *e*-bonds (as well as at *trans-3* and *cis-2* bonds). The transition states of the addition leading to **16** might be further lowered in energy by the generation of two isolated benzenoid rings as shown in *Scheme 4*; additions to any other 6-6 bonds in **12** fail to generate such benzenoid ring substructures.

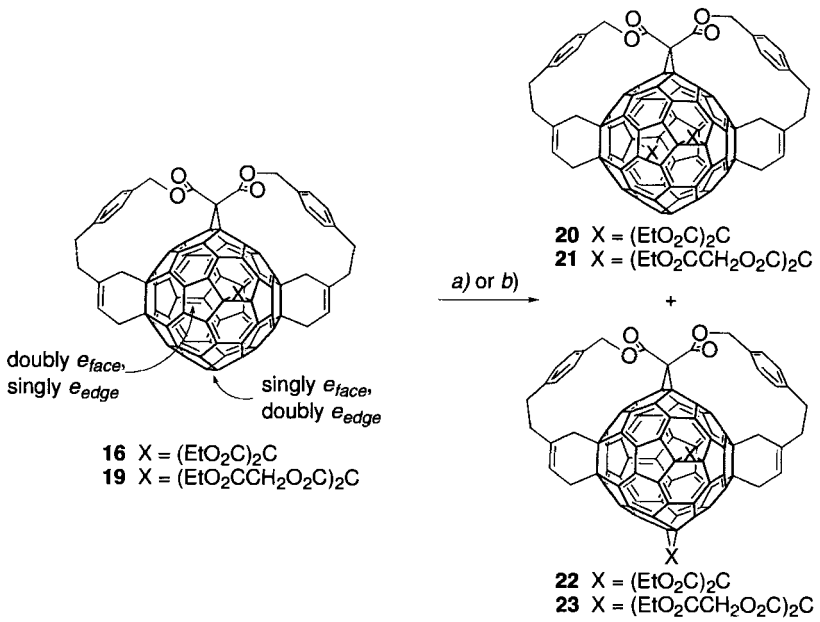
To facilitate the separation of regioisomeric pentakis-adducts (see below), bis(2-ethoxy-2-oxoethyl) 2-bromomalonate (**17**) with significantly more $R_f$-determining ester groups than those in the corresponding diethyl ester was reacted with tris-adduct **12**. Compound **17** was prepared in two steps from malonyl dichloride *via* **18** (*Scheme 4*). Thus, reaction of **12** with a large excess of **17** (7.5 equiv.) and DBU (7.5 equiv.) at room temperature in PhCl provided unreacted starting material, tetrakis-adducts, and some pentakis-adduct, which were separated chromatographically ($SiO_2$-*H*, $CH_2Cl_2$). The major product (70%) was the expected $C_s$-symmetrical tetrakis-adduct **19** which was separated from three other minor tetrakis-adducts resulting presumably from addition to less activated 6-6 bonds. The lower selectivity observed in the formation of **19**, as compared to **16**, is presumably due to increased steric interactions of the bulkier new addend with the three ones already in place, which offset the intrinsic electronic preferences of the system. Tetrakis-adduct **19** showed excellent solubility in $CHCl_3$, PhCl, THF, and even $Me_2SO$; it can be precipitated by addition of cyclohexane in which it is insoluble.

2.5. *Synthesis of Pentakis-adducts of $C_{60}$: Solvent Effects in the* Bingel *Reaction and* $e_{face}$ vs. $e_{edge}$ *Directing Effects.* When tetrakis-adduct **16** was reacted with diethyl 2-bromomalonate (5 equiv.) and DBU (5 equiv.) in PhCl at room temperature, a mixture of the orange-colored pentakis-adducts **20** and **22** was obtained in a total yield of 70% (*Scheme 5*). The ratio **20**/**22** was determined as 8:2 by integration of the benzylic $CH_2$ $^1$H-NMR signals at 5.1 and 5.3 ppm, respectively. The initial assignment of a $C_{2v}$-symmetrical structure to **20** and a $C_s$-symmetrical structure to **22** was based on the $^1$H-NMR spectrum of the isomeric mixture which showed a *d* and a *s* for the $CH_2$ protons of the cyclohexene moieties in **20**, whereas these protons are diastereotopic in **22** and gave the expected coupling patterns. Repeated recrystallization out of $CHCl_3$/hexane gave **20** with a maximum isomeric purity of only 96%. The preparative scale column-chromatographic separation ($SiO_2$-*H*) of **20** and **22** was very tedious; only regioisomer **20** could be isolated in pure form (33% yield) from reactions of **16** with a 7.5-fold excess of diethyl 2-bromomalonate and DBU. These separation problems are due to extremely similar retention factors of the two regioisomers, resulting from the almost identical orientation of their three $R_f$-determining malonate addends on the fullerene surface. The three malonate residues in each case are *trans-1*,*e*,*e*-related, differing only in the choice of the two nonequivalent *e*-bonds. The $^{13}$C-NMR spectrum of pure **20** fully confirmed its high symmetry, showing all 17 core resonances expected for a $C_{2v}$-symmetrical fullerene derivative.

We explored the solvent and temperature dependency of the *Bingel* reaction in the preparation of the pentakis-adducts in order to possibly increase the regioselectivity. When the addition was conducted in $CH_2Cl_2$ at $-40°$, the ratio **20**/**22** was 75:25. In contrast, when the reaction was conducted in $CCl_4$ at room temperature, a much higher selectivity of 91:9 was observed. Use of a less polar solvent such as cyclohexane, which presumably would have given a further enhanced regioselectivity, was not possible for solubility reasons.

The regioselectivity observed for attack at one triply *e*-6-6 bond, leading to **20**, over attack at another triply *e*-6-6 bond, leading to **22**, was actually quite remarkable. Close examination of the molecular structure of tetrakis-adduct **16** revealed that the more reactive bond is doubly $e_{face}$ and singly $e_{edge}$ (*Fig. 1*, *Scheme 5*), whereas the less reactive 6-6 bond is doubly $e_{edge}$ and once $e_{face}$ with regard to the addends already in place. This

Scheme 5. *Synthesis of Pentakis-adducts* **20**–**23**




*a*) $(EtO_2C)_2CHBr$ (5 equiv.), DBU (7.5 equiv.), PhCl, r.t.; 33% (**20**). *b*) **17** (1 equiv.), DBU (1 equiv.) PhCl, r.t.; 28% (**21**), 11% (**23**), 31% (recovered **19**).

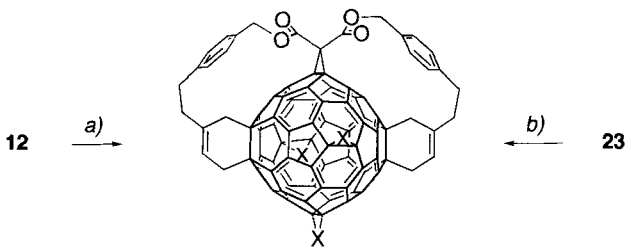
can be considered as the first experimental evidence for the enhanced reactivity of $e_{face}$ bonds over $e_{edge}$ bonds, which had previously been predicted in computational studies by *Hirsch* and coworkers [9e].

A complete separation of the formed pentakis-adducts was possible if the fourth and fifth addends were bis(2-ethoxy-2-oxoethyl)malonates which generate larger differences in the $R_f$ values. When tetrakis-adduct **19** was reacted with **17** (1 equiv.) and DBU (1 equiv.) in PhCl at room temperature, chromatographic workup ($SiO_2$-*H*, $CH_2Cl_2$/AcOEt 100:1.5) afforded isomerically pure $C_{2v}$-pentakis-adduct **21** (28%) and $C_s$-pentakis-adduct **23** (11%) (isomer ratio 72:28; *Scheme 5*), along with trace quantities of a third product. The colors and, accordingly, the UV/VIS spectra [24] of **21** and **23** are remarkably different: whereas a solution of **21** in $CH_2Cl_2$ is pale-orange, the corresponding solution of **23** is orange-red. The $^{13}C$-NMR spectrum of **23** displayed 30 of the 32 resonances expected for the fullerene core in a $C_s$-symmetrical adduct.

2.6. *Synthesis of Hexakis-adducts of* $C_{60}$. When a suspension of tris-adduct **12** was treated with diethyl 2-bromomalonate (10 equiv.) and DBU (10 equiv.) at room temperature in dry PhCl, the mixture became rapidly homogeneous, and, after 2 h, flash-chromatographic workup yielded the bright-yellow hexakis-adduct **24** in 73% yield (*Scheme 6*). Compound **24** possesses a pseudo-octahedral *e,e,e,e,e,e*-addition pattern similar to other hexakis-adducts described in the literature [7a] [9e] [19–21] and was formed with complete regioselectivity. Its structure was conclusively demonstrated by X-ray crystallography [12] [39]. In solution, the compound has averaged $C_{2v}$-symmetry

as revealed by the presence of 16 of the 17 expected resonances for fullerene C-atoms and three nonequivalent $CO_2Et$ groups in its $^{13}C$-NMR spectrum. Hexakis-adduct **24** is highly soluble and dissolves readily in chlorinated and aromatic solvents; more than 40 mg can be dissolved in 1 ml of $CHCl_3$. It is a thermally robust solid which showed no sign of decomposition or melting up to 270° and is significantly more stable to light and air than the mono- to pentakis-adducts described above. Apparently, hexakis-adducts are no longer able to efficiently photosensitize the formation of $^1O_2$, which would undergo destructive $^1O_2$-ene reaction at the cyclohexene moieties, as discussed above (*Sect. 2.2*). The high regioselectivity observed in the formation of **24** can be attributed to the preference for additions at *e*-bonds due to enhanced LUMO coefficients at these 6-6 bonds [9e] and to the generation of a 'cubic' cyclophane substructure [13] with eight stable benzenoid rings which, in the X-ray crystal structure, show reduced bond length alteration [39]. Formation of the stable benzenoid structure should energetically lower the transition state(s) of the sixth addition step. A similar hexakis-adduct **25** was also formed in 85% yield by *Bingel* addition of **17** to pentakis-adduct **23** (*Scheme 6*).

Scheme 6. *Synthesis of Hexakis-adducts* **24** *and* **25**

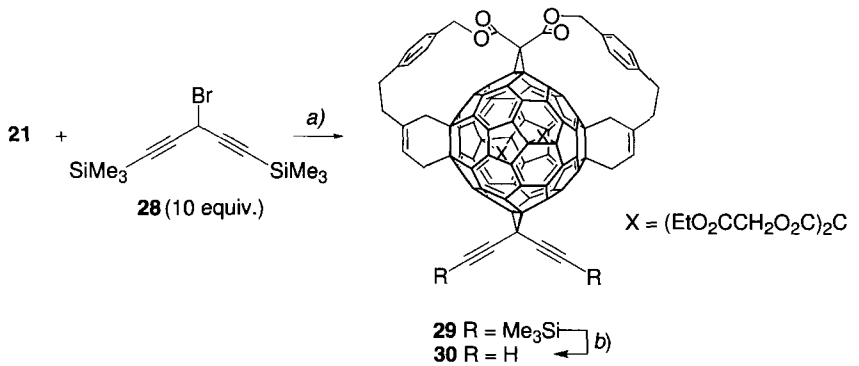



*a*) $(EtO_2C)CHBr$ (10 equiv.), DBU (10 equiv.), PhCl, r.t.; 73%. *b*) **17** (2 equiv.), DBU (2 equiv.), PhCl, r.t.; 85%.

For the construction of derivatives of the novel fullerene-acetylene hybrid carbon allotropes **26** and **27** described below, a diethynylmethano residue was introduced into the remaining reactive *e*-6-6 bond of pentakis-adduct **21**. First, 3-bromo-1,5-bis(trimethylsilyl)penta-1,4-diyne (5 equiv.; **28**) [40] was reacted with **19** in the presence of DBU (5 equiv.) in PhCl. However, no conversion was observed, and unchanged starting material was recovered, whereas $C_{60}$ is readily cyclopropanated under these conditions [23]. Tris-adduct **12** also was unreactive under these conditions which again illustrates the significant changes in reactivity of the fullerene that occur with increasing functionalization and reduction of its conjugated $\pi$-chromophore. To lower the activation barriers of this polar *Bingel*-type addition reaction, we switched to more polar solvents. Whereas, with **21**, no reaction occurred in $CH_2Cl_2$, partial conversion was observed in THF, and in $Me_2SO$, ultimately a clean, rapid conversion to the dialkynylmethanofullerene **29** [20] was observed (*Scheme 7*). Thus, reaction of **21** with **28** (10 equiv.) and DBU (10 equiv.) in $Me_2SO$ gave, after chromatography, hexakis-adduct **29** in 88% yield.

