157. Macrocyclization on the Fullerene Core: Direct Regio- and Diastereoselective Multi-Functionalization of [60]Fullerene, and Synthesis of Fullerene-dendrimer Derivatives

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The macrocyclization between buckminsterfullerene, C_{60}, and bis-malonate derivatives in a double *Bingel* reaction provides a versatile and simple method for the preparation of covalent bis-adducts of C_{60} with high regio- and diastereoselectivity. A combination of spectral analysis, stereochemical considerations, and X-ray crystallography (*Fig. 2*) revealed that out of the possible *in-in*, *in-out*, and *out-out* stereoisomers, the reaction of bis-malonates linked by *o*-, *m*-, or *p*-xylylene tethers afforded only the *out-out* ones (*Scheme 1*). In contrast, the use of larger tethers derived from 1,10-phenanthroline also provided a first example, (±)-**19** (*Scheme 2*), of an *in-out* product. Starting from optically pure bis-malonate derivatives, the new bis-functionalization method permitted the diastereoselective preparation of optically active fullerene derivatives (*Schemes 4* and *5*) and, ultimately, the enantioselective preparation (enantiomeric excess ee > 97%) of optically active *cis-3* bis-adducts whose chirality results exclusively from the addition pattern (*Fig. 6*). The macrocyclic fixation of a bis-malonate with an optically active, 9,9′-spirobi[9*H*-fluorene]-derived tether to C_{60} under generation of **24** and *ent*-**24** with an achiral addition pattern (*Scheme 4*) was found to induce dramatic changes in the chiroptical properties of the tether chromophore such as strong enhancement and reversal of sign of the *Cotton* effects in the circular dichroism (CD) spectra (*Figs. 4* and *5*). By the same method, the functionalized bis-adducts **50** and **51** (*Schemes 10* and *11*) were prepared as initiator cores for the synthesis of the fullerene dendrimers **62**, **63**, and **66** (*Schemes 12* and *13*) by convergent growth. Finally, the new methodology was extended to the regio- and diastereoselective construction of higher cyclopropanated adducts. Starting from mono-adduct **71**, a clipping reaction provided exclusively the all-*cis-2* tris-adduct (±)-**72** (*Scheme 14*), whereas the similar reaction of bis-adduct **76** afforded the all-*cis-2* tetrakis-adduct **77** (*Scheme 15*). Electrochemical investigations by steady-state voltammetry (*Table 2*) in CH_2Cl_2 (+ 0.1M Bu_4NPF_6) showed that all macrocyclic bis(methano)fullerenes underwent multiple reduction steps, and that regioisomerism was not much influencing the redox potentials. All *cis-2* bis-adducts gave an instable dianion which decomposed during the electrochemical reduction. In CH_2Cl_2, the redox potential of the fullerene core in dendrimers **62**, **63**, and **66** is not affected by differences in size and density of the surrounding poly(ether-amide) dendrons. The all-*cis-2* tris- and tetrakis(methano)fullerenes (±)-**72** and **77**, respectively, are reduced at more negative potential than previously reported all-*e* tris- and tetrakis-adducts with methano bridges that are also located along an equatorial belt. This indicates a larger perturbation of the original fullerene π-chromophore and a larger raise in LUMO energy in the former derivatives.

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1. Introduction. – Tether-directed remote functionalization is *the* method of choice for the regioselective preparation of multiple adducts of C_{60}. In 1994, we introduced a first powerful methodology [1], which provided access to a great variety of unprecedented bis- to hexakis-adducts of the C-sphere [2] [3]. Other protocols for multifunctionalization relying on tether control have since then been developed in several laboratories [4].

During the synthesis of precursors of poly(triacetylene)s with pendant fullerene moieties, we found in 1996 that the reaction of C_{60} with a bis(2-bromomalonate) directly yielded macrocyclic bis-adducts resulting from double *Bingel* addition [5] to one carbon sphere with high regio- and diastereoselectivity [6]. The general character of this second tether-dependent methodology from our laboratory for the selective preparation of C_{60} multiple adducts was subsequently reported in a preliminary communication [7]. Its utility for the construction of supramolecular assemblies with defined geometry was recently illustrated with the synthesis of the first fullerene-containing [2]catenane [8].

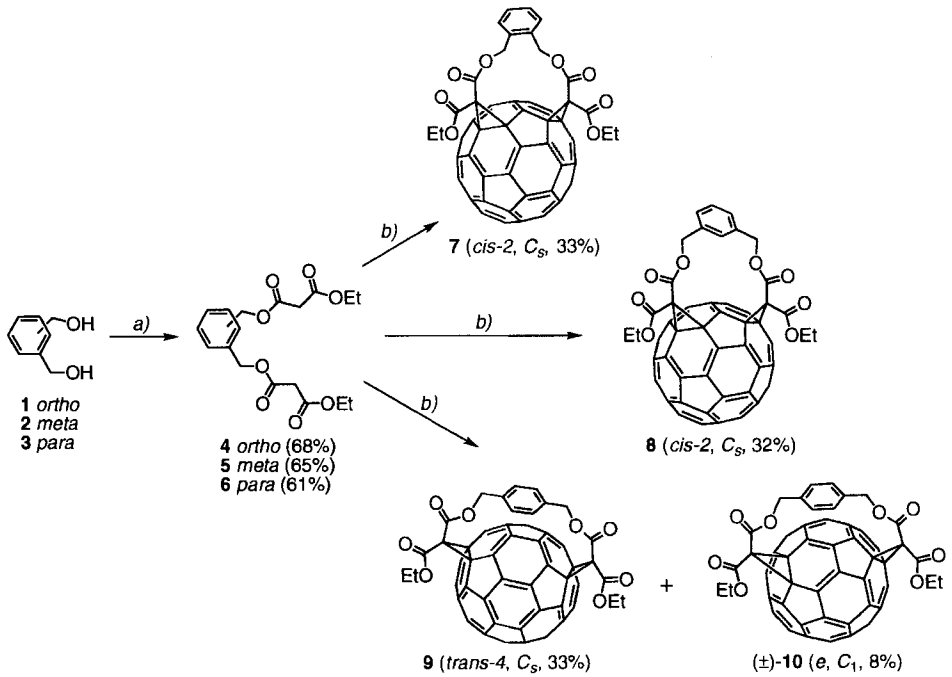
Here, we give a full account of our new, versatile C_{60} bis-functionalization method. We describe the highly regio- and diastereoselective synthesis of a large series of fullerene bis-adducts and, starting from bis-malonates with optically active tethers, the enantioselective preparation of optically active bis-adducts whose chirality exclusively results from the addition pattern [9–13]. Subsequently, we report the application of this method to the preparation of initiator cores for the construction of fullerene dendrimers [14] [15] by convergent growth strategy [16] [17]. Finally, we demonstrate an important extension of the new methodology which allows the preparation of higher multiple adducts with unprecedented addition patterns.

2. Results and Discussion. – 2.1. *Direct Bis-functionalization of C_{60} by Macrocyclization of Bis-malonates Containing* o-, m-, *or* p-*Xylylene Tethers.* We first established the general character of this methodology by starting from the three commercially available isomeric benzenedimethanols **1**–**3** (*Scheme 1*).

In a typical procedure, diols **1**–**3** were treated with ethyl 3-chloro-3-oxopropanoate in the presence of C_5H_5N in CH_2Cl_2 at room temperature to give the bis(ethyl malonyl) derivatives **4**–**6**, respectively, in 61–68% yield. The corresponding 2-halomalonates were prepared *in situ* with I_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [18a], and the one-pot reaction of C_{60} with compounds **4**–**6**, I_2, and DBU in PhMe at room temperature afforded the bis-adducts **7**–(±)-**10**. The relative position of the two cyclopropane rings on the C_{60} surface in **7**–(±)-**10** was determined based on the molecular symmetry deduced from the ^{1}H- and ^{13}C-NMR spectra, and on UV/VIS spectral comparisons. *Hirsch* and coworkers had previously shown that the UV/VIS spectra of C_{60} bis-adducts are highly dependent on the addition pattern and characteristic for each regioisomer [11a,e]. They also introduced a positional notation system for bis-adducts [11a] [2e], which is also applied to the compounds prepared in this study (*Fig. 1*). The UV/VIS spectra of **7**–(±)-**10** in CH_2Cl_2 are fully consistent with those previously reported for analogous tetrakis(ethyl esters) [11a,e] [13]. The colors of bis-adducts **7**–(±)-**10** in CH_2Cl_2 solutions are also different and quite characteristic of the addition pattern. Solutions of *cis-2* bis-adducts **7** and **8** are red-orange-colored, those of the *e* bis-adduct (±)-**10** are red, and of the *trans-4* bis-adduct **9** brown.

In theory, each macrocyclic regioisomer could be formed as a mixture of different diastereoisomers, depending on how the EtOCO residues at the two methano-bridge

Scheme 1. *Preparation of Bis-adducts* **7**–(±)-**10**



a) EtO_2CCH_2COCl, C_5H_5N, CH_2Cl_2, 0° → r.t. *b*) C_{60}, DBU, I_2. PhMe, r.t.

C-atoms are oriented with respect to each other (*in-in*, *in-out*, and *out-out* stereoisomerism) [19]. This is illustrated in *Fig. 2* for the *cis-2* bis-adduct resulting from the macrocyclization of **4** on the C_{60} core.

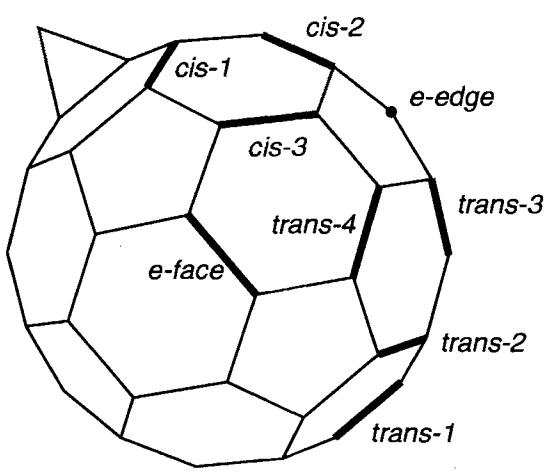


Fig. 1. *Positional notation for bis-adducts of* C_{60}. For identical addends, a second attack onto *e*-face or *e*-edge positions leads to identical products.

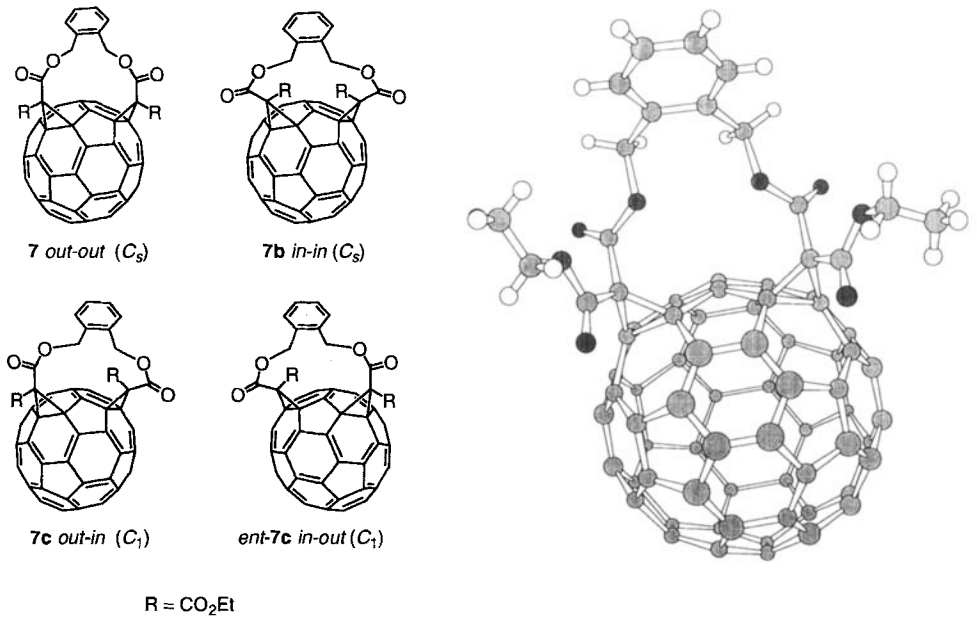


Fig. 2. *All four possible stereoisomers for the* cis-2 *bis-adducts with the* o-*xylylene tether, and ball and stick representation of the X-ray crystal structure of* **7** *showing unambiguously the formation of the* out-out *isomer* [7]

For potential *cis-1*, *cis-2*, and *trans-4* bis-adducts formed by the described macrocyclization, there exist two C_s-symmetrical (*in-in*, *out-out*) and one C_1-symmetrical (*in-out*) diastereoisomers. For *cis-3*, *trans-2*, and *trans-3* bis-adducts, two C_2-symmetrical (*in-in*, *out-out*) and one C_1-symmetrical (*in-out*) diastereoisomers can form. The *e* bis-addition can give two C_1-symmetrical diastereoisomers (*out-out*, *in-out*), and *trans-1* addition can yield one C_{2v}-symmetrical (*out-out*) and one C_2-symmetrical (*in-out*) diastereoisomer. Actually, taking into consideration the pairs of enantiomers in C_1- and C_2-symmetrical compounds, a total of 37 different isomeric bis-adducts could theoretically be formed in one macrocyclization. Nevertheless, each regioisomer **7**-(±)-**10** was isolated as a single, achiral compound or as a single racemate; therefore, the second intramolecular *Bingel* addition occurs not only regio- but also diastereoselectively.

Isomer assignments were made as illustrated in the following for the macrocyclic bis-adduct obtained from **4** and C_{60}. The compound displayed a similar UV/VIS spectrum to that of the corresponding *cis-2* tetraethyl ester reported in [11a,e]. Assuming the *cis-2* addition pattern, four structures are possible (*Fig. 2*). Its ^{1}H-NMR spectrum is broad at room temperature, indicating that ring inversion in the 13-membered ring occurs on the NMR time scale. A variable-temperature study, however, showed a perfectly reversible narrowing of all the peaks at higher temperature, with a sharp spectrum being obtained at 373 K which clearly supported the presence of a C_s-symmetrical compound. Therefore, only **7** (*out-out* diastereoisomer) and **7b** (*in-in* diastereoisomer) appear as possible structures. Steric considerations based on molecular and computer modeling indicated that the two cyclopropane rings on the C_{60} surface of the *cis-2* bis-adduct should be linked in an *out-out* manner. Effectively, after the first *Bingel*

addition to the C_{60} sphere, the second malonate moiety could react intramolecularly with one out of four possible 6-6 bonds to give a *cis-2* addition pattern. With respect to the initially introduced cyclopropane ring, two of these bonds are on the same side as the reactive malonate group, whereas the two others are on the opposite side. Macrocyclization at one of the former two bonds could only produce **7** (*out-out* diastereoisomer) or (±)-**7c** (*in-out* diastereoisomer); whereas reaction at the latter two bonds could only yield **7b** (*in-in* diastereoisomer) or (±)-**7c** (*in-out* diastereoisomer). For evident steric reasons, the malonate moiety should add to the 6-6 bonds located on the same side, and, since the cyclization product is C_s-symmetric, its correct structure is **7**. A similar reasoning was applied to identify the structures of the other bis-functionalization products described in this paper.

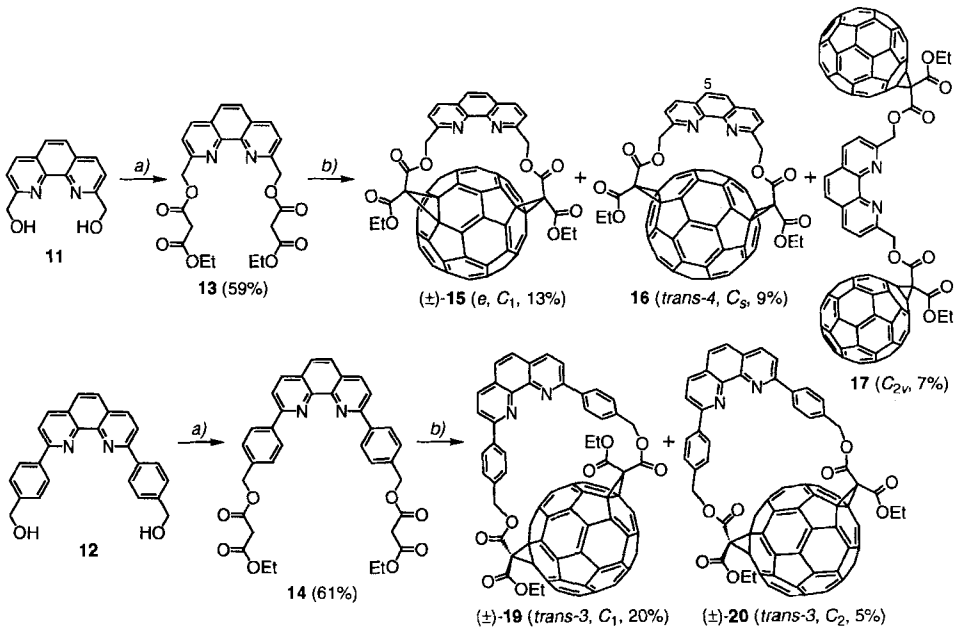
The X-ray crystal-structure analysis of **7** (*Fig. 2*) [7] finally confirmed its *cis-2* addition pattern and showed unambiguously the *out-out* orientation of the EtOCO residues. Similarly, the C_s-symmetrical *cis-2* bis-adduct **8** should be the *out-out* diastereoisomer. Because of the limited length of the linker between the two cyclopropane rings, only the *out-out* diastereoisomers appeared reasonable for bis-adducts **9** with *trans-4* and (±)-**10** with *e* addition patterns.

2.2. *Bis-functionalization by Macrocyclization of C_{60} with Bis-malonates Containing 1,10-Phenanthroline Tethers.* We became interested in attaching in a geometrically defined way a metal ion-coordinating 1,10-phenanthroline moiety to the fullerene surface in order to explore the electronic interactions between the carbon sphere and the ionic center [20]. The new macrocyclization reaction, starting from the 1,10-phenanthroline-based diols **11** and **12** (*Scheme 2*), seemed ideal to construct this ion-binding site in close proximity to the fullerene surface. Diol **11** was prepared in two steps from 2,9-dimethyl-1,10-phenanthroline ('neocuproine') according to the method reported by *Chandler et al.* [21], and diol **12** was obtained in three steps from 1,10-phenanthroline as previously described by *Sauvage* and coworkers [22].

Reaction of **11** and **12** with ethyl 3-chloro-3-oxopropanoate under typical conditions yielded bis-malonates **13** and **14**, respectively. In contrast to all of the other bis-malonate derivatives reported in this paper, compound **13** is a crystalline solid, and crystals suitable for X-ray crystal-structure analysis (*Fig. 3,a*) were obtained by very slow diffusion of PhH into a CH_2Cl_2 solution of **13**. The crystal packing analysis (*Fig. 3,b*) showed infinite stacks of **13**, with each 1,10-phenanthroline moiety sandwiched between two other anti-parallel 1,10-phenanthroline rings at an intermolecular stacking distance of *ca.* 3.6 Å. Noteworthy are also the two short, intermolecular, bifurcated H-bond-type contacts $C(sp^3)-H\cdots N$ (2.530 and 2.878 Å, *Fig. 3,b*) between one of the two acidic malonic C*H* and the two basic N-atoms of a 1,10-phenanthroline moiety in a neighboring stack.

Reaction of **13** with C_{60}, I_2, and DBU in PhMe at room temperature yielded the two macrocyclic bis-adducts (±)-**15** and **16** in 13 and 9% yield, respectively, together with bis(methanofullerene) derivative **17** (7%). The ^{1}H-NMR spectrum of **16** depicted at room temperature the presence of two conformers in a 3:2 ratio, since ring inversion in the 20-membered macrocycle is slow on the NMR time scale, whereas, at 373 K, the spectrum of a single compound with C_s-symmetry was obtained. By monitoring the coalescence of the uncoupled phenanthroline resonance H–C(5) (*Scheme 2*) in a variable-temperature study, the coalescence temperature was determined as T_c = 323 K and

Scheme 2. *Preparation of 1,10-Phenanthroline-Bridged Fullerene Derivatives*



a) EtO_2CCH_2COCl, C_5H_5N, CH_2Cl_2, 0° → r.t. *b*) C_{60}, DBU, I_2, PhMe, r.t.

the free energy barrier for the conformational equilibrium was calculated as $\Delta G^{\ddagger} = 67\,kJ\,mol^{-1}$ [23]. The C_s-symmetrical macrocyclic bis-adduct **16** exhibited the characteristic UV/VIS spectrum of a *trans-4* bis-adduct [11], and, considering the length of the linker between the two cyclopropane rings, only the *out-out* diastereoisomer appears reasonable. The ^1H- and ^{13}C-NMR spectra of bis-adduct (±)-**15** depicted molecular C_1-symmetry, and the UV/VIS spectrum was consistent with an *e* addition pattern. Again, by considering the length of the linker between the two cyclopropane rings, the *out-out* diastereoisomer is the only sterically reasonable structure for compound (±)-**15**. The relative position of the two cyclopropane rings on the C_{60} core was confirmed by transformation of (±)-**15**, *via* transesterification (K_2CO_3, EtOH/THF) [2f] [6], into the known C_s-symmetrical tetraethyl ester **18** [11a] [2f] (*Scheme 3*).

The macrocyclization reaction of **14** with C_{60} yielded bis-adducts (±)-**19** and (±)-**20** in 20 and 5% yield, respectively (*Scheme 2*). Although the UV/VIS spectra of both (±)-**19** and (±)-**20** are similar and both consistent with a *trans-3* addition pattern, their ^1H- and ^{13}C-NMR spectra are very different, revealing different molecular symmetries. Compound (±)-**19** is C_1-symmetric, whereas (±)-**20** exhibits C_2-symmetry. Both (±)-**19** and (±)-**20** are *trans-3* macrocyclic bis-adducts, they are, therefore, diastereoisomers; (±)-**19** being the *in-out* and (±)-**20** the *out-out* isomer. Steric considerations based on molecular and computer modeling indeed had indicated that the large tether in **14** could lead to the formation of the two diastereoisomers with similar steric strain energy. Furthermore, transesterification (K_2CO_3, EtOH/THF) of (±)-**19**, which is the only *in-out* diastereoisomer isolated in this study, yielded the corresponding known C_2-sym-

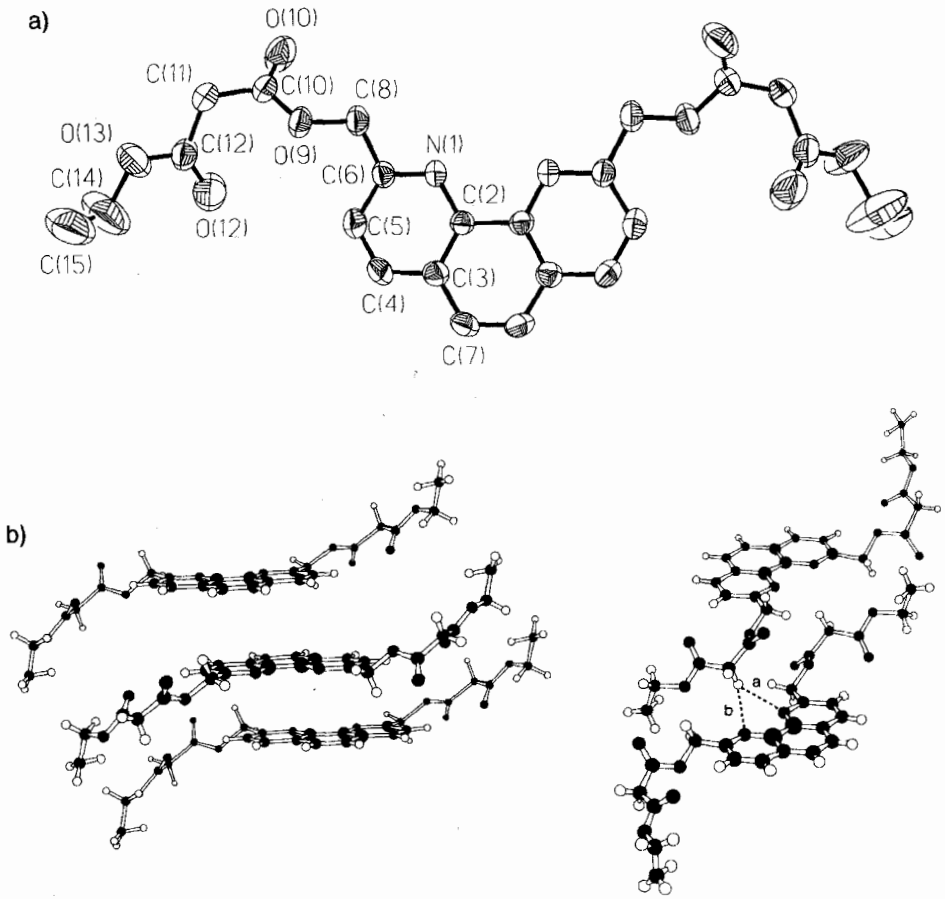
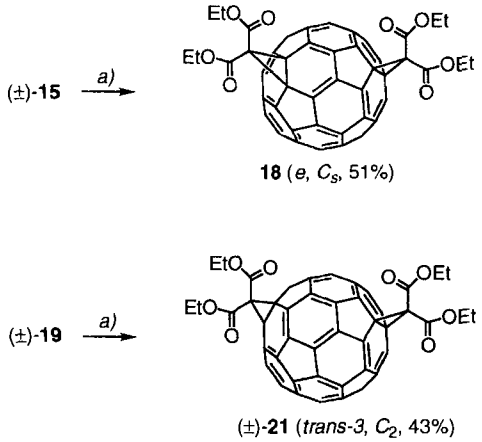


Fig. 3. a) *X-Ray crystal structure of* **13**. b) *Crystal packing of* **13** *showing the stacking between the 1,10-phenanthroline rings* (left) *and the bifurcated H-bonds between the malonic CH and the two N-atoms of a 1,10-phenanthroline moiety in a neighboring stack* (right). H-bond *a*: H ··· N distance 2.530 Å, C–H ··· N angle: 146.0°; H-bond *b*: H ··· N distance: 2.878 Å, C–H ··· N angle: 117.8°

metrical tetraethyl ester (±)-**21** [11a] (*Scheme 3*), thus fully confirming the *trans-3* addition pattern.

