Synthesis of Amphiphilic Fullerene Derivatives and Their Incorporation in *Langmuir* and *Langmuir-Blodgett* Films

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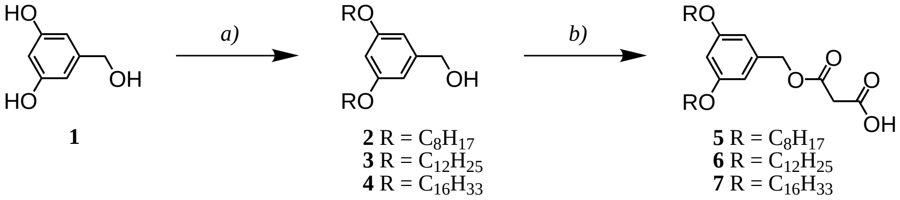
Various amphiphilic fullerene derivatives were prepared by functionalization of [5,6]fullerene-C_{60}-I_h (C_{60}) with malonate or bis-malonate derivatives obtained by esterification of the malonic acid mono-esters **5**–**7**. Cyclopropafullerene **10** was obtained by protection of the carboxylic acid function of **6** as a *tert*-butyl ester, followed by *Bingel* addition to C_{60} and a deprotection step (*Scheme 2*). The preparation of **10** was also attempted directly from the malonic acid mono-ester **6** under *Bingel* conditions. Surprisingly, the corresponding 3′-iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-C_{60}-I_h-3′-carboxylate **11** was formed instead of **10** (*Scheme 3*). The general character of this new reaction was confirmed by the preparation of **15** and **16** from the malonic acid mono-esters **13** and **14**, respectively (*Scheme 4*). All the other amphiphilic fullerene derivatives were prepared by taking advantage of the versatile regioselective reaction developed by *Diederich* and co-workers which led to macrocyclic bis-adducts of C_{60} by a cyclization reaction at the C-sphere with bis-malonate derivatives in a double *Bingel* cyclopropanation. The bis-adducts **37**–**39** with a carboxylic acid polar head group and four pendant long alkyl chains of different length were prepared from diol **22** and acids **5**–**7**, respectively (*Scheme 9*). In addition, the amphiphilic fullerene derivatives **45**, **46, 49**, **54**, and **55** bearing different polar head groups and compound **19** with no polar head group were synthesized (*Schemes 11*–*13*, *15*, and *5*, resp.). The ability of all these compounds to form *Langmuir* monolayers at the air-water interface was investigated in a systematic study. The films at the water surface were characterized by their surface pressure *vs.* molecular area isotherms, compression and expansion cycles, and *Brewster*-angle microscopy. The spreading behavior of compound **10** was not good, the two long alkyl chains in **10** being insufficient to prevent aggregation resulting from the strong fullerene-fullerene interactions. While no films could be obtained from compound **19** with no polar head group, all the corresponding amphiphilic fullerene bis-adducts showed good spreading characteristics and reversible behavior upon successive compression/expansion cycles. The encapsulation of the fullerene in a cyclic addend surrounded by four long alkyl chains is, therefore, an efficient strategy to prevent the irreversible aggregation resulting from strong fullerene-fullerene interactions usually observed for amphiphilic C_{60} derivatives at the air-water interface. The balance of hydrophobicity to hydrophilicity was modulated by changing the length of the surrounding alkyl chains or the nature of the polar head group. The best results in terms of film formation and stability were obtained with the compounds having the largest polar head group, *i.e.* **45** and **46**, and dodecyl chains. Finally, the *Langmuir* films obtained from the amphiphilic fullerene bis-adducts were transferred onto solid substrates, yielding high-quality *Langmuir-Blodgett* films.

1. Introduction. – In the light of their special electrochemical and photophysical properties, fullerene derivatives are currently being intensively investigated with the aim of generating new advanced materials for electronic, photonic, and nonlinear optical applications [1]. Since the incorporation of fullerenes into thin films is required for the preparation of many optoelectronic devices, the past several years have seen considerable growth in the use of fullerene-based derivatives at surfaces and interfaces [2]. One possible approach towards structurally ordered fullerene assemblies is the preparation of *Langmuir* films at the air-water interface and their subsequent transfer onto solid substrates [2]. However, all the studies on the spreading behavior of pure fullerenes at the air-water interface revealed the formation of collapsed films due to the nonamphiphilic nature of these compounds and to aggregation phenomena resulting from strong fullerene-fullerene interactions [3]. Furthermore, all attempts to create well-defined *Langmuir-Blodgett* (*LB*) films have failed. Two approaches have been used to overcome these problems. The first consists in preventing fullerene-fullerene interactions by incorporating the fullerenes into a matrix of an amphiphilic compound to produce mixed *Langmuir* films. Fatty acids or long-chain alcohols have been used for this purpose [4]; however, the expected protection is not always very effective, and fullerene aggregation remains a problem. Amphiphilic molecules containing a cavity able to incorporate the fullerene such as azacrowns [5] or calixarenes [6] have been found to be the most suitable matrices for the preparation of fullerene-containing composite *Langmuir* films of good quality. The second approach is achieved by chemical modification of the fullerene molecule, in general by covalent attachment of a hydrophilic head group onto the fullerene core to obtain an adduct with amphiphilic character. Even if such a modification may alter the physical properties of the fullerenes, desirable properties such as facile reducibility [7] and optical limiting capability [8] that are characteristic of the parent fullerenes are maintained at low degree of functionalization [9]. Attachment of a hydrophilic head group to the fullerene core has led to significant improvement of the spreading behavior. The polar head group is responsible for attractive interaction with the aqueous subphase, thus preventing three-dimensional aggregation and allowing the preparation of monolayers at the air-water interface [10][11]. However, in most cases, once the fullerene cores are in contact with each other in compressed *Langmuir* films, they irreversibly aggregate, and the monolayer does not return to the initial expanded state. The resulting *Langmuir* films are also usually rigid, and, as a result, their transfer onto solid substrates is difficult. It is only recently that fullerene derivatives with good spreading characteristics and reversible compression/expansion behavior have been described [12–15]. For example, fullerene derivatives bearing dendritic branches with peripheral acylated glucose units have been investigated [12]. The dendritic portion is bulky enough to prevent contact between neighboring fullerenes when the film is compressed, thus the irreversible aggregation usually observed for amphiphilic fullerene derivatives cannot occur. As part of this research, we have shown that good spreading characteristics and a reversible compression/decompression behavior can be obtained by the encapsulation of the fullerene in a cyclic addend surrounded by long alkyl chains [13] or cholesterol subunits [14]. Using an alternative approach, we have also shown that the fullerenes can be attached into the branching shell of a diblock dendritic structure [15]. In this case, the fullerene units are buried in the middle of the dendritic structure which is capable of providing a compact insulating layer around the C-spheres, thus preventing the irreversible three-dimensional aggregation resulting from strong fullerene-fullerene interactions. In addition, the peripheral substitution of the diblock globular dendrimer with hydrophobic chains on one hemisphere and hydrophilic groups on the other provides the perfect hydrophobic/hydrophilic balance allowing the formation of stable *Langmuir* films.

Herein, we report a full account of the synthesis and characterization of a complete series of amphiphilic fullerene derivatives bearing two or four long alkyl chains and various polar head groups. We also describe some of the interesting reactivity encountered during the synthesis of these molecules, specifically, the synthesis of 3′-iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-C_{60}-I_h-3′-carboxylates from [5,6]fullerene-C_{60}-I_h (C_{60}) and malonic acid mono-esters. The *Langmuir* films of the different compounds have been characterized by their surface pressure *vs.* molecular area (Π/A) isotherms and *Brewster*-angle microscopy (BAM) observations. Preliminary experiments of *LB* transfers of the monolayers onto solid substrates are also described. Part of this work has been previously reported in preliminary communications [13][16].

2. Results and Discussions. – 2.1. *Synthesis.* The preparation of the various amphiphilic fullerene derivatives is based on the functionalization of the C_{60} core with malonate or bis-malonate derivatives obtained by esterification of the malonic acid mono-esters **5**–**7**. The preparation of the precursors **5**–**7** is depicted in *Scheme 1.* Reaction of 5-(hydroxymethyl)benzene-1,3-diol (**1**) with 1-bromooctane, 1-bromododecane, and 1-bromohexadecane under classical *Williamson* conditions (K_2CO_3, DMF, 80°) afforded the 3,5-bis(alkyloxy)benzyl alcohols **2**, **3**, and **4**, respectively. Compound **2** was obtained as an oil, and column chromatography was required for its purification. In contrast, the corresponding derivatives bearing $C_{12}H_{25}$ (**3**) and $C_{16}H_{33}$ (**4**) chains were obtained as crystalline solids and were easily purified by recrystallization. The mono-esters **5**–**7** were then prepared by heating the corresponding alcohols **2**–**4** with 2,2-dimethyl-1,3-dioxane-4,6-dione (= *Meldrum*'s acid) [17]. No purification was required after this step, and compounds **5**–**7** were used in the following reactions as obtained.

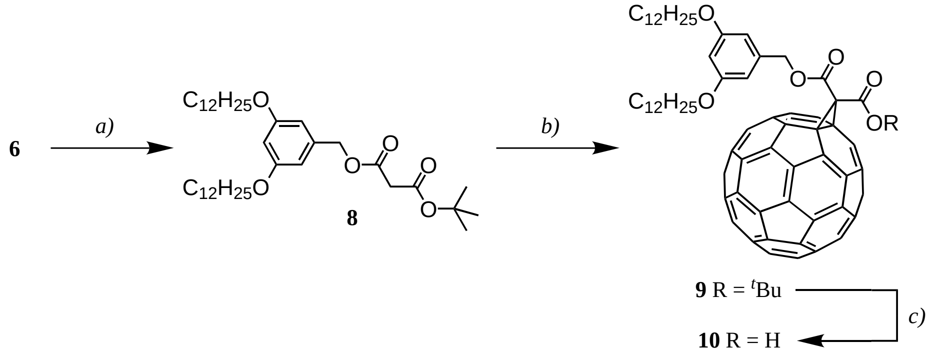
Scheme 1. *Preparation of Malonic Mono-esters* **5**–**7**



a) 1-Bromoalkane, K_2CO_3, DMF, 80°, 24 h; 90% (**2**), 70% (**3**), 63% (**4**). *b*) *Meldrum*'s acid, 120°, 3 h; 99% (**5**), 99% (**6**), 99% (**7**).

The amphiphilic C_{60} derivative **10** was prepared in three steps from compound **6** (*Scheme 2*). The carboxylic acid function of **6** was first protected as a *tert*-butyl ester. Treatment of **6** with *tert*-butyl alcohol and *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of *N*,*N*-dimethylpyridin-4-amine (DMAP) gave **8** in 76% yield. The functionalization of C_{60} with **8** is based on the *Bingel* reaction [18]. Nucleophilic addition of a stabilized α-halocarbanion to the C_{60} core, followed by an intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}. It has been shown that the α-halomalonate can be generated *in situ*, and direct treatment of C_{60} with malonates in the presence of I_2 [19] or CBr_4 [20] under basic conditions affords the corresponding cyclopropafullerenes in good yields. The reaction of C_{60} with compound **8**, I_2, and 1,8-

Scheme 2. *Preparation of Compound* **10**

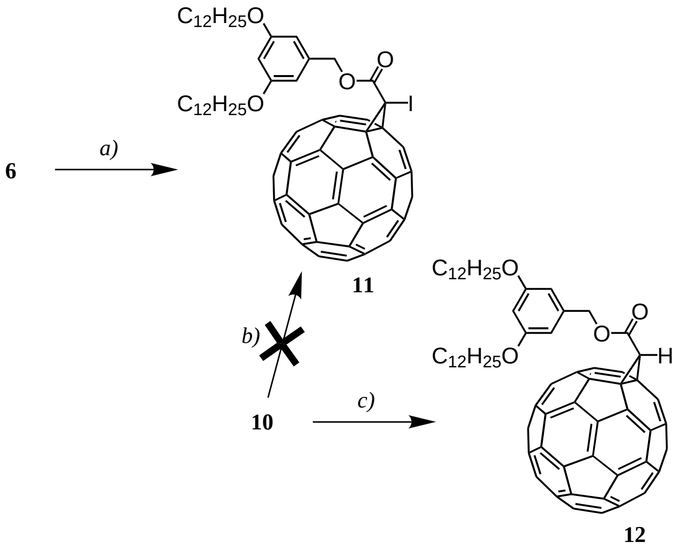


a) ᵗBuOH, DCC, DMAP, CH_2Cl_2, r.t., 12 h; 76%. *b*) C_{60}, DBU, I_2, toluene, r.t., 12 h; 46%. *c*) CF_3CO_2H, CH_2Cl_2, r.t., 4 h; 97%.

diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature gave cyclopropafullerene **9** in 46% yield. The selective cleavage of the *tert*-butyl ester moiety of **9** was first attempted with *p*-toluenesulfonic acid (TsOH) in refluxing toluene [21]. However, under these conditions, the reaction was not selective, and both *tert*-butyl and benzyl ester functions of **9** were hydrolyzed. In contrast, treatment of **9** with CF_3CO_2H in CH_2Cl_2 [21] at room temperature afforded the desired carboxylic acid derivative **10**. In this case, the benzyl ester function remained unchanged, and compound **10** was thus obtained in 97% yield.

The preparation of cyclopropafullerene **10** was also attempted from the malonic acid mono-ester **6** without protection of the carboxylic acid function (*Scheme 3*). However, compound **10** was not formed by treatment of C_{60} with **6** in the presence of I_2 and DBU in toluene at room temperature. Surprisingly, the corresponding 3′-iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-C_{60}-I_h-3′carboxylate **11** was thus obtained in 25% yield. The structure of **11** was confirmed by FAB-MS, which depicted the expected molecular-ion peak at *m*/*z* 1363.2. The ^{13}C-NMR spectrum recorded in $CDCl_3$ was also in full accordance with the structure of **11**. The 32 expected fullerene resonances (31 between δ 136 and 148 ppm, four of which show half intensity, and one at δ 75.47 ppm) as well as the 19 expected non-fullerene signals were observed for C_s-symmetrical **11**. Whereas the resonance of the cyclopropa C-atom in **11** was observed at δ 14.37, the cyclopropa C-atom of corresponding C–H analogues is typically seen around 39 ppm. This shielding effect is characteristic of the presence of an I-atom [22]. Since the malonic acid derivatives of C_{60} are known to decarboxylate easily under basic conditions [19], the formation of cyclopropafullerene **11** could be the result of decarboxylation of the *Bingel* addition product derived from **6**, followed by quenching of the resulting carbanion with I_2. To establish the formation of the *Bingel* addition product as an intermediate, compound **10** was subjected to the reaction conditions used for the preparation of **11** from **6** (DBU, I_2, toluene, room temperature). Only traces of **11** could be detected (< 1%), and compound **12** was the only isolable product (30–40% yield). To prevent the reaction of the carbanion resulting from decarboxylation with

Scheme 3. *Preparation of Compounds* **11** *and* **12**

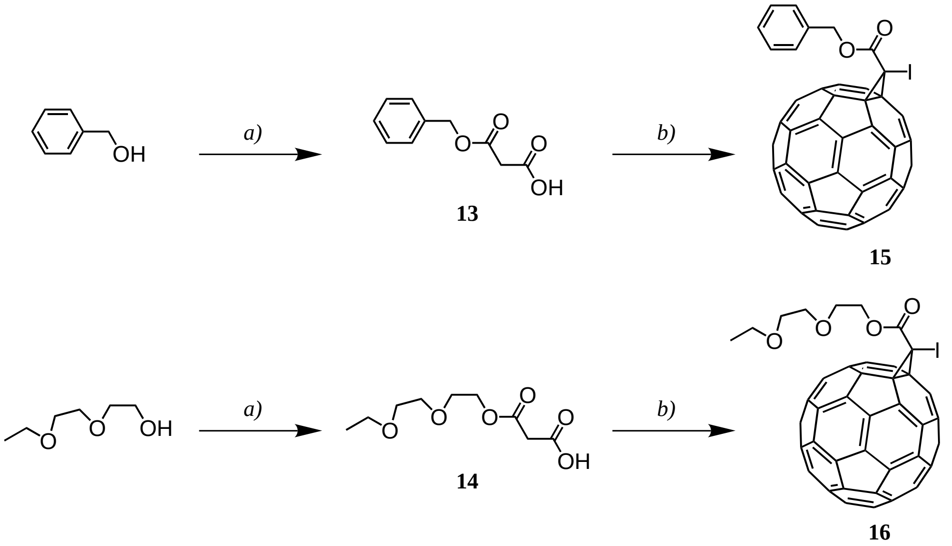


a) C_{60}, DBU, I_2, toluene, r.t.; 25%. *b*) DBU, I_2, toluene, r.t. *c*) DMAP, CH_2Cl_2, r.t., 6 h; 71%.