The $^1H$-NMR spectrum of **29** displayed a single $Me_3Si$ resonance indicating the symmetrical attachment of the dialkynylmethylene group. The 17 resonances for the

Scheme 7. *Synthesis of the Dialkynylmethanofullerenes* **29** *and* **30**



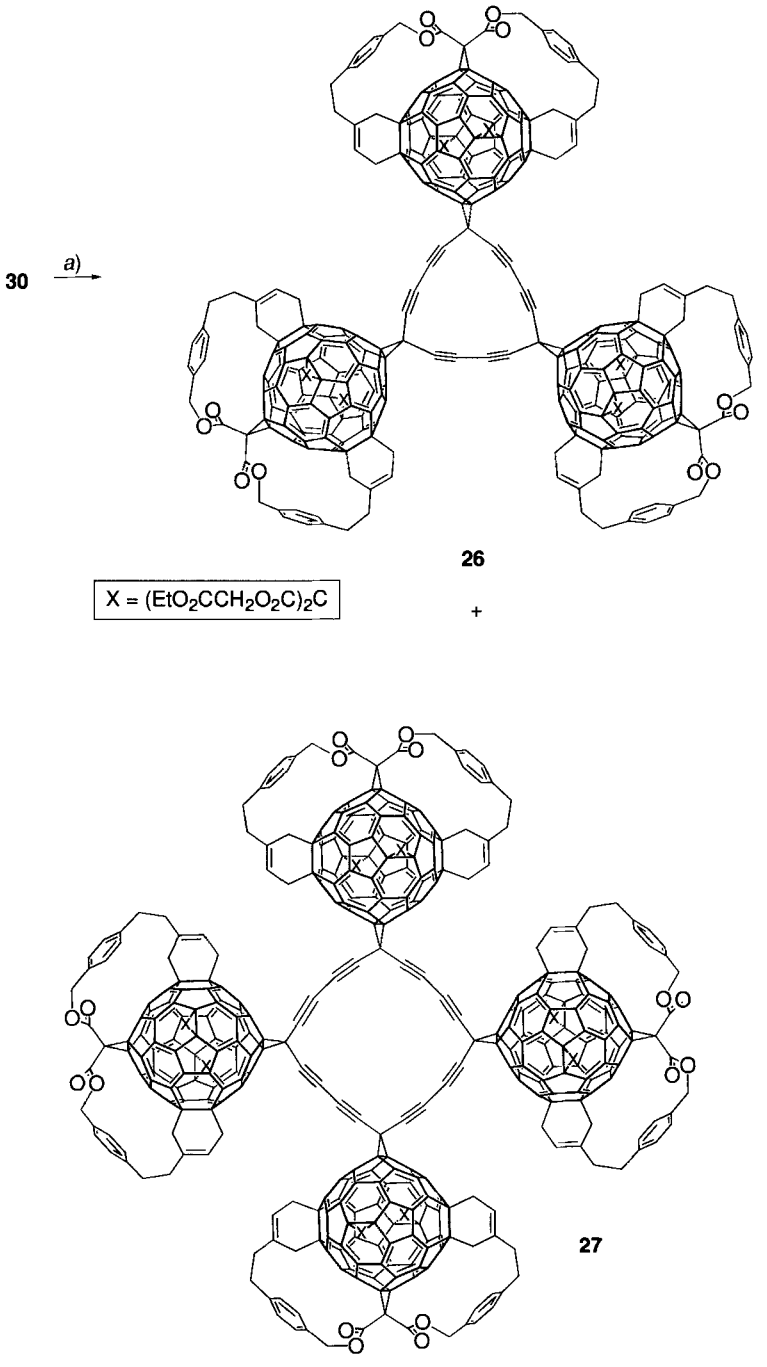

*a*) DBU (10 equiv.), $Me_2SO$, r.t.; 88%. *b*) TBAF (2.75 equiv.) on $SiO_2$, dry THF, r.t.; 90%.

fullerene C-atoms in the $^{13}$C-NMR spectrum provided conclusive proof for the depicted $C_{2v}$-symmetrical structure. The MALDI-TOF mass spectrum in α-cyano-4-hydroxycinnamic acid (CCA) as the matrix gave the expected molecular ion at *m/z* 1918, but the base peak was the fragment at *m/z* 1711 resulting from loss of the dialkynylmethylene group from the molecule under regeneration of the pentakis-adduct ion $\mathbf{21}^{+\cdot}$ [12]. It has in the meanwhile been confirmed by another study [20] that the diethynylmethano group is bound less tightly to the fullerene core than malonate addends and, therefore, splits off first under the MALDI-TOF MS conditions.

Attempts to remove the $Me_3Si$ protecting groups in **29** under basic conditions ($K_2CO_3$, MeOH/THF) were unsuccessful and led to products resulting from cleavage of the benzyl ester moieties. In contrast, treatment of **29** with $Bu_4NF$ on $SiO_2$ in anhydrous THF caused a very clean deprotection affording the diethynyl derivative **30** in 90% yield after chromatography ($SiO_2$-*H*, $CH_2Cl_2$/AcOEt 100:1.5) [12] [20]. This successful reaction again illustrates the differences in reactivity between lower and higher $C_{60}$-adducts: when *Rubin* and coworkers applied $Bu_4NF$ to deprotect 61,61-bis[(trimethylsilyl)-ethynyl]-1,2-dihydro-1,2-methano[60]fullerene, mainly decomposition and polymerization of the mono-adduct occurred, presumably induced by attack of the nucleophilic $F^-$ anion [41]. The MALDI-TOF mass spectrum of **30** again showed a pronounced preference for loss of the diethynylmethano over the malonate ester groups.

2.7. *Synthesis of Soluble Derivatives of $C_{195}$ and $C_{260}$.* With the $C_{2v}$-symmetrical hexakis-adduct **30**, an ideal precursor for the oxidative cyclization to acetylenic macrocycles [42] with appended fullerenes had been prepared. Chemical equivalency of the two ethynyl residues in **30** should ensure formation of isomerically pure compounds rather than diastereoisomer mixtures, and the extra functional groups on the fullerene sphere were expected to render the targeted multinanometer-sized products sufficiently soluble for full characterization. Oxidative cyclization of **30** ($c$ = 0.3 mM) under *Glaser-Hay* conditions [42c] [43] (CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), air, $CH_2Cl_2$) failed to produce isolable amounts of the cyclic oligomers. However, when a solution of **30** ($c$ = 0.16 mM) was subjected to the *Eglinton-Glaser* coupling conditions [44], two major products were detected by TLC ($SiO_2$/AcOEt 100:5). Isolation of the two yellow compounds was achieved by chromatography ($SiO_2$-*H*, $CH_2Cl_2$/AcOEt 100:5

Scheme 8. *Synthesis of Soluble Derivatives* **26** *and* **27** *of* $C_{195}$ *and* $C_{260}$, *Respectively*




*a*) $Cu(OAc)_2$ (200 equiv.), $C_5H_5N$, molecular sieves (4 Å), Ar, 28 h, r.t; 32% (**26**), 21% (**27**).

then 100:8.5), and their structures were established as cyclic trimeric $D_{3h}$- symmetrical **26** and cyclic tetrameric $D_{4h}$- symmetrical **27** based on their spectroscopic properties (*Scheme 8*). The combined yield of **26** and **27** was a remarkable 53%. Larger cyclic oligomers were not detected in the reaction mixture, perhaps due to steric interaction between the laterally appended fullerene spheres.

The $^1$H-NMR spectra of both cyclic oligomers showed no signals for terminal acetylenic protons, two independent sets of $CH_2COOEt$ resonances, and one set of peaks for the tether-cyclohexene moieties. In the $^{13}$C-NMR spectra of both **26** and **27**, 17 resonances were visible for the fullerene-core C-atoms implying local $C_{2v}$ symmetry which, when combined with a single peak for the methano C-atom and only two acetylenic C-atom resonances, indicates overall $D_{nh}$ symmetry. The acetylenic C-atom resonances in **26** appeared at 88.41 and 71.77 ppm, whereas those in **27** are located at 75.77 and 69.49 ppm, with the differences in chemical shift presumably reflecting the different bending of the butadiynediyl fragments from linearity in the two compounds. The UV/VIS spectra of **26** and **27** are similar to those of monomeric **30**, with the exception of the increase in molar extinction coefficients as the number of fullerene moieties per molecule increases (*Fig. 3*). This close spectral resemblance is an indication for the absence of strong homo-conjugation in the acetylenic macrorings as well as for the absence of particular interactions between the laterally appended fullerene chromophores.

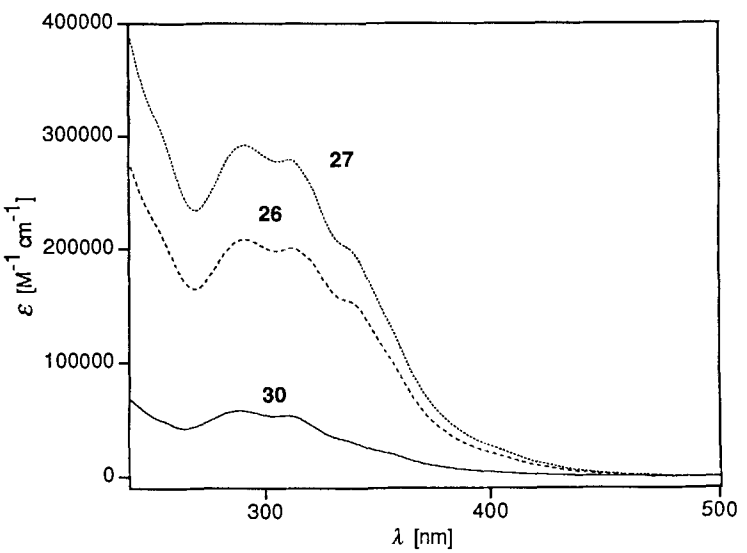



Fig. 3. *Electronic absorption spectra recorded for* **30** (——), **26** (– – –), *and* **27** (·····) *in* $CH_2Cl_2$

The size of the cyclic oligomers was determined by MALDI-TOF MS. In the spectrum of **26** (*Fig. 4, a*), the product with the higher $R_f$ value, the expected molecular ion appeared at $m/z$ 5317 ($C_{348}H_{174}O_{60}$ requires 5314) along with weaker peaks at higher masses which can be ascribed to matrix adducts of the cyclic oligomers. Strong fragment ions confirmed the large propensity of dialkynylmethanofullerenes, as noted above for

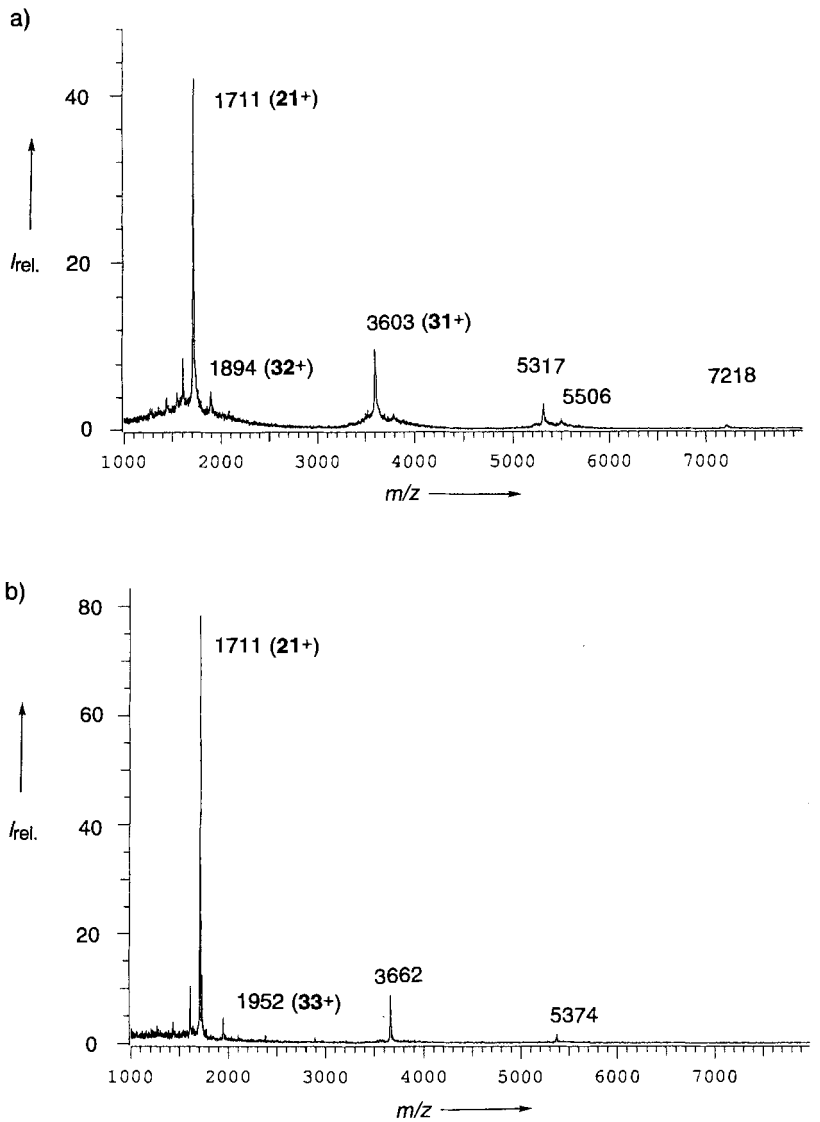
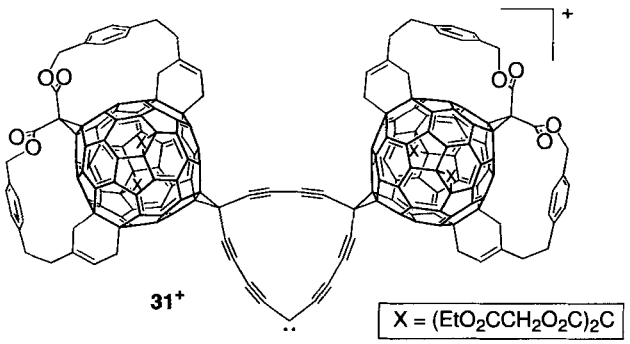
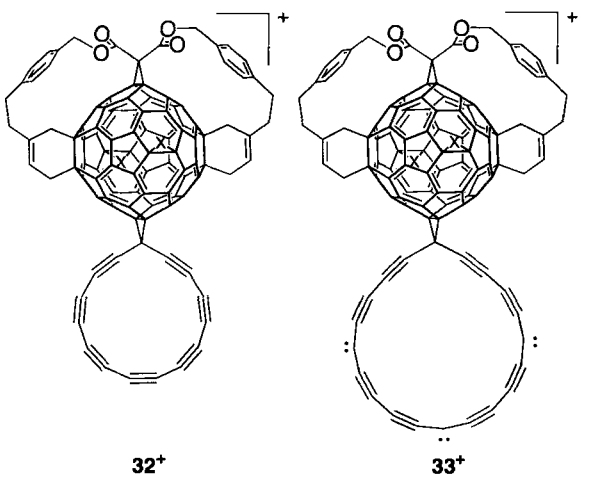