2.3. *Diastereoselective Synthesis of Optically Active Fullerene Derivatives by Macrocyclization of Bis-malonates with Optically Active Tethers: Enantioselective Synthesis of Bis-adducts (*^{f}C*)-***28** *and (*^{f}A*)-***28**. Since the new methodology for C_{60} bis-functionalization is not only regio- but also diastereoselective, we became interested in applying it to the preparation of new optically active fullerene derivatives [9a] by starting from bis-malonates with optically pure tethers. Furthermore, since several bis-addition patterns on the C_{60} core (*cis-3*, *trans-2*, and *trans-3*) are chiral [10] [11], the use of an optically active tether could allow the diastereoselective formation of only one diastereoisomer resulting from the combination of the chiral tether with a chiral addition pattern as the elements of chirality. Subsequent removal of the tether, which is used as chiral auxiliary, *via*

Scheme 3. *Transesterification of Bis-adducts (±)-15 and (±)-19*

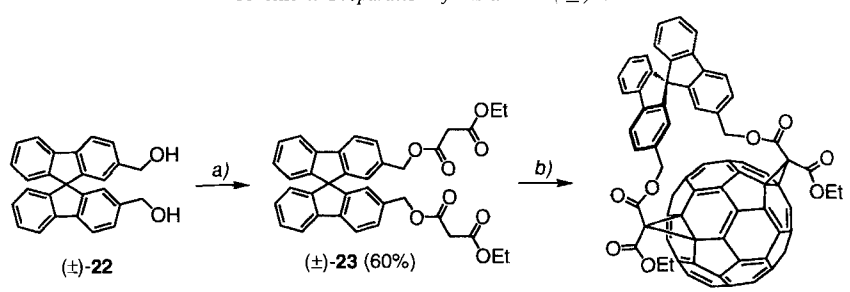


a) K_2CO_3, EtOH/THF, r.t.

transesterification would then yield the optically pure bis-adduct. Previously, the enantioselective synthesis of optically active C_{60} bis-adducts had only been achieved by the asymmetric *Sharpless* osmylation of C_{60} [10b].

In a first experiment, we started from the racemic 9,9′-spirobi[9*H*-fluorene]-2,2′-dimethanol (±)-**22** and, later on, from the corresponding pure enantiomers (+)-(*R*)-**22** and (−)-(*S*)-**22** (*Scheme 4*), which were prepared as previously reported by *Prelog* and coworkers [24].

Scheme 4. *Preparation of Bis-adduct (±)-24*



a) EtO_2CCH_2COCl, C_5H_5N, CH_2Cl_2, 0° → r.t. *b*) C_{60}, DBU, I_2, PhMe, r.t.

Diesterification of (±)-**22** with ethyl 3-chloro-3-oxopropanoate and subsequent reaction of (±)-**23** with C_{60} afforded C_1-symmetrical (±)-**24**. Compound (±)-**24** is formed by *e* attack (*Fig. 1*), and two *out-out* diastereoisomeric pairs of enantiomers could, in principle, be obtained as a result of the two elements of chirality in the molecule. The 2,2′-disubstituted 9,9′-spirobifluorene moiety is chiral, and additional chirality is introduced by the orientation of the two EtOCO residues and the macrocyclic bridge (which is the only origin of chirality in (±)-**10** (*Scheme 1*) or (±)-**15** (*Scheme 2*)), the *e* addition

pattern itself is not chiral. However, (±)-**24** was obtained as a diastereoisomerically pure racemic mixture; therefore, only one of the two possible diastereoisomeric pairs of enantiomers, with one specific orientation of EtOCO residues and macrocyclic bridge, was formed. Clearly, the chiral tether is at the origin of a very high asymmetric induction in the second intramolecular *Bingel* addition. Hence, by starting from pure (−)-(*S*)-**23** or (+)-(*R*)-**23**, which were prepared from the optically pure diols (−)-(*S*)-**22** and (+)-(*R*)-**22**, respectively, the two enantiomers **24** and *ent*-**24** were obtained. The enantiomeric excess (ee) determined by HPLC on the (*S,S*)-*Whelk-01* chiral stationary phase (CSP) for both **24** and *ent*-**24** was higher than 96%, which corresponds to the ee of the starting diols, (−)-(*S*)-**22** and (+)-(*R*)-**22**.

The mirror-image circular-dichroism (CD) spectra of **24** and *ent*-**24** (*Fig. 4*) display *Cotton* effects in two separate wavelength regions. We propose that the intense bands ($\Delta\varepsilon$ up to 30 cm^2 $mmol^{-1}$) between 250 and 350 nm result mainly from the chiroptical contributions of the chiral spirobifluorene tether which displays strong optical absorption bands in this range. It is well documented that optically active fullerene derivatives with chiral, weakly absorbing addends but achiral addition patterns do not display strong CD effects in this region [25] [26] (see also the discussion for **25** and *ent*-**25** below). A comparison between the CD spectra of the two enantiomers of **24** to those of the starting bis-malonates (−)-(*S*)-**23** and (+)-(*R*)-**23** (*Fig. 5*) reveals that the two major bands in these compounds appear at similar wavelengths (*Table 1*). However, there are some dramatic differences. First, the *Cotton* effects of the macrocyclic fullerene derivatives in this region are stronger by nearly one order of magnitude (in $\Delta\varepsilon$) as compared to those measured for the bis-malonate precursors. Secondly, the sign of the *Cotton* effects changes upon passing from (−)-(*S*)-**23** to **24** and from (+)-(*R*)-**23** to *ent*-**24**. This remarkable change in sign clearly demonstrates a strong electronic coupling between the fullerene and spirobifluorene chromophores in **24** and *ent*-**24** when interacting with the photons from the linearly polarized light.

Between 400 and 720 nm appear weak *Cotton* effects which we assign to an induced CD originating from the perturbation of the achiral fullerene chromophore by the attached optically active tether [25]. Overall, the chiroptical properties of **24**/*ent*-**24** are less pronounced than those measured for fullerenes with optically active addition patterns (see below) [7] [11d] [26] or for optically active derivatives of inherently chiral fullerenes [27], which display *Cotton* effects with $\Delta\varepsilon$ values well exceeding 100 cm^2 $mmol^{-1}$.

By the same methodology, the two enantiomeric *cis-2* bis-adducts **25** and *ent*-**25**, together with the two enantiomeric *cis-3* bis-adducts **26** and *ent*-**26**, were obtained from the tethered bis-malonates (−)-**29** and (+)-**29**, which, in return, were prepared from the commercially available optically pure diols (+)-**27** and (−)-**27**, respectively (*Scheme 5*).

The macrocyclization was again highly diastereoselective, and only one of the possible diastereoisomers could be detected in each case. In each reaction, two diastereoisomeric *out-out cis-3* bis-adducts are possible due to the chiral addition pattern; however, the very high asymmetric induction in the second intramolecular *Bingel* addition leads to the formation of **26** or *ent*-**26** only. Transesterification (K_2CO_3, EtOH/THF) of **26** and *ent*-**26** yielded the *cis-3* tetraethyl esters **28** and *ent*-**28**, respectivey, as enantiomerically pure compounds; the two enantiomers with the configurational assignments (^{f}*C*)-**28** and (^{f}*A*)-**28** (f = fullerene, *C* = clockwise, *A* = anticlockwise) [9b] [26] are depicted in *Fig. 6*. The ee determined by HPLC is higher than 97% for **28** and 99% for *ent*-**28**,

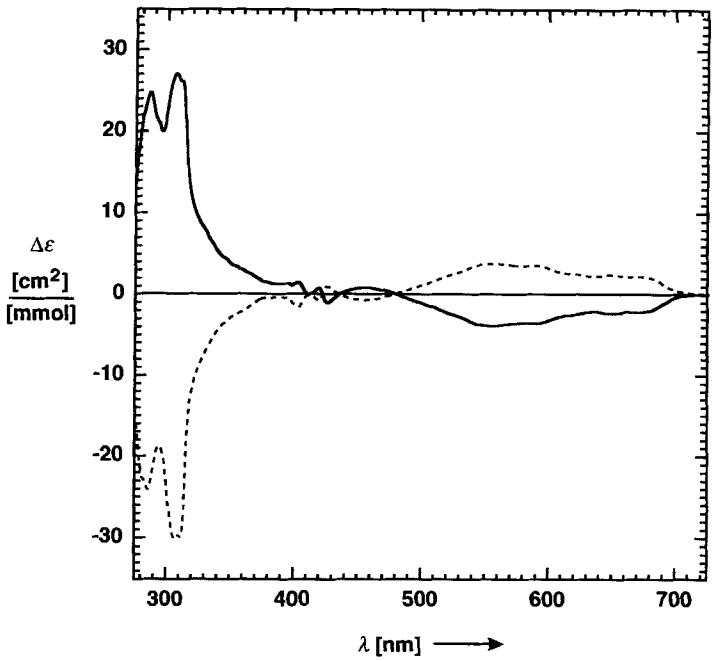


Fig. 4. *CD Spectra of* **24** (————) *and* ent-**24** (- - - - - - -) *in* CH_2Cl_2

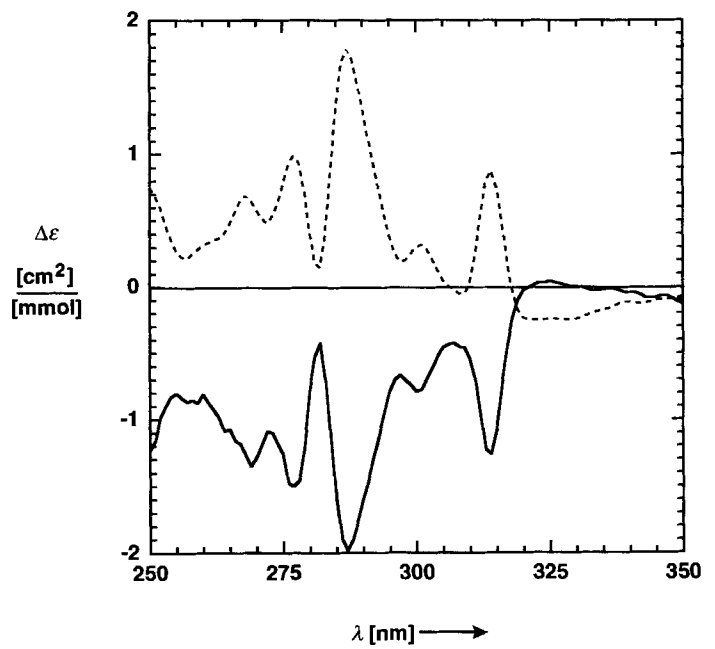


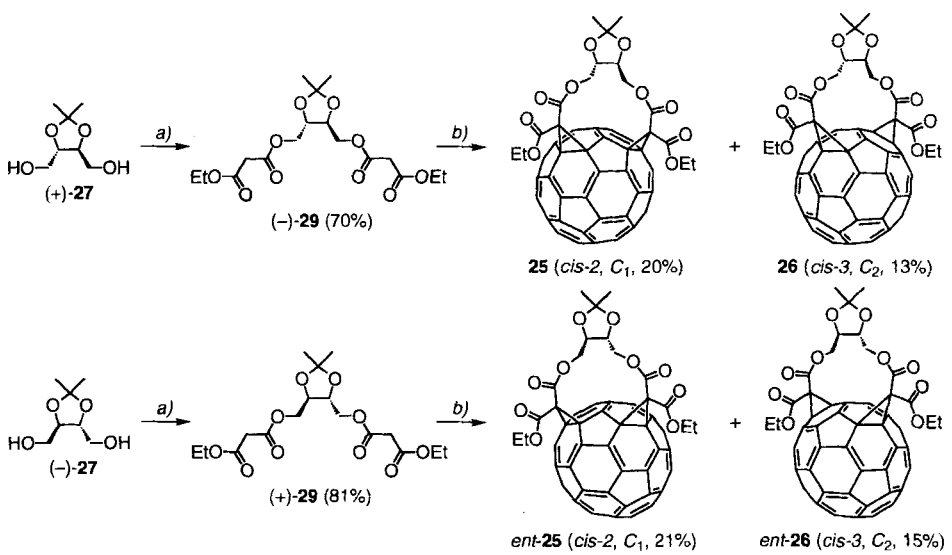
Fig. 5. *CD Spectra of* (−)-(S)-**23** (————) *and* (+)-(R)-**23** (- - - - - - -) *in* CH_2Cl_2

Table 1. *CD Spectra* (λ_{max} [nm] ($\Delta\varepsilon$ [cm^2 $mmol^{-1}$])) *of Bis-malonates* (+)-(R)-**23** *and* (−)-(S)-**23**, *and of the Fullerene Bis-adducts* **24** *and* ent-**24** *in* CH_2Cl_2 *at 293 K*

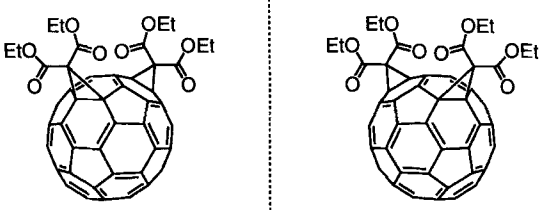
(+)-(*R*)-**23**	(−)-(*S*)-**23**	**24**	*ent*-**24**
268 (0.7)	269 (−1.4)	286 (24.8)	286 (−24.0)
272 (0.5)	272 (−1.1)	296 (20.0)	296 (−18.8)
277 (1.0)	277 (−1.5)	307 (27.1)	307 (−30.1)
282 (0.1)	282 (−0.4)	311 (26.0)	322 (−29.6)
287 (1.9)	287 (−2.0)	312 (26.1)	312 (−29.9)
297 (0.2)	297 (−0.7)	391 (0.6)	391 (−0.5)
301 (0.3)	300 (−0.8)	395 (1.5)	395 (−1.7)
309 (−0.1)	308 (−0.4)	399 (1.2)	399 (−1.2)
314 (0.9)	314 (−1.2)	403 (1.5)	404 (−1.5)
322 (−0.3)	325 (0.0)	412 (0.0)	412 (−0.1)
		420 (0.7)	420 (−0.8)
		426 (−1.1)	426 (0.9)
		457 (0.8)	456 (−0.7)
		556 (−3.9)	558 (3.8)
		582 (−3.5)	580 (3.5)
		589 (−3.6)	590 (3.6)
		637 (−2.1)	637 (2.1)
		650 (−2.4)	650 (2.4)
		664 (−2.1)	665 (2.2)
		672 (−2.2)	673 (2.2)

reflecting the ee's of the corresponding starting diols. Thus, with similar efficiency to the asymmetric *Sharpless* osmylation of C_{60} [10b], the addition of the chirally tethered bis-malonate (+)-**29** or (−)-**29** enables the overall enantioselective synthesis of optically active C_{60} bis-adducts in which the chirality results exclusively from the addition pattern.

Scheme 5. *Synthesis of Bis-adducts* **25** *and* **26** *and Their Enantiomers* ent-**25** *and* ent-**26**



a) EtO_2CCH_2COCl, C_5H_5N, CH_2Cl_2, 0° → r.t. *b*) C_{60}, DBU, I_2, PhMe, r.t.



(*f A*)-**28** (*cis-3*, C_2) (*f C*)-**28** (*cis-3*, C_2)

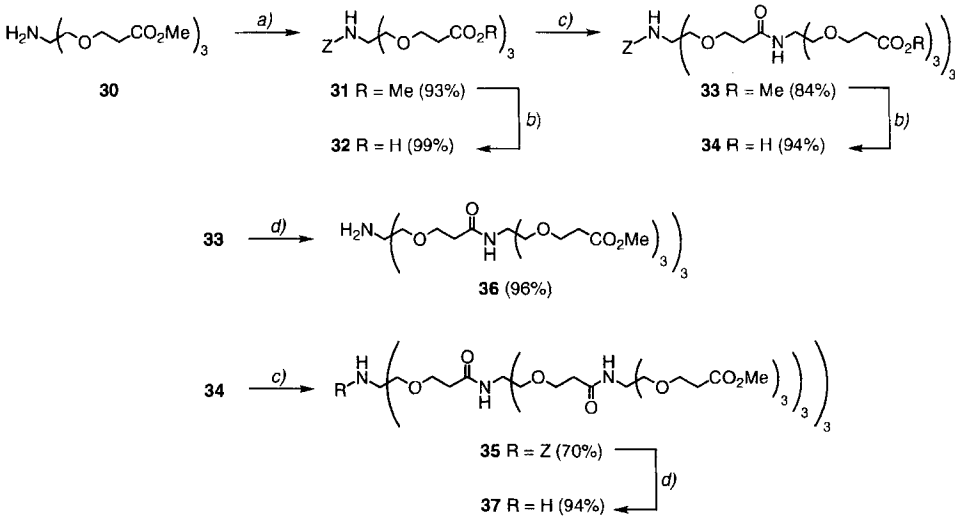
Fig. 6. *The two enantiomeric tetraethyl esters* (*f*A)-**28** *and* (*f*C)-**28** *prepared by enantioselective synthesis.* f = Fullerene, *A* = anticlockwise, *C* = clockwise.

An investigation of the chiroptical properties revealed that the intensities of the mirror-image bands between 230 and 500 nm in the CD spectra (CH_2Cl_2) of the *cis-2* compounds **25** and *ent*-**25** with achiral addition pattern were too weak to be measured reproducibly. Apparently, the chiral tether is too remote from the fullerene sphere to generate substantial induced CD effects. The CD spectra of **26**, *ent*-**26**, **28**, and *ent*-**28** [7], however, displayed large *Cotton* effects between 250 and 750 nm with $\Delta\varepsilon$ values approaching 150 $cm^2\ mmol^{-1}$, predominantly due to strong chiroptical contributions from the chiral *cis-3* addition pattern of the fullerene [26]. Chiroptical contributions from the poorly absorbing chiral tether are once more not detectable in a reproducible way: the CD spectra of **26** and **28**, or of *ent*-**26** and *ent*-**28** are pairwise nearly identical.

2.4. *Synthesis of Fullerene-dendrimer Derivatives.* The spherical fullerene framework with its various possible degrees and patterns of addition is an ideal core for the construction of new dendrimers. The first attachments of a dendron to a C_{60} mono-adduct were reported by *Fréchet* and coworkers [14], and, very recently, the preparation of a T_h-symmetrical hexakis-adduct of C_{60} bearing twelve dendritic branches of first generation was described by *Hirsch* and coworkers [15]. Dendrimers have been constructed around electroactive chromophores [28] [29] or receptor-binding sites [30] in order to explore influences of the specific microenvironment inside the macromolecule on the properties of the functional core. Similarly, it was of interest to explore how the polarity of the dendritic surroundings would affect the redox and photophysical properties of a central fullerene core. The single dendron in the earlier systems [14], however, did not efficiently encapsulate the fullerene mono-adduct core to create a specific microenvironment. Furthermore, most of the characteristic properties of the C-sphere, such as facile multiple reversible one-electron reductions, have vanished in the dendrimer grown from the C_{60} hexakis-adduct, due to the high degree of functionalization and corresponding strong reduction in the conjugated fullerene π chromophore [2b,f]. Therefore, we were interested in growing multiple, encapsulating dendritic branches of higher generations from a lower adduct of C_{60} as the initiator core which better retains the desirable physical properties of the free C-sphere. Suitable cores displaying characteristic fullerene properties are fullerene bis-adducts [2f] such as those accessible by the new bis-functionalization method.

We decided to prepare the dendrimers *via* the convergent growth methodology [16] [17] in order to avoid structural defects with increasing dendritic generation. For this purpose, poly(ether-amide) dendrons [31] of second and third generations were synthe-

Scheme 6. *Synthesis of Dendrons* **36** *and* **37**



a) $PhCH_2OCOCl$, $NaHCO_3$, NaOH, H_2O, 0°. *b*) NaOH, H_2O, MeOH, r.t. *c*) **30**, DCC, BtOH, THF, 0° → r.t. *d*) HCO_2NH_4, 10% Pd/C, EtOH, 40°, Z = (benzyloxy)carbonyl.

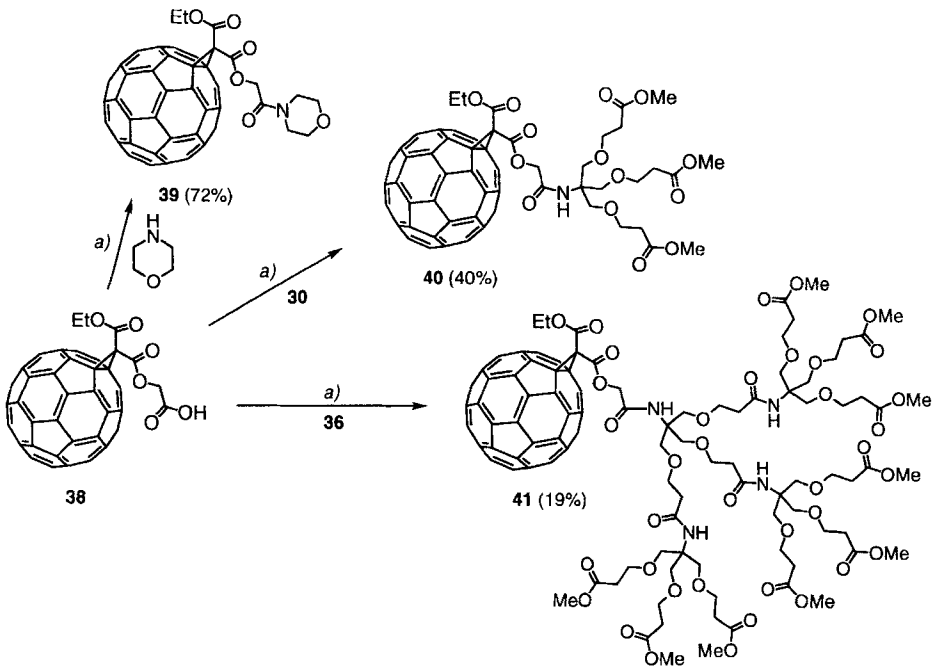
sized. Attachment of these dendrons to a central fullerene core was first realized in a model reaction on a mono-functionalized C_{60} derivative, then on macrocyclic C_{60} bis-adducts.

The synthesis of the dendrons followed the branching methodology of *Newkome et al.* [31] (*Scheme 6*). The amine monomer **30** was protected with the (benzyloxy) carbonyl group (Z) [32] to give **31**, and hydrolysis of the three ester groups afforded the tris(carboxylic acid) **32**. Reaction of **32** with **30** under peptide coupling conditions using *N,N'*-dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (BtOH) [33] led to the Z-protected dendron **33** of second-generation in 84% yield. Hydrolysis to nonakis-acid **34** followed by coupling with **30** yielded the third-generation derivative **35**. The cleavage of the Z group in **33** and **35** was performed by catalytic hydrogenation ($HCOONH_4$, Pd/C) [32] and afforded dendrons **36** (96% yield) and **37** (94% yield), respectively. In addition to ^1H- and ^{13}C-NMR data, mass-spectrometric investigations provided support for the structures assigned to the dendrons of second and third generation. The matrix-assisted laser-desorption-ionization time-of-flight mass spectrum (MALDI-TOF-MS) of **37** displayed the molecular-ion peak as the base peak at *m/z* 4547 besides a strong peak for the sodium-molecular ion complex at *m/z* 4568 ($^{13}C_2$-$^{12}C_{194}H_{329}N_{13}O_{105}Na$ requires 4570).

Methanofullerene **38** [6] was used as the first initiator core, and its reaction with morpholine to give **39** demonstrated its compatibility with peptide-coupling conditions. The coupling reactions of the first- and second-generation dendrons **30** and **36** with acid **38** yielded the expected dendritic fullerene derivatives **40** (40%) and **41** (19%), respectively (*Scheme 7*), but the reaction of the third-generation dendron **37** with **38** did not produce isolable amounts of **42** (*Scheme 8*). The preparation of **42** was also attempted by a semiconvergent approach consisting of the condensation reaction of first-generation

triacid **43** with the second-generation dendron **36** (*Scheme 8*). For the preparation of **43**, the Z-protected triacid **32** was esterified with *t*-BuOH and the Z group of the resulting **44** was cleaved to yield amine **45** [31c], which was coupled with acid **38** to give **46**. Selective hydrolysis of the *tert*-butyl-ester groups under acidic conditions [6] afforded the first-generation triacid **43**, but the subsequent coupling with the second-generation dendron **36** also failed.