DBU-H^+ and the formation of **12**, NaH was used as base; however, only decomposition products were obtained and no traces of **11** could be detected. It has to be noted that the reaction of compound **10** with a catalytic amount of DMAP [19] in CH_2Cl_2 at room temperature afforded **12** in good yield (72%). In this case, the unstable carbanion resulting from the decarboxylation reaction is immediately quenched by the more acidic DMAP-H^+ resulting from the reaction of DMAP with the carboxylic acid function of **10**; therefore, the conversion of **10** to **12** is clean under these conditions. Since all attempted transformations of **10** to **11** failed under the experimental conditions used for the preparation of **11** from **6**, the cyclopropanation of C_{60} with the malonic acid mono-ester **6** in the presence of I_2 and DBU seems not to occur *via* the formation of the corresponding *Bingel* addition product. As an alternative, we suppose that the α-iodocarbanion formed *in situ* might be not nucleophilic enough to react with C_{60} and the formation of the corresponding diiodomalonate derivative occurs. Subsequent decarboxylation and I-displacement could yield a carbenoid intermediate able to react with C_{60} to form the corresponding cyclopropafullerene. This cyclopropanation appears to be similar to the addition of dichlorocarbene to C_{60} described by *Nogami* and co-workers [23]. The pyrolysis of sodium trichloroacetate in a mixture of benzene and diglyme generates dichlorocarbene, which then adds to C_{60} to give the corresponding cyclopropafullerene in 26% yield.

The general character of this reaction [16] was then confirmed by the preparation of **15** and **16** from the corresponding malonic acid mono-esters (*Scheme 4*). Compounds **13** and **14** were obtained by treatment of benzyl alcohol and diethylene glycol monomethyl ether, respectively, with *Meldrum*'s acid. As observed for the reaction of **6** with C_{60}, the treatment of C_{60} with **13** and **14** in the presence of DBU and I_2 afforded the

Scheme 4. *Preparation of Compounds* **15** *and* **16**

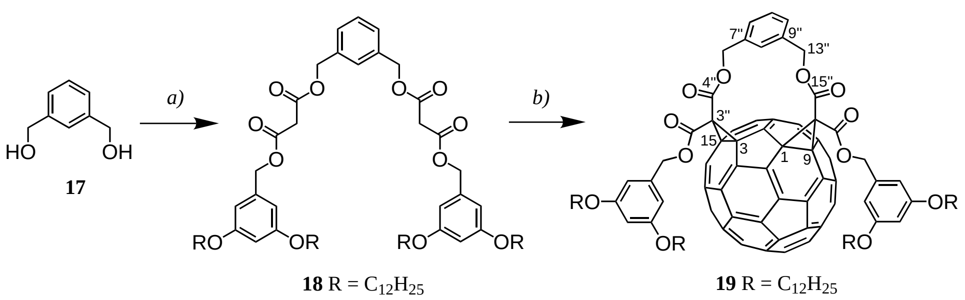


a) *Meldrum*'s acid, 120°, 3 h; 99% (**13**), 99% (**14**). *b*) C_{60}, DBU, I_2, toluene, r.t., 12 h; 28% (**15**), 26% (**16**).

3′-iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-C_{60}-I_h-3′ carboxylates **15** and **16**, respectively. The characteristic shielding effect due to the presence of the I-atom was observed for the cyclopropa C-atom in the ^{13}C-NMR spectra of both **15** and **16** (δ 14.81 (**15**) and 14.47 (**16**)).

All other fullerene derivatives reported in this paper were prepared by taking advantage of the versatile regioselective reaction developed by *Diederich* and co-workers [24] [25], which led to macrocyclic bis-adducts of C_{60} by a cyclization reaction at the C-sphere with bis-malonate derivatives in a double *Bingel* cyclopropanation. The cyclic fullerene bis-adduct **19** with no polar head group was obtained in two steps from **6** and 1,3-benzenedimethanol (**17**) (*Scheme 5*). Reaction of diol **17** with acid **6** in CH_2Cl_2

Scheme 5. *Preparation of* **19**

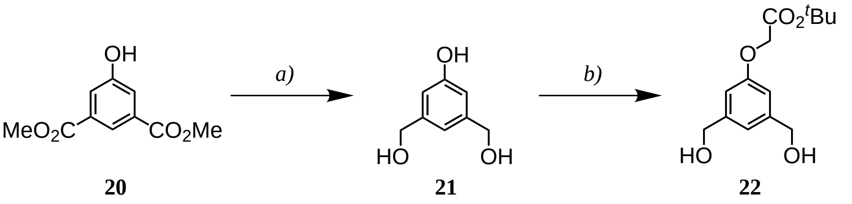


a) **6**, DCC, DMAP, CH_2Cl_2, 0° to r.t., 12 h; 60%. *b*) C_{60}, DBU, I_2, toluene, r.t., 12 h; 42%.

under esterification conditions (DCC, DMAP) gave bis-malonate **18** in 60% yield. Subsequent reaction with C_{60}, I_2, and DBU in toluene at room temperature afforded the desired cyclization product in 42% yield. The relative position of the two cyclopropane rings in **19** at the C_{60} core was determined based on the molecular symmetry deduced from the ^{1}H- and ^{13}C-NMR spectra (C_s) as well as on its UV/VIS spectrum. It was shown [25][26] that the absorption spectra of C_{60} bis-adducts are highly dependent on the addition pattern and characteristic for each regioisomer; the UV/VIS spectrum of **19** is fully consistent with those of previously reported analogous *cis-2* bis-adducts. In addition, it is well-established that the 1,3-phenylenebis(methylene)-tethered bis-malonates produce regioselectively the *cis-2* addition pattern at C_{60} [25][27].

The key building block for the preparation of the amphiphilic fullerene derivatives **37**–**39** bearing a carboxylic acid polar head group is dihydroxy ester **22**. The synthesis of this compound can be achieved in two steps starting from dimethyl 5-hydroxyisophthalate (**20**) (*Scheme 6*). The reduction of **20** by treatment with lithium aluminum hydride ($LiAlH_4$) in THF gave triol **21**. However, the yield of this reaction was found to be poorly reproducible (50–90%). This is mainly associated with the poor solubility of compound **21** in usual organic solvents and its tendency to stick to the aluminum salts resulting from the oxidation of $LiAlH_4$. Reaction of **21** with *tert*-butyl bromoacetate in DMF at 80° in the presence of K_2CO_3 afforded the desired diol **22**. The yield of this alkylation step was not too good (40–70%). Actually, by-products resulting from *C*-alkylations were also obtained, making the purification of **22** particularly difficult. It was quite surprising to observe *C*-alkylations under the conditions used for the preparation of **22** (K_2CO_3, DMF, 80°). Indeed, phenoxides usually undergo *O*-alkylation, and *C*-alkylation is not observed [28]. However, it has been shown that, in solvents such as water, which forms particularly strong H-bonds with the O-atom of the phenolate anion, this strong solvation decreases the reactivity at the O-atom and favors *C*-alkylation [29]. In our case, it is reasonable to ascribe the abnormally high proportion of *C*-alkylation to the presence of alcohol functions in **21** capable of giving intermolecular H-bonds with phenolate anions. As a result, the reactivity at the O-atoms is sufficiently decreased to allow competition between *C*- and *O*-alkylation.

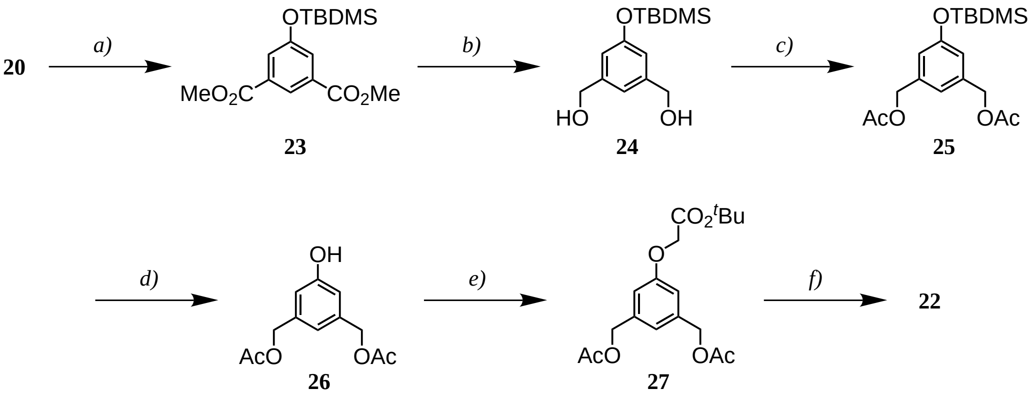
Scheme 6. *Preparation of Compound* **22**



a) $LiAlH_4$, THF, 0°, 4 h; 50–90%. *b*) *tert*-Butyl bromoacetate, K_2CO_3, DMF, 80°, 24 h; 40–70%.

To prevent this effect, it was decided to protect the two methanol functions of **21**. The new synthetic route for the preparation of **22** is depicted in *Scheme 7*. The phenol function of **20** was protected as a (*tert*-butyl)dimethylsilyl (TBDMS) ether by treatment with TBDMSCl in the presence of 1*H*-imidazole. Reduction of **23** with

Scheme 7. *Preparation of Compound* **22**



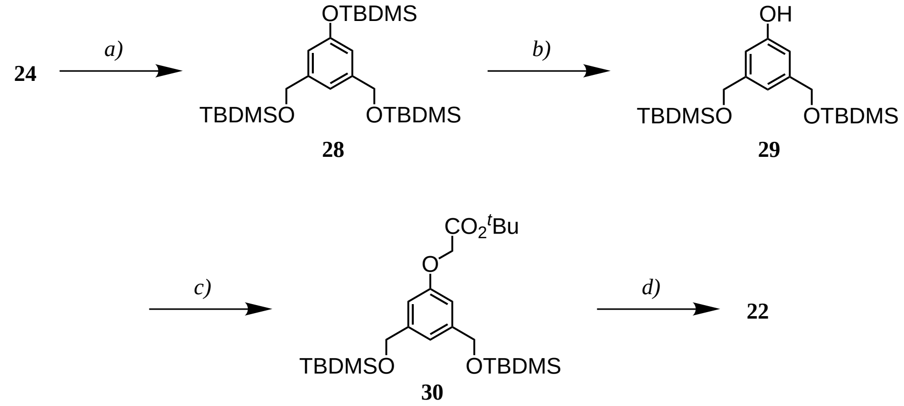
a) TBDMSCl, 1*H*-imidazole, DMF, 0°, 3 h; 86%. *b*) $LiAlH_4$, THF, 0°, 5 h; 97%. *c*) AcCl, pyridine, CH_2Cl_2, 0°, 1 h; 98%. *d*) Bu_4NF, THF, 0°, 30 min; 86%. *e*) *tert*-Butyl bromoacetate, K_2CO_3, DMF, 70°, 24 h; 90%. *f*) $NaHCO_3$, EtOH, H_2O, r.t., 24 h; 50%.

$LiAlH_4$ and reaction of the resulting **24** with acetyl chloride (AcCl) in CH_2Cl_2 in the presence of pyridine afforded **25**. Subsequent treatment with tetrabutylammonium fluoride (Bu_4NF) in THF gave phenol **26** in 86% yield. Reaction of **26** with *tert*-butyl bromoacetate in DMF at 80° in the presence of K_2CO_3 afforded the desired alkylation product **27** in 90% yield. In this case, by-products resulting from *C*-alkylation reactions could not be detected, showing that the unprotected methanol functions certainly play an important role for the abnormally high proportion of *C*-alkylation observed during the reaction of **21** with *tert*-butyl bromoacetate under the same conditions.

The hydrolysis of the two acetate protecting groups in **27** was attempted under various conditions, and the best results were obtained by treatment with $NaHCO_3$ in H_2O/MeOH 1:1 at room temperature. However, the yield of this step was always limited by partial hydrolysis of the *tert*-butyl ester. It was, therefore, decided to change the protecting groups of the two methanol functions (*Scheme 8*). Treatment of **24** with TBDMSCl in the presence of 1*H*-imidazole afforded **28** in 85% yield. The selective cleavage of the phenolic TBDMS ether in **28** was accomplished by Bu_4NF [30]. It has been shown that, under these conditions, the cleavage of phenolic TBDMS ethers is fast, whereas the desylilation of benzylic TBDMS ethers occurs slowly, allowing selective deprotection of the phenol group [30]. Treatment of **28** with 1 equiv. of Bu_4NF in THF at 0° for 15 min afforded indeed phenol **29** in good yields (88%) without significant cleavage of the benzylic TBDMS ether functions. Reaction of **29** with *tert*-butyl bromoacetate in DMF at 80° in the presence of K_2CO_3 afforded **30** in 95% yield. Subsequent treatment with a slight excess of Bu_4NF in THF at 0° for 3 h gave diol **22** in 99% yield. This last route for the preparation of **22** from **20** is the most efficient (overall yield of 58%) and allowed us to easily prepare this compound on a multigram scale.

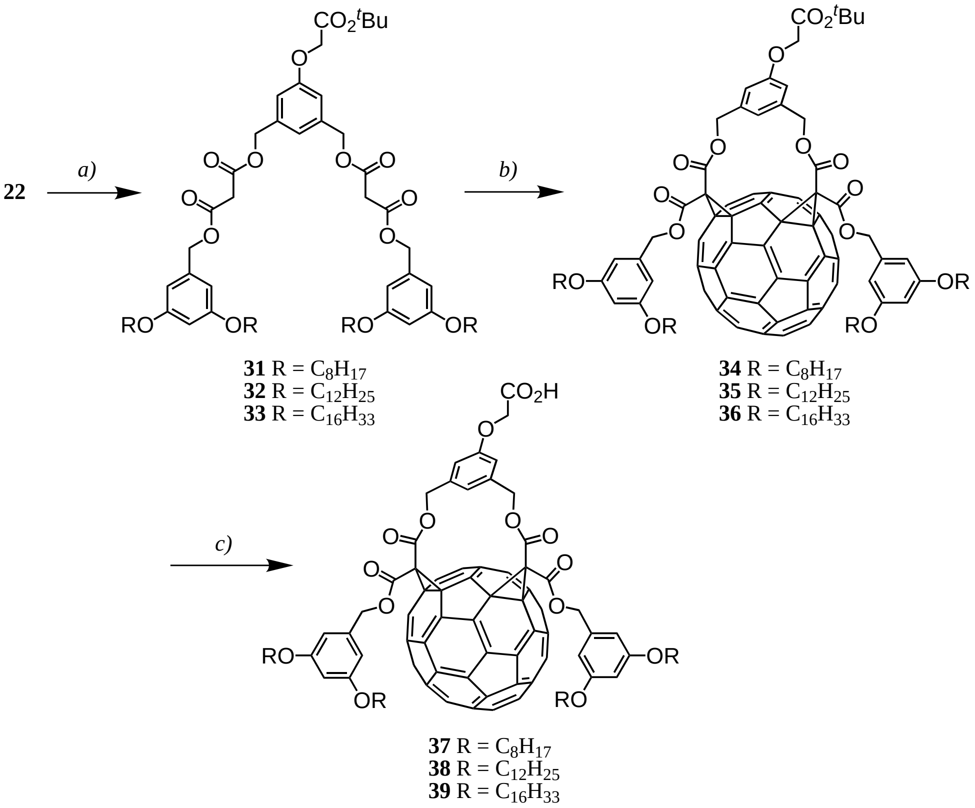
Reaction of diol **22** with acids **5**–**7** under esterification conditions (DCC, DMAP) yielded bis-malonates **31**–**33** (*Scheme 9*). Subsequent reaction with C_{60}, I_2, and DBU

Scheme 8. *Preparation of Compound* **22**



a) TBDMSCl, 1*H*-imidazole, DMF, 0°, 3 h; 85%. *b*) Bu_4NF (1 equiv.), THF, 0°, 15 min; 88%. *c*) *tert*-Butyl bromoacetate, K_2CO_3, DMF, 70°, 72 h; 95%. *d*) Bu_4NF (2.2 equiv.), THF, 0°, 3 h; 99%.