Fig. 4. *MALDI-TOF Mass spectra* a) *of* **26** *recorded in* α*-cyano-4-hydroxycinnamic acid* (CCA) *and* b) *of* **27** *in 2,5-dihydroxybenzoic acid* (DHB)

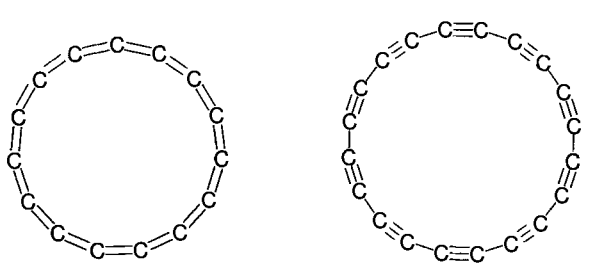
**29** and **30**, to undergo *retro*-addition with loss of the fullerene moiety. The base peak appeared at *m/z* 1711, which corresponds to the fullerene pentakis-adduct ion $\mathbf{21}^+$. This interesting fragmentation also explains the relatively intense fragment ions at *m/z* 3603 ($C_{237}H_{116}O_{40}$ requires 3602) and 1894 ($C_{126}H_{58}O_{20}$ requires 1891) which arise from loss of one and two fullerene pentakis-adducts **21**, generating $\mathbf{31}^+$ and $\mathbf{32}^+$. The latter ions correspond to bis- and mono-fullerene adducts of *cyclo*-$C_{15}$ respectively. Unfortunately,




**31**$^+$



**32**$^+$ **33**$^+$



*cyclo*-$C_{15}$ *cyclo*-$C_{20}$

it was not possible to observe a peak for *cyclo*-$C_{15}^+$ itself, resulting from *retro*-addition of all three fullerene moieties, since matrix peaks severely obscured the spectrum in the mass region around $m/z$ 180. The corresponding spectrum recorded without matrix assistance also did not yield the cyclocarbon ion peak since, at the required higher laser power, significant fragmentation of the solubilizing groups occurred, once again obscuring the mass region around $m/z$ 180.

The MALDI-TOF mass spectrum of the cyclization product **27** with the lower $R_f$ value did not show a peak at masses expected for tetrameric (*m/z* 7085), pentameric (*m/z* 8856), or hexameric (*m/z* 10628) cyclic oligomers (*Fig. 4,b*). However, a weak peak was observed at *m/z* 5374 ($C_{353}H_{174}O_{60}$ requires 5374) and a relatively strong one at *m/z* 3662 ($C_{242}H_{116}O_{40}$ requires 3662). In analogy to the fragmentation pattern observed for trimeric **26**, these peaks correspond to ions formed by successive loss of one and two molecules of pentakis-adduct **21** from cyclic tetrameric **27**. The weak peak at *m/z* 1952 ($C_{131}H_{58}O_{20}$ requires 1951) resulted from the loss of a third equivalent of **21** and corresponds to $\mathbf{33}^+$, an adduct between fullerene derivative **21** and *cyclo*-$C_{20}$. These characteristic fragment peaks provide strong support for the assignment of the cyclic tetrameric structure **27** to the product with lower $R_f$ value. Just as in the spectrum of cyclic trimeric **26**, matrix peaks prevented the unambiguous observation of a peak for free *cyclo*-$C_{20}^+$. The formation and observation of free *cyclo*-$C_{15}$ and *cyclo*-$C_{20}$ ions, starting from **26** and **27**, respectively, and study of their gas-phase ion-molecule coalescence reactions requires further investigation by *Fourier*-transform mass spectrometry, a technique which had previously been successfully applied to the study of other cyclocarbon molecules [45–47].

**3. Conclusions.** – The concept of tether-directed remote functionalization, which had been previously developed by *Breslow* [10] for the efficient, regioselective functionalization of steroids and long-chain alkanes, is a similarly powerful methodology when applied to the regioselective formation of $C_{60}$ multiple adducts. Some of the specific multiple addition patterns displayed by the compounds in this paper may also be accessed by stepwise functionalization accompanied, however, by tedious chromatographic separations, whereas others can only be obtained by tether-directed synthesis. As an example, the addition pattern in $C_{2v}$-symmetrical tris-adduct **12**, which is a versatile intermediate in the regioselective synthesis of many other higher adducts of $C_{60}$ and is available in multi-gram quantities through use of the described new methodology, cannot be accessed otherwise.

Starting from **12**, a series of tetrakis- to hexakis-adducts of $C_{60}$ was prepared *via* the amazing succession of stepwise *e*-additions which had been demonstrated first by *Hirsch* and coworkers [9e]. In an extension of the regioselectivity concept of preferential *e*-additions, experimental evidence for the enhanced reactivity of $e_{face}$ over $e_{edge}$ bonds was obtained for the first time. The four hexakis-adducts **24**, **25**, **29**, and **30** all possess a pseudo-octahedral addition pattern, and the chromophore of the carbon sphere in these derivatives is reduced to a 'cubic cyclophane'-type substructure with eight benzenoid rings. X-Ray crystallographic analysis of **24** [39] had shown that bond alteration in these benzenoid rings is significantly reduced as compared to that seen for 6-6 (shorter) and 6-5 bonds (longer) in the parent fullerene and in lower adducts [23].

Oxidative cyclization of diethynylmethanofullerene **30** under *Eglinton-Glaser* conditions afforded the first soluble derivatives of $C_{195}$ and $C_{260}$, **26** and **27**, respectively, which are members of a new class of fullerene-acetylene hybrid C-allotropes with the general formula $C_{n(60+5)}$. Particularly intriguing were the MALDI-TOF-MS of **26** and **27** which showed sequential loss of the fullerene spheres generating ions corresponding to mono-fullerene adducts of the cyclocarbons *cyclo*-$C_{15}$ and *cyclo*-$C_{20}$. This paper once again confirms [48] in an impressive way, that MALDI-TOF-MS is the

premier method for the analysis of the molecular composition of large all-C and C-rich materials.

With increasing functionalization and corresponding reduction of the conjugated fullerene $\pi$-chromophore, the reactivity and the physical properties of the carbon spheres change dramatically. In this paper, we briefly discussed the changes in color from magenta-purple ($C_{60}$) to yellow (hexakis-adducts **24**, **25**, **29**, and **30**) as a consequence of chromophore reduction. Also mentioned were changes in chemical reactivity such as the reduced ability of the hexakis-adducts to act as photosensitizers for $^1O_2$ formation or the reduced electrophilicity of higher adducts due to the increase in LUMO energy with increasing $\pi$-chromophore reduction. A full discussion of the changes in fullerene properties with increasing functionalization is given in the following paper [24], which also reports an important extension of the synthetic methodology presented here. By removal of the tether-reactive-group conjugate, a variety of other multiply functionalized fullerenes with unprecedented addition patterns have become available.

This work was supported by the *Swiss National Science Foundation*. We also thank Ms. *Brigitte Brandenberg* for recording highfield $^{13}$C-NMR spectra and Dr. *Walter Amrein* and Mr. *Hans-Ulrich Hediger* for the MALDI-TOF mass spectra.

## Experimental Part

*General.* Reagents and solvents were reagent-grade commercials and were used without further purification. Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona, AZ 85706, USA. Crude fullerene-enriched soot, containing 5% soluble fullerenes, was purchased from *Polygon Enterprises*, Waco, Texas, USA, and *Texas Fullerene Corporation*, Houston, Texas, USA. $C_{60}$ was purified as previously reported [49]. THF was freshly distilled from sodium benzophenone ketyl, $CH_2Cl_2$ from $CaH_2$. $Me_2SO$ was distilled from $CaH_2$ onto activated molecular sieves (4 Å) and stored under $N_2$. Anh. PhCl was dried over molecular sieves (4 Å) for several days before use. Molecular sieves (4 Å) were activated by heating in a drying pistol to 300° for 6 h and stored in a dessicator over NaOH. All reactions were performed in standard glassware under an inert atmosphere ($N_2$ or Ar). Reactions involving the multiply functionalized fullerenes were conducted under strict exclusion of light and air. Degassing of solvents was performed by repetitive freeze-pump-thaw cycles or by sparging with Ar before use. Evaporation and concentration was done at water-aspirator pressure; if not stated otherwise, isolated solid products were dried at $10^{-1}$ Torr. Column chromatography (CC) and flash chromatography (FC): $SiO_2$-*60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck* or *Macherey-Nagel* and $SiO_2$-*H* (0.005–0.040 mm) from *Fluka*. Thin-layer chromatography (TLC): plastic sheets pre-coated with $SiO_2$-*G* $UV_{254}$ from *Macherey-Nagel* and glass-backed $SiO_2$-*60* $F_{254}$ from *Merck*, visualization by UV light. Melting points: *Büchi Smp-20*; uncorrected. UV/VIS Spectra: *Varian-Cary-5* spectrophotometer; $\lambda_{max}$ in nm ($\varepsilon$). IR Spectra ($cm^{-1}$): *Perkin-Elmer 1600-FTIR*. NMR Spectra: *Bruker AM 500* ($^{13}$C) and *Varian Gemini 300* or *200* ($^1$H) at 296 or 300 K, with $Me_4Si$ or solvent peaks ($CHCl_3$ at 7.26 ($^1$H) and 77.0 ($^{13}$C), $C_6HD_5$ at 7.15 and 128.0, $CHCl_2CDCl_2$ at 5.91 and 74.2, and $CHD_2COCD_3$ at 2.04 and 29.8 ppm) as reference. MALDI-TOF Mass spectra (*m/z* (%)): *Bruker REFLEX* spectrometer with 2,5-dihydroxybenzoic acid (DHB), 2-(4-hydroxyphenylazo)benzoic acid (HABA), or α-cyano-4-hydroxycinnamic acid (CCA) as matrix, positive-ion mode; a 1-µl sample of the mixture of a soln. of the fullerene derivative (1 µl; 1 mg $ml^{-1}$) and a soln. of the matrix (1 µl) in MeCN/EtOH/$H_2O$ 50:45:5 was deposited on the probe tip, dried under mild vacuum, and analyzed. FAB-MS (*m/z*, (%)): *VG-ZAB-2-SEQ* instrument; 3-nitrobenzyl alcohol as matrix. For MALDI-TOF and FAB mass spectra of fullerene derivatives, the experimentally observed highest peak in the molecular-ion cluster is reported, followed in parenthesis by the isotopic molecular formula corresponding to the calculated most intense peak in the cluster. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich. Fullerene derivatives were named by the *Chemical Abstracts Service* (*CAS*) and adjusted for publication.