Scheme 7. *Preparation of First- and Second-Generation Dendritic Fullerenes* **40** *and* **41**

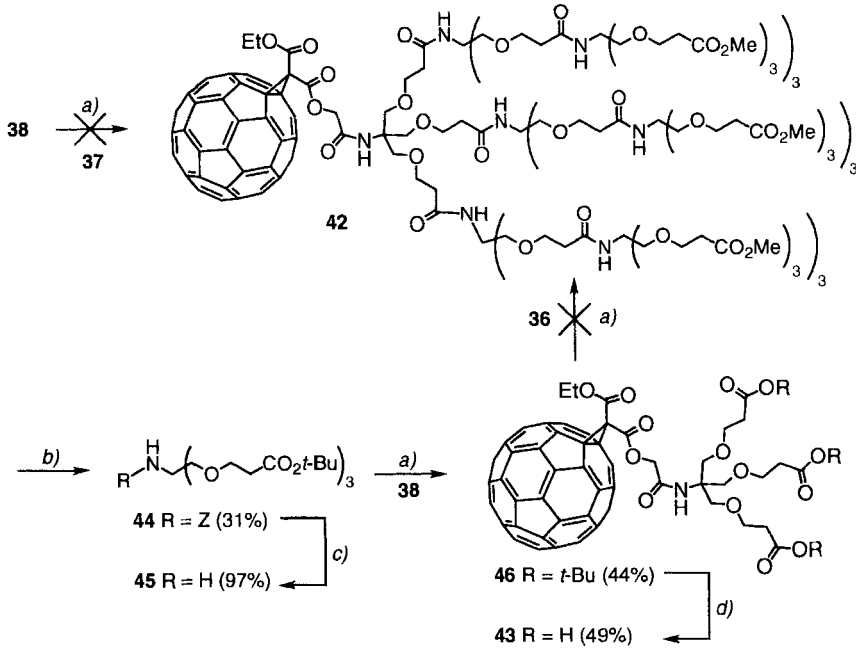


a) DCC, BtOH, CH_2Cl_2, 0° → r.t.

The low-yield coupling (19%) of methanofullerenecarboxylic acid **38** with the second-generation dendron **36**, and the unsuccessful attempts to prepare the third-generation dendritic fullerene **42** indicate a very low reactivity of the NH_2 group in **36** and **37**. The steric bulk of the substituents at the adjacent quarternary C-atom apparently causes a poor accessibility of this focal point in the dendron. We, therefore, extended the distance between the bulky poly(ether-amide) wedge and the primary amine focal point by introducing a short spacer (*Scheme 9*). By coupling the third-generation dendron **37** to Z-glycine under forcing conditions (10 equiv. of Z-glycine, 5 d reaction time, heating to 60° for 12 h), compound **47** was obtained in 67% yield.

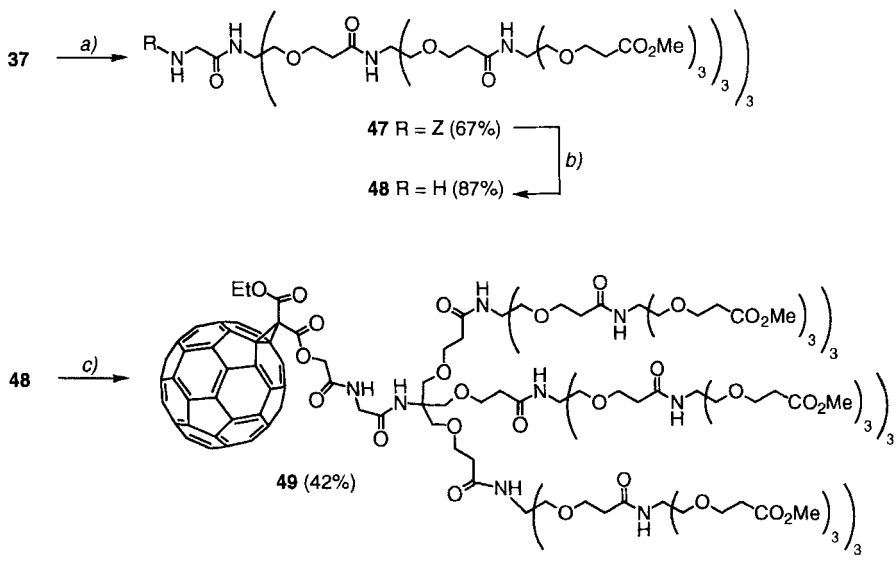
The cleavage of the Z group in **47** gave the third-generation dendron **48** which now could be coupled to acid **38** to give the third-generation dendrimer **49** in 42% yield. A comparison of this yield to the 19% obtained in the preparation of the second-generation derivative **41** and the failure to prepare the third-generation compound **42** clearly demonstrates the advantage of introducing the short glycine linker between the reactive amino group and the bulky poly(ether-amide) wedge of the dendron.

Scheme 8. *Attempted Preparation of the Third-Generation Dendritic Fullerene* **42**



a) DCC, BtOH, CH_2Cl_2, 0° → r.t. *b*) *t*-BuOH, DCC, DMAP, THF, r.t. *c*) HCO_2NH_4, 10% Pd/C, EtOH, 40°. *d*) TsOH · H_2O, PhMe, Δ. TsOH = toluene-4-sulfonic acid.

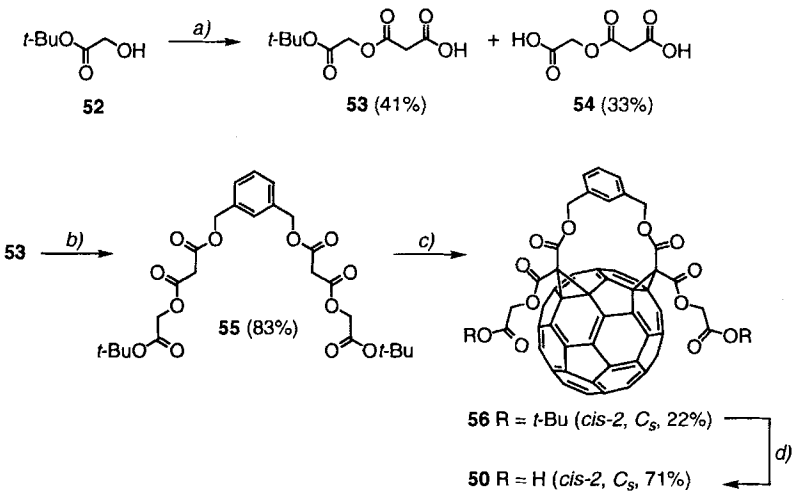
Scheme 9. *Preparation of Third-Generation Dendritic Fullerene* **49**



a) *Z*-glycine (10 equiv.), DCC, BtOH, THF, 0° → 60°. *b*) HCO_2NH_4, 10% Pd/C, EtOH, 40°. *c*) **38**, DCC, BtOH, CH_2Cl_2, 0° → r.t.

Following this experience, bis-adducts **50** (*Scheme 10*) and **51** (*Scheme 11*) with multiple carboxylic-acid residues were prepared as central cores of dendritic fullerenes in which the branches encapsulate efficiently the C-sphere. Heating alcohol **52** [34] with 2,2-dimethyl-1,3-dioxane-4,6-dione ('*Meldrum*'s acid') [35] gave the malonic acid monoester derivative **53** in 41% yield together with **54** (33%) resulting from partial ester hydrolysis (*Scheme 10*). DCC-Mediated esterification of diol **2** with acid **53** afforded the bis-malonate derivative **55** (83%) from which the C_s-symmetrical *cis-2* bis-adduct **56** was obtained in 22% yield by macrocyclization with C_{60}. Subsequent selective cleavage of the *tert*-butyl-ester functions (71%) provided the desired diacid core **50**.

Scheme 10. *Preparation of Diacid* **50**

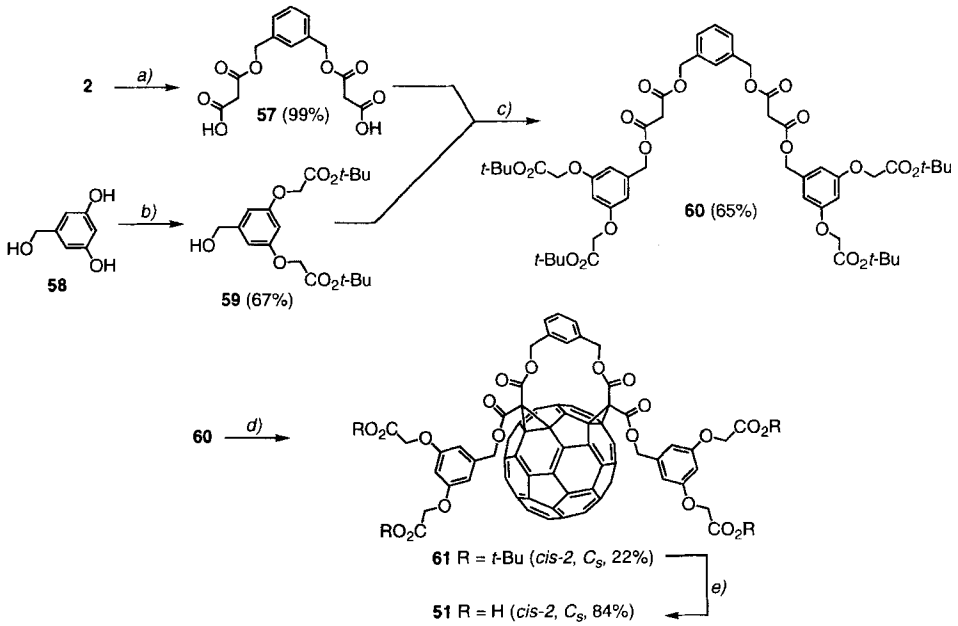


a) *Meldrum*'s acid, 110°. *b*) **2**, DCC, DMAP, THF, 0° → r.t. *c*) C_{60}, DBU, I_2, PhMe, r.t. *d*) TsOH · H_2O, PhMe, Δ.

For the preparation of the second core **51**, diacid **57** was obtained in quantitative yield by heating diol **2** with *Meldrum*'s acid to 120°. Alkylation of diphenol **58** with *tert*-butyl 2-bromoacetate (K_2CO_3/Cs_2CO_3, DMF) afforded **59**, and subsequent DCC-mediated esterification with **57** gave the bis-malonate derivative **60**. Reaction of **60** with C_{60}, DBU, and I_2 in PhMe led to the macrocyclic *cis-2* bis-adduct **61** in 22% yield from which the tetraacid core **51** was obtained in 84% yield by selective cleavage of the *tert*-butyl-ester functions.

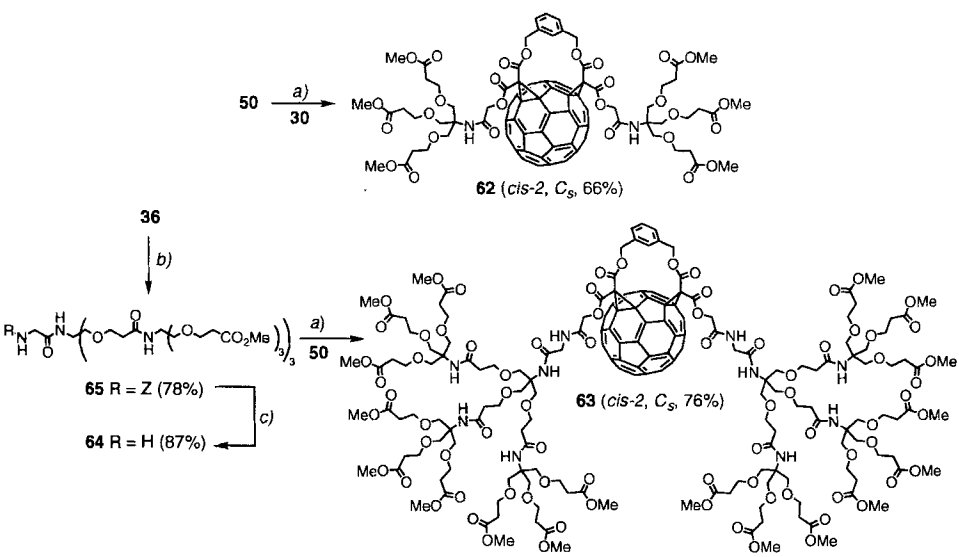
The coupling (DCC/BtOH) of the diacid core **50** to the dendritic branch **30** in THF afforded the first-generation dendrimer **62** in 66% yield (*Scheme 12*). The corresponding second-generation derivative **63** was obtained in 76% yield by the condensation of **50** with dendron **64**, which was prepared by coupling **36** to Z-glycine to give **65**, followed by cleavage of the Z group. The second-generation fullerene dendrimer **66** was obtained as a dark-orange glassy compound by DCC/BtOH coupling (34% yield) of **51** with **64** (*Scheme 13*). The UV/VIS spectra of all three fullerene dendrimers **62**, **63**, and **66** display the characteristic absorptions of a *cis-2* bis-adduct of C_{60}. Their ^{1}H- and ^{13}C-NMR data are fully consistent with the proposed structures and show clearly the C_s symmetry of the compound as well as the presence of both fullerene bis-adduct core and dendritic branch-

Scheme 11. *Preparation of Tetraacid* **51**



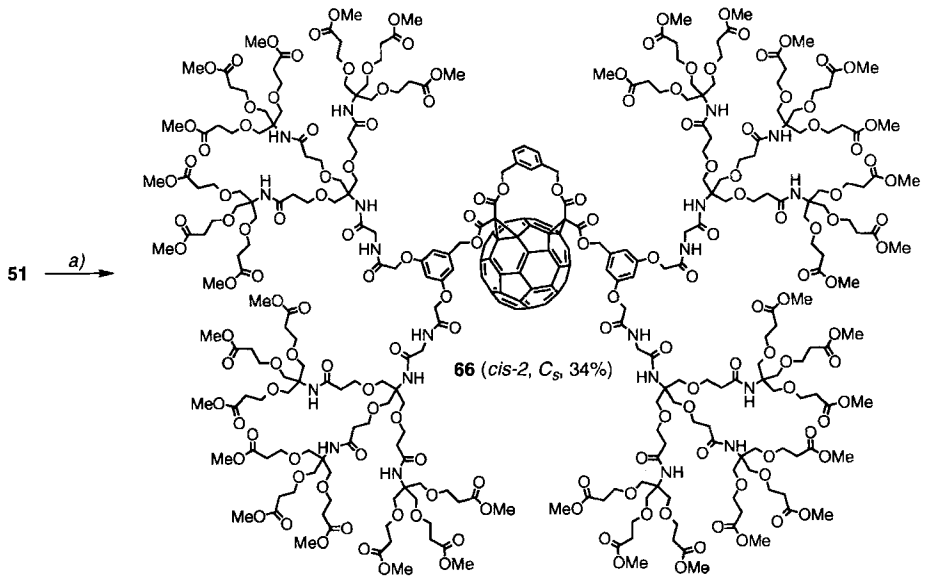
a) *Meldrum*'s acid, 120°. *b*) *tert*-Butyl 2-bromoacetate, K_2CO_3, Cs_2CO_3, DMF, 80°. *c*) DCC, DMAP, THF, 0° → r.t. *d*) C_{60}, DBU, I_2, PhMe, r.t. *e*) CF_3COOH, CH_2Cl_2, r.t.

Scheme 12. *Preparation of Fullerene-dendrimers* **62** *and* **63**



a) DCC, BtOH, THF, 0° → r.t. *b*) Z-glycine, DCC, BtOH, THF, 0° → r.t. *c*) HCO_2NH_4, 10% Pd/C, EtOH, 40°.

Scheme 13. *Preparation of Fullerene-dendrimer* **66**



a) **64**, DCC, BtOH, THF, 0° → r.t.

es in each case. The mass spectra also confirmed the structures of **62**, **63**, and **66**, with no peaks corresponding to defected dendrons being observed. The MALDI-TOF-MS of **66** (*Fig. 7*) displays the sodium-molecular ion complex at *m/z* 7368 ($^{13}C_4{}^{12}C_{344}H_{450}N_{20}O_{152} \cdot Na$ requires 7368) as the base peak and provides clear evidence for the monodispersity of **66**.

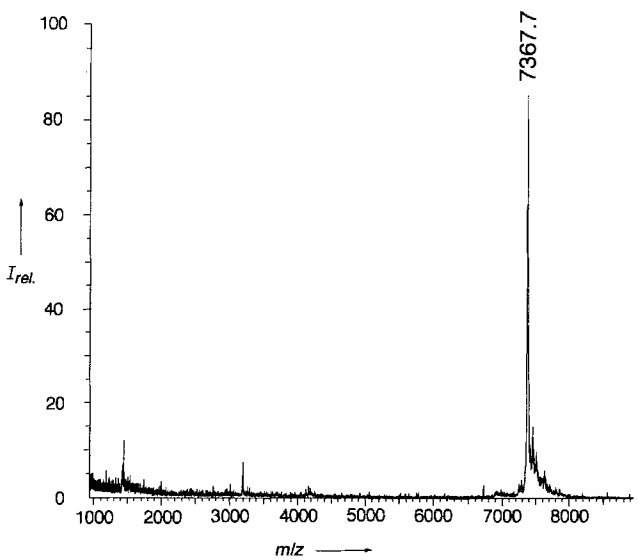
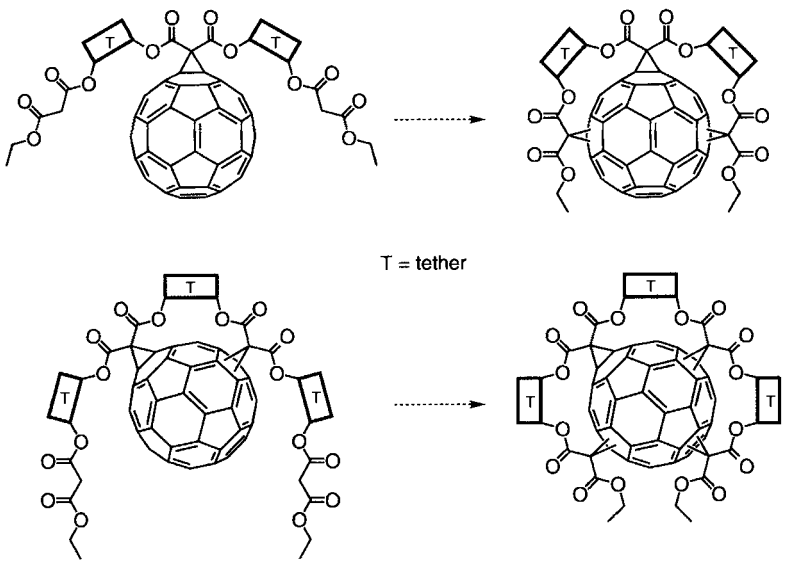


Fig. 7. *MALDI-TOF Mass spectrum of* **66**

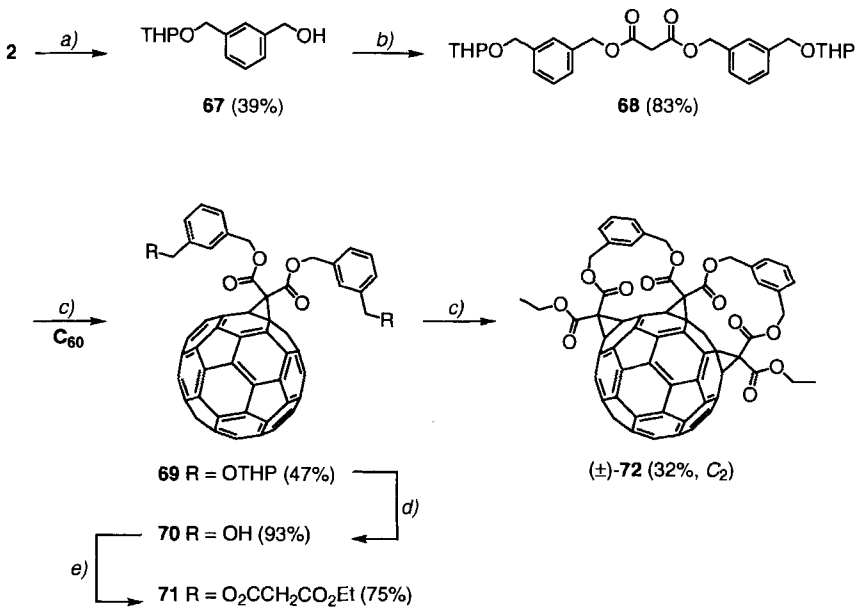
2.5. *Tether-directed Preparation of Higher Multiple Adducts.* An obvious extension of the new methodology for the synthesis of bis-adducts was the construction of higher adducts of C_{60} by multiple macrocylizations. The proposed principle for the regioselective preparation of covalent tris- and tetrakis-adducts of C_{60} is outlined in *Scheme 14*. Starting from a mono-adduct bearing two pendant malonate moieties, a clipping reaction on the C_{60} core should lead to a selected tris-adduct depending on the nature of the tethers. In a similar manner, the clipping reaction starting from a bis-adduct should give a selected tetrakis-adduct. By a judicious combination of tethers, a rich variety of specific tris- and tetrakis-adducts of C_{60} with original addition patterns are theoretically accessible *via* this route. Here, we describe the preparation of tris-adduct (±) **72** and tetrakis-adduct **77** using *m*-xylylene tethers (*Schemes 15* and *16*).

Scheme 14. *Regioselective Preparation of Tris- and Tetrakis-adducts of C_{60} by Multiple Macrocyclization (Clipping) Reactions*



Reaction of mono-protected **67**, which was obtained in 39% yield from diol **2** and 3,4-dihydro-2*H*-pyran (DHP), with malonyl dichloride in CH_2Cl_2 in the presence of C_5H_5N yielded **68** as a mixture of diastereoisomers (*Scheme 15*). Subsequent addition to C_{60} formed mono-adduct **69**, and deprotection (TsOH, EtOH/PhMe) afforded diol **70**. Double esterification of **70** with ethyl 3-chloro-3-oxopropanoate gave the desired C_{60} mono-adduct **71** bearing two pendant malonate groups. Reaction of **71** with DBU/I_2 in PhMe under high-dilution conditions yielded tris-adduct (±)-**72** as a single isolable product. In *Sect. 2.1*, we showed that the *m*-xylylene tether directs a bis-functionalization to a *cis-2* addition pattern. It could, therefore, be expected that the two new (external) methano bridges in tris-adduct (±)-**72** would be formed in *cis-2* positions relative to the central bridge already in place. With this assumption, three different structures are possible depending on the relative position of the two external addends. Starting from **71**, after the first intramolecular cyclization, there are three *cis-2* C=C bonds available

Scheme 15. *Preparation of Tris-adduct (±)-72*

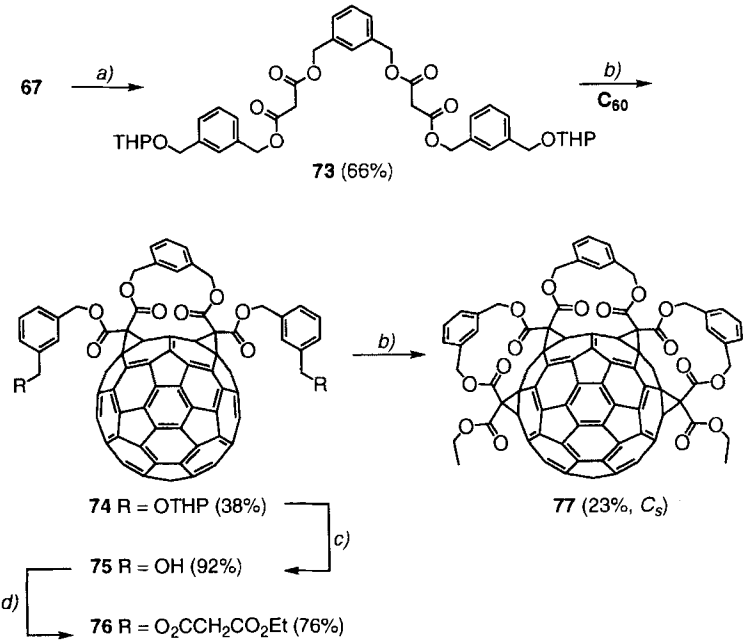


a) DHP (1 equiv.), TsOH · H_2O (cat.), MeCN, r.t. *b*) $ClCOCH_2COCl$, C_5H_5N, CH_2Cl_2, 0° → r.t. *c*) DBU, I_2, PhMe, r.t. *d*) TsOH · H_2O, EtOH, PhMe, 80°. *e*) EtO_2CCH_2COCl, C_5H_5N, CH_2Cl_2, 0° → r.t. THP = 3,4,5,6-tetrahydro-2*H*-pyran-2-yl.

for the second intramolecular *Bingel* addition. The relative positions of the two external cyclopropane rings could be *cis-1*, *trans-3*, or *trans-4*, and the molecular symmetry of the resulting tris-adduct is different in each case. With the (for *cis-2* addition, see *Sect. 2.1*) expected preference for *out-out* stereoisomers, the (*cis-2*, *cis-2*, *cis-1*) tris-adduct should be C_s-symmetrical, the (*cis-2*, *cis-2*, *trans-3*) C_2-symmetrical, and the (*cis-2*, *cis-2*, *trans-4*) C_1-symmetrical, with the third entry in the functional descriptors in parentheses describing the relative position of the two external methano bridges. Formation of the C_s-symmetrical tris-adduct is not expected due to severe steric hindrance between the two COOEt groups of the external addends in the *cis-1* positional relationship. The formation of the C_1-symmetrical tris-adduct should also be disfavored, since one of the tethers would be oriented in an *in-out* manner. Therefore, the tris-adduct should be C_2-symmetrical with a (*cis-2*, *cis-2*, *trans-3*) addition pattern. This symmetry and addition pattern of tris-adduct (±)-**72** were readily confirmed by ^{13}C-NMR spectroscopy. The presence of three fullerene sp^3-C-signals (66.70, 66.98, and 70.58 ppm) and 33 resonances in the sp^2-C-atom region (27 fullerene C-atoms and six aromatic C-atoms) in the ^{13}C-NMR spectrum of (±)-**72** demonstrates conclusively the formation of the C_2-symmetrical tris-adduct. Four different fullerene sp^3-C-atom and 28 fullerene sp^2-C-atom resonances would be expected for a C_s-symmetrical derivative.