Scheme 9. *Preparation of the Amphiphilic Fullerene Derivatives* **37**–**39**



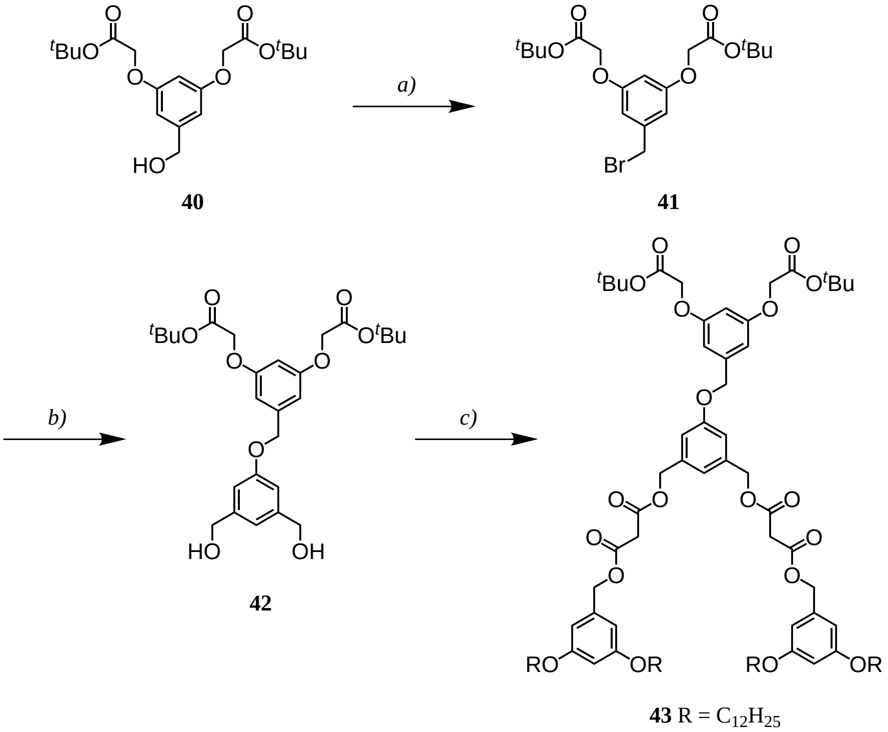
a) **5**, **6**, or **7**, DCC, DMAP, CH_2Cl_2, 0° to r.t., 12 h; 93% (**31**), 73% (**32**), 85% (**33**). *b*) C_{60}, DBU, I_2, toluene, r.t., 12 h; 59% (**34**), 45% (**35**), 53% (**36**). *c*) CF_3CO_2H, CH_2Cl_2, r.t., 4 h; 98% (**37**), 99% (**38**), 99% (**39**).

in toluene at room temperature afforded the corresponding C_s-symmetric *cis-2* bis-adducts **34**–**36** in remarkable yields (45–59%). Selective hydrolysis of the *tert*-butyl ester residue with CF_3CO_2H then afforded the desired amphiphilic fullerene derivatives **37**–**39** in quantitative yields.

For the synthesis of the related amphiphilic fullerene derivative **45** with two carboxylic acid groups, compound **40** was first prepared from 5-(hydroxymethyl)benzene-1,3-diol (**1**) and *tert*-butyl bromoacetate according to the procedure described by *Diederich* and co-workers [25]. Treatment of benzylic alcohol **40** with tetrabromomethane (CBr_4) and triphenylphosphine (PPh_3) in THF at 0° gave **41** in 83% yield (*Scheme 10*). Thanks to the increased reactivity of the benzyl bromide **41** when compared to *tert*-butyl bromoacetate, the alkylation of **21** with **41** could be performed in refluxing acetone in the presence of K_2CO_3 and 1,4,7,10,13,16-hexaoxacyclooctadecane ([18]crown-6). Under these conditions, by-products resulting from *C*-alkylation reactions were not formed as observed during the alkylation of **21** with *tert*-butyl bromoacetate in DMF, and compound **42** was thus obtained in 88% yield.

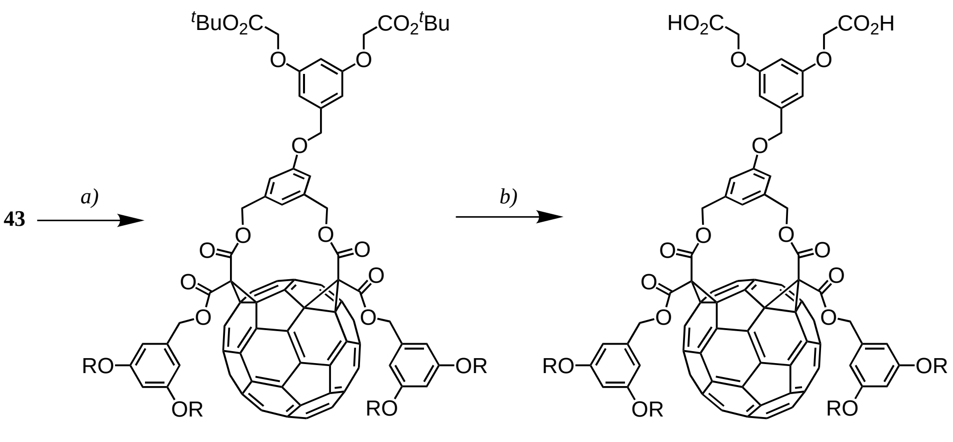
Esterification of diol dihydroxy compound **42** with carboxylic acid **6** in the presence of DCC and DMAP yielded bis-malonate **43** (84%) from which the C_3-symmetrical *cis-2* bis-adduct **44** was obtained in 44% yield by macrocyclization with C_{60} (*Scheme 11*).

Scheme 10. *Preparation of Bis-malonate* **43**



a) CBr_4, PPh_3, THF, 0°, 3 h; 73%. *b*) **21**, K_2CO_3, [18]crown-6, acetone, Δ, 12 h; 88%. *c*) **6**, DCC, DMAP, CH_2Cl_2, 0° to r.t., 12 h; 84%.

Scheme 11. *Preparation of the Amphiphilic Fullerene Derivative* **45**



44 R = $C_{12}H_{25}$ **45** R = $C_{12}H_{25}$

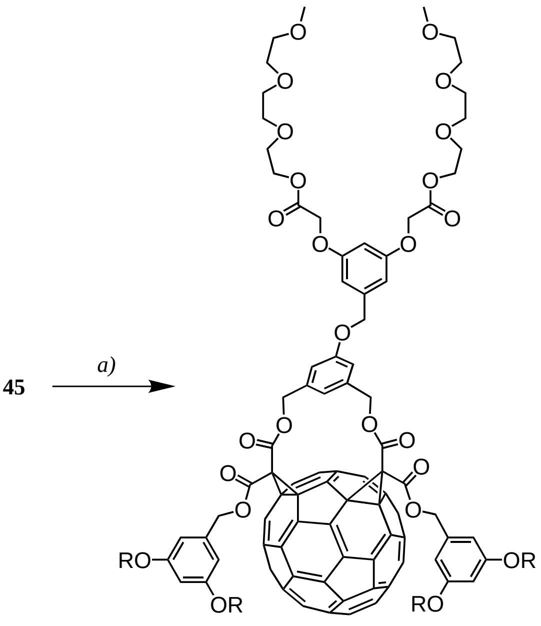
a) C_{60}, DBU, I_2, toluene, r.t., 12 h; 44%. *b*) CF_3CO_2H, CH_2Cl_2, r.t., 4 h; 98%.

Subsequent selective cleavage of the *tert*-butyl ester functions under acidic conditions provided the desired diacid **45**.

Amphiphilic fullerene derivatives **46** and **49** bearing ethylene glycol moieties as polar head groups were also prepared (*Schemes 12* and *13*). Compound **46** was obtained by esterification of **45** with triethylene glycol monomethyl ether. The bis-malonic acid **47** was prepared according to a previously reported procedure [14]. Reaction of **47** with alcohol **2** under esterification conditions (DCC, DMAP) yielded bis-malonate **48**. Subsequent reaction with C_{60}, I_2, and DBU in toluene at room temperature afforded the C_s-symmetric *cis-2* bis-adduct **49** in 45% yield.

Esterification of diol (+)-**50** with the malonic acid mono-ester **6** (DCC, DMAP, CH_2Cl_2) yielded bis-malonate (−)-**51** (*Scheme 14*). Treatment of C_{60} with (−)-**51**, I_2, and DBU in toluene afforded the two regioisomeric bis-adducts **52** and **53** in 12 and 20% yield, respectively. The relative positions of the two cyclopropa components in **52** and **53** at the C_{60} core was determined based on the molecular symmetry deduced from the ^{1}H- and ^{13}C-NMR spectra (C_1 for **52** and C_2 for **53**) as well as on the UV/VIS spectra. As previously mentioned, the absorption spectra of C_{60} bis-adducts are highly dependent on the addition pattern and characteristic for each regioisomer [25]; the UV/VIS spectra of **52** and **53** are fully consistent with those of previously reported analogous bis-adducts [25]. It is worth noting that the addition pattern in the *cis-3* bis-adduct **53** is chiral; therefore, two diastereoisomeric bis-adducts are possible; however, the very high asymmetric induction in the second intramolecular *Bingel* addition leads to the formation of **53** only. The diastereoselectivity of the tether-directed bis-cyclopropanation of the diethyl ester analog of (−)-**51** ((−)-(4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diylbis(methylene) diethyl dipropanedioate) has been previously established by *Diederich* and co-workers [25]. Furthermore, the absolute configuration of the resulting *cis-3* bis-adduct has been assigned by comparison of the theoretical and

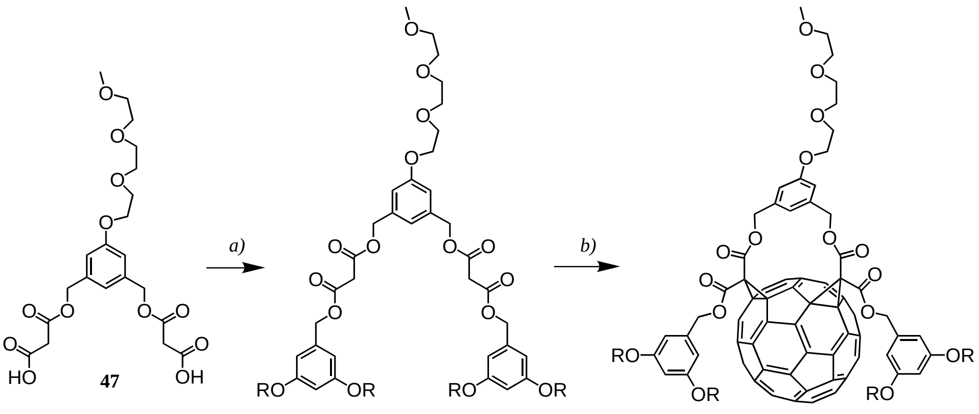
Scheme 12. *Preparation of the Amphiphilic Fullerene Derivative* **46**



46 R = $C_{12}H_{25}$

a) Triethylene glycol monomethyl ether, DCC, DMAP, CH_2Cl_2, 0° to r.t., 12 h; 88%.

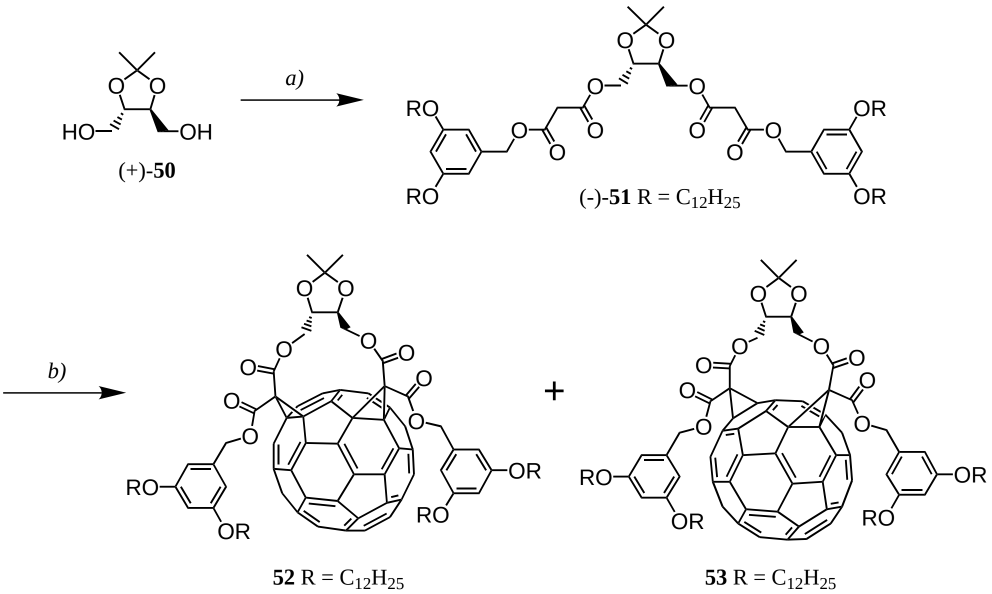
Scheme 13. *Preparation of the Amphiphilic Fullerene Derivative* **49**



48 R = C_8H_{17} **49** R = C_8H_{17}

a) **2**, DCC, DMAP, CH_2Cl_2, 0° to r.t., 24 h; 40%. *b*) C_{60}, DBU, I_2, toluene, r.t., 12 h; 45%.

Scheme 14. *Preparation of* **52** *and* **53**



a) **6**, DCC, DMAP, CH_2Cl_2, 0° to r.t., 12 h; 51%. *b*) C_{60}, DBU, I_2, toluene, r.t., 12 h, 12% (**52**), 20% (**53**).

experimental circular dichroism (CD) spectra by *Harada*, *Diederich*, and co-workers [31]. By analogy to this previously reported stereochemical assignment, the enantiomer of **53** obtained by double *Bingel* addition of (−)-**51** ((*S*,*S*)) to C_{60} has the absolute configuration (*S*,*S*,${}^{f}C$)¹).

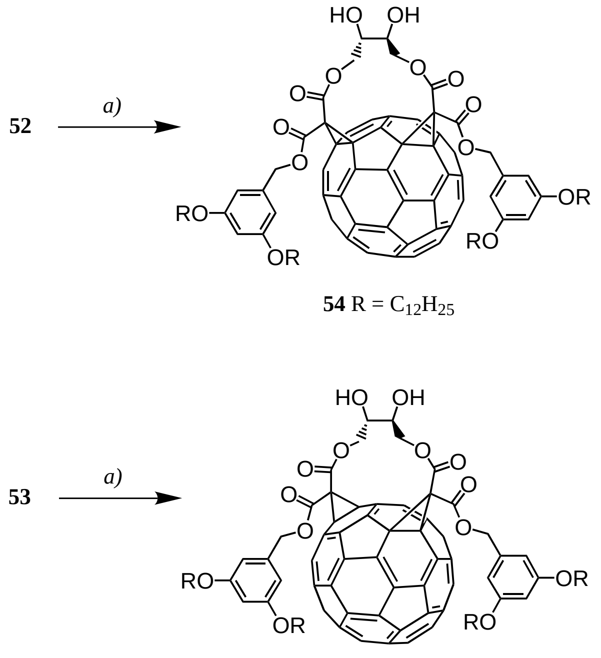
The cyclic isopropylidene acetal protecting group of the 1,2-diol function in **52** was cleaved by treatment with an excess of CF_3CO_2H in CH_2Cl_2/H_2O 2:1 at room temperature (*Scheme 15*). Complete deprotection was achieved after 2 days, and, despite this long reaction time, the various ester functions remained unchanged. Compound **54** was thus obtained in good yield (89%). The deprotection of **53** was carried out under similar conditions affording compound **55** in 69% yield.

2.2. Langmuir *Films at the Air-Water Interface.* While monolayers of pure C_{60} at the air-water interface are difficult to achieve, modification of the fullerene core with hydrophilic addends lead to significant improvements [10][11]. However, in most cases, aggregation remains a problem, and the resulting *Langmuir* films are rigid due to the strong intermolecular fullerene-fullerene interactions. Therefore, their transfer onto solid substrates appears to be difficult. On the other hand, it has also been shown that the incorporation of fullerenes into a matrix of an amphiphilic compound to produce mixed *Langmuir* films is efficient in preventing fullerene-fullerene interactions [4]. We decided to prepare a compound that combines the advantages of these two approaches, meaning a C_{60} derivative substituted at the same time with a polar head group (to

---

¹) For the specification of the absolute configuration of fullerene derivatives with a chiral functionalization pattern by a single descriptor ${}^{f}A$ (f = fullerene, *A* = anticlockwise) or ${}^{f}C$ (*C* = clockwise), see [32].

Scheme 15. *Preparation of the Amphiphilic Fullerene Derivatives* **54** *and* **55**



54 R = $C_{12}H_{25}$

55 R = $C_{12}H_{25}$

a) CF_3CO_2H, CH_2Cl_2, H_2O, 48 h; 89% (**54**), 67% (**55**).

obtain an adduct with an amphiphilic character) and long alkyl chains (to prevent the fullerene-fullerene interactions). Therefore, compound **10** was synthesized. The *Π*/*A* isotherm of compound **10** is depicted in *Fig. 1*.