*4-(Bromomethyl)benzyl Acetate* (**7**). A mixture of **6** (10.0 g, 37.9 mmol), AcOK (3.72 g, 37.9 mmol), MeCN (300 ml), and [18]crown-6 (0.50 g, 1.9 mmol) in MeCN (300 ml) was stirred at r.t. for 16 h. The residue obtained by evaporation was dissolved in $Et_2O$, washed with 0.1M HCl, $H_2O$, and sat. aq. NaCl soln., and dried ($MgSO_4$). After concentration, FC ($SiO_2$, PhMe/hexane 2:1) gave **7** (4.37 g, 47%) as a colorless oil which solidified on

standing in the freezer overnight. White solid. M.p. *ca.* 25°. IR (neat): 3031*w*, 2958*w*, 2889*w*, 1740*s*, 1515*w*, 1440*m*, 1421*m*, 1379*m*, 1361*m*, 1229*s*, 1030*m*, 968*w*, 822*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.39 (*d*, $J$ = 8.2, 2H); 7.34 (*d*, $J$ = 8.2, 2H); 5.10 (*s*, 2H); 4.49 (*s*, 2H); 2.11 (*s*, 3H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.7; 137.7; 136.2; 129.2; 128.5; 65.7; 32.9; 21.0. EI-MS: 244/242 (0.9, $M^+$), 202/200 (0.3), 185/183 (1.5), 163 (51), 43 (100, $CH_3CO^+$). HR-MS: 241.9946 ($M^+$, $C_{10}H_{11}{}^{79}BrO_2^+$, calc. 241.9943). Anal. calc. for $C_{10}H_{11}BrO_2$ (243.10): C 49.41, H 4.56, Br 32.87; found: C 49.17, H 4.61, Br 33.01.

*4-(3-Methylidenepent-4-enyl)benzyl Acetate* (**8**). Granulated Zn cut into small pieces (3.626 g, 55.47 mmol) was activated by heating with 1,2-dibromoethane (268 mg, 1.43 mmol) in THF (5 ml) near reflux for 2 min. After decanting the solvent, **7** (8.66 g, 35.6 mmol) in THF (30 ml) was added over 75 min by syringe pump to the activated Zn cooled to 5°. After 3 h at 5°, the soln. was transferred by syringe into a soln. of CuCN (*caution*!) (3.19 g, 35.6 mmol) and LiCl (3.10 g, 73.0 mmol) in THF (45 ml) at −75°. The resultant mixture was brought to −20° for 5 min and then cooled to below −70°. After 2-(bromomethyl)buta-1,3-diene (4.19 g, 28.5 mmol) was added by syringe, the mixture was allowed to warm to r.t. over 14 h, then quenched with 25% aq. $NH_4OH$/sat. aq. $NH_4Cl$ soln. 1:1, diluted with $Et_2O$, and washed with 25% aq. $NH_4OH$/sat. aq. $NH_4Cl$ soln. 1:1 until the washings were colorless. After washing with 0.1M HCl, sat. aq. $NaHCO_3$ soln., $H_2O$, and sat. aq. NaCl soln., the org. phase was dried ($MgSO_4$) and evaporated. CC ($SiO_2$, PhMe) gave **8** (3.99 g, 61%). Colorless oil. IR (neat): 3089*w*, 3011*w*, 2936*w*, 2861*w*, 1741*s*, 1594*w*, 1515*w*, 1379*m*, 1361*m*, 1229*s*, 1020*m*, 899*m*, 811*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.30 (*d*, $J$ = 8.3, 2H); 7.21 (*d*, $J$ = 8.3, 2H); 6.41 (*dd*, $J$ = 17.8, 10.8, 1H); 5.35–4.95 (*m*, 4H); 5.08 (*s*, 2H); 2.90–2.75 (*m*, 2H); 2.60–2.45 (*m*, 2H); 2.10 (*s*, 3H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 170.9; 145.4; 142.3; 138.7; 133.9; 128.5; 128.4; 116.1; 113.2; 66.1; 34.1; 33.1; 21.0. EI-MS: 230 (0.5, $M^+$), 170 (100, $[M - C_2H_4O_2]^+$). HR-MS: 230.1340 ($M^+$, $C_{15}H_{18}O_2^+$, calc. 230.1307).

*4-(3-Methylidenepent-4-enyl)benzenemethanol* (**2**). A mixture of **8** (1.240 g, 5.38 mmol) and $K_2CO_3$ (3.720 g, 26.92 mmol) in MeOH (50 ml) was stirred at r.t. for 1 h. Dilution with $Et_2O$, washing with 0.1M HCl, $H_2O$, sat. aq. NaCl soln., drying ($MgSO_4$), and CC ($SiO_2$, $CH_2Cl_2$) gave **2** (0.975 g, 96%). Colorless oil. IR (neat): 3339*s*, 3083*m*, 2927*s*, 2861*m*, 1593*s*, 1513*m*, 1419*m*, 1215*w*, 1038*m*, 1014*s*, 992*s*, 897*s*, 803*m*, 756*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.30 (*d*, $J$ = 8.0, 2H); 7.21 (*d*, $J$ = 8.0, 2H); 6.41 (*dd*, $J$ = 17.7, 10.8, 1H); 5.35–4.95 (*m*, 4H); 4.66 (*s*, 2H); 2.90–2.75 (*m*, 2H); 2.60–2.45 (*m*, 2H); 1.90–1.60 (br. *s*, 1H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 145.5; 141.7; 138.7; 138.4; 128.6; 127.1; 116.1; 113.3; 65.2; 34.2; 33.3. EI-MS: 188 (9, $M^+$), 170 (8), 158 (40), 129 (47), 121 (100, $C_8H_9O^+$), 91 (40), 77 (30). HR-MS: 188.1217 ($M^+$, $C_{13}H_{16}O^+$, calc. 188.1201). Anal. calc. for $C_{13}H_{16}O$ (188.27): C 82.94, H 8.57; found: C 82.67, H 8.47.

*[4-(3-Methylidenepent-4-enyl)phenyl]methyl 3'H-Cyclopropa[1,9][5,6]fullerene-$C_{60}$-$I_h$-3'-carboxylate* (**3**) and *3',6'-Dihydro-5',3''-(Ethano[1,4]benzenomethanoxymethano)-3''H-benzo[1,9]cyclopropa[16,17][5,6]fullerene-$C_{60}$-$I_h$-17'-one* (**4**). To **1** (100 mg, 0.128 mmol) in PhBr (20 ml) was added sequentially DCC (26.5 mg, 0.128 mmol), HOBt (17.4 mg, 0.128 mmol), DMAP (15.7 mg, 0.128 mmol), and **2** (48.4 mg, 0.256 mmol). After stirring at r.t. for 19 h, the mixture was loaded directly onto a column and chromatographed ($SiO_2$, PhMe/hexane 2:1), yielding a soln. of **3** which was evaporated to remove the hexane and then diluted with PhMe to a total volume of 500 ml. The resulting soln. was deoxygenated by purging with Ar for 10 min, further degassed by two freeze-pump-thaw cycles, and then heated to 80° for 44 h. After concentration to 100 ml, the orange-red soln. was chromatographed ($SiO_2$, PhMe/hexane 2:1) to afford one main product which was recrystallized from $CS_2$/MeOH, then from $CS_2$/hexane, and dried to give **4** (27.7 mg, 23%).

**3**: Wine-red soln. UV/VIS (PhMe): 692, 495, 429, 331.

**4**: Black solid. M.p. > 270°. TLC (PhMe/hexane 2:1) $R_f$ 0.51. UV/VIS ($CH_2Cl_2$): 508 (sh, 2180), 449 (3050), 427 (4030), 399 (4000, sh), 397 (3250, sh), 349 (15300, sh), 309 (32000, sh), 279 (51400, sh), 248 (77100). IR (KBr): 2919*w*, 1740*m*, 1725*m*, 1638*s*, 1617*s*, 1511*s*, 1383*m*, 1181*m*, 1156*m*, 525*m*. $^1$H-NMR (300 MHz, $CS_2$/$(CD_3)_2CO$ capillary): 7.06 (*s*, 4H); 6.47 (*t*, $J$ = 5.4, 1H); 5.09 (*s*, 2H); 4.47 (*s*, 1H); 3.66 (*d*, $J$ = 5.4, 2H); 3.33 (*s*, 2H); 3.06 (*s*, 4H). $^{13}$C-NMR (125 MHz, $CS_2$/$(CD_3)_2CO$ capillary): 163.46; 160.19; 156.41; 149.16; 148.35; 147.90; 147.42; 146.81; 146.53; 146.32; 146.29; 146.26; 145.99; 145.86; 145.33; 145.20; 145.09; 144.99; 144.69; 144.23; 144.11; 144.01; 143.20; 143.14; 142.59; 142.49; 142.22; 140.32; 139.09; 138.97; 138.60; 136.59; 132.72; 130.79; 128.51 (br.); 125.98; 69.60; 68.00; 65.78; 64.99; 43.77; 41.71; 40.14; 35.67; 34.75. MALDI-TOF-MS (DHB): 964 (49, $[M + O]^+$, $^{12}C_{75}H_{16}O_3^+$; formed during sample preparation for MS), 948 (100, $M^+$, $^{12}C_{75}H_{16}O_2^+$). Anal. calc. for $C_{75}H_{16}O_2 \cdot 0.8\ CS_2$ (1009.87): C 90.15, H 1.60; found: C 89.90, H 1.76.

*Methyl 4-(3-Methylidenepent-4-enyl)benzyl Propanedioate* (**11**). To a soln. of **2** (1.00 g, 5.31 mmol) in $CH_2Cl_2$ (20 ml) at −5°, methyl 3-chloro-3-oxopropanoate (725 mg, 0.57 ml, 5.31 mmol) and $C_5H_5N$ (420 mg, 0.43 ml, 5.31 mmol) were added by syringe. After 1.25 h, the mixture was poured into $Et_2O$, washed with sat. aq. $NaHCO_3$ soln., 0.1M HCl, $H_2O$, and sat. aq. NaCl soln. After evaporation, FC ($SiO_2$, $CH_2Cl_2$) afforded **11** (1.233 g, 81%). Colorless oil. TLC ($CH_2Cl_2$/hexane 1:1) $R_f$ 0.28. IR (neat): 3089*w*, 3007*w*, 2951*m*, 2863*w*, 1757*s*, 1736*s*, 1594*m*,

1517*m*, 1438*m*, 1410*m*, 1377*m*, 1335*s*, 1274*s*, 1200*m*, 1149*s*, 1019*m*, 992*m*, 901*m*, 813*m*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.35-7.15 (*AA'BB'*, 4H); 6.41 (*dd*, *J* = 10.8, 17.4, 1H); 5.27 (*d*, *J* = 17.4, 1H); 5.18 (*s*, 2H); 5.10 (*d*, *J* = 10.8, 1H); 5.04 (br. *s*, 1H); 5.00 (br. *s*, 1H); 3.74 (*s*, 3H); 3.43 (*s*, 2H); 2.90–2.75 (*m*, 2H); 2.60–2.45 (*m*, 2H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 166.9; 166.4; 145.5; 142.6; 138.7; 132.8; 128.6; 128.5; 116.1; 113.3; 67.1; 52.3; 41.2; 34.0; 33.0. EI-MS: 288 (0.2, $M^+$), 221 (12), 170 (100, $C_{13}H_{14}^+$). Anal. calc. for $C_{17}H_{20}O_4$ (288.34): C 70.81, H 6.99; found: C 71.03, H 6.85.

*Methyl 4-(3-Methylidenepent-4-enyl)benzyl 2-Bromopropanedioate* (**10**). To a soln. of **11** (1.10 g, 3.81 mmol) in THF (20 ml), DBU (696 mg, 4.47 mmol) was added by syringe. After 5 min, the mixture was cooled to −78° and, after 5 min at −78°, a soln. of $CBr_4$ (1.516 g, 4.57 mmol) in THF (5 ml) was added by syringe. The yellow mixture was quenched after 20 min with 0.1M HCl, diluted with $Et_2O$, washed with 0.1M HCl, sat. aq. $NaHCO_3$, and sat. aq. NaCl soln., and dried ($MgSO_4$). After evaporation, CC ($SiO_2$, $CH_2Cl_2$/hexane 1:1) provided **10** (955 mg, 68%). Colorless oil. TLC ($CH_2Cl_2$/hexane 1:1): $R_f$ 0.40. IR (neat): 3088*w*, 3006*w*, 2954*w*, 2861*w*, 1767*s*, 1747*s*, 1594*m*, 1516*w*, 1436*m*, 1376*w*, 1308*m*, 1288*m*, 1144*s*, 1015*m*, 994*m*, 900*m*, 816*w*, 651*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.35–7.20 (*AA'BB'*, 4H); 6.41 (*dd*, *J* = 10.8, 17.5, 1H); 5.28 (*d*, *J* = 17.5, 1H); 5.23 (*s*, 2H); 5.10 (*d*, *J* = 10.8, 1H); 5.05 (br. *s*, 1H); 5.00 (br. *s*, 1H); 4.89 (*s*, 1H); 3.81 (*s*, 3H); 3.90–3.75 (*m*, 2H); 2.60–2.45 (*m*, 2H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 164.9; 164.3; 145.3; 142.8; 138.6; 132.0; 128.6; 128.4; 116.1; 113.3; 68.6; 53.8; 41.9; 34.1; 33.1. EI-MS: 368/366 (1, $M^+$), 170 (100, $C_{13}H_{14}^+$). Anal. calc. for $C_{17}H_{19}BrO_4$ (367.24): C 55.60, H 5.21, Br 21.76; found: C 55.86, H 5.22, Br 21.66.