In the preparation of tetrakis-adduct **77**, DCC-mediated esterification of diacid **57** with alcohol **67** yielded bis-malonate **73** as a mixture of diastereoisomers (*Scheme 16*). Macrocyclization of **73** with C_{60} gave the *cis-2* bis-adduct **74**, and subsequent deprotec-

Scheme 16. *Preparation of Tetrakis-adduct* **77**



a) **57**, DCC, DMAP, THF, 0° → r.t. *b*) DBU, I_2, PhMe, r.t. *c*) TsOH · H_2O, EtOH, PhMe, 80°. *d*) EtO_2CCH_2COCl, C_5H_5N, CH_2Cl_2, 0° → r.t.

tion (TsOH, EtOH/PhMe) afforded diol **75**. The reaction of **75** with ethyl 3-chloro-3-oxopropanoate in the presence of C_5H_5N in CH_2Cl_2 at room temperature led to **76** in 76% yield. Finally, treatment of **76** with DBU/I_2 in PhMe under high-dilution conditions afforded tetrakis-adduct **77** in 23% yield as the single isolable product. By applying similar stereochemical considerations as described for tris-adduct (±)-**72**, the most reasonable addition pattern for tetrakis-adduct **77** appears to be (*cis-2*, *cis-2*, *cis-2*, *trans-1*); compound **77** should, therefore, have C_s-symmetry. The ^{13}C-NMR spectrum of **77** is in full agreement with this proposed symmetry and displays the 38 expected resonances in the typical fullerene and aromatic region (28 for the fullerene sp^2-C-atoms and ten for the aromatic sp^2-C-atoms) as well as the expected 15 non-aromatic signals (163.90, 163.23, 163.02, 162.46 ppm for the C=O groups; 68.83, 67.28, 66.60, 65.67 ppm for the fullerene sp^3-C-atoms; 67.37, 67.16, 67.02, 63.28 ppm for the CH_2O groups; 44.73, 41.60 ppm for the methano-bridge C-atoms; and 14.24 ppm for the Me groups).

2.6. *Physical Properties of the New Multiple Adducts of* C_{60}. 2.6.1. *Electronic-Absorption Spectroscopy*. Compounds **8**, (±)-**72**, and **77** constitute an interesting new series of bis-, tris-, and tetrakis-adducts of C_{60}, respectively, with a *cis-2* relationship between neighboring addends that are progressively introduced along an equatorial belt on the fullerene sphere. Whereas bis-adduct **8** is orange-red-colored in CH_2Cl_2 solution, tris-adduct (±)-**72** is orange and visually indistinguishable from tetrakis-adduct **77**. The UV/VIS spectra of the three compounds in CH_2Cl_2 are depicted in *Fig. 8*. The characteristic bis-adduct absorption band of **8** at λ_{max} 437 nm has expectedly vanished in the spectra

of the higher adducts [2f]. The visible range in the spectrum of (±)-**72** is dominated by a broad band at λ_{max} 461 nm, but, overall, the absorptions of the tris-adduct in this spectral range are less intense than those of tetrakis-adduct **77**. Whereas band shapes and positions vary significantly in the spectra of (±)-**72** and **77**, the end absorptions of the two compounds occur at nearly the same wavelength (at *ca.* 625 nm). Thus, the end absorption of these compounds with an all-*cis-2* positional relationship between the addends is hypsochromically shifted by *ca.* 25 nm compared to that of tris- and tetrakis-adducts with an all-*e* positional relationship between malonate addends, that are also located along an equatorial belt [2f].

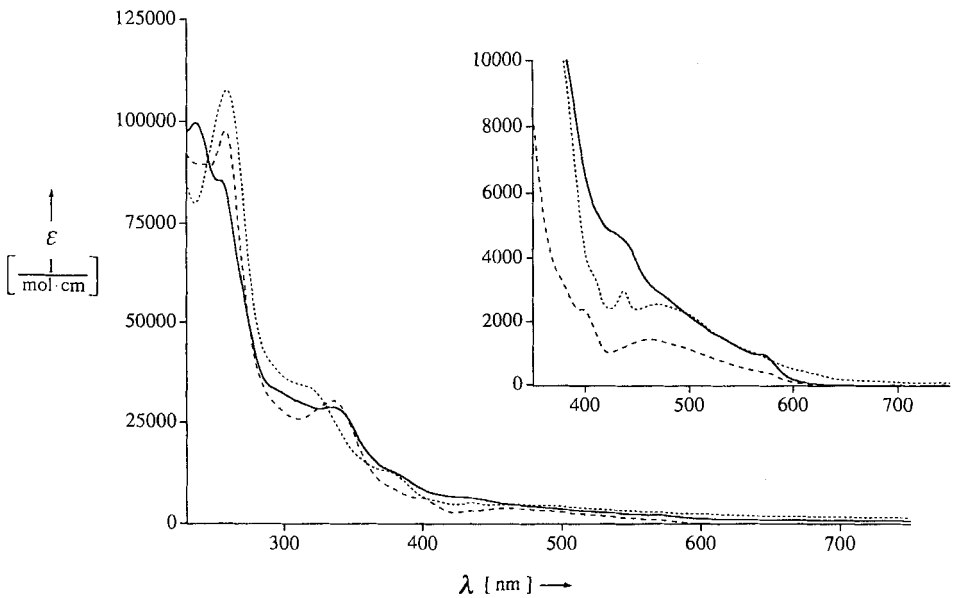


Fig. 8. *UV/VIS Spectra of* **8** (·····), *(±)-***72** (– – –), *and* **77** (——) *in* CH_2Cl_2

2.6.2. *Electrochemistry.* The electrochemical investigations on the new fullerene adducts were carried out as previously described [2b] by steady-state voltammetry (SSV) in CH_2Cl_2 (+ 0.1M Bu_4NPF_6) on a glassy C-electrode. All redox processes in *Table 2* are reported *vs.* the ferrocene/ferricinium couple (Fc/Fc^+). All macrocyclic bis(methano)-fullerenes undergo multiple reduction steps with the first electron transfer occurring in a narrow potential range between −1.10 to −1.13 V. Thus, on the bis-adduct stage, regioisomerism (*cis-2*, *cis-3*, *e*, *trans-4*, *trans-3*) does not seem to influence fullerene redox properties, which is in agreement with previous findings [2f] [36]. Also, the nearly identical first three reduction potentials of the *cis-2* bis-adducts **7**, **8**, and **25** demonstrate that there exists no particular intramolecular electronic communication between the fullerene and aromatic rings in the macrocyclic bridges.

Cyclic voltammetric studies in CH_2Cl_2 (+ 0.1M Bu_4NPF_6, glassy C-electrode) revealed that the first reduction step in bis-adducts **7**–(±)-**10**, (±)-**19**–(±)-**21**, **25**, and *ent*-**26** was a reversible one-electron reduction. The second reduction step was reversible for all species with the exception of the *cis-2* derivatives, which exhibited irreversible

Table 2. *Reduction and Oxidation Characteristics* (V *vs.* Fc/Fc^+) *of Covalent Fullerene Adducts in Comparison to* C_{60} *Measured by Steady-State Voltammetry on a Rotating Glassy C Disk Electrode in* CH_2Cl_2 + 0.1M Bu_4NPF_6. The degree of addition increases sequentially going down the *Table*.

Compound	Reduction[a])					Oxidation[a])
	E_1	E_2	E_3	E_4	E_5	E_1
C_{60}	−0.98 (57)	−1.37 (59)	−1.81 (57)			
70	−1.04 (62)	−1.41 (62)	−1.90 (64)			+1.36 (121)
7	−1.12 (62)	−1.49 (60)	−1.77 (65)[b])	−2.00 (60)	−2.18 (64)	
8	−1.10 (64)	−1.46 (60)	−1.73 (59)[b])	−2.15 (61)	−2.37 (74)	
9	−1.13 (64)	−1.54 (62)	−2.00 (62)	−2.23 (60)		
(±)-**10**	−1.11 (64)	−1.51 (62)	−2.02 (100)[c])			
(±)-**19**	−1.12 (62)	−1.49 (64)	−2.04 (66)			+1.11 (91)
(±)-**20**	−1.11 (68)	−1.49 (66)	−2.07 (67)			+1.14 (88)
(±)-**21**	−1.14 (67)	−1.53 (70)	[d])			+1.11 (70)
25	−1.11 (66)	−1.47 (60)	−1.73 (61)[b])	−2.16 (64)		
ent-**26**	−1.10 (61)	−1.47 (60)	−1.97 (59)[c])			
62	−1.10 (62)	−1.43 (61)	−1.72 (60)[b])	−2.11 (60)		+1.18 (97)
63	−1.10 (63)	−1.44 (80)	−1.71 (61)[b])	−2.06 (64)		+1.16 (115)
66	−1.10 (63)	−1.48 (88)	−1.72 (60)	−2.16 (111)		+1.19 (115)
(±)-**72**	−1.25 (63)	−1.43 (57)	−1.84 (60)[c])	−2.20 (84)		+1.21 (71)
77	−1.25 (56)	−1.35 (63)	−1.88 (67)[c])			+1.16 (72)

[a]) Values quoted: $E_{1/2}$ in V and, in parenthesis, the slope $\log(I/(I_d - I))$ in mV; one electron is transferred unless indicated otherwise. [b]) 0.5 Electron transferred. [c]) Two electrons transferred. [d]) Poorly resolved one-electron reduction step.

electron transfers at sweep rates lower than 1 $V\,s^{-1}$. The evolution of the peak characteristics with the sweep rate clearly demonstrated that the second electron transfer in the *cis-2* derivatives was followed by a chemical reaction, generating a species reducible at *ca.* −1.75 V. Indeed, this third reduction at *ca.* −1.75 V is measured for all *cis-2* derivatives and is not observed for either C_{60}, mono-adducts, or bis-adducts with other addition patterns. It cannot be excluded that the generated *cis-2* dianion is unstable and decomposes during the electrochemical reduction [37].

The dendritic bis-adducts **62**, **63**, and **66** all undergo multiple reductions at very similar potentials, identical to those of the other *cis-2* bis-adducts such as **7** or **8**. Clearly, in CH_2Cl_2 the redox potential of the fullerene core is not affected by size and density of surrounding poly(ether-amide) dendrons. Interestingly however, cyclic voltammetry revealed that the first reduction step is irreversible in the case of the first- and second-generation compounds **62** and **63**, whereas it is reversible in **66** with a more encapsulated fullerene core.

Upon changing from the bis-adducts to the all-*cis-2* tris- and tetrakis-adducts (±)-**72** and **77**, respectively, the first reduction potential expectedly becomes more negative. The first electron transfer to both compounds occurs at −1.25 V, which is at −0.11 V and −0.06 V more negative potential than the first reduction of all-*e* tris(methano)- and tetrakis(methano)fullerenes in which the addends are located along an equatorial belt [2f]. These differences correlate with the observed differences in the optical end absorptions, which are shifted by *ca.* 25 nm to shorter wavelength in the UV/VIS spectra of the

all-*cis*-2 as compared to the previously reported all-*e* derivatives (see *Sect. 2.6.1*). The reduction parameters indicate that multiple all-*cis*-2 addition patterns cause a larger perturbation of the initial fullerene π chromophore and a larger raise in LUMO energy than multiple all-*e* patterns.

3. Conclusions. – With the invention of a second, broadly applicable tether-directed remote functionalization reaction in our laboratory, the regioselective access to selected fullerene multiple adducts has been greatly improved. A large variety of multifunctional fullerene building blocks for three-dimensional molecular construction should rapidly become available by this facile methodology, consisting of the direct macrocyclization of bis-malonates with the fullerene sphere in a double *Bingel* addition. The few applications described in this paper already demonstrate nicely the broad scope of this reaction. Thus, the macrocyclization reaction is not only regio- but also highly diastereoselective and use of optically active tethers allows the synthesis of optically active fullerene derivatives and, after removal of the tether, of those whose chirality results exclusively from the addition pattern.

By the double fixation through macrocyclization, metal-ion binding sites such as the phenanthroline moieties in (±)-**15**, **16**, (±)-**19**, and (±)-**20** are attached in a defined way atop the surface of the C-sphere. The methodology should find multiple applications in supramolecular devices, which rely on control of geometry for the expression of function. Already, the macrocyclization reaction has been applied in the synthesis of the first fullerene-containing [2]catenane featuring an unprecedented acceptor-donor-acceptor-donor-acceptor π stack [8]. The construction of the fullerene dendrimers **62**, **63**, and **66** illustrates another advantage of the new method: multiple derivatizations can be performed in the macrocyclic bridge rather than on the adjacent fullerene surface. In this way, the number of addends to the C-sphere in extensively functionalized systems is reduced, and desirable properties such as facile multiple reducibility or efficient photosensitization of singlet oxygen that are characteristic of the parent fullerenes and lower adducts, but not of higher adducts, are maintained [2f].

Finally, an extension of the new macrocyclization for the construction of selected higher adducts was developed. Starting from the C_{60} mono-adduct **71** bearing two pendant malonate groups, a clipping reaction provided the all-*cis*-2 tris-adduct (±)-**72** with high regioselectivity. In a similar manner, the clipping reaction starting from bis-adduct **76** afforded the all-*cis*-2 tetrakis-adduct **77**. These multiple adducts are not accessible by stepwise additions of non-tethered malonates. By a judicious combination of tethers, whose choices are limited by imagination only, a rich variety of specific multiple-adducts with original addition patterns will become accessible *via* this route.

Experimental Part

General. Reagents and solvents were purchased reagent-grade and used without further purification. PhMe and THF were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2 or dried over molecular sieves (4 Å). Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona, AZ 85706, USA, and C_{60} was purified as reported in [38]. Compounds **11** [21], **12** [22], **22** [24], **30** [31], **38** [6], and **52** [34] were prepared as previously reported. All reactions were performed in standard glassware under an inert atmosphere of N_2 or Ar. Evaporation and concentration *in vacuo* were done at water-aspirator pressure, and compounds were dried at 10^{-2} Torr. The electrochemical investigations were carried out as described in [2b].

Column chromatography (CC): SiO_2 *60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck*. Gel permeation chromatography (GPC): *Biorad Biobeads SX-1*. For the optically active derivatives, the ee was determined by HPLC (eluent hexane/CH_2Cl_2 7:3) on the CSP (*S,S*)-*Whelk-01* (5 μm, 250 mm × 4.6 mm) from *Regis Chemical Company*, Morton Grove, IL, USA; *Knauer HPLC Pump 64*, high-pressure gradient pumps, *Variable Wavelength Monitor* UV/VIS detector from *Knauer*, with detector wavelength fixed at λ 310 nm; flow rate 2 ml min^{-1}. TLC: glass sheets coated with SiO_2 *60* F_{254} from *E. Merck*; visualization by UV light. Prep. TLC (PTLC): pre-coated plates with SiO_2 *60* F_{254} from *E. Merck*; visualization by UV light. M.p.: *Büchi Smp-20*, uncorrected. Optical rotation: *Perkin-Elmer-241* polarimeter; at r.t. (295 ± 1 K). Due to the very dark color of the solns. optical rotations could not be determined for the fullerene derivatives **24**/*ent*-**24**, **25**/*ent*-**25**, **26**/*ent*-**26**, and **28**/*ent*-**28**. UV/VIS Spectra (λ_{max} in nm (ε)): *Varian Cary-5* spectrophotometer. CD Spectra (λ_{max} and λ_{min} in nm ($\Delta\varepsilon$)): *Jasco-J-710* spectropolarimeter. IR Spectra (cm^{-1}): *Perkin Elmer 1600-FTIR*. NMR Spectra: *Bruker AM 500* and *Varian Gemini 300* or *200* spectrometers at 296 or 300 K, with solvent peaks as reference. EI-MS (*m/z* (%)): *VG Tribrid* instrument, 70 eV; FAB-MS (*m/z* (%)): *VG ZAB 2SEQ* instrument, 3-nitrobenzyl alcohol as matrix; MALDI-TOF-MS: measured with reflectron detection in the positive- or negative-ion mode, acceleration voltage 15–20 kV, on a *Bruker-REFLEX* spectrometer; matrices are 2,5-dihydroxybenzoic acid (DHB, 0.1M in MeCN/EtOH/H_2O 50:45:5), α-cyano-4-hydroxycinnamic acid (CCA, 0.1M in MeCN/EtOH/H_2O 50:45:5) or anthracene-1,8,9-triol (dithranol; 0.05M in $CHCl_3$/MeOH 1:1). Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie, ETH-Zürich*.

1,2-Bis{[(ethoxycarbonyl)acetoxy]methyl}benzene (**4**). Ethyl 3-chloro-3-oxopropanoate (2.3 ml, 18.09 mmol) was added to a stirred soln. of **1** (1.00 g, 7.24 mmol) and C_5H_5N (1.5 ml, 18.09 mmol) in CH_2Cl_2 (100 ml) at 0°. The soln. was allowed to slowly warm to r.t. (over 1 h) and then stirred for 3 h. The mixture was washed with sat. aq. NH_4Cl soln. (2×), dried ($MgSO_4$), and evaporated to dryness. CC (SiO_2, CH_2Cl_2/MeOH 97:3) yielded **4** (1.81 g, 68%). Colorless oil. IR (neat): 1733 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.22 (*t*, *J* = 7.1, 6 H); 3.40 (*s*, 4 H); 4.17 (*q*, *J* = 7.1, 4 H); 5.26 (*s*, 4 H); 7.34–7.41 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.97; 41.55; 61.64; 64.69; 129.06; 130.04; 134.14; 166.45 (2×). FAB-MS: 367 (58, MH^+), 235 (100, $[M - O_2CCH_2CO_2Et]^+$). Anal. calc. for $C_{18}H_{22}O_8 \cdot 0.1\ CH_2Cl_2$ (374.9): C 57.99, H 5.97; found: C 57.95, H 5.76.

1,3-Bis{[(ethoxycarbonyl)acetoxy]methyl}benzene (**5**). Starting from diol **2**, synthesis was performed as for **4**, yielding **5** (1.71 g, 65%). Colorless oil. IR (neat): 1737 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.22 (*t*, *J* = 7.1, 6 H); 3.39 (*s*, 4 H); 4.16 (*q*, *J* = 7.1, 4 H); 5.15 (*s*, 4 H); 7.31 (br. *s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.73, 41.25; 61.27; 66.47; 127.65; 127.91; 128.58; 135.48; 166.06 (2×). FAB-MS: 367 (70, MH^+), 235 (100, $[M - O_2CCH_2CO_2Et]^+$). Anal. calc. for $C_{18}H_{22}O_8 \cdot 0.15\ CH_2Cl_2$ (379.1): C 57.50, H 5.93; found: C 57.59, H 6.04.

1,4-Bis{[(ethoxycarbonyl)acetoxy]methyl}benzene (**6**). Starting from diol **3**, synthesis was performed as for **4**, yielding **6** (1.61 g, 61%). Colorless oil. IR (neat): 1735 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.19 (*t*, *J* = 7.1, 6 H); 3.36 (*s*, 4 H); 4.13 (*q*, *J* = 7.1, 4 H); 5.12 (*s*, 4 H); 7.30 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.70, 41.22; 61.23; 66.34; 128.09; 135.27; 166.02 (2×). FAB-MS: 367 (6, MH^+), 235 (100, $[M - O_2CCH_2CO_2Et]^+$). Anal. calc. for $C_{18}H_{22}O_8 \cdot 0.2\ CH_2Cl_2$ (383.4): C 57.02, H 5.89; found: C 57.16, H 5.77.

Diethyl endo,endo-*(o-Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**7**). DBU (0.4 ml, 2.496 mmol) was added at r.t. to a soln. of C_{60} (300 mg, 0.416 mmol), I_2 (211 mg, 0.832 mmol), and **4** (152 mg, 0.416 mmol) in PhMe (600 ml). The soln. was stirred for 5 h. The crude material was filtered through a short plug (SiO_2), eluting first with PhMe (to remove unreacted C_{60}) and then with CH_2Cl_2. CC (SiO_2, CH_2Cl_2/hexane 2:1) and recrystallization (hexane/$CHCl_3$) provided **7** (151 mg, 33%). Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (90800), 318 (28700), 372 (10900), 437 (2690), 469 (2310). IR (KBr): 1743 (C=O). ^{1}H-NMR ($CDCl_2CDCl_2$, 500 MHz, 373 K): 1.36 (*t*, *J* = 7.1, 6 H); 4.32–4.44 (*m*, 4 H); 5.31 (*AB*, *J* = 12.1, 4 H); 7.49 (br. *s*, 2 H); 7.57 (br. *s*, 2 H). FAB-MS: 1083 (100, MH^+), 720 (74, C_{60}^+). Anal. calc. for $C_{78}H_{18}O_8 \cdot 1.5\ CHCl_3$ (1262.1): C 75.66, H 1.56; found: C 75.58, H 1.64. X-Ray: see *Fig. 2*.

Diethyl endo,endo-*(m-Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**8**). Starting from **5**, synthesis was performed as for **7**. CC (SiO_2, CH_2Cl_2/hexane 9:5) and recrystallization (hexane/CH_2Cl_2) provided **8** (143 mg, 32%). Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 259 (107700), 318 (33800), 378 (12800), 437 (2960), 469 (2540). IR (KBr): 1742 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.34 (*t*, *J* = 7.1, 6 H); 4.34–4.46 (*m*, 4 H); 5.16 (*d*, *J* = 12.8, 2 H); 5.86 (*d*, *J* = 12.8, 2 H); 7.27 (*dd*, *J* = 7.5, 1.5, 2 H); 7.38 (*t*, *J* = 7.5, 1 H); 7.52 (*t*, *J* = 1.5, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.15; 49.36; 63.25; 67.07; 67.41; 70.74; 123.73; 126.59; 128.68; 135.93; 136.33; 136.67; 137.63; 139.98; 141.10; 141.31; 142.39; 143.09; 143.33; 143.66; 143.84; 144.03; 144.24; 144.32; 144.50; 144.66; 145.11; 145.24; 145.26; 145.43; 145.71; 145.78; 145.82; 146.14; 146.17; 147.39; 147.54; 147.59; 148.83; 162.87; 163.04. FAB-MS: 1083 (100, MH^+), 720 (32, C_{60}^+). Anal. calc. for $C_{78}H_{18}O_8 \cdot 0.5\ CH_2Cl_2$ (1125.5): C 83.78, H 1.70; found: C 83.53, H 1.75.

Diethyl endo,endo-*(*p-*Phenylenedimethyl) 1,2:34,35-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**9**), *and (±)-Diethyl* endo,endo-*(*p-*Phenylenedimethyl) 1,2:18,36-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((±)-(**10**). Starting from **6**, synthesis was performed as for **7**. CC (SiO_2) eluting with CH_2Cl_2/hexane 9:5 yielded (±)-**10** which was recrystallized from $CHCl_3$/hexane (34 mg, 8%), and with CH_2Cl_2/hexane 2:1 **9** which was also recrystallized from $CHCl_3$/hexane (149 mg, 33%).

Data of **9**: Brown solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 243 (94900), 314 (37500), 417 (3280), 473 (2110), 633 (580), 698 (400). IR (KBr): 1743 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.50 (*t*, *J* = 7.1, 6 H); 4.52–4.58 (*m*, 4 H); 5.00 (*d*, *J* = 11.3, 2 H); 6.02 (*d*, *J* = 11.3, 2 H); 7.16 (*d*, *J* = 1.8, 2 H); 7.52 (*d*, *J* = 1.8, 2 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.27; 49.01; 63.51; 68.18; 70.45; 70.75; 130.48; 131.45; 131.65; 135.75; 138.15; 140.97; 141.08; 141.15; 141.20; 141.37; 141.39 (2×); 141.91; 142.07; 142.28; 142.75; 142.90; 142.97; 143.11; 144.15; 144.32; 144.72; 144.98; 145.12; 145.17; 145.30; 145.32; 145.86; 145.95; 146.40; 146.85; 146.94; 148.15; 163.82; 164.00. FAB-MS: 1083 (100, MH^+), 720 (30, C_{60}^+). Anal. calc. for $C_{78}H_{18}O_8 \cdot 1.2\ CHCl_3$ (1226.3): C 77.58, H 1.58; found: C 77.71, H 1.62.