Even if compound **10** behaves slightly better than pure C_{60}, a strong tendency to escape from the air-water interface to form three-dimensional aggregates is observed. Indeed, the molecular area extrapolated to zero surface pressure is $A_0 \approx 80$ Å^2, which is obviously too small for such a molecule, and BAM observations of the films obtained from **10** reveal the presence of defects in the structure. In addition, once the fullerene cores are in contact with each other, they irreversibly aggregate, and the layer does not expand back anymore. It appears that the expected protection resulting from the presence of the two long alkyl chains is not efficient enough, and fullerene-aggregation still occurs. To improve the spreading behavior of the amphiphilic fullerene derivatives, two additional long alkyl chains were attached to the C_{60} sphere, leading to **37**. In the design of this compound, it is worth noting that a cyclic structure was chosen to encapsulate the fullerene core in its addend and thus to prevent more efficiently the aggregation observed with other amphiphilic C_{60} derivatives such as **10**. The *Π*/*A* isotherm obtained with **37** is shown in *Fig. 2,a*. The surface pressure rises around $A \approx$ 145 Å^2, and the molecular area extrapolated at zero surface pressure A_0 is *ca.* 136 Å^2, in good agreement with the value estimated by molecular modeling. These films show

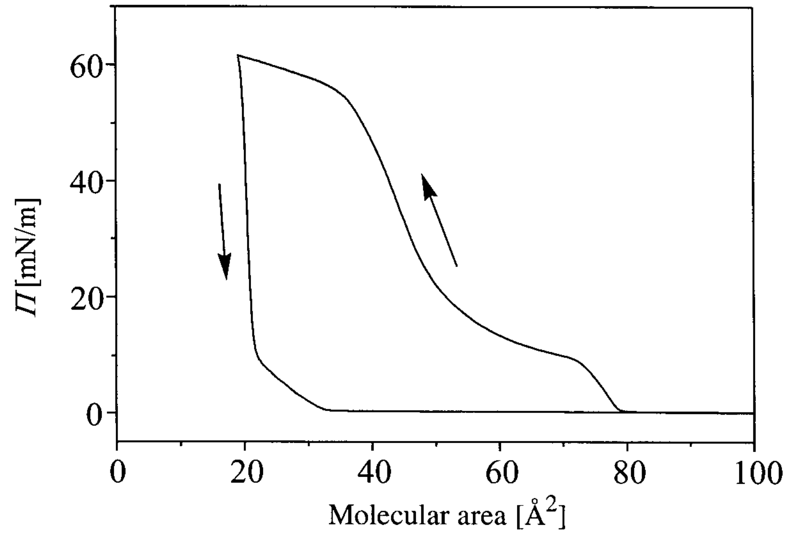


Fig. 1. *Hysteresis curve showing the irreversibility of the isotherm of* **10**

excellent reversibility if Π is kept below the collapse pressure $\Pi_c \approx 18$ mN · m^{-1}. The latter observation clearly indicates that the four alkyl chains are able to efficiently prevent the aggregation resulting from fullerene-fullerene interactions. At this point, it is also important to note that compound **19**, which has the same chemical structure as **37** but is deprived of the polar head group, does not form any film on the air-water interface. The surface pressure never increases, even at unrealistically small molecular areas. This observation illustrates the crucial need for a polar head group responsible for an attractive interaction with the aqueous subphase, thus forcing the molecules towards the water surface in a two-dimensional arrangement.

BAM Observations show that the film obtained from **37** is discontinuous at large molecular areas, with holes through which water can be seen (*Fig. 3,a*). These small circular domains shrink and disappear when the surface pressure reaches $\Pi \approx 10$ mN · m^{-1}, and, as long as the film does not enter the collapse regime, only homogeneous surfaces are observed. Simultaneous measurements of the surface potential were also performed (*Fig. 2, b*). The onset of the surface potential occurs at a molecular area $A \approx$ 180 Å^2. This is the area at which the molecules interact sufficiently for the film to be electrically homogeneous. The surface potential then grows rapidly and levels off at $A \approx 150$ Å. At this value, the surface pressure starts to increase as the molecules become mechanically squeezed together. This plateau in the surface potential indicates the formation of a homogeneous film as observed by BAM (*Fig. 3,b*). When the molecular area reaches $A \approx 120$ Å^2, the surface potential increases again. At the same time, a change of slope appears in the surface-pressure curve, indicating a greater compressibility of the film. The increase in the surface potential is the result of a thickening of the film, molecules being expelled from the water surface because the pressure becomes too high. Defects are then seen in the BAM pictures. This behavior indicates that the hydrophilic/hydrophobic balance is not very good for compound **37**,

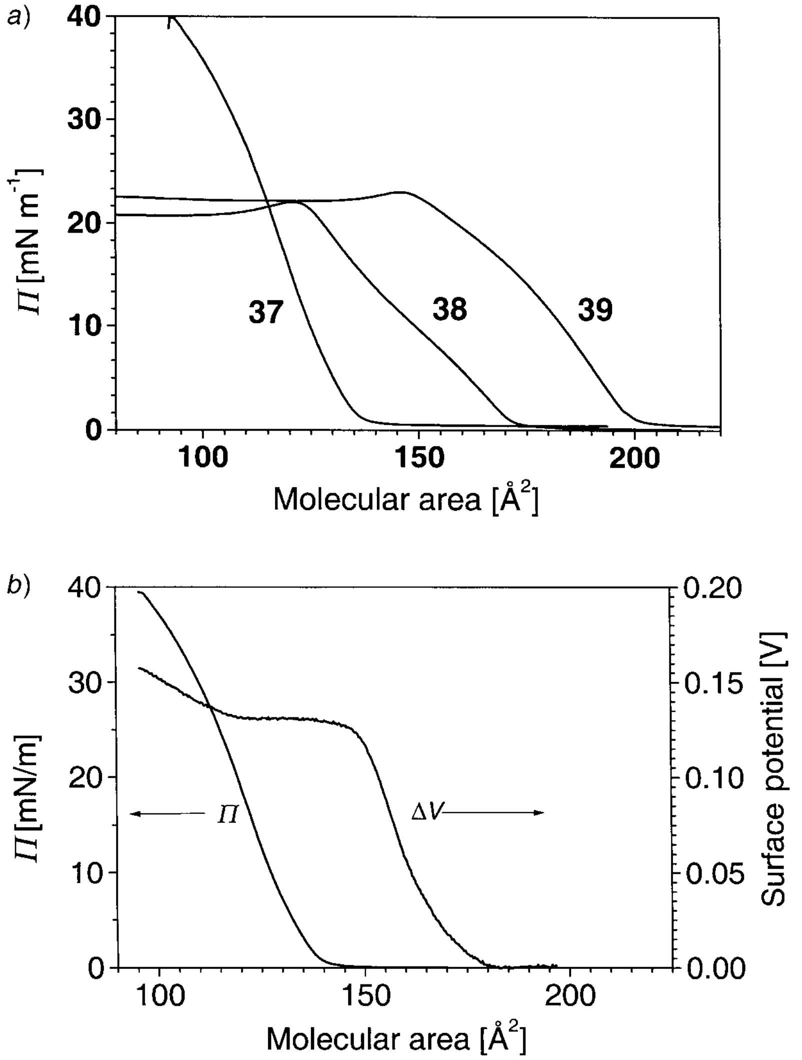


Fig. 2. a) *Pressure-area isotherms for* **37**–**39** *and* b) *surface pressure and surface potential as a function of molecular area for* **37**

the molecules being able to leave the air-water interface at rather low surface pressures (*ca.* 20 mN · m^{-1}).

Compounds **38** and **39**, the $C_{12}H_{25}$ and $C_{16}H_{33}$ analogues of **37**, respectively, also form good-quality *Langmuir* films, with collapse pressures around 20 mN · m^{-1} (*Fig. 2,a*). However, upon compression, **38** and **39** exhibit behavior somewhat different when compared to **37**. Indeed, the pressure levels off and becomes almost independent of the molecular area. Actually, when the chain length is increased, the hydrophobic/hydrophilic balance becomes less favorable, and as a result, the molecules are easier to

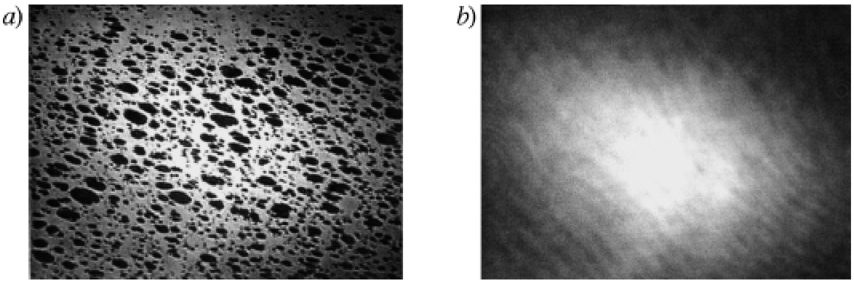


Fig. 3. Brewster-*angle microscopy images for* **37** *at* a) A = *180* $Å^2$ *and* b) A = *135* $Å^2$

expel from the surface. It is also interesting to note the values obtained for the molecular area extrapolated to zero surface pressure as a function of the chain length: $A_0 \approx 136$ $Å^2$ (C_8H_{17}), 170 $Å^2$ ($C_{12}H_{25}$), and 204 $Å^2$ ($C_{16}H_{33}$). This increase of the extrapolated molecular area with the chain length indicates that the chains are not perpendicular to the water surface.

The Π/A isotherm obtained for the amphiphilic fullerene bis-adduct **49** bearing a triethylene glycol polar head group is shown in *Fig. 4,a*. As observed for **37**–**39**, the films obtained from **49** show excellent reversibility upon successive compression/decompression cycles as long as the collapse pressure (20 $mN \cdot m^{-1}$) is not exceeded, and BAM observations reveal the good quality of the films (*Fig. 4,b–d*).

As seen in *Fig. 4,a*, the surface pressure takes off rather sharply at $A \approx 160$ $Å^2$, and the molecular area extrapolated to zero pressure is $A_0 \approx 158$ $Å^2$. This value is slightly higher than the one observed for the corresponding C_8H_{17} compound **37** with a carboxylic acid polar head group. We believe that the conformation of the molecules at the air-water interface must be similar, and the difference observed for the molecular area may be the result of a better anchoring of the carboxylic acid function on the water surface when compared to the triethylene glycol chain. Therefore, the repulsion of the C_8H_{17} chains from the water surface must be more effective in the case of **37**, and as a result, the molecule adopts a more compact structure, as schematically shown in *Fig. 5*. The long alkyl chains being not perpendicular to the water surface, this model is also in good agreement with the increase of the extrapolated molecular area with the chain length observed for **37**–**39**.

The Π/A isotherms of compounds **54** and **55** are very similar to that of **38**. The films obtained from **54** or **55** show also excellent reversibility upon successive compression/decompression cycles as long as the collapse pressure is not exceeded (*Fig. 6*), and the BAM pictures at the end of the compression look exactly like the picture shown in *Fig. 3,b* for **37**. The molecular area extrapolated to zero pressure and the collapse pressure being the same for **38**, **54**, and **55**, the hydrophilic-hydrophobic balance and the anchoring at the water surface must be similar for these three compounds.

For compound **46** with two triethylene glycol units and $C_{12}H_{25}$ chains, a sizeable increase in collapse pressure is observed when compared to the $C_{12}H_{25}$ analogues **38**, **54**, and **55** described above, indicating a more favorable hydrophilic-hydrophobic balance and better anchoring of the molecules at the water surface. The isotherm shows nice behavior: the surface pressure starts to increase smoothly at $A \approx 140$ $Å^2$ until the

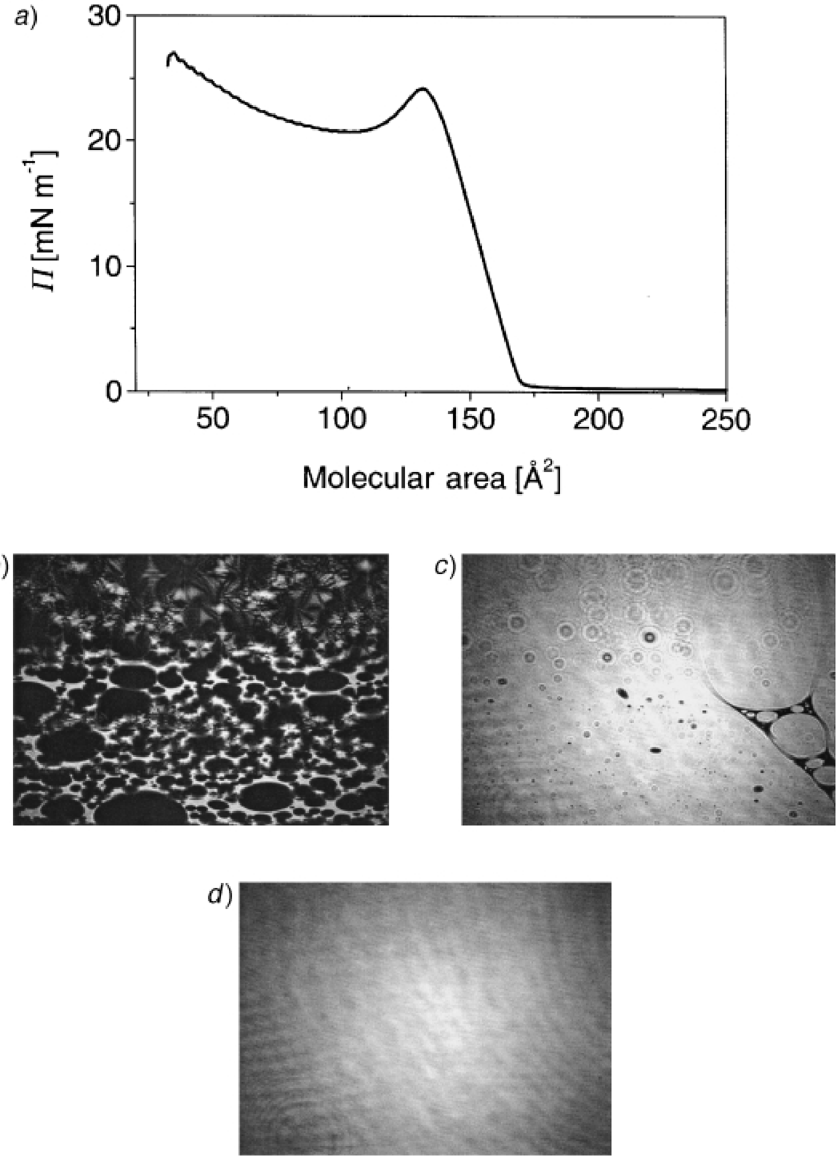


Fig. 4. a*) Pressure-area isotherm for* **49** *and* b–d*)* Brewster-*angle microscopy images for* **49** *at* b*)* A = *500 Å²,* c*)* A = *180 Å², and* d*)* A = *135 Å²*

collapse, which occurs at $\Pi_c \approx 40$ mN · m^{-1} (*Fig. 7,a*). Here again, the behavior is reversible if Π_c is not exceeded. A closer look at the shape of the various isotherms reveals that, for the compounds with a small polar head group, the surface pressure starts to increase steadily at some point, with almost constant compressibility, whereas, in the case of **46**, there is a first regime between $A \approx 145$ and 110 Å^2 where the

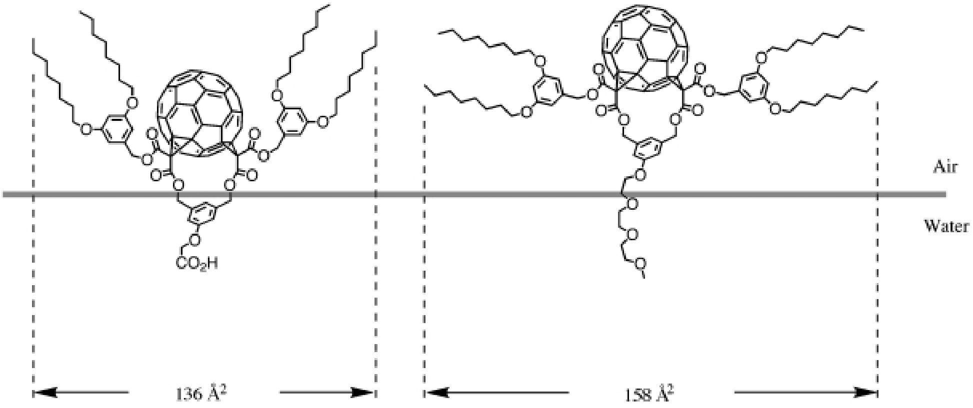


Fig. 5. *Schematic representation of* **37** *and* **49** *at the air-water interface showing how* **37** *adopts a more compact structure as compared to* **49**

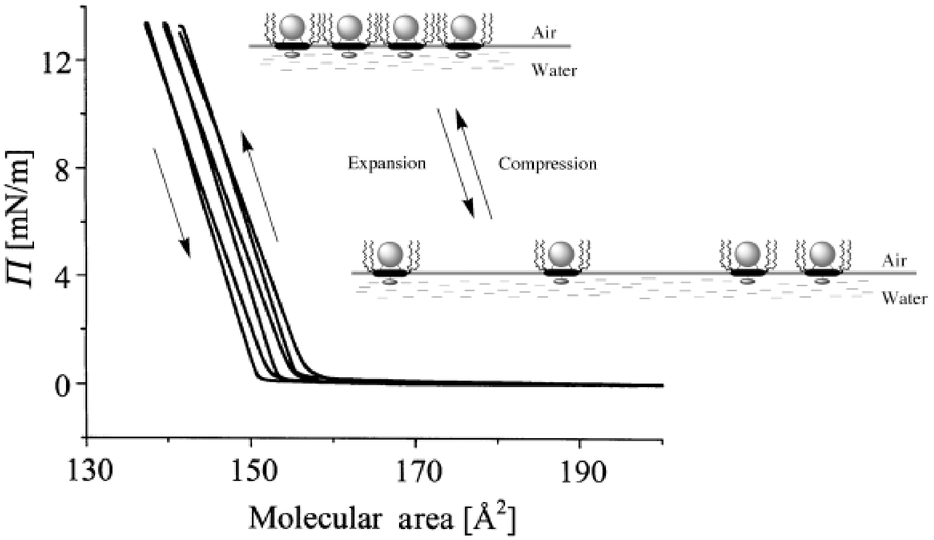


Fig. 6. *Successive compression/expansion cycles with a monolayer of* **54**, *showing the reversibility of the process* (the small shift observed for the successive cycles results from a film migration on the trough border and on the barriers at high pressure)

compressibility gradually increases before remaining constant. The molecular area extrapolated to zero pressure A_0 is *ca.* 120 Å^2. When compared to **38**, **54**, and **55** for which $A_0 \approx 170$ Å^2, the lower value obtained for **46** points to higher film density and, hence, better molecular packing. We believe that this smaller A_0 value and the observation of a 'liquid expanded phase' between 145 and 110 Å^2 must result from better anchoring of **46** when compared to analogous compounds with a smaller polar-head group. Indeed, the molecules being not easily expelled from the water surface at high pressure, they are forced to adopt a compact conformation in which the long alkyl chains are pushed perpendicular to the water surface. BAM Observations reveal a film