*Methyl 3',6-Dihydro-17'-oxo-5',3''-(ethano[1,4]benzenomethanoxymethano)-3''H-benzo[1,9]cyclopropa-[16,17][5,6]fullerene-$C_{60}$-$I_h$-3''-carboxylate* (**9**). To a soln. of $C_{60}$ (735 mg, 1.02 mmol) and **10** (250 mg, 0.68 mmol) in PhMe (500 ml), DBU (104 mg, 0.680 mmol) in PhMe (3 ml) was added by syringe. After 1 h, the mixture was concentrated to 200 ml, diluted with hexane (200 ml), and submitted to CC ($SiO_2$, PhMe/hexane 1:1 then 2:1): wine-red soln. of the methanofullerene mono-adduct. After evaporation of hexane, the remaining soln. was diluted with PhMe (to 1 l), deoxygenated by bubbling Ar through for 10 min, and heated to reflux for 39 h. Concentration to 100 ml and CC ($SiO_2$, PhMe), followed by recrystallization from $CS_2$/MeOH, yielded **9** (340 mg, 50%). Brown solid. M.p. > 250°. TLC (PhMe): $R_f$ 0.70. UV/VIS ($CH_2Cl_2$): 500 (sh, 2120), 450 (2940), 428 (3830), 399 (sh, 3560), 338 (sh, 21100), 305 (sh, 39500), 271 (sh, 61100), 249 (85700). IR (KBr): 2944*w*, 2914*w*, 2831*w*, 1747*s*, 1725*s*, 1513*w*, 1446*m*, 1431*m*, 1321*m*, 1288*m*, 1097*m*, 1061*m*, 585*w*, 533*m*, 524*m*. $^1$H-NMR (200 MHz, $CS_2$/$CDCl_3$ 1:1): 7.30–7.05 (br. *m*, 4H); 6.55 (*t*, *J* = 5.5, 1H); 5.30–5.10 (br. *s*, 2H); 4.01 (*s*, 3H); 3.72 (*d*, *J* = 5.5, 2H); 3.48 (br. *s*, 2H); 3.11 (br. *s*, 4H). $^{13}$C-NMR (125 MHz, $CS_2$/$C_2D_2Cl_4$ 1:1): 163.99; 162.11; 160.62; 156.28 (br.); 149.19; 148.36; 148.01; 147.35; 147.01; 146.40 (br.); 146.23; 146.22; 145.81; 145.74; 144.96; 144.90; 144.84; 144.55; 144.25; 144.10; 144.06; 143.28; 142.80; 142.68 (br.); 142.55; 142.53; 141.58; 140.27; 139.70 (br.); 138.85; 138.43 (br.); 132.08; 130.32; 128.46 (br.); 126.03; 69.95; 68.55; 65.22; 64.92; 53.78; 52.42; 43.84; 40.03; 35.89; 33.92. FAB-MS: 1007 (44, $MH^+$, $^{13}C^{12}C_{76}H_{18}O_4^+$), 720 (100, $C_{60}^+$). Anal. calc. for $C_{77}H_{18}O_4 \cdot 0.15\ CS_2$ (1018.41): C 90.99, H 1.78; found: C 90.87, H 1.84.

*Bis[4-(3-methylidenepent-4-enyl)benzyl] Propanedioate* (**14**). To a soln. of **2** (829 mg, 4.40 mmol) and propanedioyl dichloride (310 mg, 2.20 mmol) in $CH_2Cl_2$ (20 ml) at 0°, $C_5H_5N$ (348 mg, 0.36 ml, 4.40 mmol) was added by syringe. After stirring for 3 h, the mixture was diluted with $Et_2O$, the soln. washed with sat. aq. $NaHCO_3$ soln., 0.1M HCl, $H_2O$, sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated, and the residue chromatographed ($SiO_2$, $CH_2Cl_2$): **14** (780 mg, 80%). Colorless oil. IR (neat): 3087*w*, 2936*w*, 2862*w*, 1753*s*, 1736*s*, 1594*m*, 1515*m*, 1459*w*, 1410*w*, 1377*m*, 1330*m*, 1269*m*, 1146*m*, 992*m*, 900*m*, 812*m*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.27 (*d*, *J* = 8.2, 4H); 7.19 (*d*, *J* = 8.2, 4H); 6.40 (*dd*, *J* = 17.6, 10.8, 2H); 5.35–4.95 (*m*, 8H); 5.14 (*s*, 4H); 3.46 (*s*, 2H); 2.90–2.75 (*m*, 4H); 2.60–2.45 (*m*, 4H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 166.4; 145.5; 142.6; 138.8; 132.8; 128.6; 128.5; 116.2; 113.3; 67.1; 41.5; 34.1; 33.1. EI-MS: 444 (2, $M^+$), 104 (100, $C_8H_8^+$). HR-MS: 444.2290 ($M^+$, $C_{29}H_{32}O_4^+$, calc. 444.2300). Anal. calc. for $C_{29}H_{32}O_4$ (444.58): C 78.35, H 7.26; found: C 78.45, H 7.31.

*Bis[4-(3-methylidenepent-4-enyl)benzyl] 2-Bromopropanedioate* (**13**). To a soln. of **14** (472 mg, 1.06 mmol) in THF (20 ml) at r.t., DBU (194 mg, 1.27 mmol) in THF (3 ml) was added. After 5 min, the mixture was cooled to −78°, and $CBr_4$ (423 mg, 1.27 mmol) in THF (5 ml) was added. Within 75 min, the soln. was warmed to −65° and quenched with 0.1M HCl, diluted with $Et_2O$, washed with 0.1M HCl, $H_2O$, sat. aq. NaCl soln., dried ($MgSO_4$) and evaporated. CC ($SiO_2$, hexane/$CH_2Cl_2$ 1:1) afforded **13** (441 mg, 79%). Colorless oil. IR (neat): 3087*w*, 2939*w*, 1763*s*, 1744*s*, 1594*m*, 1515*w*, 1458*w*, 1421*w*, 1374*w*, 1281*m*, 1231*m*, 1142*m*, 992*m*, 899*m*, 814*m*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.25 (*d*, *J* = 8.4, 4H); 7.18 (*d*, *J* = 8.4, 4H); 6.40 (*dd*, *J* = 17.4, 10.8, 2H); 5.35–4.95 (*m*, 8H); 5.19 (*s*, 4H); 4.90 (*s*, 1H); 2.90–2.75 (*m*, 4H); 2.60–2.45 (*m*, 4H). $^{13}$C NMR (50 MHz, $CDCl_3$): 164.1; 145.3; 142.6; 138.6; 132.0; 128.5; 128.4; 116.1; 113.2; 68.5; 42.3; 34.1; 33.0. EI-MS: 524/522 (1, $M^+$), 171 (91), 104 (100, $C_8H_8^+$). Anal. calc. for $C_{29}H_{31}BrO_4$ (523.47): C 66.54, H 5.97, Br 15.26; found: C 66.66, H 6.11, Br 15.21.

*Bis[4-(3-methylidenepent-4-enyl)phenyl]methyl 3'H-Cyclopropa[1,9][5,6]fullerene-$C_{60}$-$I_h$-3',3'-dicarboxylate* (**15**) *and 3',3'',6',6''-Tetrahydro-5',3''':5'',3'''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H-dibenzo[1,9:52,60]-cyclopropa[16,17][5,6]fullerene-$C_{60}$-$I_h$-17',17''-dione* (**12**). To a soln. of $C_{60}$ (2.753 g, 3.82 mmol) and **13** (1.0 g, 1.91 mmol) in PhMe (700 ml), DBU (320 mg, 2.10 mmol) in PhMe (50 ml) was added over 5 min. After 3 h, the mixture was concentrated to 100 ml, diluted with hexane (100 ml), and chromatographed ($SiO_2$, PhMe/hexane 1:1, then 2:1): wine-red methanofullerene **15**. After evaporation of hexane, PhMe was added to give a total volume of 2.5 l, then the soln. was deoxygenated by purging with Ar for 1.5 h and heated to reflux for 36 h. Concentration and CC ($SiO_2$, PhMe), followed by recrystallization from $CHCl_3$/MeOH and drying gave **12** (1.335 g, 60%).

**15**: Wine-red soln. UV/VIS (PhMe): 691, 489, 429, 330. $^1$H-NMR (300 MHz, $Cl_2CDCDCl_2$): aromatic resonances obscured; 6.62 (*dd*, $J$ = 11.0, 17.8, 2H); 5.63 (*s*, 4H); 5.48 (*d*, $J$ = 17.8, 2H); 5.31 (*d*, $J$ = 11.0, 2H); 5.26 (*s*, 2H); 5.21 (*s*, 2H); 3.05–2.95 (*m*, 4H); 2.75–2.65 (*m*, 4H). **12**: Brown solid. M.p. > 270°. TLC (PhMe) $R_f$ 0.60. UV/VIS ($CH_2Cl_2$): 498 (3120), 468 (1660), 368 (sh, 6320), 337 (sh, 13800), 308 (sh, 21000), 264 (41400). IR (KBr): 2919*w*, 1746*m*, 1718*m*, 1638*s*, 1617*s*, 1384*w*, 1288*w*, 1256*w*, 1229*m*, 1208*m*, 1168*w*, 1098*w*, 1061*m*, 1001*w*, 946*w*, 885*w*, 799*m*, 744*m*, 625*m*, 537*m*, 525*m*. $^1$H-NMR (300 MHz, $Cl_2CDCDCl_2$): 7.13 (br. *s*, 8H); 6.52 (*t*, $J$ = 5.3, 2H); 5.18 (*s*, 4H); 3.80 (*d*, $J$ = 5.3, 4H); 3.42 (*s*, 4H); 3.06 (*s*, 8H). $^{13}$C-NMR (125 MHz, $Cl_2DCCDCl_2$): 162.88; 158.36; 153.58; 146.97; 146.50; 146.24; 145.70; 145.51; 145.19; 144.60; 143.09; 142.81; 142.27 (br.); 140.17; 139.90; 139.72; 139.57; 132.02; 130.61; 128.62 (br.); 125.93; 69.34; 69.13; 62.89; 62.85; 54.45; 43.53; 39.93; 35.49; 34.49. MALDI-TOF-MS (DHB): 1178 (23, $[M + O]^+$, $^{12}C_{89}H_{30}O_5^+$, formed during sample preparation for MS), 1162 (100, $M^+$, $^{12}C_{89}H_{30}O_4^+$). Anal. calc. for $C_{89}H_{30}O_4 \cdot 0.75\ CHCl_3$ (1252.76): C 86.05, H 2.47; found: C 85.94, H 2.74.

*Bis(2-ethoxy-2-oxoethyl) Propanedioate* (**18**). To a soln. of propanedioyl dichloride (1.35 g, 9.60 mmol) in $CH_2Cl_2$ (50 ml) at 0°, ethyl hydroxyacetate (2.00 g, 19.2 mmol) and $C_5H_5N$ (1.52 g, 19.2 mmol) were added over 15 min by syringe. After 75 min at 0°, the ice bath was removed, and stirring was continued at r.t. for 14 h. The mixture was diluted with $Et_2O$, washed with sat. aq. $NaHCO_3$ soln., 0.1M HCl, $H_2O$, sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated after which bulb-to-bulb distillation (140°/0.2 Torr) provided **18** (1.95 g, 73%). Pale-yellow oil. IR (neat): 2986*m*, 1748*s*, 1425*s*, 1383*s*, 1292*s*, 1211*s*, 1144*s*, 1071*s*, 1028*s*, 943*w*, 854*m*, 790*w*, 731*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 4.62 (*s*, 4H); 4.18 (*q*, $J$ = 7.2, 4H); 3.57 (*s*, 2H); 1.23 (*t*, $J$ = 7.2, 6H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 166.9; 165.2; 61.4; 61.3; 40.3; 13.9. EI-MS: 277 (0.5, $MH^+$), 105 (100, $C_4H_9O_3^+$). Anal. calc. for $C_{11}H_{16}O_8$ (276.24): C 47.83, H 5.84; found: C 47.79, H 5.82.