*Data of (±)-***10**: Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 253 (84150), 307 (sh, 34300), 358 (sh, 13200), 397 (3500), 408 (sh, 2200), 421 (1980), 482 (2500). IR (KBr): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.45 (*t*, *J* = 7.1, 3 H); 1.46 (*t*, *J* = 7.1, 3 H); 4.46–4.55 (*m*, 4 H); 4.88 (*d*, *J* = 11.3, 1 H); 5.07 (*d*, *J* = 11.8, 1 H); 5.72 (*d*, *J* = 11.8, 1 H); 5.86 (*d*, *J* = 11.3, 1 H); 6.90 (*dd*, *J* = 7.5, 1.5, 1 H); 7.01 (*dd*, *J* = 7.5, 1.5, 1 H); 7.63 (*dd*, *J* = 8.0, 1.5, 1 H); 7.66 (*dd*, *J* = 8.0, 1.5, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.21; 14.25; 52.09; 52.78; 63.34; 63.44; 68.20; 68.90; 70.55; 70.83; 71.04; 71.88; 128.51; 129.93; 130.23; 132.73; 135.34; 137.38; 138.17; 138.36; 139.05; 141.04; 141.09; 141.11; 141.44; 141.54; 141.72; 141.78; 142.09; 142.12; 142.30; 142.80; 142.92; 143.07; 143.12; 143.15; 143.26; 143.46; 143.54; 143.60; 143.64; 143.70; 143.95; 144.02; 144.10; 144.38; 144.39; 144.46; 144.51; 144.63; 144.72; 144.76; 144.80; 144.85; 144.88; 145.50; 145.56; 145.89; 145.96; 146.08; 146.16; 146.42; 146.44; 146.48; 146.65; 146.81; 147.18; 147.24; 162.56; 162.66; 162.98; 163.73. FAB-MS: 1083 (100, MH^+), 720 (20, C_{60}^+).

2,9-Bis{[(ethoxycarbonyl)acetoxy]methyl}-1,10-phenanthroline (**13**). Ethyl 3-chloro-3-oxopropanoate (0.55 ml, 4.162 mmol) was added to a stirred soln. of **11** (400 mg, 7.24 mmol) and C_5H_5N (0.35 ml, 1.665 mmol) in CH_2Cl_2 (100 ml) at 0°. The soln. was allowed to slowly warm to r.t. (over 1 h) and was then stirred for 12 h. The mixture was washed with H_2O (3×), dried ($MgSO_4$), and evaporated to dryness. CC (SiO_2, CH_2Cl_2/MeOH 99:1) followed by recrystallization (hexane/CH_2Cl_2) yielded **13** (458 mg, 59%). Pale-yellow crystals. M.p. 94°. IR (neat): 1734 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.29 (*t*, *J* = 7.1, 6 H); 3.56 (*s*, 4 H); 4.24 (*q*, *J* = 7.1, 4 H); 5.74 (*s*, 4 H); 7.78 (*d*, *J* = 7.7, 2 H); 7.81 (*s*, 2 H); 8.30 (*d*, *J* = 7.7, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz); 11.58, 39.13, 59.26; 65.99; 118.84; 124.20; 126.01; 134.93; 142.80; 153.98; 164.04; 164.20. FAB-MS: 469 (MH^+). Anal. calc. for $C_{24}H_{24}N_2O_8$ (468.5): C 61.53, H 5.16, N 5.98: found: C 61.24, H 5.15, N 6.04. X-Ray: see *Fig. 3*.

(±)-Diethyl endo,endo-*[(1,10-Phenanthroline-2,9-diyl)dimethyl] 1,2:18,36-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((±)-**15**), *Diethyl* endo,endo-*[(1,10-Phenanthroline-2,9-diyl)dimethyl] 1,2:34,35-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**16**), *and Diethyl [(1,10-Phenanthroline-2,9-diyl)dimethyl] Bis(1,2-methano[60]fullerene-61,61-dicarboxylate)* (**17**). DBU (0.3 ml, 1.83 mmol) was added at r.t. to a soln. of C_{60} (200 mg, 0.278 mmol), I_2 (176 mg, 0.695 mmol), and **13** (143 mg, 0.306 mmol) in PhMe (500 ml), and the mixture was stirred for 5 h. The product was filtered through a short plug (SiO_2) eluting first with PhMe to remove unreacted C_{60} (31 mg) then with CH_2Cl_2/MeOH (92:8). CC (SiO_2) with gradient elution (PhMe/AcOEt 10:1 to 5:1) gave **17**, followed by **16**, and finally (±)-**15**. Recrystallization (CH_2Cl_2/hexane) yielded **17** (19 mg, 7%), **16** (29 mg, 9%), and (±)-**15** (42 mg, 13%), respectively.

*Data of (±)-***15**: Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 256 (110600), 308 (sh, 38780), 358 (sh, 13850), 397 (3900), 409 (2410), 421 (2170), 480 (2800). IR (KBr): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.47 (*t*, *J* = 7.1, 3 H); 1.50 (*t*, *J* = 7.1, 3 H); 4.48–4.62 (*m*, 4 H); 5.62 (*d*, *J* = 13.8, 1 H); 5.80 (*d*, *J* = 10.6, 1 H); 5.85 (*d*, *J* = 10.6, 1 H); 6.12 (*d*, *J* = 13.8, 1 H); 7.65 (*d*, *J* = 8.2, 1 H); 7.75 (*s*, 2 H); 7.90 (*d*, *J* = 8.2, 1 H); 8.22 (*d*, *J* = 8.2, 1 H); 8.27 (*d*, *J* = 8.2, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.21; 14.29; 51.01; 54.14; 63.33; 63.46; 67.91; 69.98; 70.55; 71.23; 71.92; 121.67; 125.04; 126.51; 127.01; 128.16; 128.49; 136.92; 137.12; 138.10; 138.34; 138.87; 140.51; 140.72; 141.42; 141.45; 141.51; 141.72; 142.43; 142.67; 142.74; 142.91; 143.19; 143.23; 143.30; 143.35; 143.53; 143.57; 143.62; 143.79; 143.83; 143.95; 144.03; 144.18; 144.23; 144.37; 144.39; 144.48; 144.63; 144.73; 144.81; 144.84; 144.87; 145.18; 145.24; 145.43; 145.64; 145.86; 145.93; 145.95; 146.08; 146.24; 146.34; 146.38; 146.47; 147.02; 147.10; 147.18; 148.31; 153.82; 154.51; 163.40; 163.49; 163.65; 164.15. FAB-MS: 1185 (100, MH^+), 720 (19, C_{60}^+). Anal. calc. for $C_{84}H_{20}N_2O_8 \cdot 1.4\ CH_2Cl_2$ (1304.0): C 78.66, H 1.76, N 2.15; found: C 78.61, H 2.14, N 2.13.

Data of **16**: Brown solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 257 (104800), 322 (sh, 31700), 393 (sh, 5000), 405 (sh, 3750), 415 (sh, 3000), 467 (2200), 628 (480), 688 (310). IR (KBr): 1745 (C=O). ^{1}H-NMR ($CDCl_2CDCl_2$,

500 MHz, 393 K): 1.47 (*t*, *J* = 7.1, 6 H); 4.54 (*q*, *J* = 7.1, 4 H); 5.66 (*d*, *J* = 10.4, 2 H); 5.91 (br. *s*, 2 H); 7.68 (*s*, 2 H); 7.84 (*d*, *J* = 8.2, 2 H); 8.17 (*d*, *J* = 8.2, 2 H). FAB-MS: 1185 (51, MH$^+$), 720 (100, C_{60}^+). Anal. calc. for $C_{84}H_{20}N_2O_8 \cdot 1.2\ CH_2Cl_2$ (1287.0): C 79.51, H 1.75, N 2.18; found: C 79.67, H 1.98, N 2.17.

Data of **17**: Brown solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (196270), 326 (62280), 393 (sh, 10390), 403 (sh, 7840), 413 (sh, 6350), 426 (6000), 474 (3890), 685 (870). IR (KBr): 1742 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.46 (*t*, *J* = 7.1, 6 H); 4.58 (*q*, *J* = 7.1, 4 H); 6.06 (*s*, 4 H); 7.88 (*s*, 2 H); 7.97 (*d*, *J* = 8.3, 2 H); 8.38 (*d*, *J* = 8.3, 2 H). FAB-MS: 1906 (100, M^+), 720 (15, C_{60}^+).

2,9-Bis(4-{[(ethoxycarbonyl)acetoxy]methyl}phenyl)-1,10-phenanthroline (**14**). Ethyl 3-chloro-3-oxopropanoate (1.2 ml, 9.362 mmol) was added to a stirred soln. of **12** (1.47 g, 3.745 mmol) and C_5H_5N (0.75 ml, 9.362 mmol) in CH_2Cl_2 (250 ml) at 0°. The soln. was allowed to slowly warm to r.t. (over 1 h) and was then stirred for additional 4 h. The resulting mixture was washed with H_2O (4 ×) and dried ($MgSO_4$), the solvent was removed *in vacuo*, and CC (SiO_2, CH_2Cl_2/MeOH 500:1) yielded **14** (1.41 g, 61%). Pale-yellow glassy product. IR (neat): 1746, 1732 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.27 (*t*, *J* = 7.2, 6 H); 3.48 (*s*, 4 H); 4.22 (*q*, *J* = 7.2, 4 H); 5.30 (*s*, 4 H); 7.58 ('*d*', *J* = 8.4, 4 H); 7.76 (*s*, 2 H); 8.11 (*d*, *J* = 8.4, 2 H); 8.28 (*d*, *J* = 8.4, 2 H); 8.45 ('*d*', *J* = 8.4, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.13; 41.77; 61.77; 67.08; 120.22; 126.40; 128.08; 128.29; 128.96; 136.76; 137.29; 139.81; 146.36; 156.46; 166.80; 166.86. FAB-MS: 621 (MH$^+$). Anal. calc. for $C_{36}H_{32}N_2O_8 \cdot 1.4\ CH_2Cl_2$ (739.6): C 60.74, H 4.74, N 3.79; found: C 60.77, H 4.80, N 3.65.

(±)-Diethyl endo,exo-*[(1,10-Phenanthroline-2,9-diyl)bis(*p*-phenylenemethyl)]1,2:33,50-Bis(methano)[60]-fullerene-61,61,62,62-tetracarboxylate* ((±)-**19**) *and (±)-Diethyl* endo-endo-*[(1,10-Phenanthroline-2,9-diyl)bis(*p*-phenylenemethyl)] 1,2:33,50-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((±)-**20**). A soln. of **14** (413 mg, 0.665 mmol) in CH_2Cl_2 (15 ml) was added at r.t. to a soln. of C_{60} (400 mg, 0.555 mmol) and I_2 (338 mg, 1.332 mmol) in PhMe (800 ml). DBU (507 mg, 3.330 mmol) was added, and the resulting mixture was stirred overnight. Filtration through a short plug (SiO_2), first eluting with PhMe, then with CH_2Cl_2/MeOH 9:1, followed by CC (SiO_2, CH_2Cl_2/hexane 1:1 to 2:1), and PTLC (SiO_2, CH_2Cl_2/hexane 4:1) yielded (±)-**20** (38 mg, 5%) and (±)-**19** (149 mg, 20%).

*Data of (±)-***19**: Brown solid. M.p. > 250°. UV/VIS (CH_2Cl_2): 244 (153900), 266 (119600), 299 (sh, 60900), 311 (sh, 55600), 329 (sh, 41200), 343 (sh, 29400), 381 (sh, 8000), 399 (sh, 4500), 411 (3700), 422 (2900), 487 (2600), 571 (sh, 1200), 624 (470), 685 (140). IR (KBr): 1744, 1728 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.43 (*t*, *J* = 7.1, 3 H); 1.55 (*t*, *J* = 7.1, 3 H); 4.49 (*q*, *J* = 7.1, 2 H); 4.62 (*q*, *J* = 7.1, 2 H); 5.28 (*d*, *J* = 12.5, 1 H); 5.45 (*d*, *J* = 12.8, 1 H); 5.70 (*d*, *J* = 12.8, 1 H); 5.95 (*d*, *J* = 12.5, 1 H); 7.46 (*d*, *J* = 8.2, 2 H); 7.54 (*d*, *J* = 8.2, 2 H); 7.75 (*s*, 2 H); 8.09 (*d*, *J* = 8.4, 1 H); 8.14 (*d*, *J* = 8.4, 1 H); 8.23–8.32 (*m*, 2 H); 8.34 (*d*, *J* = 8.2, 2 H); 8.39 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.16; 14.30; 51.91; 51.93; 63.45; 63.57; 68.29; 69.22; 71.17; 71.43; 71.57; 71.64; 119.88; 120.19; 126.20; 127.76; 128.14; 128.16; 128.33; 128.49; 135.39; 135.90; 136.95; 136.99; 138.00; 138.93; 139.48; 139.54; 139.93; 140.26; 140.31; 140.54; 140.76; 141.04; 141.63; 141.84; 141.87; 141.89; 142.30; 142.46; 142.47; 142.53; 142.93; 143.18; 143.32; 143.37; 143.39; 143.53; 143.54; 143.70; 143.93; 144.00; 144.11; 144.15; 144.28; 144.41; 144.59; 144.69; 144.75; 145.20; 145.21; 145.32; 145.64; 146.16; 146.27; 146.28; 146.38; 146.40; 146.42; 146.54; 146.55; 146.59; 146.99; 147.01; 147.16; 147.37; 155.88; 156.00; 163.25; 163.40; 163.46; 164.86. FAB-MS: 1338 (100, MH$^+$), 720 (9, C_{60}^+). HR-FAB-MS: 1337.1909 (MH$^+$, $C_{96}H_{29}N_2O_8^+$, calc. 1337.1923).

*Data of (±)-***20**: Brown solid. M.p. > 250°. UV/VIS (CH_2Cl_2): 244 (111500), 266 (103400), 300 (sh, 51400), 313 (sh, 46300), 329 (sh, 34900), 343 (sh, 24800), 382 (sh, 6500), 398 (sh, 3800), 411 (3050), 423 (2500), 485 (2100), 579 (730), 626 (sh, 260), 684 (90). IR (KBr): 1744, 1722 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.51 (*t*, *J* = 7.1, 6 H); 4.59 (*q*, *J* = 7.1, 4 H); 5.27 (*d*, *J* = 12.9, 2 H); 5.63 (*d*, *J* = 12.9, 2 H); 7.40 ('*d*', *J* = 8.3, 4 H); 7.79 (*s*, 2 H); 8.16 (*d*, *J* = 8.4, 2 H); 8.31 (*d*, *J* = 8.4, 2 H); 8.42 ('*d*', *J* = 8.3, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.21; 52.11; 63.51; 68.42; 71.59; 71.79; 119.73; 126.15; 127.80; 128.13; 135.65; 136.95; 137.24; 137.56; 139.42; 140.62; 141.66; 141.94; 142.55; 143.37; 143.41; 143.44; 143.54; 143.56; 143.63; 143.85; 144.18; 144.46; 144.52; 145.19; 145.32; 145.49; 146.03; 146.12; 146.17; 146.45; 146.48; 146.67; 146.71; 147.03; 147.13; 147.31; 155.85; 163.39; 163.44. FAB-MS: 1338 (100, MH$^+$), 720 (18, C_{60}^+). HR-FAB-MS: 1337.1919 (MH$^+$, $C_{96}H_{29}N_2O_8^+$; calc. 1337.1923).

Tetraethyl 1,2:18,36-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate (**18**). K_2CO_3 (43 mg, 0.312 mmol) was added to a soln. of (±)-**15** (37 mg, 0.031 mmol) in THF/EtOH 1:1 (30 ml), and the mixture was stirred at r.t. for 2 h. The solvent was removed *in vacuo*, and the resulting residue was filtered through a plug of SiO_2 (CH_2Cl_2). CC (SiO_2, CH_2Cl_2/hexane 2:1) followed by recrystallization (CH_2Cl_2/hexane) yielded **18** (16.6 mg, 51%). Dark-red solid. M.p. > 250°. IR, UV/VIS, ^{1}H-NMR, and FAB-MS: identical to those reported in [11a].

(±)-Tetraethyl 1,2:33,50-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate ((±)-**21**). K_2CO_3 (223 mg, 1.616 mmol) was added to a soln. of (±)-**19** (30 mg, 0.022 mmol) in THF/EtOH 1:1 (30 ml). The mixture was stirred at r.t. for 35 min, then filtered through a plug (SiO_2), and evaporated to dryness. CC (SiO_2, CH_2Cl_2/hexane 3:2 to 7:3), followed by recrystallization (CH_2Cl_2/hexane), yielded (±)-**21** (10 mg, 43%). Brown solid. M.p. > 250°. IR, UV/VIS, ^{1}H-NMR, and FAB-MS: identical to those reported in [11a].

(±)-2,2'-Bis{[(ethoxycarbonyl)acetoxy]methyl}-9,9'-spirobifluorene ((±)-**23**). Ethyl 3-chloro-3-oxopropanoate (0.43 ml, 3.32 mmol) was added to a stirred soln. of (±)-**22** (500 mg, 1.33 mmol) and C_5H_5N (0.27 ml, 3.32 mmol) in CH_2Cl_2 (100 ml) at 0°. The soln. was allowed to slowly warm to r.t. (over 1 h), and stirring was continued for 3 h. The resulting mixture was washed with sat. aq. NH_4Cl soln. (2×), dried ($MgSO_4$), and the solvent was evaporated to dryness. CC (SiO_2, CH_2Cl_2/hexane 6:1) yielded (±)-**23** (480 mg, 60%). Colorless oil. UV/VIS (CH_2Cl_2): 269 (29500), 278 (28500), 300 (13400), 311 (19500). IR (neat): 1745, 1734 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.20 (*t*, *J* = 7.1, 6 H); 3.35 (*s*, 4 H); 4.10 (*q*, *J* = 7.1, 4 H); 5.05 (*s*, 4 H); 6.71 (*s*, 2 H); 6.72 (*d*, *J* = 6.6, 2 H); 7.13 (*dd*, *J* = 7.6, 6.6, 2 H); 7.40 (*dd*, *J* = 8.0, 7.6, 2 H); 7.42 (*d*, *J* = 8.0, 2 H); 7.88 (*d*, *J* = 8.0, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.05; 41.58; 61.51; 65.83; 67.13; 120.27; 124.05; 124.15; 127.99; 128.24; 128.30; 134.97; 141.16; 142.21; 148.84; 166.40 (2×). FAB-MS: 604 (45, M^+), 473 (100, $[M - O_2CCH_2CO_2Et]^+$). Anal. calc. for $C_{37}H_{32}O_8$ (604.7): C 73.50, H 5.33; found: C 73.01, H 5.12.

(−)-(S)-2,2'-Bis{[(ethoxycarbonyl)acetoxy]methyl}-9,9'-spirobifluorene ((−)-(*S*)-**23**). Ethyl 3-chloro-3-oxopropanoate (0.09 ml, 0.68 mmol), (−)-(*S*)-**22** (85 mg, 0.23 mmol), and C_5H_5N (0.48 ml, 0.60 mmol) in CH_2Cl_2 (100 ml) reacted as described for (±)-**23** to give (−)-(*S*)-**23** (75 mg, 57%). Colorless oil. $[\alpha]_D^{25} = -27.4$ (*c* = 1.30, $CHCl_3$). CD: see *Table 1*.

(+)-(R)-2,2'-Bis{[(ethoxycarbonyl)acetoxy]methyl}-9,9'-spirobifluorene ((+)-(*R*)-**23**). Ethyl 3-chloro-3-oxopropanoate (0.16 ml, 1.27 mmol), (+)-(*R*)-**22** (160 mg, 0.42 mmol), and C_5H_5N (0.08 ml, 0.99 mmol) in CH_2Cl_2 reacted as described for (±)-**23** to give (+)-(*R*)-**23** (139 mg, 55%). Colorless oil. $[\alpha]_D^{25} = +27.5$ (*c* = 1.46, $CHCl_3$). CD: see *Table 1*.

(±)-Diethyl endo,endo-*[(9,9'-Spirobifluorene-2,2'-diyl)dimethyl] 1,2:18,36-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((±)-**24**). Starting from (±)-**23**, (251 mg, 0.416 mmol) the synthesis was performed as for **7**. CC (SiO_2, CH_2Cl_2/hexane 1:1) and recrystallization (hexane/CH_2Cl_2) provided (±)-**24** (230 mg, 44%). Dark-red solid. M.p. > 250°. UV/VIS (CH_2Cl_2): 252 (121100), 279 (sh, 81400), 300 (49000), 312 (50200), 355 (15000), 398 (3900), 409 (sh, 2500), 422 (2300), 480 (2600). IR (KBr): 1744 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.34 (*t*, *J* = 7.1, 3 H); 1.42 (*t*, *J* = 7.1, 3 H); 4.38 (*q*, *J* = 7.1, 2 H); 4.44 (*q*, *J* = 7.1, 2 H); 4.80 (*d*, *J* = 11.3, 1 H); 5.14 (*d*, *J* = 14.3, 1 H); 5.81 (*d*, *J* = 14.3, 1 H); 5.95 (*d*, *J* = 11.3, 1 H); 6.49 (*d*, *J* = 7.5, 1 H); 6.57 (*d*, *J* = 1.1, 1 H); 6.67 (*d*, *J* = 7.5, 1 H); 6.70 (*d*, *J* = 1.1, 1 H); 7.01 (*ddd*, *J* = 7.5, 7.5, 1.1, 1 H); 7.07 (*ddd*, *J* = 7.5, 7.5, 1.1, 1 H); 7.23 (*ddd*, *J* = 7.5, 7.5, 1.1, 1 H); 7.29 (*ddd*, *J* = 7.5, 7.5, 1.1, 1 H); 7.33 (*dd*, *J* = 8.0, 1.4, 1 H); 7.53 (*d*, *J* = 7.5, 1 H); 7.60 (*dd*, *J* = 7.8, 1.4, 1 H); 7.73 (*d*, *J* = 7.8, 1 H); 7.79 (*d*, *J* = 7.8, 1 H); 7.86 (*d*, *J* = 8.0, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz); 14.14; 50.98; 53.45; 63.43; 66.13; 67.92; 68.81; 70.17; 71.36; 71.43; 71.55; 120.02; 120.10; 120.88; 121.04; 123.35; 123.70; 124.98; 126.18; 127.63; 127.83; 127.99; 128.20; 129.03; 130.42; 130.55; 134.52; 134.77; 138.50; 138.64; 140.23; 140.26; 140.45; 140.47; 140.72; 141.11; 141.35; 141.49; 141.53; 141.80; 142.11; 142.37; 142.44; 142.78; 142.80; 143.00; 143.04; 143.07; 143.13; 143.18; 143.24; 143.47; 143.56; 143.67; 143.74; 144.03; 144.14; 144.28; 144.35; 144.42; 144.54; 144.61; 144.66; 144.73; 144.79; 144.98; 145.13; 145.17; 145.19; 145.22; 145.58; 145.71; 145.72; 146.03; 146.10; 146.15; 146.36; 146.48; 146.52; 147.06; 147.25; 147.27; 147.97; 148.57; 148.88; 149.10; 149.24; 163.36; 163.53; 163.79; 163.83. FAB-MS: 1321 (100, MH^+), 720 (8, C_{60}^+).

(S)-Diethyl endo,endo-*[(9,9'-Spirobifluorene-2,2'-diyl)dimethyl] 1,2:18,36-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**24**). DBU (0.10 ml, 0.669 mmol) was added at r.t. to a soln. of C_{60} (37 mg, 0.075 mmol), I_2 (47 mg, 0.188 mmol), and (−)-(*S*)-**23** (50 mg, 0.083 mmol) in PhMe (200 ml), and the mixture was stirred for 5 h. The crude material was filtered through a short plug (SiO_2), eluting first with PhMe (to remove unreacted C_{60}) and then with CH_2Cl_2. CC (SiO_2, CH_2Cl_2/hexane 1:1) and recrystallization (hexane/CH_2Cl_2) provided **24** (37 mg, 40%). Dark-red solid. M.p. > 250°. CD: see *Table 1*.

(R)-Diethyl endo,endo-*[(9,9'-Spirobifluorene-2,2'-diyl)dimethyl] 1,2:18,36-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (*ent*-**24**). DBU (0.08 ml, 0.535 mmol), C_{60} (65 mg, 0.090 mmol), I_2 (52 mg, 0.205 mmol), and (+)-(*R*)-**23** (60 mg, 0.099 mmol) in PhMe (200 ml) reacted as described for **24**, yielding *ent*-**24** (52 mg, 43%). Dark-red solid. M.p. > 250°. CD: see *Table 1*.

(−)-(4S,5S)-Bis{[(ethoxycarbonyl)acetoxy]methyl}-2,2-dimethyl-1,3-dioxolane ((−)-**29**). Ethyl 3-chloro-3-oxopropanoate (2.0 ml, 15.41 mmol) was added to a stirred soln. of (+)-**27** (1.00 g, 6.16 mmol) and C_5H_5N (1.2 ml, 15.41 mmol) in CH_2Cl_2 (100 ml) at 0°. The soln. was allowed to slowly warm to r.t. (over 1 h), and stirring was continued for 5 h. The resulting mixture was washed with sat. aq. NH_4Cl soln. (2×), dried ($MgSO_4$), the solvent was removed *in vacuo*, and CC (SiO_2, CH_2Cl_2/MeOH 98:2) yielded (−)-**29** (1.69 g, 70%). Colorless oil. $[\alpha]_D^{25} = -10.8$ (*c* = 1.19, CH_2Cl_2). IR (neat): 1734 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.25 (*t*, *J* = 7.0, 6 H); 1.38 (*s*, 6 H); 3.40 (*s*, 4 H); 4.05 (*t*, *J* = 2.5, 2 H); 4.17 (*q*, *J* = 7.0, 4 H); 4.20–4.35 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.99; 26.81; 41.26; 61.67; 64.53; 75.54; 110.43; 166.24; 166.30. FAB-MS: 391 (38, MH^+), 375 (100, $[M - Me]^+$), 259 (8, $[M - O_2CCH_2CO_2Et]^+$). Anal. calc. for $C_{17}H_{26}O_{10}$ (390.4): C 52.30, H 6.71; found: C 52.23, H 6.67.