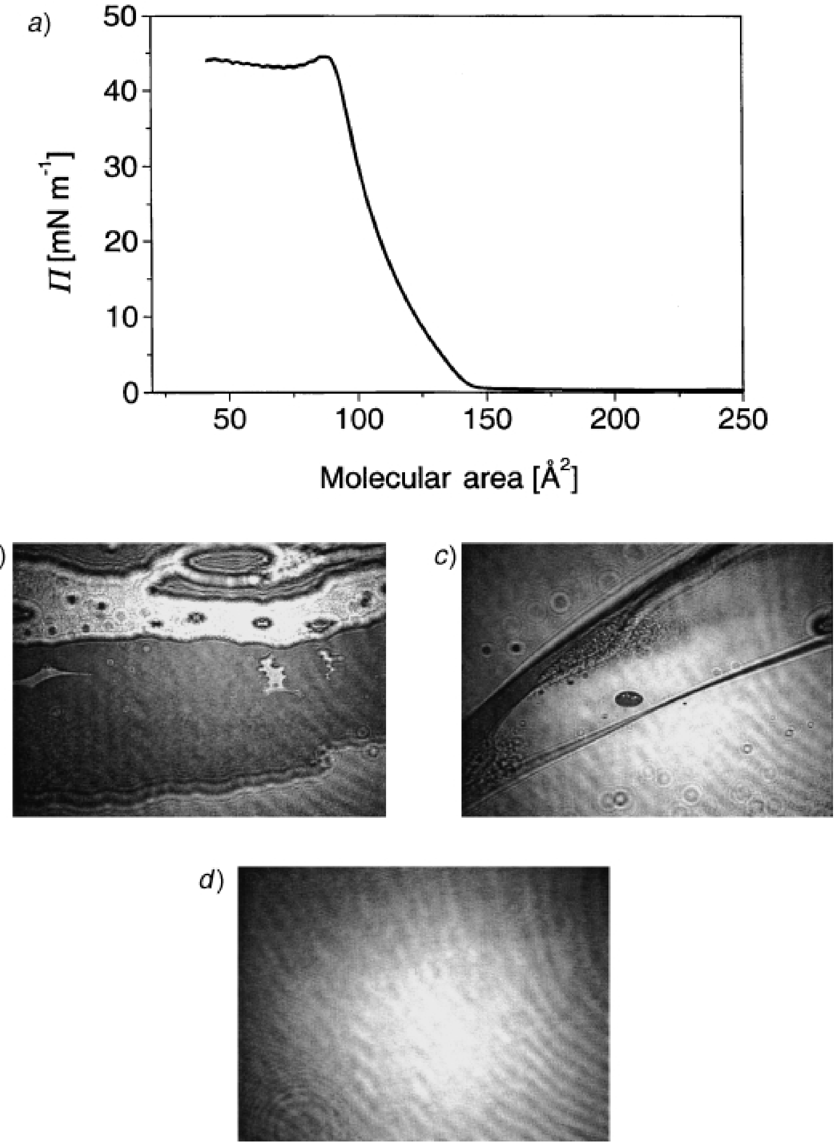


Fig. 7. a) *Pressure-area isotherm for* **46** *and* b–d) Brewster-*angle microscopy images for* **46** *at* b) $A = 290$ Å^2, c) $A = 200$ Å^2, *and* d) $A = 120$ Å^2

formation slightly different from that of the previous compounds: large islands cover the surface and gently merge upon compression, yielding a continuous and homogeneous *Langmuir* film (*Fig. 7,b–d*).

The Π/A isotherm obtained with compound **45** (*Fig. 8,a*) is similar to that of **46**, but the collapse pressure is slightly higher ($\Pi_c \approx 50$ mN · m^{-1}), and the surface pressure starts to rise even more gradually. BAM Observations show very nice merging of

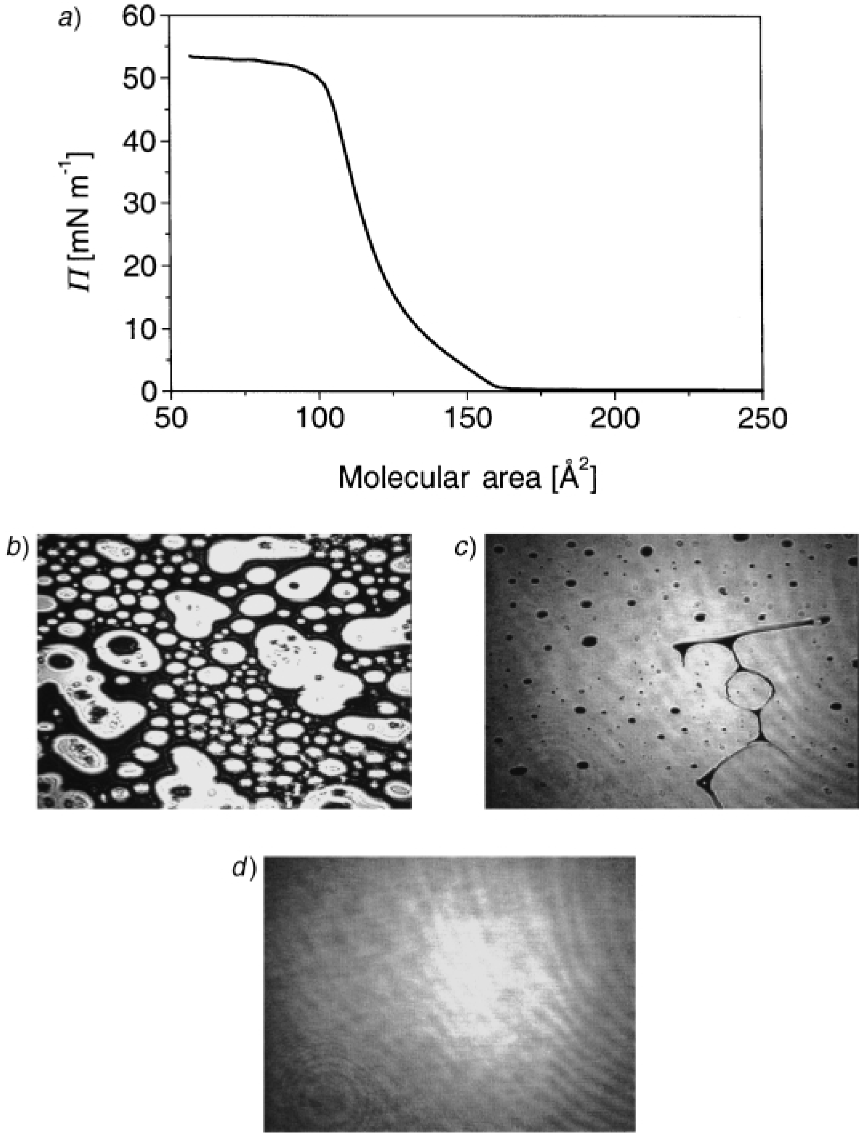


Fig. 8. a) *Pressure-area isotherm for* **45** *and* b–d) Brewster-*angle microscopy images for* **45** *at* b) A = *600* Å^2, c) A = *155* Å^2, *and* d) A = *108* Å^2

round-shaped domains, ending with a perfect film. The adjacent domains merge without any grain boundary being left as shown in *Fig. 8,b–d*.

2.3. Langmuir-Blodgett *Films*. The *Langmuir* films obtained from all amphiphilic fullerene bis-adducts were transferred onto solid substrates with the *LB* technique. It must be noted that, whereas hydrophobic substrates had to be used for the deposition of **37**–**39**, hydrophilic substrates could be used for the transfer of the other compounds, *i.e.* of **45**, **46**, **49**, **54**, and **55**. A great number of layers could be deposited without any problem. The excellent quality of the *LB* films prepared with these amphiphilic fullerene bis-adducts was deduced from the plot of their UV/VIS absorbance as a function of the layer number which results in straight lines, indicating an efficient stacking of the layers. Typical examples are shown in *Fig. 9*. The main feature of the

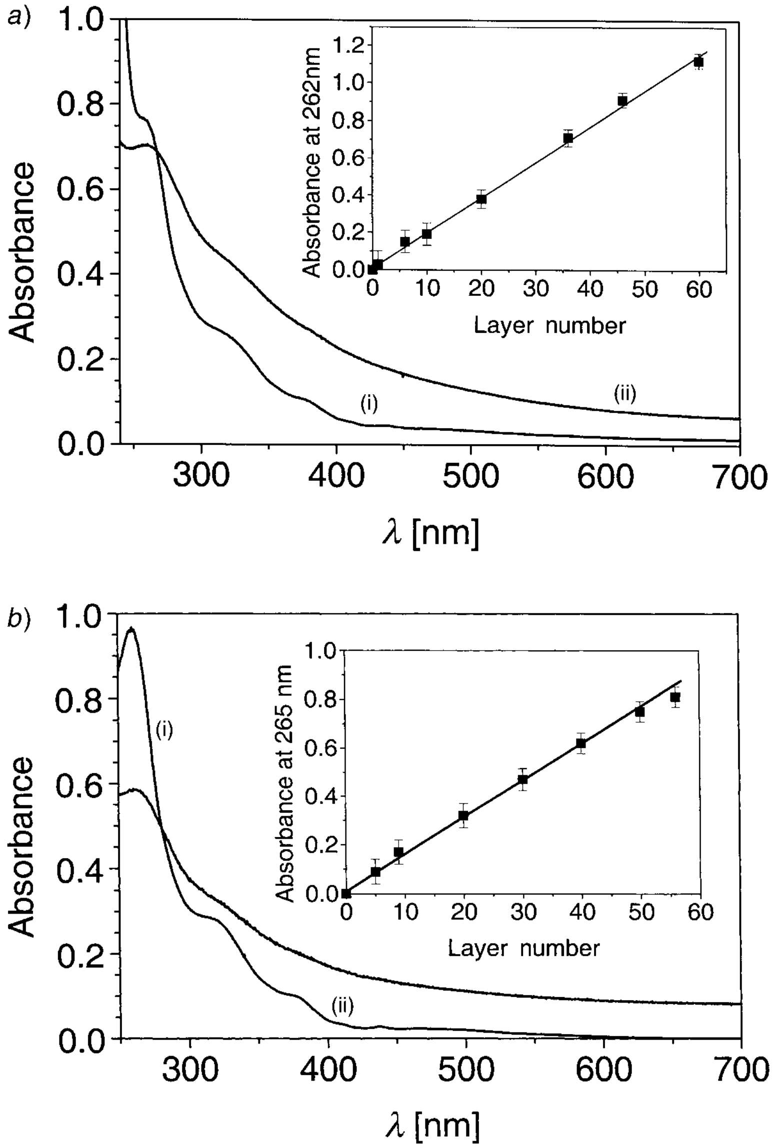


Fig. 9. a) *UV/VIS spectra of* **49** *in* CH_2Cl_2 (i) *and for* LB *film* (ii) (inset: plot of the absorbance at 265 nm against the layer number for *LB* films of **49**) *and* b) *UV/VIS spectra of* **45** *in* CH_2Cl_2 (i) *and for LB film* (ii) (inset: plot of the absorbance at 265 nm against the layer number for *LB* films of **45**)

UV/VIS spectra is the broadening of the absorption in the *LB* films when compared to the solution. The latter observation is indicative for fullerene-fullerene interactions within the *LB* films [10][33]. Due to the presence of the long alkyl chains around the C_{60} subunits within a layer, we believe that these fullerene-fullerene interactions may be the result of the contact of C-spheres from neighboring layers rather than within the layers.

3. Conclusions. – Some of the fundamental architectural requirements needed for the design of amphiphilic fullerene derivatives capable of forming stable *Langmuir* films were reported. The encapsulation of the fullerene in a cyclic addend surrounded by long alkyl chains is an efficient strategy to prevent the irreversible aggregation resulting from the strong fullerene-fullerene interactions usually observed for amphiphilic C_{60} derivatives at the air-water interface. Being repelled both from the water surface and from the C_{60} core, the four long alkyl chains act like buffers between the molecules and allow them to interact in an elastic way. All amphiphilic fullerene bis-adducts showed good spreading characteristics and reversible behavior upon successive compression/expansion cycles. We also showed that the balance of hydrophobicity to hydrophilicity can be easily modulated by changing the length of the surrounding alkyl chains or the nature of the polar-head group. The best results in terms of film formation and stability were obtained with compounds **45** and **46** having the largest polar-head group and dodecyl chains. We are currently investigating the physical properties of *LB* films made from these molecules, and more specifically their optical behavior in view of optical limiting applications.

Experimental Part

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **2** [34], **3** [35], **4** [15], **5** [34], **7** [15], **33** [15], **36** [15], **39** [15], **40** [25], and **47** [14] were prepared according to the literature. All reactions were performed in standard glassware under Ar. Evaporation and concentration were done at water-aspirator pressure and drying at 10^{-2} Torr. Column chromatography (CC): silica gel *60* (230 – 400 mesh, 0.040 – 0.063 mm) from *E. Merck*. TLC: glass sheets coated with silica gel *60 F_{254}* from *E. Merck*; visualization by UV light. Optical rotation: *Perkin-Elmer 241* polarimeter at $30 \pm 1°$. Due to the very dark color of the solns. optical rotation could not be determined for the fullerene derivatives **52** – **55**. UV/VIS spectra (λ_{max} in nm (ε)): *Hitachi U-3000* spectrophotometer. IR spectra (cm^{-1}): *ATI-Mattson Genesis-Series FTIR* instrument. NMR Spectra: *Bruker AC-200* (200 MHz) or *Bruker AM-400* (400 MHz); solvent peaks as reference; δ in ppm, *J* in Hz. FAB Mass spectra (*m*/*z*): *ZA-HF* instrument; 4-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg, France.

Langmuir *and* Langmuir-Blodgett *Films.* Spreading solns. were prepared by dissolving the compounds in $CHCl_3$ (analysis grade from *Carlo Erba*) at *ca.* 1.0 mg/ml concentrations. For a typical experiment, 50 µl of the fresh soln. was spread on the water surface with a microsyringe, and the film was then left 15 – 20 min to equilibrate before the compression started. Data were collected with a *KSV-LB5000* system (*KSV Instruments*, Helsinki, Finland) using a symmetrical compression *Teflon* trough and hydrophilic barriers in a dust-free environment. The whole setup was in a *Plexiglas* enclosure resting on a vibration-free table, and the trough temp. was controlled to $\pm 0.1°$. All isotherms were taken at 20°. Ultra-pure water ($\rho = 18.2\ M\Omega \cdot cm$) obtained from a *Milli-RO3-Plus* system combined with a *Milli-Q185 Ultra-Purification* system from *Millipore* was used for the subphase. Surface pressure was measured with the *Wilhelmy* plate method. The monolayers were compressed with speeds ranging from 2.5 to 10 $Å^2$/(molecule · min), with almost no incidence of the barrier velocity on the observed behavior. *Brewster*-angle microscopy (BAM) was performed with a *BAM-2-Plus* setup from *Nanofilm Technologies GmbH*. Illumination came from an Ar laser, images were recorded on a *CCD* camera; the field was 620 µm width × 500 µm height. *Langmuir-Blodgett* (*LB*) films were obtained by transfer onto quartz slides. Dipping parameters were not very stringent, and usually a dipping speed $V_{dip} \approx 2$ mm/min was applied. Transfers were performed at surface pressures of 15 (**37**–**39**, **49**, **54**, and **55**) or 40 mN/m (**45** and **46**). In all the cases, the transfer ratios were 1 ± 0.1 and Y-type multilayer films were obtained.

[3,5-Bis(dodecyloxy)phenyl]methyl Hydrogen Propanedioate (**6**). A mixture of **3** (26.64 g, 55.87 mmol) and *Meldrum*'s acid (8.05 g, 55.87 mmol) was heated at 120° for 3 h. Cooling and drying (10^{-2} Torr, 24 h) provided **6** (31.10 g, 99%). Pale yellow crystals. M.p. 40°. IR (CH_2Cl_2): 1748 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.88 (*t*, *J* = 6, 6 H); 1.26 (*m*, 36 H); 1.77 (*m*, 4 H); 3.50 (*s*, 2 H); 3.93 (*t*, *J* = 6, 4 H); 5.14 (*s*, 2 H); 6.42 (*t*, *J* = 2, 1 H); 6.47 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.05; 22.62; 25.97; 29.16; 29.29; 29.34; 29.55; 31.87; 40.78; 67.46; 68.00; 101.22; 106.38; 136.88; 160.39; 166.37; 171.38.