*Bis(2-ethoxy-2-oxoethyl) 2-Bromopropanedioate* (**17**). To a soln. of **18** (2.25 g, 8.14 mmol) in THF (20 ml), DBU (1.49 g, 9.77 mmol) was added. After 5 min at r.t., the mixture was cooled to −70°, and a soln. of $CBr_4$ (3.24 g, 9.77 mmol) in THF (5 ml) was added rapidly by syringe. The resulting suspension was allowed to warm to r.t. overnight. Dilution with $Et_2O$, washing with $H_2O$, sat. aq. NaCl soln., drying ($MgSO_4$), and bulb-to-bulb distillation (140°/0.05 Torr) gave **17** (6.12 g, 75%) contaminated by 3% each of starting material and dibrominated product ($^1$H-NMR). Further purification by distillation or CC was not possible, but the minor impurities did not affect the subsequent *Bingel* addition and were readily removed afterwards. Pale-yellow oil. IR (neat): 2985*m*, 1753*s*, 1424*m*, 1381*s*, 1301*s*, 1208*s*, 1146*s*, 1063*m*, 1030*m*, 943*w*, 858*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 5.07 (*s*, 1H); 4.78 (*d*, $J$ = 15.7, 2H); 4.69 (*d*, $J$ = 15.7, 2H); 4.24 (*q*, $J$ = 7.2, 4H); 1.29 (*t*, $J$ = 7.2, 6H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 166.3; 163.6; 62.4; 61.7; 40.7; 14.0. EI-MS: 356/354 (1, $M^+$), 253/251 (50), 207/205 (49), 173 (100, $C_7H_9O_5^+$), 105 (99), 69 (59). HR-MS: 353.9933 ($M^+$, $C_{11}H_{15}{}^{79}BrO_8^+$, calc. 353.9951).

*Diethyl 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3'''-Bis(ethano[1,4]benzenomethanoxymethano)-3'''H,3''''H-dibenzo[1,9:52,60]dicyclopropa[16,17:21,40][5,6]fullerene-$C_{60}$-$I_h$-3'''',3''''-dicarboxylate* (**16**). To a suspension of **12** (25.0 mg, 0.0215 mmol) and diethyl 2-bromopropanedioate (25.7 mg, 0.107 mmol) in dry PhCl (19.5 ml), DBU (16.4 mg, 0.107 mmol) in PhCl (0.5 ml) was added. After 135 min, the mixture was directly chromatographed ($SiO_2$, PhMe then $CH_2Cl_2$) to give a bright-red soln. of **16**. Concentration and precipitation by addition of MeOH, followed by drying yielded **16** (20.4 mg, 72%). Red solid. M.p. > 270°. TLC (PhMe): $R_f$ 0.13. UV/VIS ($CH_2Cl_2$): 578 (1040), 556 (sh, 1350), 533 (sh, 2370), 492 (3550), 459 (3880), 414 (sh, 5620), 386 (8740), 278 (71700). IR ($CHCl_3$): 3053*w*, 1740*m*, 1719*m*, 1264*s*, 1015*m*, 908*w*, 704*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 7.20 (br. *s*, 4H); 7.12 (br. *s*, 4H); 6.41 (*t*, $J$ = 5.3, 2H); 5.19 (*s*, 4H); 4.40–4.20 (*m*, 4H); 3.60 (*dd*, $J$ = 5.3, 14.1, 2H); 3.56 (*dd*, $J$ = 5.3, 14.1, 2H); 3.28 (*d*, $J$ = 14.3, 2H); 3.18 (*d*, $J$ = 14.3, 2H); 3.06 (br. *s*, 8H); 1.32 (*t*, $J$ = 7.1, 3H); 1.30 (*t*, $J$ = 7.1, 3H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 163.43; 163.19; 162.42; 158.10; 156.70; 153.27; 152.16; 150.21; 148.14; 147.23; 147.14; 146.19; 146.11; 145.82; 145.35; 145.31; 145.08; 145.00; 144.45 (2×); 142.65; 142.44 (2×) ; 141.95; 141.93; 141.85; 141.16; 140.78; 139.82; 139.51; 139.47; 131.85; 130.37; 130.28; 128.25; 125.39; 71.82; 68.61; 67.49; 67.28; 62.74; 62.63; 62.47; 62.25; 53.60; 52.72; 42.82; 39.32; 35.02; 34.23; 14.13 (2×). MALDI-TOF-MS (HABA): 1352 (31, $[M + 2\ O]^+$, $^{12}C_{96}H_{40}O_{10}^+$), 1336 (31, $[M + O]^+$, $^{12}C_{96}H_{40}O_9^+$) (both peaks due to oxidation during sample preparation for MS), 1320 (100, $M^+$, $^{12}C_{96}H_{40}O_8^+$).

*Bis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-Bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3''''H-dibenzo[1,9:52,60]dicyclopropa[16,17:21,40][5,6]fullerene -$C_{60}$-$I_h$-3'''',3''''-dicarboxylate* (**19**). To a suspension of **12** (200 mg, 0.172 mmol) in PhCl (100 ml), **17** (458 mg, 1.29 mmol) and DBU (196 mg, 1.29 mmol) in PhCl (1 ml) were added. The soln. was stirred at r.t for 125 min, then chromatographed ($SiO_2$, PhMe then $CHCl_3$/EtOH 99:1) to separate unreacted starting material from higher adducts. A second CC ($SiO_2$-*H*, $CH_2Cl_2$) gave traces of three isomeric tetrakis-adducts followed by bright-red **19**, along with higher adducts. Recrystallization from $CH_2Cl_2$/MeOH and drying afforded **19** (173 mg, 70%). Red solid. M.p. 230° (dec.). TLC ($CH_2Cl_2$): $R_f$ 0.48. UV/VIS ($CH_2Cl_2$): 578 (750), 493 (2790), 459 (3090), 414 (sh, 4370), 385 (6900), 278 (53400), 241 (sh, 63100). IR (KBr): 2919*w*, 1751*s*, 1636*w*, 1617*w*, 1449*w*, 1383*m*, 1288*m*, 1257*m*, 1233*m*, 1193*s*, 1106*m*, 1061*w*, 801*w*, 667*m*, 536*w*, 528*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.19 (*s*, 4H); 7.13 (*s*, 4H); 6.40 (*t*, *J* = 5.4, 2H); 5.18 (br. *m*, 4H); 4.76 (*s*, 2H); 4.73 (*s*, 2H); 4.22 (*q*, *J* = 7.1, 2H); 4.19 (*q*, *J* = 7.1, 2H); 3.64 (*dd*, *J* = 5.4, 14.4, 2H); 3.55 (*dd*, *J* = 5.4, 14.4, 2H); 3.28 (*d*, *J* = 14.2, 2H); 3.18 (*d*, *J* = 14.2, 2H); 3.05 (br. *s*, 8H); 1.35–1.15 (*m*, 6H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 166.51; 166.36; 162.39; 162.31; 162.17; 158.05; 156.67; 153.24; 152.11; 150.20; 148.09; 147.32; 147.10; 146.17; 146.06; 145.96; 145.78; 145.45; 145.29; 145.10; 144.93; 144.54; 144.45; 142.66; 142.52; 142.38; 141.91; 141.32; 141.12; 140.71; 139.74; 139.59; 139.43; 131.74; 130.29; 128.39 (br.); 128.15 (br.); 125.34; 70.97; 68.58; 67.43; 67.16; 62.41; 62.31; 62.18; 61.60; 61.55; 53.56; 51.33; 42.79; 39.23; 34.98; 34.13; 33.94; 14.10; 14.04. MALDI-TOF-MS (DHB): 1459 (42, $[M + Na]^+$, $^{12}C_{100}H_{44}O_{12}Na^+$), 1437 (100, $M^+$, $^{13}C^{12}C_{99}H_{44}O_{12}^+$), 1335 (13), 1165 (22). Anal. calc. for $C_{100}H_{44}O_{12}$ (1437.44): C 83.56, H 3.09; found: C 82.35, H 3.38.

*Tetraethyl 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3''''H,3'''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:30,31][5,6]fullerene-$C_{60}$-$I_h$-3''''',3'''''',3''''''',3'''''''-tetracarboxylate* (**20**) *and Tetraethyl 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'', 3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H,3''''H,3'''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:44,45][5,6]fullerene-$C_{60}$-$I_h$-3''''',3'''''', 3''''''',3'''''''-tetracarboxylate* (**22**). To a soln. of **16** (764 mg, 0.578 mmol) in PhCl (50 ml) was added at 0° DBU (660 mg, 4.337 mmol) and diethyl 2-bromopropanedioate (1.04 g, 4.34 mmol). The resulting mixture was stirred for 90 min, then washed with sat. aq. $NH_4Cl$ and sat. aq. NaCl soln., and dried ($MgSO_4$). Evaporation and re-dissolution of the red viscous residue in a minimum amount of $CH_2Cl_2$, followed by precipitation with pentane, afforded an orange powder which was chromatographed ($SiO_2$-*H*, $CH_2Cl_2$/hexane 9:1) to yield hexakis-adduct **24** (412 mg, 44%; see below) and **20** (280 mg, 33%), as well as mixed fractions containing **20** and **22**.

**20**: Orange solid. M.p. 235–245° (dec.). UV/VIS ($CH_2Cl_2$): 526 (1960), 387 (sh, 7020), 356 (sh, 17100), 285 (59900). IR (KBr): 2978*w*, 2922*w*, 2833*w*, 1747*s*, 1444*m*, 1367*m*, 1350*s*, 1290*m*, 1077*m*, 1063*m*, 1031*m*, 1011*m*, 854*w*, 753*m*, 707*m*, 661*w*, 590*w*, 538*m*, 528*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.07 (br. *s*, 8H); 6.27 (*t*, *J* = 5.3, 2H); 5.11 (br. *s*, 4H); 4.36 (*q*, *J* = 7.1, 4H); 4.33 (*q*, *J* = 7.1, 4H); 3.42 (*d*, *J* = 5.3, 4H); 3.05–2.90 (*m*, 12H); 1.34 (*t*, *J* = 7.1, 6H); 1.33 (*t*, *J* = 7.1, 6H). $^{13}$C-NMR (100 MHz, $CDCl_3$): 163.89; 163.64; 162.39; 157.96; 153.47; 147.56; 145.90; 145.68; 145.37; 145.24; 143.34; 142.50; 142.43; 141.95; 141.78; 141.57; 141.48; 138.29; 131.80; 130.20; 128.19; 125.30; 70.99; 68.47; 66.73; 62.78; 62.67; 62.36; 61.90; 53.61; 45.47; 42.43; 38.98; 34.89; 34.27; 14.16. FAB-MS: 1528.3 (12, $[M + 2\ O]^+$), 1512.0 (49, $[M + O]^+$) (both peaks due to oxidation during sample preparation for MS), 1480.6 (100, $M^+$), 1479.6 (82), 1478.7 (82).

**22**: $^1$H-NMR (200 MHz, $CDCl_3$): 7.10 (br. *s*, 8H); 6.27 (*t*, *J* = 5.1, 2H); 5.28 (br. *s*, 4H); 4.45–4.15 (*m*, 8H); 3.44 (*dd*, *J* = 5.1, 14.0, 2H); 3.32 (*dd*, *J* = 5.1, 14.0, 2H); 3.21 (*d*, *J* = 14.2, 2H); 3.11 (*d*, *J* = 14.2, 2H); 3.05–2.90 (*m*, 8H); 1.45–1.20 (*m*, 12H).

*Tetrakis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-Bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3''''H,3'''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:30,31][5,6] fullerene-$C_{60}$-$I_h$-3''''', 3''''',3'''''',3''''''-tetracarboxylate* (**21**) *and Tetrakis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3'':5'',3'''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H,3''''H,3'''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21, 40:44, 45][5,6]fullerene-$C_{60}$-$I_h$-3''''',3''''',3'''''',3''''''-tetracarboxylate* (**23**). To a soln. of **19** (89.9 mg, 0.063 mmol) in PhCl (0.5 ml), DBU (9.5 mg, 0.063 mmol) and **17** (22.2 mg, 0.063 mmol) were added, each in PhCl (0.1 ml). The resulting mixture was stirred for 22 h at r.t., then chromatographed ($SiO_2$-*H*, $CH_2Cl_2$/ACOEt 100:1.5) to elute first unreacted **19** (28.1 mg, 31%), followed by the two isomeric **21** and **23**. Trace quantities of a non-characterized third compound running slightly faster than **21** were also separated. The product fractions were diluted with cyclohexane and concentrated. The precipitated solids were washed with MeOH and dried to give **21** (30.0 mg, 28%) and **23** (12.3 mg, 11%).