(+)-(4R,5R)-Bis{[(ethoxycarbonyl)acetoxy]methyl}-2,2-dimethyl-1,3-dioxolane ((+)-**29**). Ethyl 3-chloro-3-oxopropanoate (2.0 ml, 15.41 mmol), (−)-**27** (1.00 g, 6.16 mmol), and C_5H_5N (1.2 ml, 15.41 mmol) in CH_2Cl_2 (100 ml) reacted as described for (−)-**29** to give (+)-**29** (1.95 g, 81%). Colorless oil. $[\alpha]_D^{25} = +12.9$ ($c = 0.95$, CH_2Cl_2).

Diethyl endo,endo-*[(4S,5S)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)dimethyl] 1,2:7,21-Bis(methano)[60]-fullerene-61,61,62,62-tetracarboxylate* (**25**) *and Diethyl* endo,endo-*[(4S,5S)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)dimethyl] 1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**26**). DBU (0.25 ml, 1.662 mmol) was added at r.t. to C_{60} (200 mg, 0.277 mmol), I_2 (155 mg, 0.609 mmol), and (−)-**29** (119 mg, 0.305 mmol) in PhMe (400 ml), and the mixture was stirred for 8 h. The crude material was filtered through a short plug (SiO_2), eluting first with PhMe to remove unreacted C_{60} and then with CH_2Cl_2/MeOH 97:3. CC (SiO_2) eluting with CH_2Cl_2/hexane 9:1 yielded **25** which was precipitated from $CHCl_3$/hexane (61 mg, 20%), and eluting with CH_2Cl_2/MeOH 199:1 gave **26** which was precipitated from CH_2Cl_2/hexane (41 mg, 13%).

Data of **25**. Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (108500), 320 (sh, 32500), 374 (sh, 10700), 409 (sh, 3300), 437 (2700), 468 (2300). IR (KBr): 1746 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.36 (*t*, *J* = 7.1, 3 H); 1.37 (*t*, *J* = 7.1, 3 H); 1.46 (*s*, 3 H); 1.47 (*s*, 3 H); 4.05 (*t*, *J* = 10.5, 1 H); 4.15 (*dd*, *J* = 10.5, 2.6, 1 H); 4.22 (*dt*, *J* = 10.5, 2.6, 1 H); 4.33–4.47 (*m*, 4 H); 4.60 (*dt*, *J* = 10.5, 2.6, 1 H); 4.84 (*t*, *J* = 10.5, 1 H); 4.98 (*dd*, *J* = 10.5, 2.6, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.12, 14.13; 28.48; 28.55; 48.90 (2×); 63.46 (2×); 66.89; 67.08 (2×); 67.16; 70.10; 70.17; 78.25; 78.29; 111.35; 133.55; 137.55; 137.73; 137.83; 138.06; 138.33; 138.48; 138.55; 140.92; 140.95; 141.30; 141.33; 141.89; 142.09; 142.42; 142.45; 143.15; 143.20; 143.64; 143.66; 143.89; 143.94; 144.19; 144.25; 144.39; 144.57; 144.58; 144.69; 144.72; 144.90; 145.03; 145.18; 145.19; 145.21; 145.27; 145.32; 145.33; 145.35; 145.64; 145.71; 145.75; 145.77; 146.00; 146.04; 146.15; 146.19; 147.33; 147.43; 147.53; 149.38; 149.51; 162.63; 162.68; 162.92; 162.99. FAB-MS: 1107 (100, MH$^+$), 720 (42, C_{60}^+). Anal. calc. for $C_{77}H_{22}O_{10} \cdot CHCl_3$ (1226.4): C 76.39, H 1.89; found: C 76.66, H 1.88.

Data of **26**. Brown solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 255 (110200), 317 (36400), 399 (sh, 4750), 408 (sh, 4000), 454 (1800), 468 (1750), 632 (490), 697 (280). CD (CH_2Cl_2): 706 (−37), 658 (−1), 639 (−11), 618 (sh, −2), 599 (4), 574 (−2), 546 (sh, 2), 489 (19), 422 (−8), 411 (−1), 396 (−13), 393 (−12), 381 (−23), 363 (sh, 7), 341 (49), 326 (3), 313 (27), 300 (−1), 281 (89), 261 (−146), 241 (−42), 234 (−52). IR (KBr): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.44 (*t*, *J* = 7.1, 6 H); 1.50 (*s*, 6 H); 4.31–4.36 (*m*, 2 H); 4.39–4.44 (*m*, 2 H); 4.44–4.57 (*m*, 4 H); 4.70–4.75 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.22; 27.79; 48.92; 63.71; 64.95; 69.05; 71.91; 75.95; 109.99; 130.20; 136.41; 139.45; 139.73; 141.27; 141.30; 141.36; 141.96; 142.11; 142.48; 142.66; 143.92; 144.48; 144.68; 144.74; 144.99; 145.18; 145.31; 145.35; 145.50; 145.63; 145.88; 145.94; 146.75; 146.98; 163.61; 163.72. FAB-MS: 1107 (100, MH$^+$), 720 (67, C_{60}^+). Anal. calc. for $C_{77}H_{22}O_{10} \cdot 1.2\ CH_2Cl_2$ (1208.9): C 77.69, H 2.03; found: C 77.91, H 2.09.

Diethyl endo-endo-*[(4R,5R)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)dimethyl] 1,2:7,21-Bis(methano)[60]-fullerene-61,61,62,62-tetracarboxylate* (*ent*-**25**) *and Diethyl* endo-endo-*[(4R,5R)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)-dimethyl] 1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (*ent*-**26**). DBU (0.43 ml, 2.913 mmol), C_{60} (350 mg, 0.485 mmol), I_2 (271 mg, 1.068 mmol), and (+)-**29** (208 mg, 0.534 mmol) in PhMe (700 ml) reacted as described for **25**/**26** to give *ent*-**25** (114 mg, 21%) and *ent*-**26** (84 mg, 15%).

Data of ent-**25**: Dark-red solid. M.p. > 280°.

Data of ent-**26**. Brown solid. M.p. > 280°. CD (CH_2Cl_2): 703 (37), 658 (1), 640 (12), 618 (sh, 2), 597 (−4), 579 (2), 546 (sh, −2), 487 (−20), 421 (4), 412 (−2), 396 (9), 393 (9), 381 (19), 363 (sh, −10), 341 (−49), 325 (−4), 313 (−30), 300 (−2), 280 (−92), 261 (141), 241 (47), 234 (54).

Tetraethyl 1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate (**28**). K_2CO_3 (260 mg, 1.886 mmol) was added to **26** (21 mg, 0.019 mmol) in THF/EtOH 1:1 (28 ml), and the mixture was stirred at r.t. for 1.5 h, then filtered, and evaporated to dryness. CC (SiO_2, PhMe) followed by precipitation from CH_2Cl_2/hexane yielded **28** (8 mg, 40%). Brown solid. M.p. > 250°. CD (CH_2Cl_2): 705 (−29), 658 (4), 639 (−6), 622 (sh, 2), 599 (8), 573 (2), 547 (sh, 5), 490 (20), 423 (−8), 410 (4), 393 (sh, −10), 380 (−23), 339 (58), 323 (18), 313 (27), 300 (1), 280 (89), 261 (−133), 236 (−51) [7]. UV/VIS, IR, ^{1}H-NMR, and FAB-MS: identical to those reported for (±)-**28** in [11a].

Tetraethyl 1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate (*ent*-**28**). K_2CO_3 (314 mg, 2.276 mmol) and *ent*-**26** (35 mg, 0.031 mmol) in THF/EtOH 1:1 (34 ml) reacted as described for **28** to give *ent*-**28** (28 mg, 83%). Brown solid. M.p. > 250°. CD (CH_2Cl_2): 706 (49), 657 (12), 639 (21), 619 (sh, 10), 597 (1), 572 (7), 536 (sh, −2), 488 (−18), 422 (12), 410 (−2), 396 (12), 380 (26), 339 (−60), 323 (−18), 313 (−28), 300 (−2), 280 (−90), 261 (138), 241 (62) [7]. UV/VIS, IR, ^{1}H-NMR, and FAB-MS: identical to those reported for (±)-**28** in [11a].

Benzyl N-*Tris{[2-(methoxycarbonyl)ethoxy]methyl}methylcarbamate* (**31**). Benzyl chloroformate (0.73 g, 4.279 mmol) was added to **30** (1.10 g, 2.902 mmol) in sat. aq. $NaHCO_3$ soln. (10 ml) at 0°. The mixture was stirred

for 1 h, while additional portions of benzyl chloroformate (0.36 g, 2.13 mmol) and NaOH (0.20 g, 5.0 mmol) were added every 20 min. After addition of conc. aq. HCl soln., the mixture was extracted with Et_2O (2×), the org. layers were dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 98:2) yielded **31** (1.38 g, 93%). Colorless oil. IR (neat): 1731 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.45 (*t*, *J* = 6.4, 6 H); 3.58 (*s*, 15 H); 3.60 (*t*, *J* = 6.4, 6 H); 4.96 (*s*, 2 H); 5.21 (*s*, 1 H); 7.19–7.28 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 34.38; 51.24; 58.37; 65.75; 66.41; 68.96; 127.57 (2×); 128.06; 136.39; 154.68; 171.54. FAB-MS: 514 (100, M^+); 470 (16, $[M - CO_2]^+$); 406 (41, $[M - OCH_2Ph]^+$). Anal. calc. for $C_{24}H_{35}NO_{11}$ (513.5): C 56.13, H 6.87, N 2.73; found: C 56.06, H 6.73, N 2.92.

Benzyl N-*Tris[(2-carboxyethoxy)methyl]methylcarbamate* (**32**). A mixture of **31** (0.80 g, 1.559 mmol), 2M aq. NaOH (2.5 ml, 5.00 mmol), and MeOH (3 ml) was stirred at r.t. for 5 h, then diluted with H_2O (10 ml). After addition of conc. aq. HCl soln. and extraction with $CHCl_3$ (2×) and AcOEt, the org. layers were dried ($MgSO_4$) and the solvent was removed *in vacuo* to afford **32** (0.73 g, 99%). Colorless oil. IR (neat): 3033 (O–H), 1716 (C=O). ^{1}H-NMR (CD_3COCD_3, 200 MHz): 2.54 (*t*, *J* = 6.3, 6 H); 3.68 (*s*, 6 H); 3.69 (*t*, *J* = 6.3, 6 H); 5.03 (*s*, 2 H); 5.78 (*s*, 1 H); 7.28–7.40 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 34.87; 59.55, 65.92; 67.39; 69.66; 128.29 (2×); 128.90; 138.08; 155.54; 172.99. FAB-MS: 472 (100, MH^+), 428 (29, $[M - CO_2]^+$), 338 (21, $[M - O(CH_2)_2CO_2H]^+$). Anal. calc. for $C_{21}H_{29}NO_{11} \cdot CHCl_3$ (590.8): C 44.72, H 5.12, N 2.37; found: C 44.55, H 5.38, N 2.53.

Benzyl N-*Tris[2-({[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]-methylcarbamate* (**33**). DCC (2.16 g, 10.485 mmol) and BtOH (1.42 g, 10.485 mmol) were added to **32** (1.10 g, 2.335 mmol) and **30** (3.98 g, 10.501 mmol) in THF (15 ml) at 0°, and, after slowly warming to r.t. (4 h), the mixture was stirred for 3 d. Filtration, dilution with CH_2Cl_2, washing with aq. $NaHCO_3$ soln. and H_2O, drying ($MgSO_4$), and evaporation to dryness were followed by GPC (PhMe) and CC (SiO_2, CH_2Cl_2/MeOH 98:2 to 96:4) to yield **33** (3.05 g, 84%). Colorless oil. IR (neat): 1733 (C=O ester), 1670 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.30 (*t*, *J* = 6.0, 6 H); 2.44 (*t*, *J* = 6.3, 18 H); 3.54-3.64 (*m*, 75 H); 4.94 (*s*, 2 H); 5.52 (*s*, 1 H); 6.09 (*s*, 3 H); 7.20–7.29 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.62; 37.28; 51.57; 58.83; 59.67; 65.97; 66.65; 67.47; 69.01; 69.24; 127.85; 127.95; 128.34; 136.71; 155.06; 170.93; 171.95. FAB-MS: 1555 (100, MH^+), 1451 (18, $[M - O(CH_2)_2CO_2Me]^+$). Anal. calc. for $C_{69}H_{110}N_4O_{35} \cdot 2.5\ CH_2Cl_2$ (1768.0): C 48.57, H 6.56, N 3.17; found: C 48.69, H 6.78, N 3.32.

Benzyl N-*Tris({[({2-tris[(2-carboxyethoxy)methyl]methyl}amino)carbonyl]ethoxy}methyl)methylcarbamate* (**34**). A mixture of **33** (3.00 g, 1.930 mmol), 2M aq. NaOH (30 ml, 60 mmol), and MeOH (30 ml), was stirred at r.t. for 5 d, and, after concentration, conc. aq. HCl soln. was added. Extraction with AcOEt (3×), drying of the org. layers ($MgSO_4$), and evaporation afforded **34** (2.60 g, 94%). Colorless oil. IR (neat): 3338 (O–H), 1720 (C=O ester), 1637 (C=O amide). ^{1}H-NMR (CD_3SOCD_3, 200 MHz): 2.31 (*t*, *J* = 6.0, 6 H); 2.41 (*t*, *J* = 6.3, 18 H); 3.46–3.60 (*m*, 48 H); 4.96 (*s*, 2 H); 6.43 (*s*, 1 H); 7.10 (*s*, 3 H); 7.30–7.40 (*m*, 5 H); 12.08 (*s*, 9 H). ^{13}C-NMR (CD_3SOCD_3, 50 MHz): 34.16; 35.89; 59.25; 59.36; 66.27; 66.93; 67.78; 127.18; 127.27; 127.88; 136.69; 154.00; 171.61; 172.25. FAB-MS: 1429 (100, M^+), 1109 (12, $[M - C(CH_2O(CH_2)_2CO_2H)_3]^+$).

Tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]methylamine (**36**). A mixture of **33** (1.80 g, 1.158 mmol), HCO_2NH_4 (0.29 g, 4.603 mmol), and 10% Pd/C (0.45 g) in EtOH (5 ml) was stirred at 40° for 4 h, while N_2 was bubbled through. Filtration through *Celite* (CH_2Cl_2/AcOEt 1:1), washing with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation provided **36** (1.58 g, 96%). Colorless oil. IR (neat): 1735 (C=O ester), 1669 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.34 (*t*, *J* = 6.0, 6 H); 2.41 (*t*, *J* = 6.2, 18 H); 3.50–3.56 (*m*, 69 H); 3.60 (*t*, *J* = 6.0, 6 H); 6.46 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.48; 36.58; 51.61; 59.66; 59.82; 66.58; 67.51; 67.66; 68.76; 171.41; 172.07. FAB-MS: 1422 (100, MH^+), 1334 (33, $[M - O(CH_2)_2CO_2Me]^+$). Anal. calc. for $C_{61}H_{104}N_4O_{33} \cdot CH_2Cl_2$ (1506.4): C 49.43, H 7.09, N 3.72; found: C 49.50, H 6.81, N 3.74.

Benzyl N-*Tris(2-{[({[(tris-{2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)-methyl]methyl}amino)carbonyl]ethoxy}methyl)methylcarbamate* (**35**). DCC (2.25 g, 10.902 mmol) and BtOH (1.47 g, 10.902 mmol) were added to a soln. of **34** (1.30 g, 0.910 mmol) and **30** (4.14 g, 10.902 mmol) in THF (10 ml) at 0°. The mixture was allowed to slowly warm to r.t. (4 h) and, after stirring for 3 d, filtered, diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated to dryness. GPC (PhMe) yielded **35** (3.00 g, 70%). Colorless oil. IR (neat): 1733 (C=O ester), 1667 (C=O amide). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.33 (*t*, *J* = 6.1, 24 H); 2.50 (*t*, *J* = 6.3, 54 H); 3.50–3.66 (*m*, 237 H); 4.90 (*s*, 2 H); 5.60 (*s*, 1 H); 6.13 (*s*, 9 H); 6.25 (*s*, 3H); 7.22–7.30 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.77; 37.02; 37.27; 51.74; 58.84; 59.91; 60.00; 65.95; 66.88; 67.66; 67.79; 69.24; 128.10; 128.19; 128.66; 136.98; 155.39; 171.02; 171.32; 172.38. MALDI-TOF-MS (CCA): 4703 (100, $[M + Na]^+$; calc. for $^{13}C_2{}^{12}C_{202}H_{335}N_{13}O_{107}Na$: 4704). Anal. calc. for $C_{204}H_{335}N_{13}O_{107} \cdot 2\ CH_2Cl_2$ (4851.8): C 50.00, H 7.04, N 3.75; found: C 49.96, H 6.85, N 3.73.

Tris(2-{[(tris{[(2-[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]-methyl}amino)carbonyl]ethoxy}methyl)methylamine (**37**). A mixture of **35** (1.00 g, 0.237 mmol), HCO_2NH_4 (63 mg, 1.00 mmol), and 10% Pd/C (0.25 g) in EtOH (5 ml) was stirred at 40° for 6 h while N_2 was bubbled through. After cooling to r.t. and stirring for 12 h, an additional portion of HCO_2NH_4 (63 mg, 1.00 mmol) was added, and stirring was continued at 60° for 4 h. Filtration through *Celite* (CH_2Cl_2/AcOEt 1:1), washing with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation provided **37** (0.91 g, 94%). Colorless oil. IR (neat): 1738 (C=O ester), 1668 (C=O amide). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.42 (*t*, *J* = 6.3, 24 H); 2.57 (*t*, *J* = 6.3, 54 H); 3.55–3.75 (*m*, 237 H); 6.20 (*s*, 12 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 34.35; 36.61; 51.31; 59.59; 59.83; 66.41; 66.99; 68.20; 68.70; 170.94; 171.08; 171.75. MALDI-TOF-MS (CCA): 4568 (70, $[M + Na]^+$; calc. for $^{13}C_2{}^{12}C_{194}H_{329}N_{13}O_{105}Na$: 4570), 4547 (100, M^+). Anal. calc. for $C_{196}H_{329}N_{13}O_{105} \cdot 2\ CH_2Cl_2$ (4717.7): C 50.41, H 7.11, N 3.86; found: C 50.55, H 7.09, N 3.92.

Ethyl (Morpholin-4-yl)carbonylmethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**39**). DCC (38 mg, 0.185 mmol) and BtOH (21 mg, 0.154 mmol) were added to a soln. of **38** (140 mg, 0.154 mmol) and morpholine (13.5 mg, 0.154 mmol) in CH_2Cl_2 (50 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 12 h, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 198:2) followed by recrystallization ($CHCl_3$/hexane) yielded **39** (109 mg, 72%). Dark-red powder. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (114600), 326 (35600), 393 (sh, 4960), 401 (sh, 3730), 413 (sh, 2760), 426 (sh, 2680), 479 (1570), 685 (180). IR (KBr): 1746 (C=O ester), 1673 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.50 (*t*, *J* = 7.5, 3 H); 3.48 (br. *s*, 2 H); 3.69 (br. *s*, 2 H); 3.70–3.80 (*m*, 4 H); 4.59 (*q*, *J* = 7.5, 2 H); 5.09 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.32; 42.39; 45.35; 51.98; 63.59; 63.89; 66.52; 66.90; 71.57; 139.09; 139.53; 141.27; 142.17; 142.20; 142.49; 143.27; 143.30; 143.37; 144.18; 144.95; 145.20; 145.42; 145.49; 145.57; 145.63; 163.49; 163.53; 164.06. FAB-MS: 978 (48, MH$^+$), 720 (100, C_{60}^+).

Ethyl {[(Tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}methyl 1,2-Methano[60]-fullerene-61,61-dicarboxylate (**40**). DCC (24.5 mg, 0.119 mmol) and BtOH (16 mg, 0.119 mmol) were added to a soln. of **38** (90 mg, 0.099 mmol) and **30** (45 mg, 0.119 mmol) in CH_2Cl_2 (100 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 24 h, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 95:5) followed by GPC (PhMe) yielded **40** (50 mg, 40%). Dark-red glassy product. UV/VIS (CH_2Cl_2): 257 (107400), 324 (35500), 393 (sh, 9800), 402 (sh, 5050), 413 (sh, 4050), 425 (3680), 470 (2340), 682 (190). IR (neat): 1740 (C=O ester), 1691 (C=O amide). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.47 (*t*, *J* = 7.1, 3 H); 2.56 (*t*, *J* = 6.3, 6 H); 3.67 (*s*, 9 H); 3.70 (*t*, *J* = 6.3, 6 H); 3.73 (*s*, 6 H); 4.57 (*q*, *J* = 7.1, 2 H); 4.85 (*s*, 2 H); 6.55 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.20; 34.69; 49.13; 51.66; 60.14; 63.72; 64.85; 66.81; 68.88; 71.28; 138.97; 139.22; 140.94; 140.96; 141.86; 141.87; 142.19 (2×); 142.96; 142.99; 143.03; 143.08; 143.86; 144.59; 144.64; 144.69; 144.78; 144.91; 145.03; 145.10; 145.14; 145.18; 145.20; 145.28; 162.45; 163.36; 165.52; 171.94. FAB-MS: 1270 (100, MH$^+$), 1166 (41, $[M - O(CH_2)_2CO_2Me]^+$), 720 (95, C_{60}^+). MALDI-TOF-MS (DHB): 1269 (100, M^+).

Ethyl [({Tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]methyl}-amino)carbonyl]methyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**41**). DCC (24.5 mg, 0.119 mmol) and BtOH (14.4 mg, 0.107 mmol) were added to a soln. of **38** (81 mg, 0.089 mmol) and **36** (152 mg, 0.107 mmol) in CH_2Cl_2 (100 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 2 d, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 97:3) followed by GPC (PhMe) yielded **41** (39 mg, 19%). Dark-red glassy product. UV/VIS (CH_2Cl_2): 254 (105400), 325 (50900), 426 (sh, 7740), 470 (5140), 688 (140). IR (neat): 1740 (C=O ester), 1671 (C=O amide). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.49 (*t*, *J* = 7.1, 3 H); 2.43 (*t*, *J* = 6.5, 6 H); 2.54 (*t*, *J* = 6.3, 18 H); 3.52–3.81 (*m*, 75 H); 4.58 (*q*, *J* = 7.1, 2 H); 4.94 (*s*, 2 H); 6.14 (*s*, 3 H); 7.09 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.17; 34.69; 37.09; 51.61; 51.89; 59.77; 60.19; 63.67; 64.66; 66.72; 67.57; 68.91; 69.11; 71.44; 138.73; 139.32; 140.85; 140.92; 141.76; 141.87; 142.16; 142.91; 142.96; 142.98; 143.03; 143.04; 143.83; 143.84; 144.57; 144.59; 144.63; 144.65; 144.86; 144.94; 145.07; 145.14; 145.15; 145.17; 145.22; 145.24; 145.42; 162.72; 163.30; 165.51; 171.00; 171.98. FAB-MS: 2313 (100, MH$^+$), 2209 (10, $[M - O(CH_2)_2CO_2Me]^+$), 1861 (7, $[M - O(CH_2)_2CONHC(CH_2O(CH_2)_2CO_2Me)_3]^+$), 720 (42, C_{60}^+). MALDI-TOF-MS (CCA): 2311 (100, M^+).

Benzyl N-*Tris({2-[(*tert-*butoxy)carbonyl]ethoxy}methyl)methylcarbamate* (**44**). A mixture of DCC (1.48 g, 7.184 mmol), DMAP (0.58 g, 4.747 mmol), *t*-BuOH (1.5 ml, 160 mmol), and **32** (0.75 g, 1.592 mmol) in THF (10 ml) was stirred at r.t. for 24 h, then filtered, and evaporated to dryness. CC (SiO_2, Et_2O/hexane 1:1) yielded **44** (310 mg, 31%). Colorless oil. IR (neat): 1729 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.44 (*s*, 27 H); 2.44 (*t*, *J* = 6.2, 6 H); 3.65 (*t*, *J* = 6.2, 6 H); 3.67 (*s*, 6 H); 5.04 (*s*, 2 H); 5.24 (*s*, 1 H); 7.28–7.40 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 28.09; 36.25; 58.79; 66.18; 67.17; 69.48; 80.53; 128.05; 128.11; 128.55; 136.93; 155.31; 171.02. FAB-MS: 640 (M^+).