[3,5-Bis(dodecyloxy)phenyl]methyl 1,1-Dimethylethyl Propanedioate (**8**). DCC (806 mg, 3.91 mmol) was added to a stirred soln. of **6** (2.0 g, 3.55 mmol), ^{t}BuOH (290 mg, 3.91 mmol), and DMAP (87 mg, 0.71 mol) in CH_2Cl_2 (100 ml) at 0°. After 1 h, the mixture was allowed to slowly warm to r.t. (within 1 h), then stirred for 12 h, filtered, and evaporated. CC (SiO_2, hexane/CH_2Cl_2 4:3) yielded **8** (1.68 g, 76%). Colorless oil. IR (CH_2Cl_2): 1727, 1746 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 6 H); 1.28 (*m*, 36 H); 1.46 (*s*, 9 H); 1.77 (*m*, 4 H); 3.35 (*s*, 2 H); 3.93 (*t*, *J* = 6, 4 H); 5.10 (*s*, 2 H); 6.41 (*t*, *J* = 2, 1 H); 6.49 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 25.81; 26.03; 27.85; 29.22; 29.36; 29.62; 31.90; 42.85; 66.91; 67.99; 81.98; 101.03; 106.34; 137.40; 160.43; 165.54; 166.68. Anal. calc. for $C_{38}H_{66}O_6$ (618.9): C 73.74, H 10.75; found: C 73.59; H 10.81.

*[3,5-Bis(dodecyloxy)phenyl]methyl 1,1-Dimethylethyl 3′*H*-Cyclopropa[1,9][5,6]fullerene-C_{60}-*I*$_h$-3′,3′-dicarboxylate* (**9**). DBU (0.4 ml, 2.78 mmol) was added to a stirred soln. of C_{60} (600 mg, 0.83 mmol), I_2 (212 mg, 0.83 mmol), and **8** (515 mg, 0.83 mmol) in toluene (600 ml) at r.t. The soln. was stirred for 12 h at r.t., filtered through a short plug of SiO_2 (toluene), and evaporated. CC (SiO_2, toluene/hexane 1:1) yielded **9** (508 mg, 46%). Dark red glassy product. UV/VIS (CH_2Cl_2): 257 (104900), 324 (33980), 426 (2940), 486 (1670), 688 (200). IR (CH_2Cl_2): 1740 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 6 H); 1.27 (*m*, 36 H); 1.62 (*s*, 9 H); 1.76 (*m*, 4 H); 3.93 (*t*, *J* = 6, 4 H); 5.44 (*s*, 2 H); 6.44 (*t*, *J* = 2, 1 H); 6.63 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.12; 22.67; 26.07; 27.91; 29.23; 29.32; 29.38; 29.60; 31.87; 52.97; 68.06; 68.67; 71.76; 85.14; 101.58; 107.18; 136.58; 138.73; 139.05; 140.75; 140.80; 141.80; 141.85; 142.11; 142.88; 143.78; 144.38; 144.47; 144.59; 144.73; 145.05; 145.11; 145.32; 160.46; 162.03; 163.60. Anal. calc. for $C_{98}H_{64}O_6$ (1337.6): C 88.00, H 4.82; found: C 87.91, H 4.92.

*[3,5-Bis(dodecyloxy)phenyl]methyl Hydrogen 3′*H*-Cyclopropa[1,9][5,6]fullerene-C_{60}-*I*$_h$-3′,3′-dicarboxylate* (**10**). A soln. of **9** (431 mg, 0.32 mmol) and CF_3COOH (25 ml) in CH_2Cl_2 (150 ml) was stirred at r.t. for 4 h. The mixture was then washed with H_2O, dried ($MgSO_4$), and evaporated. Recrystallization from CH_2Cl_2/hexane yielded **10** (402 mg, 97%). Dark red solid. M.p. >200°. UV/VIS (CH_2Cl_2): 258 (100200), 325 (32890), 425 (3230), 470 (1840), 687 (180). IR (CH_2Cl_2): 1740 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 6 H); 1.26 (*m*, 36 H); 1.71 (*m*, 4 H); 3.90 (*t*, *J* = 6, 4 H); 5.47 (*s*, 2 H); 6.41 (*t*, *J* = 2, 1 H); 6.61 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.16; 22.71; 28.18; 29.29; 29.38; 29.50; 29.87; 31.93; 51.87; 68.21; 69.15; 71.38; 101.90; 107.26; 136.52; 138.22; 139.77; 140.77; 141.73; 141.82; 142.11; 142.78; 142.90; 143.74; 143.80; 144.38; 144.57; 144.84; 145.05; 145.11; 145.17; 145.30; 160.37; 163.65; 167.20. Anal. calc. for $C_{94}H_{56}O_6$ (1281.5): C 88.10, H 4.40; found: C 87.99, H 4.51.

*[3,5-Bis(dodecyloxy)phenyl]methyl 3′-Iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-C_{60}-*I*$_h$-3′-carboxylate* (**11**). DBU (0.4 ml, 2.78 mmol) was added to a stirred soln. of C_{60} (300 mg, 0.42 mmol), **6** (258 mg, 0.46 mmol), and I_2 (317 mg, 1.25 mmol) in toluene (300 ml) at r.t. After 12 h, additional portions of **6** (124 mg, 0.23 mmol) and I_2 (159 mg, 0.62 mmol) were added, and the mixture was stirred for another 12 h, filtered through a pad of SiO_2 (toluene), and evaporated. CC (SiO_2, hexane/toluene 4:3) afforded **11** (141 mg, 25%). Dark red glassy product. UV/VIS (CH_2Cl_2): 256 (120700), 321 (43760), 426 (2960), 479 (1780), 682 (180). IR ($CHCl_3$): 1737 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 6 H); 1.26 (*m*, 36 H); 1.74 (*m*, 4 H); 3.90 (*t*, *J* = 6, 4 H); 5.45 (*s*, 2 H); 6.41 (*t*, *J* = 2, 1 H); 6.62 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.20; 14.37; 22.72; 26.17; 29.29; 29.39; 29.47; 29.65; 29.66; 29.67; 29.72; 31.94; 68.11; 69.26; 75.47; 101.97; 107.18; 136.60; 137.31; 139.12; 140.82; 140.96; 142.02; 142.13; 142.18; 142.36; 142.81; 142.88; 142.96; 142.98; 143.06; 143.24; 143.57; 143.77; 144.19; 144.29; 144.48; 144.67; 144.69; 144.70; 144.71; 144.74; 145.09; 145.15; 145.18; 145.25; 145.33; 145.47; 147.77; 160.43; 165.99. FAB-MS: 1363.2 (10, MH^+), 719.9 (100, C_{60}^+). Anal. calc. for $C_{93}H_{55}IO_4$ (1363.4): C 81.93, H 4.07; found: C 81.76, H 4.12.

*[3,5-Bis(dodecyloxy)phenyl]methyl 3′*H*-Cyclopropa[1,9][5,6]fullerene-C_{60}-*I*$_h$-3′-carboxylate* (**12**). A soln. of DMAP (1 mg, 0.008 mmol) and **10** (53 mg, 0.041 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 6 h and evaporated. CC (SiO_2, CH_2Cl_2/hexane 1:1) yielded **12** (37 mg, 72%). Dark red glassy product. UV/VIS (CH_2Cl_2): 258 (100430), 325 (30570), 426 (2840), 484 (1590), 688 (190). IR ($CHCl_3$): 1740 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 6 H); 1.27 (*m*, 36 H); 1.79 (*m*, 4 H); 3.97 (*t*, *J* = 6, 4 H); 4.84 (*s*, 1 H); 5.41 (*s*, 2 H); 6.48 (*t*, *J* = 2, 1 H); 6.67 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.14; 22.90; 26.09; 29.28; 29.35;

29.43; 29.63; 31.92; 38.96; 68.16; 68.18; 70.52; 101.58; 107.00; 136.38; 136.84; 140.49; 140.89; 141.12; 142.07; 142.17; 142.40; 142.78; 142.94; 143.23; 143.71; 143.93; 144.38; 144.57; 144.66; 145.05; 145.18; 145.23; 145.53; 145.62; 148.17; 160.61; 166.08. Anal. calc. for $C_{93}H_{56}O_4$ (1237.5): C 90.27, H 4.56; found: C 89.98, H 4.57.

Phenylmethyl Hydrogen Propanedioate (**13**). As described for **6**, with benzyl alcohol (2.25 g, 20.82 mmol) and *Meldrum*'s acid (3.0 g, 20.82 mmol). Cooling and drying (10^{-2} Torr, 24 h) provided **13** (3.99 g, 99%). Colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.50 (*s*, 2 H); 5.23 (*s*, 2 H); 7.38 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 40.84; 67.49; 128.29; 128.48; 128.54; 134.90; 166.37; 171.67.

2-(2-Ethoxyethoxy)ethyl Hydrogen Propanedioate (**14**). As described for **6**, with diethylene glycol monoethyl ether (2.79 g, 20.82 mmol) and *Meldrum*'s acid (3.0 g, 20.82 mmol). Cooling and drying (10^{-2} Torr, 24 h) provided **14** (4.56 g, 99%). Pale yellow oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.22 (*t*, *J* = 7, 3 H); 3.47 (*s*, 2 H); 3.55 (*q*, *J* = 7, 2 H); 3.61 (*m*, 4 H); 3.74 (*t*, *J* = 5, 2 H); 4.35 (*t*, *J* = 5, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.68; 40.68; 64.33; 66.47; 68.51; 69.37; 70.19; 166.62; 169.32.

*Phenylmethyl 3′-Iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-*C_{60}*-*I$_h$*-3′-carboxylate* (**15**). As described for **11**, with **13** (89 mg, 0.46 mmol), C_{60} (300 mg, 0.42 mmol), I_2 (317 mg, 1.25 mmol), and DBU (0.2 ml, 1.39 mmol) in toluene (300 ml). CC (SiO_2, hexane/toluene 2 : 1) afforded **15** (117 mg, 28%). Dark red solid. M.p. > 200°. UV/VIS (CH_2Cl_2): 254 (97860), 320 (35500), 426 (2350), 486 (1470), 681 (160). ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.23 (*s*, 2 H); 7.40 (*m*, 3 H); 7.53 (*m*, 2 H). ^{13}C-NMR (C_6D_6, 50 MHz): 14.81; 69.04; 76.03; 128.71; 128.01; 128.49; 135.11; 137.63; 139.39; 140.98; 141.17; 142.27; 142.30; 142.56; 142.99; 143.15; 143.17; 143.41; 143.76; 144.01; 144.40; 144.62; 144.75; 144.88; 144.97; 145.38; 145.51; 146.09; 148.13; 166.04.

*2-(2-Ethoxyethoxy)ethyl 3′-Iodo-3′*H*-cyclopropa[1,9][5,6]fullerene-*C_{60}*-*I$_h$*-3′-carboxylate* (**16**). As described for **11**, with **14** (101 mg, 0.46 mmol), C_{60} (300 mg, 0.42 mmol), I_2 (317 mg, 1.25 mmol), and DBU (0.2 ml, 1.39 mmol) in toluene (300 ml). CC (SiO_2, CH_2Cl_2/hexane 5 : 1) afforded **16** (109 mg, 26%). Dark red solid. M.p. > 200°. UV/VIS (CH_2Cl_2): 255 (128100), 320 (43300), 426 (2510), 489 (1570), 683 (190). IR ($CHCl_3$): 1739 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.22 (*t*, *J* = 7, 3 H); 3.54 (*q*, *J* = 7, 2 H); 3.60 (*m*, 4 H); 3.71 (*t*, *J* = 5, 2 H); 4.70 (*t*, *J* = 5, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.47; 15.24; 66.43; 66.75; 68.83; 69.85; 70.81; 75.50; 137.36; 139.14; 140.87; 141.06; 142.04; 142.19; 142.38; 142.84; 143.03; 143.09; 143.26; 143.61; 143.83; 144.22; 144.47; 144.60; 144.75; 144.82; 145.16; 145.24; 145.37; 145.75; 147.86; 166.05. Anal. calc. for $C_{68}H_{13}O_4I$ (1020.7): C 80.01, H 1.28; found: C 80.03, H 1.53.

1,3-Phenylenebis(methylene) Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Dipropanedioate (**18**). As described for **8**, with **17** (700 mg, 3.62 mmol), DCC (1.61 g, 7.78 mmol), DMAP (120 mg, 1.09 mmol), and **6** (4.27 g, 7.60 mmol) in CH_2Cl_2 (100 ml). CC (SiO_2, CH_2Cl_2/hexane 3 : 1) afforded **18** (2.65 g, 60%). Colorless oil. IR (CH_2Cl_2): 1754 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6.5, 12 H); 1.27 (*m*, 72 H); 1.76 (*m*, 8 H); 3.49 (*s*, 4 H); 3.92 (*t*, *J* = 6.5, 8 H); 5.10 (*s*, 4 H); 5.18 (*s*, 4 H); 6.41 (*t*, *J* = 2, 2 H); 6.47 (*d*, *J* = 2, 4 H); 7.32 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.06; 22.62; 25.99; 29.19; 29.29; 29.34; 29.55; 31.87; 41.38; 66.79; 67.20; 67.99; 101.06; 106.36; 127.84; 128.13; 128.85; 135.63; 137.10; 160.40; 166.11. Anal. calc. for $C_{76}H_{122}O_{12}$ (1227.8): C 74.35, H 10.02; found: C 74.30, H 10.11.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} 4″,15″-Dioxo-3′,3″-(methanoxymethano[1,3]benzenomethanoxymethano)-3′*H*,3″*H*-dicyclopropa[1,9 : 3,15][5,6]fullerene-*C_{60}*-*I$_h$*-3′,3″-dicarboxylate* (**19**). DBU (0.2 ml, 1.39 mmol) was added to a stirred soln. of C_{60} (200 mg, 0.28 mmol), I_2 (178 mg, 0.70 mmol), and **18** (375 mg, 0.31 mmol) in toluene (500 ml). The soln. was stirred for 12 h, then filtered through a short plug of SiO_2, eluting first with toluene (to remove unreacted C_{60}) and then with CH_2Cl_2. CC (SiO_2, CH_2Cl_2/hexane 1 : 1) to yield **19** (226 mg, 42%). Dark orange glassy product. UV/VIS (CH_2Cl_2): 259 (139470), 319 (41220), 378 (14470), 437 (4080), 466 (sh, 3340). IR (CH_2Cl_2): 1749 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6.5, 12 H); 1.27 (*m*, 72 H); 1.73 (*m*, 8 H); 3.86 (*t*, *J* = 6.5, 4 H); 5.05 (*d*, *J* = 13, 2 H); 5.23 (*d*, *J* = 12, 2 H); 5.35 (*d*, *J* = 12, 2 H); 5.84 (*d*, *J* = 12, 2 H); 6.37 (*t*, *J* = 2, 2 H); 6.48 (*d*, *J* = 2, 4 H); 7.27 (*m*, 2 H); 7.37 (*m*, 1 H); 7.51 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.13; 22.68; 26.09; 29.25; 29.35; 29.44; 29.63; 29.68; 31.90; 49.03; 66.88; 67.31; 68.06; 68.61; 70.58; 101.54; 107.06; 123.66; 126.61; 128.55; 134.48; 135.79; 136.17; 136.56; 136.69; 137.77; 140.00; 141.03; 141.12; 142.28; 142.69; 143.14; 143.55; 143.73; 143.96; 144.12; 144.31; 144.57; 144.92; 144.98; 145.14; 145.32; 145.56; 145.71; 146.04; 147.28; 147.44; 148.62; 160.37; 162.55; 162.66. Anal. calc. for $C_{136}H_{118}O_{12}$ (1944.4): C 84.01, H 6.12; found: C 84.27, H 6.16.

5-Hydroxybenzene-1,3-dimethanol (**21**). A soln. of **20** (10 g, 47.58 mmol) in dry THF (50 ml) was added dropwise within 30 min to a soln. of $LiAlH_4$ (2.71 g, 71.36 mmol) in dry THF (50 ml) at 0°. The resulting mixture was allowed to slowly warm to r.t. (within 1 h) and stirred for another 3 h. MeOH (10 ml) was then carefully added. The mixture was filtered (*Celite*), dried ($MgSO_4$), and evaporated: **21** (6.2 g, 84%). Colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.67 (*s*, 4 H); 6.77 (*d*, *J* = 2, 2 H); 6.96 (*t*, *J* = 2, 1 H). Anal. calc. for $C_8H_{10}O_3$ (154.2): C 62.33, H 6.54; found: C 62.75, H 6.27.