**21**: Orange solid. M.p. 195–198° (dec.). TLC ($CH_2Cl_2$): $R_f$ 0.18. UV/VIS ($CH_2Cl_2$): 525 (1820), 491 (1860), 391 (sh, 6390), 285 (55800), 260 (sh, 51900), 244 (sh, 69300). IR (KBr): 2922*w*, 1750*m*, 1638*m*, 1617*m*, 1383*m*, 1260*w*, 1190*m*, 1092*w*, 800*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.12 (*s*, 8H); 6.30 (*t*, *J* = 5.1, 2H); 5.13 (br. *s*, 4H); 4.84 (*s*, 4H); 4.80 (*s*, 4H); 4.30–4.10 (*m*, 8H); 3.44 (*d*, *J* = 5.1, 4H); 3.07 (*s*, 4H); 3.10–2.90 (br. *m*, 8H); 1.28

(*t*, *J* = 7.2, 6H); 1.25 (*t*, *J* = 7.1, 6H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 166.64; 166.47; 162.88; 162.68; 162.30; 157.99; 153.51; 147.71; 145.92; 145.73; 145.44; 143.46; 142.58; 142.43; 141.98; 141.81; 141.66; 141.14; 137.84; 131.74; 130.45; 128.29 (br.); 125.27; 70.47; 68.53; 66.73; 62.44; 62.39; 62.27; 62.02; 61.92; 61.66; 61.60; 53.67; 44.22; 42.47; 38.96; 34.91; 34.22; 14.15; 14.10. MALDI-TOF-MS (DHB): 1712 (100, $M^+$, $^{13}C_2^{12}C_{109}H_{58}O_{20}^+$), 1607 (27), 1733 (72), 1749 (29). Anal. calc. for $C_{111}H_{58}O_{20}$ (1711.67): C 77.89, H 3.42; found: C 77.71, H 4.09.

**23**: Orange-red solid. M.p. 190–193° (dec.). TLC ($CH_2Cl_2$): $R_f$ 0.13. UV/VIS ($CH_2Cl_2$): 570 (1050), 548 (1210), 527 (1500), 455 (2270), 364 (sh, 11900), 302 (56800), 275 (sh, 59900), 246 (sh, 68300). IR (KBr): 2922*w*, 1751*s*, 1638*w*, 1618*w*, 1447*w*, 1422*w*, 1382*m*, 1289*m*, 1254*m*, 1194*s*, 1167*m*, 1092*m*, 1058*m*, 1033*m*, 850*w*, 797*w*, 756*w*, 711*w*, 590*w*, 540*w*, 530*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.30–7.10 (br. *m*, 8H); 6.27 (*t*, *J* = 5.1, 2H); 5.40–5.20 (br. *m*, 4H); 4.75 (*s*, 4H); 4.71 (*s*, 2H); 4.66 (*s*, 2H); 4.30–4.10 (*m*, 8H); 3.45 (*dd*, *J* = 5.1, 14.0, 2H); 3.34 (*dd*, *J* = 5.1, 14.0, 2H); 3.22 (*d*, *J* = 14.2, 2H); 3.12 (*d*, *J* = 14.2, 2H); 3.10–2.90 (br. *m*, 8H); 1.30–1.15 (*m*, 12H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 166.50; 166.46; 166.40; 163.18; 162.92; 162.33; 162.21; 155.91; 153.50; 153.39; 151.35; 146.62; 146.37; 145.87; 145.70; 145.54; 144.37; 144.15; 143.99; 143.40 (br.); 143.26; 143.21; 142.99; 142.93; 142.72; 142.52 (br.); 142.38; 142.22; 142.21; 142.07; 141.66; 137.32 (br.); 136.94; 131.76; 130.37 (br.); 128.51 (br.); 128.23 (br.); 125.23; 70.36; 68.72; 66.49; 65.99; 65.93; 62.29; 62.20; 62.10; 62.02; 61.86; 61.74; 61.57; 61.54; 61.50; 52.65; 45.99; 43.60; 42.72; 39.71; 39.28; 34.93; 34.15; 14.10; 14.04; 14.01. MALDI-TOF-MS (CCA): 1735 (10, $[M + Na]^+$, $^{13}C_2^{12}C_{109}H_{58}O_{20}Na^+$), 1712 (100, $M^+$, $^{13}C_2^{12}C_{109}H_{58}O_{20}^+$), 1610 (8), 1545 (25). Anal. calc. for $C_{111}H_{58}O_{20}$ (1711.67): C 77.89, H 3.42; found: C 78.04, H 3.38.

*Hexaethyl 3′,3″,6′,6″-Tetrahydro-17′,17″-dioxo-5′,3‴:5″,3⁗-bis(ethano[1,4]benzenomethanoxymethano)-3‴H, 3⁗H,3⁗⁗H,3⁗⁗⁗H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45][5,6]fullerene-$C_{60}$-$I_h$-3⁗⁗,3⁗⁗⁗, 3⁗⁗⁗⁗,3⁗⁗⁗⁗⁗,3⁗⁗⁗⁗⁗⁗-hexacarboxylate* (**24**). To **12** (20.5 mg, 0.0176 mmol) in an oven-dried 10 ml flask under Ar, diethyl 2-bromopropanedioate (42.1 mg, 0.176 mmol) in dry PhCl (0.45 ml) was added, followed by DBU (26.8 mg, 0.176 mmol) in dry PhCl (0.55 ml). After 5 min, the initial suspension had turned into a homogeneous, bright-red mixture, and after stirring for 2 h more, CC ($SiO_2$, $CH_2Cl_2$) afforded a bright-yellow soln. of **24**, which was evaporated. Subsequent recrystallization from $CH_2Cl_2$/pentane gave **24** (21.1 mg, 73%). Yellow solid. M.p. > 270°. TLC ($CH_2Cl_2$): $R_f$ 0.41. UV/VIS ($CH_2Cl_2$): 353 (sh, 21800), 332 (sh, 35000), 308 (sh, 64400), 288 (73300). IR (KBr): 2981*w*, 2925*w*, 2847*w*, 1746*s*, 1725*m*, 1630*w*, 1444*w*, 1384*w*, 1367*w*, 1292*m*, 1254*s*, 1217*m*, 1208*m*, 1176*w*, 1095*w*, 1065*w*, 1021*w*, 856*w*, 799*w*, 754*w*, 710*w*, 531*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.25–7.05 (br. *m*, 8H); 6.16 (*t*, *J* = 5.5, 2H); 5.22 (*s*, 4H); 4.34 (*q*, *J* = 7.1, 4H); 4.28 (*q*, *J* = 7.1, 4H); 4.24 (*q*, *J* = 7.1, 4H); 3.21 (*d*, *J* = 5.5, 4H); 3.05–2.85 (*m*, 12H); 1.35 (*t*, *J* = 7.1, 6H); 1.29 (*t*, *J* = 7.1, 6H); 1.26 (*t*, *J* = 7.1, 6H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 164.14; 163.85; 163.67; 162.99; 155.27; 155.07; 145.77; 145.41; 145.29; 144.85; 143.65; 143.36; 143.14; 142.51; 139.98; 139.73; 139.34; 139.08; 131.75; 130.24; 128.26; 125.12; 70.66; 68.56; 65.88; 62.62; 62.53; 62.42; 61.70; 61.60; 45.84; 45.52; 44.54; 42.29; 39.61; 34.84; 34.23; 14.14; 14.03; 14.00. MALDI-TOF-MS (DHB): 1658 (27, $[M + Na]^+$, $^{12}C_{110}H_{60}O_{16}Na^+$), 1636 (100, $M^+$, $^{12}C_{110}H_{60}O_{16}^+$), 1591 (31), 1478 (35). Anal. calc. for $C_{110}H_{60}O_{16}$ (1637.70): C 80.68, H 3.69; found: C 79.87, H 3.31. X-Ray: see [39].

*Hexakis(2-ethoxy-2-oxoethyl) 3′,3″,6′,6″-Tetrahydro-17′,17″-dioxo-(5′,3‴:5″,3⁗-bis(ethano[1,4]benzenomethanoxymethano)-3⁗H, 3⁗⁗H,3⁗⁗⁗H,3⁗⁗⁗⁗H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21, 40:30,31:44,45][5,6]-fullerene-$C_{60}$-$I_h$-3⁗⁗,3⁗⁗⁗,3⁗⁗⁗⁗,3⁗⁗⁗⁗⁗,3⁗⁗⁗⁗⁗,3⁗⁗⁗⁗⁗⁗-hexacarboxylate* (**25**). To a soln. of **23** (60.0 mg, 0.035 mmol) in PhCl (0.5 ml), **17** (24.9 mg, 0.070 mmol) in PhCl (0.25 ml) and DBU (10.7 mg, 0.070 mmol) in PhCl (0.1 ml) were added. After stirring for 54 h, additional portions of **17** (49.8 mg, 0.14 mmol) and DBU (21.4 mg, 0.14 mmol) were each added in PhCl (0.1 ml). After an additional 21 h, the mixture was chromatographed ($SiO_2$-*H*, $CH_2Cl_2$/AcOEt 100:3); the yellow product fraction was diluted with cyclohexane, and concentration afforded a precipitate which was dried to give **25** (59.6 mg, 85%). Yellow solid. M.p. 232–234° (dec.). TLC ($CHCl_3$/EtOH 100:1): $R_f$ 0.09. UV/VIS ($CH_2Cl_2$): 355 (sh, 18200), 332 (sh, 29500), 308 (sh, 56500), 286 (69300). IR (KBr): 2993*w*, 1749*s*, 1638*m*, 1617*m*, 1383*m*, 1286*m*, 1264*m*, 1192*s*, 1094*m*, 1061*w*, 1033*w*, 853*w*, 794*w*, 756*m*, 710*w*, 614*w*, 593*w*, 532*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.16 (br. *s*, 8H); 6.16 (*t*, *J* = 4.9, 2H); 5.21 (br. *s*, 4H); 4.78 (*s*, 4H); 4.73 (*s*, 4H); 4.68 (*s*, 4H); 4.30–4.10 (*m*, 12H); 3.22 (*d*, *J* = 4.9, 4H); 3.10–2.85 (br. *m*, 12H); 1.35–1.15 (*m*, 18H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 166.57; 166.47; 166.39; 162.97; 162.79; 162.69; 155.26; 155.14; 145.75; 145.55; 145.46; 145.30; 143.89; 143.46; 142.51; 139.50; 139.16 (br.); 138.67; 131.69; 130.27; 128.39 (br.); 125.11; 70.21; 68.61; 65.90; 65.35; 62.31; 62.22; 62.19; 61.74; 61.62; 61.59; 61.57; 61.44; 45.56; 44.61; 43.34; 42.30; 39.36; 34.82; 34.17; 14.12; 14.04; 14.01. MALDI-TOF-MS (CCA): 2009 (34, $[M + Na]^+$, $^{13}C_2^{12}C_{120}H_{72}O_{28}Na^+$), 1986 (100, $M^+$, $^{13}C_2^{12}C_{120}H_{72}O_{28}^+$), 1882 (18). Anal. calc. for $C_{122}H_{72}O_{28}$ (1985.90): C 73.79, H 3.65; found: C 73.28, H 3.45.