*Tris({2-[(*tert-*butoxy)carbonyl]ethoxy}methyl)methylamine* (**45**). A mixture of **44** (0.30 g, 0.469 mmol), HCO_2NH_4 (0.15 g, 2.381 mmol), and 10% Pd/C (60 mg) in EtOH (2 ml) was stirred at 40° for 20 min, while N_2

was bubbled through. Filtration through *Celite* (CH_2Cl_2/AcOEt 1:1), washing with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation provided **45** (0.23 g, 97%). Colorless oil. IR (neat): 1731 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.44 (*s*, 27 H); 2.44 (*t*, *J* = 6.4, 6 H); 3.30 (*s*, 6 H); 3.64 (*t*, *J* = 6.4, 6 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 28.08; 36.31; 55.96; 67.13; 72.88; 80.37; 170.91. FAB-MS: 506 (MH^+). Anal. calc. for $C_{25}H_{47}NO_9$ (505.6): C 59.38, H 9.37, N 2.77; found: C 59.30, H 9.24, N 2.76.

*({[Tris({2-[(*tert*-butoxy)carbonyl]ethoxy}methyl)methyl]amino}carbonyl)methyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate* (**46**). DCC (57 mg, 0.277 mmol) and BtOH (31 mg, 0.231 mmol) were added to a soln. of **38** (210 mg, 0.231 mmol) and **45** (140 mg, 0.277 mmol) in CH_2Cl_2 (150 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 12 h, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 99:1) yielded **46** (141 mg, 44%). Dark-red glassy product. IR (neat): 1730 (C=O ester), 1691 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.44 (*s*, 27 H); 1.49 (*t*, *J* = 7.1, 3 H); 2.47 (*t*, *J* = 6.5, 6 H); 3.66 (*t*, *J* = 6.5, 6 H); 3.74 (*s*, 6 H); 4.58 (*q*, *J* = 7.1, 2 H); 4.87 (*s*, 2 H); 6.66 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.29; 28.20; 36.19; 49.15; 60.31; 63.84; 64.97; 67.27; 69.05; 71.47; 80.66; 139.23; 139.57; 141.20; 141.23; 142.16; 142.48; 143.24; 143.30; 143.37; 144.15; 144.18; 144.89; 144.92; 144.97; 145.11; 145.20; 145.36; 145.44; 145.49; 145.57; 162.82; 163.66; 165.79; 167.18. MALDI-TOF-MS (CCA): 1395 (100, M^+).

[({Tris[(2-carboxyethoxy)methyl]methyl}amino)carbonyl]methyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**43**). A soln. of **46** (135 mg, 0.097 mmol) and TsOH · H_2O (185 mg, 0.973 mmol) in PhMe (250 ml) was refluxed for 6 h, then cooled to r.t., and evaporated to dryness. The residue was dissolved in $CHCl_3$, and the resulting soln. was washed with H_2O (3 ×), dried ($MgSO_4$), and evaporated. The crude product was washed with acetone, THF, and CH_2Cl_2, then dried at 10^{-5} Torr to give **43** (58 mg, 49%) as a dark-red solid which was used without further purification. M.p. > 280°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.51 (*t*, *J* = 7.0, 3 H); 2.43–2.77 (*m*, 6 H); 3.60–3.90 (*m*, 12 H); 4.61 (*q*, *J* = 7.0, 2 H); 5.07 (*s*, 2 H). FAB-MS: 1228 (4, MH^+), 1198 (10, $[M - Et]^+$), 720 (100, C_{60}^+).

Benzyl N-*({[Tris({2-[({tris-[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)-methyl]methyl}amino)carbonyl]ethoxy}methyl)methyl]amino}carbonyl)methylcarbamate* (**47**). DCC (0.62 g, 3.00 mmol) and BtOH (0.41 g, 3.00 mmol) were added to a soln. of **37** (1.36 g, 0.300 mmol) and *Z*-glycine (0.63 g, 3.00 mmol) in THF (15 ml) at 0°. The mixture was allowed to slowly warm to r.t. (4 h) and was stirred for 3 d at this temp., then for 12 h at 60°, and for additional 24 h at r.t. The resulting suspension was filtered, diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated to dryness. GPC (PhMe) yielded **47** (0.95 g, 67%). Colorless oil. IR (neat): 1739 (C=O ester), 1670 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.37 (*t*, *J* = 6.2, 24 H); 2.52 (*t*, *J* = 6.2, 54 H); 3.54–3.78 (*m*, 237 H); 3.84 (*d*, *J* = 3.7, 2 H); 5.07 (*s*, 2 H); 6.18 (*s*, 9 H); 6.34 (*s*, 3 H); 7.26–7.31 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.75; 36.92; 37.23; 44.54; 51.74; 59.89; 60.02; 66.67; 66.86; 67.64; 67.80; 69.23; 128.18; 128.68; 137.04; 156.75; 169.33; 171.26; 171.32; 172.36. MALDI-TOF-MS (CCA): 4762 (100, $[M + Na]^+$; calc. for $^{13}C_2{}^{12}C_{204}H_{338}N_{14}O_{108}Na$: 4761).

*2-Amino-*N*-Tris({2-[({tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)-methyl]methyl}amino)carbonyl]ethoxy}methyl)methyl Acetamide* (**48**). A mixture of **47** (0.95 g, 0.200 mmol), HCO_2NH_4 (50 mg, 0.80 mmol), and 10% Pd/C (0.24 g), in EtOH (5 ml) was stirred for 6 h at 40°, then for 12 h at r.t. An additional portion of HCO_2NH_4 (50 mg, 0.80 mmol) was added, and stirring was continued for 4 h at 60°. Filtration through *Celite* (CH_2Cl_2/AcOEt 1:1), washing with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation of the solvent provided **48** (0.80 g, 87%). Colorless oil. IR (neat): 1737 (C=O ester), 1671 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.34–2.47 (*m*, 18 H); 2.52 (*t*, *J* = 6.2, 60 H); 3.54–3.76 (*m*, 239 H); 6.25 (*s*, 9 H); 6.46 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.75; 37.21; 51.75; 59.92; 60.07; 66.86; 67.67; 69.19; 171.45; 172.41. MALDI-TOF-MS (CCA): 4629 (100, $[M + Na]^+$; calc. for $^{13}C_2{}^{12}C_{196}H_{332}N_{14}O_{106}Na$: 4627).

Ethyl [({[({[Tris({2-[({tris[(2-{[tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)-methyl]methyl}amino)carbonyl]ethoxy}methyl)]methyl}amino)carbonyl]methyl}amino)carbonyl]methyl1,2Methano-[60]fullerene-61,61-dicarboxylate (**49**). DCC (17.2 mg, 0.083 mmol) and BtOH (11.3 mg, 0.083 mmol) were added to a soln. of **38** (75 mg, 0.083 mmol) and **48** (320 mg, 0.069 mmol) in CH_2Cl_2 (100 ml) at 0°. The soln. was allowed to slowly warm to r.t. (6 h) and, after stirring for 3 d, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 95:5) followed by GPC (PhMe) yielded **49** (160 mg, 42%). Dark-red glassy product. UV/VIS (CH_2Cl_2): 256 (121900), 325 (48000), 393 (sh, 8380), 402 (sh, 6740), 413 (sh, 5430), 426 (4730), 470 (3190), 685 (150). IR (neat): 1732 (C=O ester), 1662 (C=O amide). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.45 (*t*, *J* = 7.1, 3 H); 2.36 (*t*, *J* = 6.4, 18 H); 2.42 (*t*, *J* = 6.8, 6 H); 2.50 (*t*, *J* = 6.2, 54 H); 3.49–3.78 (*m*, 237 H); 4.03 (*d*, *J* = 3.9, 2 H); 4.61 (*q*, *J* = 7.1, 2 H); 4.97 (*s*, 2 H); 6.17 (*s*, 9 H); 6.34 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.22; 34.65; 36.74; 37.13; 42.38; 51.56; 59.74; 59.90; 60.07; 64.03; 64.58; 66.69; 67.48; 67.66; 69.06; 71.33; 139.07; 140.87; 140.88; 141.79; 141.80; 142.14; 142.91; 142.94; 142.97; 142.99; 143.80; 143.82; 144.57; 144.59; 144.61; 144.84; 144.94; 145.08; 145.12; 145.13; 145.21; 162.58; 163.26; 165.67; 167.84; 170.86; 170.95; 171.95. MALDI-TOF-MS (CCA): 5519 (100, $[M + Na]^+$; calc. for $^{13}C_3{}^{12}C_{262}H_{338}N_{14}O_{111}Na$: 5518).

*[(*tert*-Butoxy)carbonyl]methyl Malonate* (**53**) *and Carboxymethyl Malonate* (**54**). A mixture of **52** (9.17 g, 69.396 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (*Meldrum*'s acid, 10.0 g, 69.396 mmol) was heated for 4 h at 110°. After cooling, recrystallization (CH_2Cl_2) gave colorless crystals of **54** (3.71 g, 33%) which were collected by filtration. The mother liquor was evaporated, and CC (SiO_2, CH_2Cl_2/MeOH 95:5) yielded **53** (6.22 g, 41%).

Data of **53**: Pale-yellow oil. IR (neat): 3200 (O–H), 1746 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.48 (*s*, 9 H); 3.55 (*s*, 2 H); 4.58 (*s*, 2 H); 9.84 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 27.45; 40.09; 61.61; 82.69; 165.52; 165.96; 170.47. FAB-MS: 219 (57, MH^+), 145 (44, $[M-(t\text{-BuO})]^+$), 57 (100, $(t\text{-Bu})^+$). Anal. calc. for $C_9H_{14}O_6 \cdot 0.2\ H_2O$ (221.8): C 48.74, H 6.54; found: C 48.74, H 6.34.

Data of **54**: Colorless crystals. M.p. 72–73°. IR (neat): 3511 (O–H), 1726 (C=O). ^{1}H-NMR (CD_3OD, 200 MHz): 3.49 (*s*, 2 H); 4.67 (*s*, 2 H). ^{13}C-NMR (CD_3OD, 50 MHz): 44.69; 65.23; 171.23; 172.88; 174.02. FAB-MS: 163 (MH^+). Anal. calc. for $C_5H_6O_6$ (162.1): C 37.05, H 3.73; found: C 36.94, H 3.68.

*(Benzene-1,3-diyl)dimethyl Bis(3-{[(*tert*-butoxy)carbonyl]methoxy}-3-oxopropanoate)* (**55**). DCC (4.16 g, 20.165 mmol) and DMAP (197 mg, 1.613 mmol) were added to a soln. of **2** (1.115 g, 8.066 mmol) and **53** (4.40 g, 20.165 mmol) in THF (100 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 12 h, filtered and evaporated to dryness. CC (SiO_2, CH_2Cl_2/MeOH 199:1) yielded **55** (3.61 g, 83%). Colorless oil. IR (neat): 1749 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.45 (*s*, 18 H); 3.52 (*s*, 4 H); 4.53 (*s*, 4 H); 5.17 (*s*, 4 H); 7.30–7.38 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 27.55; 40.53; 61.45; 66.50; 82.25; 127.58; 127.83; 128.47; 135.29; 165.36; 165.45; 166.77. FAB-MS: 539 (MH^+). Anal. calc. for $C_{26}H_{34}O_{12}$ (538.6): C 57.99, H 6.36; found: C 57.99, H 6.24.

*Bis{[(*tert*-butoxy)carbonyl]methyl}* endo,endo-*(*m*-Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**56**). DBU (0.5 ml, 3.33 mmol) was added at r.t. to a soln. of C_{60} (400 mg, 0.555 mmol), I_2 (338 mg, 1.332 mmol), and **55** (359 mg, 0.666 mmol) in PhMe (700 ml), and the mixture was stirred for 5 h. The crude material was filtered through a short plug (SiO_2), eluting first with PhMe (to remove unreacted C_{60}) and then with CH_2Cl_2/MeOH 92:8. CC (SiO_2, CH_2Cl_2/hexane 9:5) and recrystallization (hexane/CH_2Cl_2) provided **56** (156 mg, 22%). Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 259 (109100), 392 (sh, 33700), 374 (sh, 10490), 409 (sh, 3190), 436 (2770), 469 (2340). IR (KBr): 1750 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.48 (*s*, 18 H); 4.66 (*d*, J_{AB} = 15.6, 2 H); 4.78 (*d*, J_{AB} = 15.6, 2 H); 5.27 (*d*, J_{AB} = 13.1, 2 H); 5.93 (*d*, J_{AB} = 13.1, 2 H); 7.34 (br. *d*, *J* = 6.6, 2 H); 7.45 (*t*, *J* = 6.6, 1 H); 7.56 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 27.23; 53.36; 62.62; 66.43; 66.89; 67.54; 82.27; 122.84; 125.82; 128.20; 135.76; 136.23; 136.49; 139.60; 140.68; 141.91; 142.39; 142.93; 143.28; 143.47; 143.66; 143.88; 143.95; 144.10; 144.16; 144.29; 144.71; 144.87; 145.02; 145.34; 145.46; 145.58; 145.72; 147.18; 148.42; 161.91; 162.20; 165.12. FAB-MS: 1254 (89, MH^+), 720 (100, C_{60}^+). Anal. calc. for $C_{86}H_{30}O_{12} \cdot 0.9\ CH_2Cl_2$ (1331.6): C 78.38; H 2.41; found: C 78.41, H 2.68.

Bis(carboxymethyl) endo,endo-*(*m*-Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61-62,62-tetracarboxylate* (**50**). A soln. of **56** (256 mg, 0.204 mmol) and TsOH · H_2O (388 mg, 2.04 mmol) in PhMe (300 ml) was refluxed for 5 h, then cooled to r.t. The dark-brown precipitate was filtered, washed with H_2O, and dissolved in THF. The resulting soln. was dried ($MgSO_4$) and evaporated to dryness yielding **50** (182 mg, 71%) as a dark-orange-red solid which was used without further purification. M.p. > 280°. ^{1}H-NMR (CD_3COCD_3, 200 MHz): 4.94 (*d*, J_{AB} = 15.8, 2 H); 5.01 (*d*, J_{AB} = 15.8, 2 H); 5.31 (*d*, J_{AB} = 13.9, 2 H); 6.03 (*d*, J_{AB} = 13.9, 2 H); 7.43–7.48 (*m*, 3 H); 7.54 (br. *s*, 1 H).

*1,3-Bis{[(*tert*-butoxy)carbonyl]methoxy}-5-(hydroxymethyl)benzene* (**59**). A mixture of **58** (1.00 g, 7.143 mmol), *tert*-butyl 2-bromoacetate (2.37 ml, 16.043 mmol), K_2CO_3 (2.96 g, 21.417 mmol), and Cs_2CO_3 (6.98 g, 21.424 mmol) in DMF (50 ml) was stirred at 80° for 20 h, then cooled to r.t. After filtration through *Celite* (AcOEt) and evaporation, the residue was dissolved in Et_2O, washed with H_2O (3×), dried ($MgSO_4$), and evaporated to dryness. CC (SiO_2, Et_2O/hexane 7:3) yielded **59** (1.76 g, 67%). Colorless oil. IR (neat): 1749 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.45 (*s*, 18 H); 4.43 (*s*, 4 H); 4.54 (*s*, 2 H); 6.35 (*t*, *J* = 2.2, 1 H); 6.48 (*d*, *J* = 2.2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 27.58; 64.34; 65.23; 82.00; 100.50; 105.42; 143.45; 158.69; 167.58. EI-MS: 368 (100, M^+), 312 (33, $[M-(t\text{-Bu})]^+$). Anal. calc. for $C_{19}H_{28}O_7$ (368.4): C 61.94, H 7.66; found: C 61.47, H 7.72.

1,3-Bis[(carboxyacetoxy)methyl]benzene (**57**). A mixture of **2** (4.00 g, 28.944 mmol) and *Meldrum*'s acid (8.34 g, 57.888 mmol) was heated for 8 h at 120°. After cooling to r.t., drying (10^{-2} Torr, 24 h) provided pure **57** (8.90 g, 99%). Pale-yellow oil. IR (neat): 3200 (O–H), 1741 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.48 (*s*, 4 H); 5.19 (*s*, 4 H); 7.30–7.40 (*m*, 4 H); 10.54 (br. *s*, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 40.69; 66.69; 127.07; 127.74; 128.44; 135.23; 165.99; 171.67. FAB-MS: 311 (MH^+). Anal. calc. for $C_{14}H_{14}O_8 \cdot H_2O$ (328.3): C 51.22, H 4.91; found: C 51.44, H 4.97.

*1,3-Bis({[(3,5-bis{[(*tert*-butoxy)carbonyl]methoxy}benzyloxy)carbonyl]acetoxy}methyl)benzene* (**60**). DCC (0.87 g, 4.223 mmol) and DMAP (220 mg, 1.800 mmol) were added to **57** (550 mg, 1.772 mmol) and **59** (1.30 g,

3.533 mmol) in THF (20 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 12 h, filtered and evaporated *in vacuo*. CC (SiO_2, Et_2O/hexane 7:3) yielded **60** (1.15 g, 65%). Colorless oil. IR (neat): 1750 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.49 (*s*, 36 H); 3.48 (*s*, 4 H); 4.48 (*s*, 8 H); 5.10 (*s*, 4 H); 5.19 (*s*, 4 H); 6.45 (*t*, *J* = 2.2, 2 H); 6.52 (*d*, *J* = 2.2, 4 H); 7.20 (*t*, *J* = 7.4, 1 H); 7.30–7.38 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 27.61; 40.98; 65.30; 66.44; 66.50; 82.06; 101.36; 106.91; 127.64; 127.90; 128.57; 135.26; 137.20; 158.79; 165.77 (2×); 167.29. FAB-MS: 1010 (M^+). HR-FAB-MS: 1010.4136 (M^+, $C_{52}H_{66}O_{20}^+$; calc. 1010.4147).

*Bis(3,5-bis{[(*tert*-butoxy)carbonyl]methoxy}benzyl)* endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)-[60]fullerene-61,61,62,62-tetracarboxylate* (**61**). DBU (380 mg, 2.497 mmol) was added at r.t. to a soln. of C_{60} (300 mg, 0.417 mmol), I_2 (233 mg, 0.918 mmol), and **60** (463 mg, 0.458 mmol) in PhMe (700 ml), and the mixture stirred for 12 h. Filtration through a short plug (SiO_2), eluting first with PhMe (to remove unreacted C_{60}) and then with CH_2Cl_2/MeOH 92:8, followed by CC (SiO_2, PhMe/AcOEt 9:1), afforded **61** (155 mg, 22%). Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 259 (90110), 392 (24540), 374 (sh, 8820), 409 (sh, 2800), 437 (2270), 471 (1950). IR (KBr): 1751 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.48 (*s*, 36 H); 4.44 (*s*, 8 H); 5.02 (*d*, J_{AB} = 12.9, 2 H); 5.15 (*d*, J_{AB} = 12.0, 2 H); 5.39 (*d*, J_{AB} = 12.0, 2 H); 5.82 (*d*, J_{AB} = 12.9, 2 H); 6.44 (*t*, *J* = 2.2, 2 H); 6.56 (*d*, *J* = 2.2, 4 H); 7.27 (*d*, *J* = 7.8, 2 H); 7.35 (*t*, *J* = 7.8, 1 H); 7.47 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 28.03; 48.97; 65.63; 66.88; 67.39; 68.20; 70.51; 82.45; 102.12; 108.07; 123.67; 126.72; 128.51; 134.50; 135.82; 136.20; 136.67; 136.97; 137.81; 140.02; 141.01; 141.23; 142.31; 142.80; 143.22; 143.58; 143.76; 143.97; 144.15; 144.21; 144.35; 144.59; 144.96; 145.12; 145.18; 145.37; 145.62; 145.73; 145.75; 145.76; 146.07; 147.31; 147.45; 147.49; 148.55; 159.13; 162.42; 162.56; 167.43. MALDI-TOF-MS: 1726 (100, MH^+). Anal. calc. for $C_{112}H_{62}O_{20}$ · AcOEt (1815.8): C 76.73, H 3.89; found: C 77.09, H 3.78.

Bis[3,5-bis(carboxymethoxy)benzyl] endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**51**). A soln. of **61** (90 mg, 0.052 mmol) in CF_3COOH/CH_2Cl_2 1:1 (2 ml) was stirred at r.t. for 20 h. The mixture was diluted with H_2O, and the dark-brown precipitate was filtered, washed with H_2O, and dissolved in THF. The resulting soln. was dried ($MgSO_4$) and evaporated *in vacuo* to yield **51** (66 mg, 84%) as a dark-orange-red solid which was used without further purification. M.p. > 280°. IR (KBr): 1739 (C=O). ^{1}H-NMR (CD_3COCD_3, 200 MHz): 4.69 (*s*, 8 H); 5.05–5.23 (*m*, 4 H); 5.43 (*d*, *J* = 11.2, 2 H); 6.10 (*d*, *J* = 13.0, 2 H); 6.54 (br. *s*, 2 H); 6.67 (br. *s*, 4 H); 7.30–7.50 (*m*, 4 H). FAB-MS: 1503 (31, MH^+), 720 (100, C_{60}^+).

Bis({[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}methyl) endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**62**). DCC (68 mg, 0.330 mmol) and BtOH (35 mg, 0.260 mmol) were added to a soln. of **50** (150 mg, 0.131 mmol) and **30** (124 mg, 0.327 mmol) in THF (70 ml) at 0°. The mixture was allowed to slowly warm to r.t. (2 h) and, after stirring for 1 d, was filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 99:1), followed by GPC (PhMe), yielded **62** (161 mg, 66%). Orange-red glassy product. UV/VIS (CH_2Cl_2): 259 (124600), 319 (sh, 39950), 378 (sh, 11920), 437 (3250), 471 (2700). IR (neat): 1739 (C=O ester), 1690 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.52 (*t*, *J* = 6.2, 12 H); 3.64 (*s*, 18 H); 3.66 (*t*, *J* = 6.2, 12 H); 3.68 (*s*, 12 H); 4.65 (*d*, J_{AB} = 14.9, 2 H); 4.77 (*d*, J_{AB} = 14.9, 2 H); 5.32 (*d*, J_{AB} = 13.1, 2 H); 5.82 (*d*, J_{AB} = 13.1, 2 H); 6.47 (*s*, 2 H); 7.31 (*d*, *J* = 7.8, 2 H); 7.40 (*t*, *J* = 7.8, 1 H); 7.52 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.74; 48.81; 51.80; 60.20; 64.81; 66.92; 67.71; 68.95; 70.56; 123.88; 126.74; 128.96; 134.88; 136.33; 136.80; 136.84; 138.15; 140.28; 141.35; 141.56; 142.61; 142.94; 143.63; 143.92; 144.16; 144.34; 144.55; 144.67; 145.01; 145.31; 145.54; 145.59; 145.70; 145.90; 145.93; 145.99; 146.14; 146.43; 147.71; 147.82; 147.90; 148.84; 161.98; 163.25; 165.86; 172.33. FAB-MS: 1865 (100, MH^+), 1762 (51, $[M - O(CH_2)_2CO_2Me]^+$), 720 (30, C_{60}^+).

Benzyl N-*{[({Tris-[(2-{[(tris-{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]-methyl}amino)carbonyl]methyl}carbamate* (**65**). DCC (0.65 g, 3.170 mmol) and BtOH (0.43 g, 3.170 mmol) were added to **36** (2.25 g, 1.583 mmol) and Z-glycine (0.64 g, 3.170 mmol) in THF (15 ml) at 0°. The mixture was allowed to slowly warm to r.t. (4 h) and stirred for 4 d. The resulting suspension was filtered, diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated to dryness. CC (SiO_2, CH_2Cl_2/MeOH 99:1 to 95:5) yielded **65** (2.00 g, 78%). Colorless oil. IR (neat): 1738 (C=O ester), 1671 (C=O amide). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.38 (*t*, *J* = 6.4, 6 H); 2.54 (*t*, *J* = 6.2, 18 H); 3.64–3.71 (*m*, 75 H); 3.89 (*d*, *J* = 5.0, 2 H); 5.10 (*s*, 2 H); 5.90 (br. *t*, 1 H); 6.15 (*s*, 3 H); 6.86 (*s*, 1 H); 7.30–7.36 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 34.69; 37.16; 44.52; 51.64; 59.80; 65.51; 66.75; 67.54; 69.00; 69.13; 128.02; 128.46; 136.69; 156.40; 169.00; 171.16; 172.11. FAB-MS: 1612 (100, M^+), 1508 (18, $[M - O(CH_2)_2CO_2Me]^+$). Anal. calc. for $C_{71}H_{113}N_5O_{36} \cdot {}^1/_2$ CH_2Cl_2 (1655.2): C 51.89, H 6.94; N 4.23; found: C 51.89, H 6.99, N 4.40.

*2-Amino-*N*-{Tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]-methyl}acetamide* (**64**). A mixture of **65** (1.75 g, 1.086 mmol), HCO_2NH_4 (290 mg, 4.603 mmol), and 10% Pd/*C* (0.35 g) in EtOH (5 ml) was stirred at 40° for 4 h, while N_2 was bubbled through. After cooling to r.t. and filtration through *Celite* (CH_2Cl_2/AcOEt 1:1), washing with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation provid-

ed **64** (1.40 g, 87%). Colorless oil. IR (neat): 1738 (C=O ester), 1670 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.37 (*t*, *J* = 6.0, 6 H); 2.51 (*t*, *J* = 6.2, 18 H); 3.33 (*s*, 2 H); 3.62–3.68 (*m*, 75 H); 6.11 (*s*, 3 H); 7.33 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 34.28, 36.88; 45.07; 51.20; 59.04; 59.33; 66.31; 67.11; 68.66; 170.63; 171.64. FAB-MS: 1479 (M^+).