1,1-Dimethylethyl [3,5-Bis(hydroxymethyl)phenoxy]acetate (**22**) *from* **21**. A soln. of **21** (3.60 g, 23.35 mmol), *tert*-butyl bromoacetate (3.62 ml, 24.52 mmol) and K_2CO_3 (6.80 g, 49.00 mmol) in DMF (150 ml) was stirred at 80° for 48 h. The mixture was evaporated, the residue taken up with Et_2O (100 ml), filtered (*Celite*), and evaporated. CC (SiO_2, 5% MeOH/CH_2Cl_2) yielded **22** (4.22 g, 70%). Colorless solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.49 (*s*, 9 H); 1.92 (*t*, *J* = 6, 2 H); 4.53 (*s*, 2 H); 4.65 (*d*, *J* = 6, 4 H); 6.83 (*d*, *J* = 2, 2 H); 6.96 (*t*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 28.00; 64.84; 65.60; 82.49; 112.04; 118.23; 142.91; 158.22; 168.12. Anal. calc. for $C_{14}H_{20}O_5$ (268.3): C 62.67, H 7.51; found: C 62.81, H 7.55.

Dimethyl 5-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}benzene-1,3-dicarboxylate (**23**). A mixture of TBDMSCl (4.99 g, 33.29 mmol), 1*H*-imidazole (4.32 g, 63.42 mmol), and **20** (6.67 g, 31.71 mmol) in DMF (125 ml) was stirred at 0° for 3 h and evaporated. The residue was taken up with Et_2O, washed with brine, dried ($MgSO_4$), and evaporated. CC (SiO_2, CH_2Cl_2) yielded **23** (8.84 g, 86%). White solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.24 (*s*, 6 H); 1.01 (*s*, 9 H); 3.94 (*s*, 6 H); 7.68 (*d*, *J* = 2, 2 H); 8.30 (*t*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): -4.54; 18.15; 25.58; 52.36; 123.63; 125.32; 131.77; 155.89; 166.08. Anal. calc. for $C_{16}H_{24}O_5Si$ (324.4): C 59.23, H 7.46; found: C 59.44, H 7.47.

5-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}benzene-1,3-dimethanol (**24**). A 1M $LiAlH_4$ soln. in dry THF (21.6 ml, 21.6 mmol) was added dropwise to a stirred soln. of **23** (5.00 g, 15.41 mmol) in dry THF (135 ml) at 0°. The resulting mixture was stirred for 5 h at 0°, then MeOH was carefully added. The resulting mixture was filtered (*Celite*) and evaporated. CC (SiO_2, 10% MeOH/CH_2Cl_2) yielded **24** (4.04 g, 97%). Colorless glassy product. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.21 (*s*, 6 H); 0.99 (*s*, 9 H); 1.69 (*t*, *J* = 6, 2 H); 4.66 (*d*, *J* = 6, 4 H); 6.78 (br. *s*, 2 H); 6.96 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): -4.42; 18.14; 25.64; 64.90; 117.61; 118.14; 142.73; 155.99.

5-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}benzene-1,3-dimethanol Diacetate (**25**). A soln. of acetyl chloride (6.20 g, 79.70 mmol) in CH_2Cl_2 (50 ml) was added dropwise within 30 min to a stirred soln. of **24** (8.56 g, 31.89 mmol) and pyridine (7.50 g, 9.57 mmol) in CH_2Cl_2 (50 ml) at 0°. The resulting soln. was stirred for 1 h at 0°, then washed with a sat. aq. NH_4Cl soln., dried ($MgSO_4$), and evaporated. CC (SiO_2, CH_2Cl_2/hexane 9:1) yielded **25** (10.14 g, 98%). Colorless oil. IR (CH_2Cl_2): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.21 (*s*, 6 H); 0.99 (*s*, 9 H); 2.19 (*s*, 6 H); 5.05 (*s*, 4 H); 6.79 (*d*, *J* = 2, 2 H); 6.93 (*t*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): -4.43; 18.17; 20.97; 25.61; 65.79; 119.48; 120.56; 137.67; 155.99; 170.77. Anal. calc. for $C_{18}H_{28}O_5Si$ (352.5): C 61.33, H 8.01; found: C 61.40, H 8.11.

5-Hydroxybenzene-1,3-dimethanol α^1,α^3-Diacetate (**26**). A 1M Bu_4NF soln. in THF (3.7 ml, 3.7 mmol) was added to a stirred soln. of **25** (1.00 g, 2.83 mmol) in THF (20 ml) at 0°. After 30 min, the mixture was evaporated. The residue was taken up with Et_2O, washed with a sat. aq. NH_4Cl soln., dried ($MgSO_4$), and evaporated. CC (SiO_2, 1% MeOH/CH_2Cl_2) yielded **26** (0.52 g, 86%). Colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.15 (*s*, 6 H); 5.14 (*s*, 4 H); 6.85 (*d*, *J* = 2, 2 H); 6.95 (*t*, *J* = 2, 1 H).

1,1-Dimethylethyl {3,5-Bis[(acetyloxy)methyl]phenoxy}acetate (**27**). As described for **22**, with **26** (0.83 g, 3.46 mmol), *tert*-butyl bromoacetate (0.54 ml, 3.64 mmol), and K_2CO_3 (1.01 g, 7.28 mmol) in DMF (20 ml). CC (SiO_2, CH_2Cl_2) yielded **27** (1.10 g, 90%). Colorless glassy product. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.49 (*s*, 9 H); 2.11 (*s*, 6 H); 4.53 (*s*, 2 H); 5.06 (*s*, 4 H); 6.85 (*d*, *J* = 2, 2 H); 6.95 (*t*, *J* = 2, 1 H).

Compound **22** *from* **27**. A soln. of **27** (450 mg, 1.27 mmol) and $NaHCO_3$ (536 mg, 6.38 mmol) in MeOH/H_2O 1:1 was stirred at r.t. for 24 h. The resulting mixture was filtered and evaporated. The residue was taken up with CH_2Cl_2, washed with H_2O, dried ($MgSO_4$), and evaporated. CC (SiO_2, 3% MeOH/CH_2Cl_2) yielded **22** (170 mg, 50%).

1-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}-3,5-bis{{[(1,1-dimethylethyl)dimethylsilyl]oxy}methyl}benzene (**28**). TBDMSCl (1.30 g, 8.66 mmol) and 1*H*-imidazole (1.13 g, 16.51 mmol) were added to a stirred soln. of **24** (1.00 g, 4.13 mmol) in DMF (20 ml) at 0°. The mixture was stirred at 0° for 3 h and evaporated. The residue was taken up with Et_2O, washed with brine, dried ($MgSO_4$), and evaporated. CC (SiO_2, CH_2Cl_2) yielded **28** (1.72 g, 85%). Colorless solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.08 (*s*, 12 H); 0.20 (*s*, 6 H); 0.90 (*m*, 27 H); 4.62 (*s*, 4 H); 6.70 (br. *s*, 2 H); 6.88 (br. *s*, 1 H). Anal. calc. for $C_{26}H_{52}O_3Si_3$ (496.9): C 62.84, H 10.55; found: C 63.01, H 10.57.

3,5-Bis{{[(1,1-dimethylethyl)dimethylsilyl]oxy}methyl}phenol (**29**). A 1M Bu_4NF soln. in THF (7.36 ml, 7.36 mmol) was added to a stirred soln. of **28** (3.63 g, 7.36 mmol) in THF (110 ml) at 0°. The mixture was stirred for 15 min and then evaporated. The residue was taken up with Et_2O, washed with a sat. aq. NH_4Cl soln., dried ($MgSO_4$), and evaporated. CC (SiO_2, CH_2Cl_2) yielded **29** (2.47 g, 88%). Colorless solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.11 (*s*, 12 H); 0.95 (*s*, 18 H); 4.68 (*s*, 4 H); 6.70 (br. *s*, 2 H); 6.82 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): -5.25; 18.43; 25.97; 64.87; 111.79; 115.81; 142.87; 155.83. Anal. calc. for $C_{20}H_{38}O_3Si_2$ (382.7): C 62.77, H 10.01; found: C 62.98, H 10.02.

1,1-Dimethylethyl {3,5-Bis{{[(1,1-Dimethylethyl)dimethylsilyl]oxy}methyl}phenoxy}acetate (**30**). As described for **22**, with **29** (2.25 g, 5.87 mmol), *tert*-butyl bromoacetate (0.93 ml, 6.24 mmol) and K_2CO_3 (1.72 g, 12.48 mmol) in DMF (60 ml) for 72 h. CC (SiO_2, CH_2Cl_2/hexane 4 : 1) yielded **30** (2.78 g, 95%). Colorless glassy product. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.10 (*s*, 12 H); 0.94 (*s*, 18 H); 1.49 (*s*, 9 H); 4.51 (*s*, 2 H); 4.69 (*s*, 4 H); 6.77 (br. *s*, 2 H); 6.89 (br. *s*, 1 H). Anal. calc. for $C_{26}H_{48}O_5Si_2$ (496.8): C 62.86, H 9.74; found: C 62.90, H 9.78.

Compound **22** *from* **30**. A 1M Bu_4NF soln. in THF (11.8 ml, 11.8 mmol) was added to a stirred soln. of **30** (2.66 g, 5.35 mmol) in THF (60 ml) at 0°. The soln. was stirred for 3 h, then evaporated. The residue was taken up with Et_2O, washed with sat. aq. NH_4Cl soln., dried ($MgSO_4$), and evaporated. CC (SiO_2, CH_2Cl_2) yielded **22** (1.42 g, 99%).

5-[2-(1,1-Dimethylethoxy)-2-oxoethoxy]-1,3-phenylenebis(methylene) Bis{[3,5-bis(octyloxy)phenyl]methyl} Dipropanedioate (**31**). As described for **8**, with DCC (1.93 g, 9.32 mmol), DMAP (180 mg, 1.50 mmol), **5** (4.20 g, 9.32 mmol), and **22** (1.00 g, 3.73 mmol) in CH_2Cl_2 (100 ml). CC (SiO_2, CH_2Cl_2) yielded **31** (3.92 g, 93%). Colorless oil. IR (CH_2Cl_2): 1752 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.29 (*m*, 40 H); 1.50 (*s*, 9 H); 1.76 (*m*, 8 H); 3.50 (*s*, 4 H); 3.91 (*t*, *J* = 6, 8 H); 4.51 (*s*, 2 H); 5.13 (*s*, 4 H); 5.15 (*s*, 4 H); 6.40 (*t*, *J* = 2, 2 H); 6.46 (*d*, *J* = 2, 4 H); 6.86 (*t*, *J* = 2, 2 H); 6.94 (*d*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.05; 22.61; 25.99; 27.97; 29.18; 29.31; 31.77; 41.34; 65.57; 66.56; 67.23; 68.02; 101.09; 106.37; 114.12; 120.56; 137.10; 137.19; 160.40; 166.11. Anal. calc. for $C_{66}H_{100}O_{15}$ (1133.5): C 69.94, H 8.89; found: C 70.16, H 9.02.

5-[2-(1,1-Dimethylethoxy)-2-oxoethoxy]-1,3-phenylenebis(methylene) Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Dipropanedioate (**32**). As described for **8**, with DCC (0.58 g, 2.79 mmol), DMAP (50 mg, 0.44 mmol), **6** (1.57 g, 2.79 mmol), and **22** (0.30 g, 1.11 mmol) in CH_2Cl_2 (30 ml). CC (SiO_2, CH_2Cl_2) yielded **32** (1.11 g, 73%). Colorless oil. IR (CH_2Cl_2): 1752 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.26 (*m*, 72 H); 1.48 (*s*, 9 H); 1.77 (*m*, 8 H); 3.48 (*s*, 4 H); 3.92 (*t*, *J* = 6, 8 H); 4.51 (*s*, 2 H); 5.10 (*s*, 4 H); 5.13 (*s*, 4 H); 6.40 (*t*, *J* = 2, 1 H); 6.47 (*d*, *J* = 2, 2 H); 6.86 (*d*, *J* = 2, 4 H); 6.96 (*t*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.03; 22.61; 25.96; 27.92; 29.15; 29.29; 29.54; 31.83; 41.28; 65.54; 66.50; 67.19; 67.96; 82.33; 101.03; 106.33; 114.06; 120.50; 137.07; 137.16; 158.19; 160.36; 166.05; 167.54. Anal. calc. for $C_{82}H_{132}O_{15}$ (1357.9): C 72.53, H 9.80; found: C 72.13, H 9.87.

*Bis{[3,5-bis(octyloxy)phenyl]methyl} 11''-[2-(1,1-Dimethylethoxy)-2-oxoethoxy]-4'',15''-dioxo-3',3''-(methanoxymethano[1,3]benzenomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9 : 3,15][5,6]fullerene-*C_{60}-I$_h$*-3',3''-dicarboxylate* (**34**). As described for **19**, with DBU (0.4 ml, 2.78 mmol), C_{60} (400 mg, 0.55 mmol), I_2 (351 mg, 1.38 mmol), and **31** (660 mg, 0.58 mmol) in toluene (850 ml). CC (SiO_2, CH_2Cl_2/hexane 9 : 1) yielded **34** (605 mg, 59%). Dark orange glassy product. UV/VIS (CH_2Cl_2): 259 (106550), 318 (61220), 378 (22550), 436 (6830), 464 (sh, 5945). IR (CH_2Cl_2): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.28 (*m*, 40 H); 1.51 (*s*, 9 H); 1.73 (*m*, 8 H); 3.86 (*t*, *J* = 6, 8 H); 4.56 (*s*, 2 H); 5.06 (*d*, *J* = 12, 2 H); 5.31 (*AB*, *J* = 12, 4 H); 5.71 (*d*, *J* = 12, 2 H); 6.38 (*t*, *J* = 2, 2 H); 6.47 (*d*, *J* = 2, 4 H); 6.78 (*d*, *J* = 2, 2 H); 7.14 (*t*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.11; 22.65; 26.06; 28.03; 29.24; 29.37; 31.80; 48.96; 65.80; 66.81; 67.14; 68.06; 68.65; 70.52; 82.55; 101.55; 107.88; 112.52; 115.91; 134.35; 135.76; 136.11; 136.52; 137.77; 138.28; 140.00; 141.02; 141.12; 142.27; 142.68; 143.14; 143.54; 143.70; 143.96; 144.12; 144.30; 144.57; 144.92; 144.98; 145.15; 145.31; 145.55; 145.71; 146.03; 147.28; 147.43; 148.59; 157.94; 160.36; 162.52; 167.58. Anal. calc. for $C_{126}H_{96}O_{15} \cdot H_2O$ (1868.1): C 81.01, H 5.29; found: C 80.92, H 5.39.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} 11''-[2-(1,1-Dimethylethoxy)-2-oxoethoxy]-4'',15''-dioxo-3',3''-(methanoxymethano[1,3]benzenomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9 : 3,15][5,6]fullerene-*C_{60}-I$_h$*-3',3''-dicarboxylate* (**35**). As described for **19**, with DBU (0.41 ml, 2.78 mmol), C_{60} (400 mg, 0.55 mmol), I_2 (352 mg, 1.38 mmol), and **32** (790 mg, 0.58 mmol) in toluene (850 ml). CC (SiO_2, CH_2Cl_2/hexane 2 : 1) yielded **35** (516 mg, 45%). Dark orange glassy product. UV/VIS (CH_2Cl_2): 259 (106760), 320 (43900), 379 (22340), 436 (3140), 463 (sh, 2860). IR (CH_2Cl_2): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.97 (*t*, *J* = 6, 12 H); 1.27 (*m*, 72 H); 1.56 (*s*, 9 H); 1.70 (*m*, 8 H); 3.86 (*t*, *J* = 6, 8 H); 4.56 (*s*, 2 H); 5.03 (*d*, *J* = 12, 2 H); 5.29 (*d*, *J* = 12, 4 H); 5.75 (*d*, *J* = 12, 2 H); 6.46 (*t*, *J* = 2, 2 H); 6.48 (*d*, *J* = 2, 4 H); 6.78 (*d*, *J* = 2, 2 H); 7.14 (*t*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.15; 22.70; 26.09; 26.89; 28.04; 29.25; 29.38; 29.44; 29.64; 31.93; 48.55; 65.83; 67.19; 68.09; 68.69; 82.59; 101.58; 107.10; 112.56; 115.96; 135.78; 136.11; 136.52; 138.31; 140.01; 141.05; 141.15; 142.29; 142.71; 143.16; 143.58; 143.74; 143.98; 144.15; 144.31; 144.59; 144.92; 144.98; 145.17; 145.33; 145.59; 145.72; 146.06; 147.31; 147.46; 148.61; 157.97; 160.36; 162.55; 167.62. Anal. calc. for $C_{142}H_{128}O_{15}$ (2074.6): C 82.21, H 6.22; found: C 82.29, H 6.41.