*Tetrakis(2-ethoxy-2-oxoethyl) 3′,3″,6′,6″-Tetrahydro-17′,17″-dioxo-3⁗⁗,3⁗⁗⁗-bis[(trimethylsilyl)ethynyl]-5′, 3‴:5″,3⁗-bis(ethano[1,4]benzenomethanoxymethano)-3‴H, 3⁗H,3⁗⁗H,3⁗⁗⁗H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45][5,6]fullerene-$C_{60}$-$I_h$-3⁗⁗,3⁗⁗⁗,3⁗⁗⁗⁗,3⁗⁗⁗⁗⁗-tetracarboxylate* (**29**). To a soln. of **21**

(149 mg, 0.087 mmol) and **28** (250 mg, 0.870 mmol) in $Me_2SO$ (8 ml) was added portionwise a soln. of DBU (132 mg, 0.870 mmol) in $Me_2SO$ (1 ml) over 2 min. The mixture immediately turned black and, after 1 h, it was diluted with PhMe, washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. CC ($SiO_2$-*H*, $CH_2Cl_2$/AcOEt 100:2) afforded the product which was precipitated from a conc. soln. in $CH_2Cl_2$ by addition of MeOH: **29** (147.2 mg, 88%). Yellow solid. M.p. 230–232° (dec.). TLC ($CH_2Cl_2$): $R_f$ 0.19. UV/VIS ($CH_2Cl_2$): 352 (sh, 22100), 336 (sh, 32500), 309 (54200), 289 (58600), 254 (sh, 49700). IR (KBr): 2955*w*, 2169*w*, 1747*s*, 1638*m*, 1617*m*, 1450*w*, 1421*w*, 1382*m*, 1250*m*, 1190*s*, 1090*m*, 1058*m*, 1032*m*, 847*m*, 757*m*, 710*w*, 647*w*, 619*w*, 592*w*, 532*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.17 (br. *s*, 8H); 6.17 (*t*, $J$ = 5.2, 2H); 5.22 (br. *s*, 4H); 4.78 (*s*, 4H); 4.75 (*s*, 4H); 4.30–4.10 (*m*, 8H); 3.17 (*d*, $J$ = 5.2, 4H); 3.10–2.85 (br. *m*, 8H); 2.97 (*s*, 4H); 1.29 (*t*, $J$ = 7.1, 6H); 1.22 (*t*, $J$ = 7.1, 6H); 0.14 (*s*, 18H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 166.60; 166.49; 162.95; 162.84; 162.74; 155.85; 155.16; 145.76; 145.55; 145.53; 145.11 (br.); 143.86; 143.37 (br.); 143.27 (br.); 142.48; 139.85; 139.46; 139.37; 139.04 (br.); 131.69; 129.70; 128.35 (br.); 124.99; 97.86; 88.33; 70.22; 69.96; 68.62; 65.93; 62.95; 62.85; 62.30; 62.23; 61.66; 61.64; 61.61; 61.56; 45.14; 44.58; 42.29; 39.27; 34.85; 34.16; 20.41; 14.14; 14.03; 0.03. MALDI-TOF-MS (CCA): 1918 ($M^+$, $^{13}C_2{}^{12}C_{120}H_{76}O_{20}Si_2^+$, 78), 1710 ($[M - C_5(SiMe_3)_2]^+$, $^{12}C_{111}H_{58}O_{20}^+$, 100). Anal. calc. for $C_{122}H_{76}O_{20}Si_2$ (1918.10): C 76.40, H 3.99; found: C 76.55, H 4.09.

*Tetrakis(2-ethoxy-2-oxoethyl) 3'''',3''''''-Diethynyl-3',3'',6',6''-tetrahydro-17',17''-dioxo-5',3''':5'',3'''-bis(ethano-[1,4]benzenomethanoxymethano)-3'''H,3''''H,3''''''H,3''''''H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30, 31:44,45][5,6]fullerene-$C_{60}$-$I_h$-3'''',3'''',3''''',3''''''-tetracarboxylate* (**30**). To a soln. of **29** (95.9 mg, 0.050 mmol) in dry THF (10 ml) under Ar was added $Bu_4NF$ on $SiO_2$ (125 mg, 0.138 mmol). After 1 h, sat. aq. $NH_4Cl$ soln. was added and the mixture poured into PhMe. The org. phase was washed with sat. aq. $NH_4Cl$ soln., $H_2O$, and sat. aq. NaCl soln, dried ($MgSO_4$), and evaporated. CC ($SiO_2$-*H*, $CH_2Cl_2$/AcOH 100:1.5) followed by recrystallization from $CHCl_3$/MeOH yielded **30** (79.9 mg, 90%). Yellow solid. M.p. > 270°. TLC ($CH_2Cl_2$): $R_f$ 0.21. UV/VIS ($CH_2Cl_2$): 353 (sh, 18700), 308 (sh, 53400), 286 (65600). IR (KBr): 3288*w*, 2925*w*, 2119*w*, 1751*s*, 1639*m*, 1617*m*, 1382*m*, 1289*m*, 1250*m*, 1192*s*, 1092*m*, 1061*m*, 1032*w*, 851*w*, 799*w*, 756*m*, 710*m*, 542*w*, 532*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.15 (br. *s*, 8H); 6.16 (*t*, $J$ = 5.2, 2H); 5.21 (br. *s*, 4H); 4.77 (*s*, 4H); 4.71 (*s*, 4H); 4.24 (*q*, $J$ = 7.2, 4H); 4.18 (*q*, $J$ = 7.2, 4H); 3.21 (*d*, $J$ = 5.2, 4H); 3.10–2.85 (br. *m*, 12H); 2.42 (*s*, 2H); 1.28 (*t*, $J$ = 7.2, 6H); 1.23 (*t*, $J$ = 7.2, 6H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 166.53; 166.48; 162.87; 162.80; 162.66; 155.88; 155.22; 145.84; 145.52; 145.49; 144.04; 143.35 (br.); 143.21 (br.); 142.49; 139.56; 139.51; 139.10 (br.); 139.03; 131.67; 130.29; 128.36 (br.); 125.02; 76.89; 71.84; 70.34; 68.63; 65.99; 62.27; 62.23; 61.71; 61.64; 61.63; 61.60; 45.20; 44.67; 42.34; 39.46; 34.83; 34.12; 18.37; 14.14; 14.06. MALDI-TOF-MS (CCA): 1796 (40, $[M + Na]^+$, $^{13}C^{12}C_{115}H_{60}O_{20}Na^+$), 1772 (100, $M^+$, $^{12}C_{116}H_{60}O_{20}^+$), 1711 (89, $[M - C_5H_2]^+$, $^{13}C^{12}C_{110}H_{58}O_{20}^+$). Anal. calc. for $C_{116}H_{60}O_{20}$ (1773.74): C 78.55, H 3.41; found: C 77.82, H 3.61.

*Dodecakis(2-ethoxy-2-oxoethyl) 3'',3''',3''''''',3''''''',3''''''''',3''''''''''',6'',6''',6''''''',6''''''''',6''''''''''', 6''''''''''''-Dodecahydro-17'',17''',17''''''',17''''''''',17''''''''''',17''''''''''''-hexaoxotrispiro[cyclopentadeca-2,4,7,9, 12,14-hexayne-1,3''''''':6,3''''''''''':11,3''''''''''''''-tris{5',3''':5'',3'''-bis(ethano[1,4]benzenomethanoxymethano)-3''' H, 3'''' H, 3''''' H,3''''''H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45][5,6]fullerene-$C_{60}$-$I_h$}]-3''''',3''''',3''''''',3''''''',3''''''''',3''''''''',3''''''''',3''''''''',3''''''''''',3''''''''''',3''''''''''',3''''''''''''''-dodecacarboxylate* (**26**) *and Hexadekakis(2-ethoxy-2-oxoethyl) 3'',3''',3''''''',3''''''''',3''''''''''',3''''''''''''',3''''''''''''''',3''''''''''''''''', 3''''''''''''''''',6'',6''',6''''''',6''''''''',6''''''''''',6''''''''''''',6''''''''''''''',6''''''''''''''''-Hexadecahydro-17'',17''', 17''''''',17''''''''',17''''''''''',17''''''''''''',17''''''''''''''',17''''''''''''''''-octaoxotetraspiro[cycloeicosa-2,4,7,9,12, 14,17,19-octayne-1,3''''''':6, 3''''''''''':11, 3''''''''''''''':16, 3''''''''''''''''''' - tetrakis {5', 3''':5'', 3''' - bis(ethano-[1,4]benzenomethanoxymethano)-3'''H,3''''H,3''''''H,3''''''H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30, 31:44,45][5,6]fullerene-$C_{60}$-$I_h$}]-3''''',3''''',3''''''',3''''''',3''''''''',3''''''''',3''''''''',3''''''''',3''''''''''',3''''''''''',3''''''''''',3''''''''''''''',3''''''''''''''',3''''''''''''''',3''''''''''''''''',3''''''''''''''''',3''''''''''''''''',3''''''''''''''''''-hexadecacarboxylate* (**27**).

To a suspension of activated molecular sieves (4 Å, 8 g) in $C_5H_5N$ (380 ml) containing $Cu(OAc)_2$ (2.345 g, 12.91 mmol) under Ar, **30** (114 mg, 0.065 mmol) in $C_5H_5N$ (20 ml) was added over 225 min by syringe pump. After 20 h, the mixture was poured into PhMe (300 ml), the soln. washed with aq. $CuSO_4$ soln. to remove $C_5H_5N$ and then with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. CC ($SiO_2$-*H*, $CH_2Cl_2$/AcOEt 100:5 then 100:8.5), followed by precipitation with cyclohexane from the concentrated yellow product fractions, and washing with MeOH gave **26** (37.1 mg, 32%) and **27** (23.8 mg, 21%).

**27**: Yellow solid. M.p. > 250°. TLC ($CH_2Cl_2$/AcOEt 100:5): $R_f$ 0.28. UV/VIS ($CH_2Cl_2$): 337 (sh, 155000), 312 (sh, 201000), 291 (209000), 250 (sh, 227000). IR (KBr): 2922*w*, 1751*s*, 1638*m*, 1617*m*, 1383*w*, 1289*w*, 1253*w*, 1192*s*, 1092*w*, 1061*w*, 1033*w*, 853*w*, 799*w*, 757*w*, 711*w*, 539*w*, 534*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.16 (br. *s*, 24H); 6.19 (*t*, $J$ = 5.4, 6H); 5.22 (br. *s*, 12H); 4.77 (*s*, 12H); 4.71 (*s*, 12H); 4.24 (*q*, $J$ = 7.2, 12H); 4.20 (*q*, $J$ = 7.2, 12H); 3.25 (*d*, $J$ = 5.4, 12H); 3.10–2.85 (br. *m*, 36H); 1.28 (*t*, $J$ = 7.2, 18H); 1.26 (*t*, $J$ = 7.2, 18H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 166.45; 166.43; 162.82; 162.75; 162.57; 155.97; 155.25; 145.81; 145.43; 145.39; 144.59 (br.);

144.18; 143.30 (br.); 143.15 (br.); 142.49; 139.71; 139.49; 139.12 (br.); 138.66; 131.66; 130.29; 128.32 (br.); 125.17; 88.41; 71.77; 70.42; 68.64; 67.77; 65.99; 62.26; 62.22; 61.74; 61.69; 61.63; 61.61; 45.20; 44.77; 42.34 (br.); 39.17 (br.); 34.84 (br.); 34.09 (br.); 21.19; 14.13. MALDI-TOF-MS (CCA): 5317 (9, $M^+$, $C_{348}H_{174}O_{60}^+$ requires 5314), 3603 (21, **31**$^+$, $C_{247}H_{116}O_{40}^+$ requires 3602), 1894 (11, **32**$^+$, $C_{126}H_{58}O_{20}^+$ requires 1891), 1712 (100, **21**$^+$, $^{13}C_2{}^{12}C_{109}H_{58}O_{20}^+$).

**26**: Yellow solid. M.p. > 250°. TLC ($CH_2Cl_2$/AcOEt 100:5): $R_f$ 0.15. UV/VIS ($CH_2Cl_2$): 337 (sh, 202000), 311 (280000), 291 (292000), 250 (sh, 322000). IR (KBr): 2925*w*, 1752*s*, 1639*w*, 1619*w*, 1449*w*, 1422*w*, 1383*m*, 1289*m*, 1250*m*, 1192*s*, 1092*m*, 1061*m*, 1033*w*, 852*w*, 799*w*, 757*w*, 710*w*, 541*w*, 532*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.18 (br. *s*, 32H); 6.17 (*t*, *J* = 5.0, 8H); 5.23 (br. *s*, 16H); 4.78 (*s*, 16H); 4.68 (*s*, 16H); 4.24 (*q*, *J* = 7.2, 16H); 4.17 (*q*, *J* = 7.2, 16H); 3.21 (*d*, *J* = 5.0, 16H); 3.10–2.90 (br. *m*, 48H); 1.29 (*t*, *J* = 7.2, 24H); 1.24 (*t*, *J* = 7.2, 24H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 166.47; 166.43; 162.80; 162.67; 155.78; 155.24; 145.84; 145.78; 145.55; 145.02; 144.23; 143.30; 143.22; 142.50; 139.76; 139.45; 139.11; 138.51; 131.69; 130.33; 128.36 (br.); 124.80; 75.77; 70.39; 69.49; 68.66; 68.52; 66.01; 62.32; 62.23; 61.74; 61.68; 61.63; 45.18; 44.84; 42.37; 39.26; 34.84; 34.24; 19.84; 14.14; 14.09. MALDI-TOF-MS (DHB): 5374 (2, $[M - \mathbf{21}]^+$, $C_{353}H_{174}O_{60}^+$ requires 5374), 3662 (11, $[M - 2 \cdot \mathbf{21}]^+$, $C_{242}H_{116}O_{40}^+$ requires 3662), 1952 (5, **33**$^+$, $C_{131}H_{48}O_{20}^+$ requires 1951), 1711 (100, **21**$^+$, $^{12}C_{111}H_{58}O_{20}^+$).

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