Bis{[({[({tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]methyl}-amino)carbonyl]methyl}amino)carbonyl]methyl} endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]-fullerene-61,61,62,62-tetracarboxylate* (**63**). DCC (45 mg, 0.220 mmol) and BtOH (24 mg, 0.180 mmol) were added to a soln. of **50** (102 mg, 0.089 mmol) and **64** (330 mg, 0.223 mmol) in THF (70 ml) at 0°, and, after warming to r.t. (2 h), the mixture was stirred for 2 d. Filtration, evaporation *in vacuo*, and CC (SiO_2, CH_2Cl_2/MeOH 95:5), followed by GPC (PhMe), yielded **63** (276 mg, 76%). Glassy orange-red product. UV/VIS (CH_2Cl_2): 259 (100700), 319 (sh, 31600), 378 (sh, 10860), 436 (3150), 472 (2640). IR (neat): 1738 (C=O ester), 1671 (C=O amide). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.38 (*t*, *J* = 6.2, 12 H); 2.52 (*t*, *J* = 6.2, 36 H); 3.62–3.70 (*m*, 150 H); 4.00 (*d*, *J* = 4.7, 4 H); 4.77 (*d*, J_{AB} = 14.9, 2 H); 4.88 (*d*, J_{AB} = 14.9, 2 H); 5.37 (*d*, J_{AB} = 13.1, 2 H); 5.88 (*d*, J_{AB} = 13.1, 2 H); 6.14 (*s*, 6 H); 7.03 (*s*, 2 H); 7.06 (*t*, *J* = 4.7, 2 H); 7.32 (*d*, *J* = 7.3, 2 H); 7.40 (*t*, *J* = 7.3, 1 H); 7.52 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 34.77; 37.18; 42.53; 48.75; 51.77; 59.91; 60.33; 64.67; 66.87; 67.71; 69.00; 69.26; 70.49; 124.49; 127.32; 128.99; 134.62; 136.29; 136.76; 136.98; 138.37; 140.38; 141.35; 141.59; 142.58; 142.90; 143.65; 143.94; 144.12; 144.36; 144.54; 144.59; 144.80; 144.99; 145.31; 145.59; 145.72; 145.86; 145.94; 146.04; 146.09; 146.43; 147.68; 147.82; 147.89; 148.74; 162.06; 163.09; 166.00; 168.29; 171.42; 172.42. FAB-MS: 4063 (M^+). MALDI-TOF-MS (CCA): 4087 (100, $[M + Na]^+$; calc. for $^{13}C_2{}^{12}C_{202}H_{224}N_{10}O_{78}Na$: 4086).

Bis(3,5-bis{[({[({tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]-methyl}amino)carbonyl]methyl}amino)carbonyl]methoxy}benzyl endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**66**). DCC (63 mg, 0.305 mmol) and BtOH (41 mg, 0.305 mmol) were added to a soln. of **51** (92 mg, 0.061 mmol) and **64** (451 mg, 0.305 mmol) in THF (70 ml) at 0°. The mixture was allowed to slowly warm to r.t. (2 h) and, after stirring for 2 d, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 95.5), followed by GPC (PhMe), yielded **66** (151 mg, 34%). Orange-red glassy product. UV/VIS (CH_2Cl_2): 259 (160190), 319 (sh, 51760), 377 (sh, 14470), 437 (4280), 470 (3520). IR (neat): 1738 (C=O ester), 1671 (C=O amide). ^{1}H-NMR ($CDCl_3$, 500 MHz): 2.40 (*t*, *J* = 6.2, 24 H); 2.54 (*t*, *J* = 6.2, 72 H); 3.64–3.71 (*m*, 300 H); 4.07 (*d*, *J* = 5.0, 8 H); 4.44 (*s*, 8 H); 5.14 (*d*, J_{AB} = 12.8, 2 H); 5.28 (br. *s*, 4 H); 5.84 (*d*, J_{AB} = 12.8, 2 H); 6.16 (*s*, 16 H); 6.62 (*d*, *J* = 2.1, 4 H); 6.52 (*t*, *J* = 2.1, 2 H); 7.00 (*s*, 4 H); 7.30–7.36 (*m*, 3 H); 7.50 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 34.64; 37.10; 42.18; 49.00; 51.50; 59.74; 60.18; 66.68; 66.88; 67.28; 67.49; 68.03; 69.10; 70.50; 101.94; 108.42; 123.88; 126.93; 128.60; 134.55; 135.80; 136.08; 136.58; 137.38; 137.77; 139.96; 140.90; 141.26; 142.23; 142.86; 143.18; 143.51; 143.71; 143.90; 144.14; 144.19; 144.21; 144.50; 144.89; 145.08; 145.12; 145.31; 145.57; 145.65; 145.69 (2×); 146.00; 147.24; 147.38; 147.45; 148.52; 158.57; 162.18; 162.60; 167.16; 168.10; 170.96; 171.90. MALDI-TOF-MS (dithranol): 7368 (100, $[M + Na]^+$; calc. for $^{13}C_4{}^{12}C_{344}H_{450}N_{20}O_{152}Na$: 7368).

3-{[(Tetrahydropyran-2-yl)oxy]methyl}benzene-1-methanol (**67**). DHP (1.8 ml, 19.54 mmol) was added at r.t. to a soln. of **2** (2.70 g, 19.54 mmol) and TsOH · H_2O (10 mg, 0.05 mmol) in MeCN (70 ml). After stirring for 4 h and evaporation *in vacuo*, CC (SiO_2), eluting with CH_2Cl_2/MeOH 100:3, yielded the bis-protected derivative and, with CH_2Cl_2/hexane 50:2, the mono-protected **67** (1.70 mg, 39%). Colorless oil. IR (neat): 3460 (O–H). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.45–1.95 (*m*, 6 H); 3.06 (br. *s*, 1 H); 3.50–3.56 (*m*, 1 H); 3.86–3.92 (*m*, 1 H); 4.47 (*d*, *J* = 11.0, 1 H); 4.62 (br. *s*, 2 H); 4.70 (br. *s*, 1 H); 4.77 (*d*, *J* = 11.0, 1 H); 7.28–7.34 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 16.79; 22.95; 28.06; 59.67; 62.43; 66.37; 95.41; 123.79; 124.01; 124.62; 126.20; 136.11; 139.03. EI-MS: 222 (1, M^+); 85 (100, THP^+).

Bis(3-{[(tetrahydropyran-2-yl)oxy]methyl}benzyl) Malonate (**68**). Malonyl dichloride (0.37 ml, 3.823 mmol) was added to a soln. of **67** (1.70 g, 7.647 mmol) and C_5H_5N (0.6 ml, 8.0 mmol) in CH_2Cl_2 (100 ml) at 0°, and the resulting mixture was allowed to warm slowly to r.t. (over 1 h). After stirring for 4 h, washing with sat. aq. NH_4Cl soln. (2×), and drying ($MgSO_4$), CC (SiO_2, CH_2Cl_2/MeOH 99:1) afforded **68** (1.62 g, 83%) as a mixture of diastereoisomers. Colorless oil. IR (neat): 1737 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.45–1.95 (*m*, 12 H); 3.48 (*s*, 2 H); 3.49–3.60 (*m*, 2 H); 3.86–3.97 (*m*, 2 H); 4.49 (*d*, *J* = 12.0, 2 H); 4.71 (br. *s*, 2 H); 4.79 (*d*, *J* = 12.0, 2 H); 5.18 (*s*, 4 H); 7.30–7.35 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 19.35; 25.48; 30.56; 41.54; 62.15; 67.19; 68.53; 97.89; 127.45; 127.64; 127.86; 128.72; 135.38; 138.88; 166.27. FAB-MS: 551 (8, $[M + K]^+$), 411 (15, $[M - THPO]^+$), 85 (100, THP^+).

Bis(3-{[(tetrahydropyran-2-yl)oxy]methyl}benzyl) 1,2-Methano[60]fullerene-61,61-dicarboxylate (**69**). DBU (0.2 ml, 1.248 mmol) was added at r.t. to a soln. of C_{60} (500 mg, 0.694 mmol), I_2 (176 mg, 0.694 mmol), and **68** (427 mg, 0.833 mmol) in PhMe (600 ml), and the resulting mixture was stirred for 12 h. Filtration through a short

plug (SiO_2), eluting first with PhMe (to remove unreacted C_{60}), then with CH_2Cl_2/MeOH 9:1, followed by CC (SiO_2, CH_2Cl_2/MeOH 200:1), provided **69** (398 mg, 47%) as a mixture of diastereoisomers. Dark-red glassy product. UV/VIS (CH_2Cl_2): 258 (108100), 325 (32700), 393 (sh, 5600), 403 (sh, 4030), 413 (sh, 3130), 426 (2830), 470 (1810), 688 (150). IR (neat): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.40–1.95 (*m*, 12 H); 3.52–3.57 (*m*, 2 H); 3.88–3.94 (*m*, 2 H); 4.46–4.52 (*m*, 2 H); 4.70–4.81 (*m*, 4 H); 5.48 (*s*, 4 H); 7.27–7.45 (*m*, 8 H). FAB-MS: 1230 (8, M^+), 720 (100, C_{60}^+).

Bis[3-(hydroxymethyl)benzyl] 1,2-Methano[60]fullerene-61,61-dicarboxylate (**70**). A mixture of **69** (752 mg, 0.611 mmol) and TsOH · H_2O (580 mg, 3.055 mmol) in EtOH/PhMe 3:2 (500 ml) was stirred at 80° for 4 h. Evaporation *in vacuo*, CC (SiO_2, CH_2Cl_2/MeOH 20:1), and recrystallization (hexane/CH_2Cl_2) provided **70** (602 mg, 93%). Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (108200), 326 (31900), 393 (sh, 4570), 402 (sh, 3220), 413 (sh, 2350), 426 (2270), 484 (1380), 688 (150). IR (KBr): 3403 (O–H), 1745 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.17 (br. *s*, 2 H); 4.66 (*s*, 4 H); 5.47 (*s*, 4 H); 7.30–7.45 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 51.88; 65.03; 68.95; 71.52; 127.38; 127.61; 128.19; 129.20; 135.18; 139.34; 141.20; 141.78; 142.12; 142.48; 143.27; 143.30; 143.37; 144.16; 144.83; 144.87; 144.97; 145.20; 145.24; 145.39; 145.47; 145.55; 163.69. FAB-MS: 1062 (25, M^+), 720 (100, C_{60}^+). Anal. calc. for $C_{79}H_{18}O_6 \cdot 0.9\,CH_2Cl_2$ (1139.5): C 84.22, H 1.75; found: C 84.16, H 1.98.

Bis(3-{[(ethoxycarbonyl)acetoxy]methyl}benzyl) 1,2-Methano[60]fullerene-61,61-dicarboxylate (**71**). Ethyl 3-chloro-3-oxopropanoate (0.15 ml, 1.175 mmol) was added to a stirred soln. of **70** (500 mg, 0.470 mmol) and C_5H_5N (0.1 ml, 1.41 mmol) in CH_2Cl_2 (150 ml) at 0°. The mixture was allowed to slowly warm to r.t. (over 1 h) and then stirred for 6 h. After washing with sat. aq. NH_4Cl soln. (2 ×), drying ($MgSO_4$), and evaporation *in vacuo*, CC (SiO_2, CH_2Cl_2/MeOH 200:1), followed by recrystallization (Et_2O/$CHCl_3$), yielded **71** (456 mg, 75%). Dark-red solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (101700), 325 (31560), 392 (sh, 5240), 402 (sh, 3790), 413 (sh, 2880), 426 (2650), 476 (1700), 688 (150). IR (KBr): 1748 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.25 (*t*, *J* = 7.0, 6 H); 3.41 (*s*, 4 H); 4.18 (*q*, *J* = 7.0, 4 H); 5.16 (*s*, 4 H); 5.48 (*s*, 4 H); 7.35–7.45 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.16; 41.63; 51.74; 61.78; 66.90; 68.71; 71.47; 128.78; 128.95; 129.03; 129.36; 135.31; 136.22; 139.31; 141.18; 142.07; 142.46; 143.25; 143.30; 143.35; 144.14; 144.79; 144.86; 144.95; 145.16; 145.34; 145.46; 145.54; 163.59; 166.66; 166.71. FAB-MS: 1291 (100, MH^+), 1159 (37, $[M - O_2CCH_2CO_2Et]^+$), 720 (78, C_{60}^+). Anal. calc. for $C_{89}H_{30}O_{12} \cdot 0.8\,CH_2Cl_2$ (1359.2): C 79.36, H 2.34; found: C 79.12, H 2.58.

(±)-61,63-Diethyl endo,endo:endo,endo-*61,62:62,63-Bis*(m-*phenylenedimethyl) 1,2:7,21:39,40-Tris(methano)[60]fullerene-61,61,62,62,63,63-hexacarboxylate* ((±)-**72**). A soln. of **71** (260 mg, 0.201 mmol) and I_2 (112 mg, 0.442 mmol) in PhMe (250 ml) was added dropwise (5 h) to DBU (0.2 ml, 1.206 mmol) in PhMe (150 ml) at r.t. with vigorous stirring. After stirring for 5 h, filtration through a short plug (SiO_2, CH_2Cl_2), followed by CC (SiO_2, CH_2Cl_2) and recrystallization (CH_2Cl_2/MeOH), yielded (±)-**72** (82 mg, 32%). Dark-orange solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (97900), 338 (30410), 397 (6160), 461 (3710), 576 (sh, 980). IR (KBr): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.39 (*t*, *J* = 7.1, 6 H); 4.36–4.52 (*m*, 4 H); 5.08 (*d*, *J* = 12.9, 2 H); 5.17 (*d*, *J* = 12.9, 2 H); 5.68 (*d*, *J* = 12.9, 2 H); 5.80 (*d*, *J* = 12.9, 2 H); 7.21–7.23 (*m*, 4 H); 7.32 (br. *s*, 2 H); 7.33 (*t*, *J* = 7.7, 2 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.18; 45.10; 48.58; 63.23; 66.70; 66.98; 67.13; 67.32; 70.58; 123.81; 126.58; 128.58; 135.15; 135.98; 136.53; 136.62; 137.21; 139.87; 139.89; 140.16; 142.12; 142.97; 143.02; 143.84; 143.88; 143.98; 144.10; 144.21; 145.15; 145.46; 145.58; 145.60; 145.79; 146.03; 146.58; 146.69; 147.11; 147.40; 147.51; 148.12; 148.44; 148.65; 162.56; 162.71; 163.27. FAB-MS: 1286 (100, MH^+), 720 (18, C_{60}^+). Anal. calc. for $C_{89}H_{26}O_{12} \cdot 2$ MeOH (1351.3): C 80.89, H 2.54; found: C 80.75, H 2.71.

(Benzene-1,3-diyl)dimethyl Bis(3-{[(tetrahydropyran-2-yl)oxy]methyl}benzyl) Bis[malonate] (**73**). DCC (4.56 g, 22.13 mmol) and DMAP (450 mg, 3.69 mmol) were added to a soln. of **57** (2.86 g, 9.22 mmol) and **67** (4.10 g, 18.44 mmol) in THF (100 ml) at 0°. The mixture was allowed to slowly warm to r.t. (1 h) and, after stirring for 12 h, filtered and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 100:1) provided **73** (4.35 g, 66%) as a mixture of diastereoisomers. Colorless oily solid. IR (neat): 1737 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.45–1.95 (*m*, 12 H); 3.50 (*s*, 4 H); 3.51–3.62 (*m*, 2 H); 3.87–3.99 (*m*, 2 H); 4.50 (br. *d*, *J* = 12.5, 2 H); 4.72 (br. *s*, 2 H); 4.80 (br. *d*, *J* = 12.5, 2 H); 5.18 (*s*, 4 H); 5.20 (*s*, 4 H); 7.25–7.40 (*m*, 12 H). FAB-MS: 757 (100, $[M + K]^+$), 717 (17, $[M - H]^+$).

Bis(3-{[(tetrahydropyran-2-yl)oxy]methyl}benzyl) endo,endo-(m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)-[60]fullerene-61,61,62,62-tetracarboxylate* (**74**). DBU (0.5 ml, 3.33 mmol) was added at r.t. to a soln. of C_{60} (400 mg, 0.555 mmol), I_2 (338 mg, 1.332 mmol), and **73** (479 mg, 0.666 mmol) in PhMe (700 ml), and the soln. was stirred for 6 h. Filtration through a short plug (SiO_2), eluting first with PhMe (to remove unreacted C_{60}) and then with CH_2Cl_2/MeOH 9:1, followed by CC (SiO_2, CH_2Cl_2/MeOH 100:1), provided **74** (303 mg, 38%) as a mixture of diastereoisomers. Dark-orange glassy product. UV/VIS (CH_2Cl_2): 258 (96580), 319 (sh, 29650), 378 (sh, 8560), 437 (2570), 470 (2400). IR (neat): 1748 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.50–1.90 (*m*, 12 H); 3.50–3.58

(*m*, 2 H); 3.85–3.93 (*m*, 2 H); 4.46 (*d*, *J* = 11.0, 2 H); 4.67–4.72 (*m*, 2 H); 4.76 (*d*, *J* = 11.0, 1 H); 4.77 (*d*, *J* = 11.0, 1 H); 4.94 (br. *d*, *J* = 12.7, 2 H); 5.26 (*d*, *J* = 10.0, 1 H); 5.27 (*d*, *J* = 10.0, 1 H); 5.48 (*d*, *J* = 10.0, 1 H); 5.49 (*d*, *J* = 10.0, 1 H); 5.80 (*d*, *J* = 12.7, 2 H); 7.20–7.40 (*m*, 12 H). FAB-MS: 1435 (6, MH^+), 720 (100, C_{60}^+).

Bis[3-(hydroxymethyl)benzyl] endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* (**75**). A mixture of **74** (1.18 g, 0.822 mmol) and TsOH · H_2O (782 mg, 4.11 mmol) in EtOH/PhMe 1:1 (600 ml) was stirred at 80° for 4 h. Evaporation *in vacuo*, CC (SiO_2, CH_2Cl_2/MeOH 100:1), and recrystallization (hexane/CH_2Cl_2) provided **75** (956 mg, 92%). Dark-orange solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (98260), 317 (30780), 378 (sh, 11790), 437 (3280), 470 (2850). IR (KBr): 3345 (O–H), 1746 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.09 (br. *s*, 2 H); 4.66 (br. *s*, 4 H); 5.05 (*d*, *J* = 12.9, 2 H); 5.31 (*d*, *J* = 11.6, 2 H); 5.48 (*d*, *J* = 11.6, 2 H); 5.81 (*d*, *J* = 12.9, 2 H); 7.20–7.50 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 49.30; 65.04; 67.00; 67.55; 68.81; 70.72; 123.88; 126.94; 127.60; 128.28; 128.93; 129.04; 134.57; 135.19; 135.91; 136.27; 136.92; 138.13; 140.30; 141.27; 141.50; 141.75; 142.61; 143.02; 143.49; 143.92; 144.10; 144.33; 144.47; 144.59; 144.65; 144.94; 145.17; 145.39; 145.52; 145.69; 145.96; 146.03; 146.07; 146.22; 146.40; 147.64; 147.79; 148.89; 163.08 (2 ×). FAB-MS: 1266 (100, M^+), 720 (43, C_{60}^+). Anal. calc. for $C_{90}H_{26}O_{10}$ · 1.6 CH_2Cl_2 (1403.1): C 78.41, H 2.10; found: C 78.30, H 2.37.

Bis(3-{[(ethoxycarbonyl)acetoxy]methyl}benzyl) endo,endo-*(*m-*Phenylenedimethyl) 1,2:7,21-Bis(methano)-[60]fullerene-61,61,62,62-tetracarboxylate* (**76**). Ethyl 3-chloro-3-oxopropanoate (0.19 ml, 1.48 mmol) was added to a stirred soln. of **75** (750 mg, 0.592 mmol) and C_5H_5N (0.14 ml, 1.78 mmol) in CH_2Cl_2 (100 ml) at 0°. After slowly warming to r.t. (over 1 h) and stirring for 4 h, the mixture was washed with sat. aq. NH_4Cl soln. (2 ×), dried, ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2, CH_2Cl_2/MeOH 200:1), followed by recrystallization ($CHCl_3$/Et_2O), yielded **76** (675 mg, 76%). Dark-orange solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 258 (114440), 319 (34900), 378 (sh, 11540), 437 (3250), 471 (2820). IR (KBr): 1748 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.24 (*t*, *J* = 7.1, 6 H); 3.40 (*s*, 4 H); 4.18 (*q*, *J* = 7.1, 4 H); 4.96 (*d*, *J* = 12.8, 2 H); 5.15 (*s*, 4 H); 5.28 (*d*, *J* = 12.1, 2 H); 5.46 (*d*, *J* = 12.1, 2 H); 5.81 (*d*, *J* = 12.8, 2 H); 7.20–7.50 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.16; 41.63; 49.05; 61.79; 66.90; 67.00; 67.48; 68.47; 70.67; 123.83; 126.92; 128.93; 128.96; 129.25; 134.68; 135.38; 136.12; 136.48; 136.92; 138.11; 140.31; 141.27; 141.51; 142.60; 143.00; 143.49; 143.91; 144.10; 144.31; 144.49; 144.57; 144.63; 144.92; 145.20; 145.43; 145.52; 145.70; 145.94; 146.03; 146.07; 146.40; 147.63; 147.80; 148.87; 162.91; 163.00; 166.67; 166.72. FAB-MS: 1495 (100, MH^+), 720 (17, C_{60}^+). Anal. calc. for $C_{100}H_{38}O_{16}$ · 0.5 $CHCl_3$ (1555.1): C 77.62, H 2.50; found: C 77.57, H 2.53.

61,64-Diethyl endo,endo:endo,endo:endo,endo-*61,62:62,63:63,64-tris(*m-*Phenylenedimethyl) 1,2:7,21:39,40:55,60-Tetrakis(methano)[60]fullerene-61,61,62,62,63,63,64,64-octacarboxylate* (**77**). A soln. of **76** (600 mg, 0.401 mmol) and I_2 (255 mg, 1.003 mmol) in PhMe (300 ml) was added dropwise (6 h) to DBU (0.3 ml, 2.406 mmol) in PhMe (200 ml) at r.t. with vigorous stirring. After stirring for 1 h, filtration through a short plug (SiO_2, CH_2Cl_2/MeOH 19:1) and CC (SiO_2, CH_2Cl_2), followed by recrystallization ($CHCl_3$/Et_2O), yielded **77** (135 mg, 23%). Orange solid. M.p. > 280°. UV/VIS (CH_2Cl_2): 237 (99770), 256 (sh, 85420), 334 (28850), 380 (sh, 10580), 434 (sh, 4660), 570 (1100). IR (KBr): 1748 (C=O). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.45 (*t*, *J* = 7.1, 6 H); 4.45–4.60 (*m*, 4 H); 5.07 (*d*, *J* = 12.8, 2 H); 5.17 (*d*, *J* = 12.7, 2 H); 5.26 (*d*, *J* = 12.8, 2 H); 5.57 (*d*, *J* = 12.7, 2 H); 5.75 (*d*, *J* = 12.8, 2 H); 5.79 (*d*, *J* = 12.8, 2 H); 7.14 (*dd*, *J* = 7.6, 1.5, 4 H); 7.20–7.30 (*m*, 4 H); 7.34 (*t*, *J* = 7.6, 2 H); 7.38 (br. *s*, 2 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.24; 41.60; 44.73; 63.28; 65.67; 66.60; 67.02; 67.16; 67.28; 67.37; 68.83; 124.13; 124.48; 126.59; 126.64; 126.84; 128.53; 128.58; 131.72; 134.58; 136.32; 136.50; 136.53; 136.61; 136.83; 138.42; 139.99; 140.10; 140.26; 141.18; 141.45; 142.68; 144.02; 144.29 (2 ×); 144.40; 144.93; 145.31; 145.70; 146.10; 146.22; 146.58; 146.97; 147.08; 147.20; 147.55; 148.15; 150.81; 151.07; 162.46; 163.02; 163.23; 163.90. FAB-MS: 1491 (100, MH^+), 720 (35, C_{60}^+). Anal. calc. for $C_{100}H_{34}O_{16}$ · 0.5 $CHCl_3$ (1551.1): C 77.83, H 2.24; found: C 77.75, H 2.47.

X-Ray Structure Analysis of **13**. $C_{24}H_{24}N_2O_8$ (M_r = 468.5). Monoclinic space group *I*2/*a*, D_c = 1.369 g cm^{-3}, *Z* = 4, *a* = 8.010(3), *b* = 18.401(11), *c* = 15.415(7) Å, β = 90.23°, *V* = 2272(2) Å^3, MoK_α (λ = 0.71073 Å) radiation, $3 \leq 2\theta \leq 40°$, 1186 measured reflections, 1064 independent reflections, *T* = 293 K. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares analysis using experimental weights (heavy atoms anisotropic, H-atoms fixed, whereby H-atom positions are based on stereochemical considerations). Final $R(F) = 0.0512$, $R_w(F) = 0.0744$ for 167 variables and 937 observed reflections with $F > 4\sigma(F)$. Further details are available on request from the Director of the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB12 1EZ (UK), on quoting the full journal citation.

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