*Bis{[3,5-bis(octyloxy)phenyl]methyl} 11''-(Carboxymethoxy)-4'',15''-dioxo-3',3''-(methanoxymethano[1,3]benzenomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9 : 3,15][5,6]fullerene-*C_{60}-I$_h$*-3',3''-dicarboxylate* (**37**). As described for **10**, with **34** (220 mg, 0.12 mmol) and CF_3COOH (25 ml) in CH_2Cl_2 (100 ml). After workup, evaporation yielded **37** (210 mg, 98%). Dark orange glassy product. UV/VIS (CH_2Cl_2): 260 (62515), 320

(17545), 379 (7020), 438 (1735), 465 (sh, 1430). IR (CH_2Cl_2): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.28 (*m*, 40 H); 1.73 (*m*, 8 H); 3.84 (*t*, *J* = 6, 8 H); 4.68 (*s*, 2 H); 5.08 (*d*, *J* = 12, 2 H); 5.29 (*s*, 4 H); 5.76 (*d*, *J* = 12, 2 H); 6.36 (*t*, *J* = 2, 2 H); 6.46 (*d*, *J* = 2, 4 H); 6.80 (*d*, *J* = 2, 2 H); 7.14 (*t*, *J* = 2, 1 H). Anal. calc. for $C_{122}H_{88}O_{15} \cdot H_2O$ (1812.0): C 80.87, H 5.01; found: C 80.78, H 5.15.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} 11″-(Carboxymethoxy)-4″,15″-dioxo-3′,3″-(methanoxymethano[1,3]benzenomethanoxymethano)-3′*H,*3″*H*-dicyclopropa[1,9:3,15][5,6]fullerene-C$_{60}$-*I$_h$*-3′,3″-dicarboxylate* (**38**). As described for **10**, with **35** (370 mg, 0.18 mmol) and CF_3COOH (25 ml) in CH_2Cl_2 (100 ml). After workup, evaporation yielded **38** (358 mg, 99%). Dark orange glassy product. IR (CH_2Cl_2): 1747 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.07 (*t*, *J* = 6, 12 H); 1.26 (*m*, 72 H); 1.72 (*m*, 8 H); 3.84 (*t*, *J* = 6, 8 H); 4.72 (*s*, 2 H); 5.03 (*d*, *J* = 12, 2 H); 5.29 (*AB*, *J* = 12, 4 H); 5.76 (*d*, *J* = 12, 2 H); 6.37 (*t*, *J* = 2, 2 H); 6.48 (*d*, *J* = 2, 4 H); 6.81 (*d*, *J* = 2, 2 H); 7.18 (*t*, *J* = 2, 1 H). UV/VIS (CH_2Cl_2): 259 (111860), 320 (33500), 379 (12245), 437 (3100), 475 (sh, 2470). Anal. calc. for $C_{138}H_{120}O_{15} \cdot H_2O$ (2036.5): C 81.39, H 6.04; found: C 81.67, H 6.22.

Bis(1,1-dimethylethyl) 2,2′-[4-(Bromomethyl)-1,3-phenylenebis(oxy)]bis[acetate] (**41**). A mixture of **40** (4.73 g, 12.84 mmol), PPh_3 (4.21 g, 16.05 mmol), and CBr_4 (4.19 g, 16.05 mmol) in dry THF (70 ml) was stirred for 3 h at 0°. Brine was added and the resulting mixture concentrated. The aq. layer was extracted with CH_2Cl_2 and the extract dried ($MgSO_4$) and evaporated. CC (SiO_2, CH_2Cl_2/hexane 3:2) yielded **41** (4.04 g, 73%). Colorless solid. M.p. 72.5°. IR (KBr): 1751 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.49 (*s*, 18 H); 4.38 (*s*, 2 H); 4.48 (*s*, 4 H); 6.42 (*t*, *J* = 2, 1 H); 6.55 (*d*, *J* = 2, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 28.02; 33.17; 65.73; 82.48; 102.06; 108.31; 138.81; 159.09; 167.61. Anal. calc. for $C_{19}H_{27}BrO_6$ (431.3): C 52.91, H 6.31; found: C 52.67, H 6.31.

Bis(1,1-dimethylethyl) 2,2′-{4-{[3,5-bis(hydroxymethyl)phenoxy]methyl}-1,3-phenylenebis(oxy)}bis[acetate] (**42**). A mixture of **21** (1.26 g, 8.20 mmol), **41** (2.95 g, 6.83 mmol), K_2CO_3 (1.89 g, 13.67 mmol), and [18]crown-6 (0.542 g, 2.05 mmol) in acetone (40 ml) was refluxed for 12 h. After cooling, the soln. was filtered and evaporated. The residue was taken up with CH_2Cl_2, washed with H_2O, dried ($MgSO_4$), and evaporated. CC (SiO_2, 1.5% MeOH/CH_2Cl_2) yielded **42** (3.03 g, 88%). Colorless oil. IR (KBr). 1740 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.49 (*s*, 18 H); 1.82 (*t*, *J* = 6, 2 H); 4.49 (*s*, 4 H); 4.65 (*d*, *J* = 6, 4 H); 5.01 (*s*, 2 H); 6.43 (*t*, *J* = 2, 1 H); 6.59 (*d*, *J* = 2, 2 H); 6.89 (*s*, 2 H); 6.95 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 28.00; 64.95; 65.67; 82.49; 101.27; 106.38; 112.34; 117.77; 138.56; 142.87; 158.99; 159.14; 167.80. Anal. calc. for $C_{27}H_{36}O_9$ (504.6): C 64.27, H 7.19; found: C 64.15; H 7.02.

5-{{3,5-Bis[2-(1,1-dimethylethoxy)-2-oxoethoxy]phenyl}methoxy}-1,3-phenylenebis(methylene) Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Dipropanedioate (**43**). As described for **18**, with DCC (0.53 g, 2.58 mmol), DMAP (0.53 g, 0.43 mmol), **42** (0.54 g, 1.08 mmol), and **6** (1.33 g, 2.37 mmol) in CH_2Cl_2 (25 ml). CC (SiO_2, 2% MeOH/CH_2Cl_2) yielded **43** (1.44 g, 84%). Pale yellow oil. IR (KBr): 1756 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz); 0.88 (*t*, *J* = 6, 12 H); 1.27 (*s*, 72 H); 1.49 (*s*, 18 H); 1.76 (*t*, *J* = 6, 8 H); 3.50 (*s*, 4 H); 3.91 (*t*, *J* = 6, 8 H); 4.49 (*s*, 4 H); 4.96 (*s*, 2 H); 5.10 (*s*, 4 H); 5.14 (*s*, 4 H); 6.40–6.47 (*m*, 7 H); 6.60 (*d*, *J* = 2, 2 H); 6.90 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.11; 22.67; 28.02; 28.0; 29.21; 29.36; 29.59; 31.90; 33.94; 41.37; 65.69; 66.7; 67.26; 68.06; 69.72; 82.39; 101.10; 101.34; 106.38; 106.49; 114.37; 120.17; 137.14; 139.17; 158.97; 158.22; 160.43; 166.20; 167.68. Anal. calc. for $C_{95}H_{148}O_{19}$ (1594.2): C 71.57, H 9.36; found: C 71.55, H 9.48.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} 11″-{{3,5-Bis[2-(1,1-dimethylethoxy)-2-oxoethoxy]phenyl}methoxy}-4″,15″-dioxo-3′,3″-(methanoxymethano[1,3]benzenomethanoxymethano-3′*H,*3″*H*-dicyclopropa[1,9:3,15][5,6]fullerene-C$_{60}$-*I$_h$*-3′,3″-dicarboxylate* (**44**). As described for **19**, with DBU (423 mg, 1.66 mmol), C_{60} (423 mg, 1.66 mmol), I_2 (845 mg, 5.55 mmol), and **43** (885 mg, 5.55 mmol) in toluene (800 ml). CC (SiO_2, CH_2Cl_2/hexane 7:3) yielded **44** (560 mg, 44%). Dark red glassy product. IR (KBr): 1752 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.88 (*t*, *J* = 6, 12 H); 1.26 (*s*, 72 H); 1.50 (*s*, 18 H); 1.70 (*m*, 8 H); 3.84 (*t*, *J* = 6, 8 H); 4.51 (*s*, 4 H); 5.02 (*d*, *J* = 12, 2 H); 5.09 (*s*, 2 H); 5.29 (*s*, 4 H); 5.75 (*d*, *J* = 13, 2 H); 6.35 (br. *s*, 2 H); 6.47 (*m*, 5 H); 6.62 (*d*, *J* = 2, 2 H); 6.83 (br. *s*, 2 H); 7.11 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.15; 22.70; 26.09; 28.04; 29.25; 29.38; 29.44; 29.64; 31.93; 65.71; 66.85; 67.28; 68.08; 68.7; 69.84; 70.55; 82.45; 101.38; 101.59; 106.48; 107.10; 112.65; 115.47; 134.30; 135.76; 136.10; 136.52; 137.80; 138.25; 139.14; 140.03; 141.06; 141.12; 142.30; 142.71; 143.16; 143.58; 143.74; 143.96; 144.15; 144.31; 144.58; 144.92; 144.98; 145.17; 145.33; 145.58; 145.72; 146.07; 147.31; 147.46; 148.62; 158.68; 159.27; 160.36; 162.60; 167.70. Anal. calc. for $C_{155}H_{144}O_{19}$ (2310.8): C 80.56, H 6.28; found: C 80.59, H 6.36.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} 11″-{[3,5-Bis(carboxymethoxy)phenyl]methoxy}-4″,15″-dioxo-3′,3″-(methanoxymethano[1,3]benzenomethanoxymethano)-3′*H,*3″*H*-dicyclopropa[1,9:3,15][5,6]fullerene-C$_{60}$-*I$_h$*-3′,3″-dicarboxylate* (**45**). As described for **10**, with **44** (530 mg, 0.23 mmol) and CF_3COOH (50 ml) in CH_2Cl_2 (50 ml). After workup, evaporation yielded **45** (522 mg, 98%). Dark orange glassy product. IR (KBr): 1749 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.26 (*s*, 72 H); 1.71 (*m*, 8 H); 3.85 (*t*, *J* = 6, 8 H); 4.68 (*s*, 4 H); 5.05 (*d*, *J* = 13, 2 H); 5.10 (*s*, 2 H); 5.29 (*s*, 4 H); 5.75 (*d*, *J* = 13, 2 H); 6.36 (*s*, 2 H); 6.46 (*m*, 5 H); 6.64

(br. *s*, 2 H); 6.81 (br. *s*, 2 H); 7.11 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.15; 22.70; 26.09; 29.25; 29.38; 29.44; 29.65; 31.93; 49.00; 53.41; 64.79; 66.80; 67.40; 68.12; 68.78; 69.58; 70.52; 100.90; 101.65; 106.90; 107.160; 112.870; 115.50; 135.80; 136.04; 136.49; 138.24; 140.00; 141.05; 142.06; 143.18; 143.57; 143.74; 144.15; 144.27; 144.60; 144.98; 145.17; 145.33; 145.71; 146.06; 147.45; 148.55; 158.51; 158.82; 160.33; 162.64; 162.76; 171.90. Anal. calc. for $C_{147}H_{128}O_{19}$ (2198.6): C 80.31, H 5.87; found: C 80.13, H 5.99.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} 11''-{{3,5-Bis[(2-oxo-3,6,9,12-tetraoxatridecyl)oxy]phenyl}methoxy}-4'',15''-dioxo-3',3''-(methanoxymethano[1,3]benzenomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9:3,15][5,6]fullerene-C$_{60}$-*I*$_h$*-3',3''-dicarboxylate* (**46**). As described for **8**, with DCC (14 mg, 0.067 mmol), DMAP (2 mg, 0.013 mmol), **45** (70 mg, 0.032 mmol), and triethylene glycol monomethyl ether (12 mg, 0.067 mmol) in CH_2Cl_2 (25 ml). CC (SiO_2, 1% MeOH/CH_2Cl_2) yielded **46** (70 mg, 88%). Dark orange glassy product. IR (KBr): 1752 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.26 (*s*, 72 H); 1.72 (*m*, 8 H); 3.38 (*s*, 6 H); 3.56 (*m*, 4 H); 3.64 (*m*, 12 H); 3.74 (*t*, *J* = 5, 4 H); 3.84 (*t*, *J* = 6, 8 H); 4.38 (*t*, *J* = 5, 4 H); 4.67 (*s*, 4 H); 5.00 (*s*, 2 H); 5.12 (*d*, *J* = 12, 2 H); 5.30 (*AB*, *J* = 13, 4 H); 5.75 (*d*, *J* = 12, 2 H); 6.35 (br. *s*, 2 H); 6.47 (*m*, 5 H); 6.66 (br. *s*, 2 H); 6.85 (br. *s*, 2 H); 7.13 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.15; 22.70; 26.09; 29.25; 29.38; 29.44; 29.64; 31.93; 59.03; 64.33; 65.25; 67.30; 68.08; 68.85; 70.57; 71.89; 101.40; 101.51; 101.61; 112.70; 128.30; 133.85; 135.76; 136.52; 138.30; 139.37; 141.12; 141.20; 142.40; 142.75; 143.16; 143.65; 143.74; 144.03; 144.15; 144.30; 144.60; 144.97; 145.30; 145.45; 145.60; 145.72; 146.11; 147.51; 148.70; 158.64; 159.13; 160.36; 162.60; 168.51. Anal. calc. for $C_{161}H_{156}O_{25}$ (2491.0): C 77.63, H 6.31; found: C 76.76, H 6.56.

5-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}-1,3-phenylenebis(methylene) Bis{[3,5-bis(octyloxy)phenyl]-methyl} Dipropanedioate (**48**). As described for **8**, with DCC (0.88 g, 4.29 mmol), DMAP (0.08 g, 0.68 mmol), **2** (1.56 g, 4.29 mmol), and **47** (0.81 g, 1.71 mmol) in CH_2Cl_2 (80 ml). CC (SiO_2, 2% MeOH/CH_2Cl_2) yielded **48** (0.79 g, 40%). Pale yellow oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.30 (*m*, 40 H); 1.68 (*m*, 8 H); 3.37 (*s*, 3 H); 3.49 (*m*, 4 H); 3.50 – 3.82 (*m*, 10 H); 3.91 (*t*, *J* = 6, 8 H); 4.12 (*t*, *J* = 6, 2 H); 5.75 (*s*, 4 H); 6.40 (*d*, *J* = 2, 2 H); 6.41 (*d*, *J* = 2, 4 H); 6.87 (*t*, *J* = 2, 2 H); 6.90 (*t*, *J* = 2, 1 H).

*Bis{[3,5-bis(octyloxy)phenyl]methyl} 11''-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}-4'',15''-dioxo-3',3''-(methanoxymethano[1,3]benzenomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9:3,15][5,6]fullerene-C$_{60}$-*I*$_h$*-3',3''-dicarboxylate* (**49**). As described for **19**, with DBU (0.32 ml, 2.12 mmol), C_{60} (306 mg, 0.42 mmol), I_2 (520 mg, 0.44 mmol), and **48** (270 mg, 1.06 mmol) in toluene (800 ml). CC (SiO_2, 5% MeOH/CH_2Cl_2) yielded **49** (320 mg, 45%). Dark orange glassy product. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6, 12 H); 1.28 (*m*, 40 H); 1.72 (*m*, 8 H); 3.40 (*s*, 3 H); 3.55 – 3.76 (*m*, 10 H); 3.85 (*t*, *J* = 6, 8 H); 4.17 (*t*, *J* = 6, 2 H); 5.05 (*d*, *J* = 12, 2 H); 5.30 (*d*, *J* = 12, 2 H); 5.75 (*d*, *J* = 12, 2 H); 6.37 (*d*, *J* = 2, 2 H); 6.48 (*d*, *J* = 2, 4 H); 6.80 (*t*, *J* = 2, 2 H); 7.09 (*t*, *J* = 2, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.62; 26.04; 29.21; 29.34; 29.63; 31.77; 48.97; 58.97; 66.79; 67.19; 67.52; 68.03; 68.59; 69.58; 70.52; 70.61; 70.81; 71.86; 101.54; 107.03; 112.39; 115.12; 134.39; 135.73; 136.07; 136.52; 137.74; 138.09; 140.00; 140.99; 141.08; 142.24; 142.69; 143.10; 143.51; 143.67; 143.90; 144.09; 144.26; 144.51; 144.86; 144.94; 145.11; 145.27; 145.52; 145.69; 146.00; 147.25; 147.39; 148.55; 158.77; 160.33; 162.51. UV/VIS (CH_2Cl_2): 259 (176000), 320 (86000), 379 (33800), 437 (3500), 466 (sh, 2900). FAB-MS: 1881.4 (12, $[M+H]^+$), 719.9 (100, C_{60}^+). Anal. calc. for $C_{127}H_{100}O_{16}$ (1882.2): C 81.04, H 5.36; found: C 81.07, H 5.42.

*(−)-(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diylbis(methylene) Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Dipropanedioate* ((−)-**51**). As described for **8**, with (+)-**50** (400 mg, 2.47 mmol), DCC (1.10 g, 5.31 mmol), DMAP (80 mg, 0.74 mmol), and **6** (2.91 g, 4.94 mmol) in CH_2Cl_2 (80 ml). CC (SiO_2, CH_2Cl_2/hexane 4:1) afforded (−)-**51** (1.58 g, 51%). Colorless oil. $[\alpha]_D^{30} = -4$ ($c = 4.61$, CH_2Cl_2). IR (CH_2Cl_2): 1755, 1738 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6.5, 12 H); 1.27 (*m*, 72 H); 1.41 (*s*, 6 H); 1.77 (*m*, 8 H); 3.49 (*s*, 4 H); 3.92 (*t*, *J* = 6.5, 8 H); 4.04 (*m*, 2 H); 4.28 (*m*, 4 H); 5.09 (*s*, 4 H); 6.41 (*t*, *J* = 2, 2 H); 6.47 (*d*, *J* = 2, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.11; 22.68; 26.03; 26.84; 29.22; 29.36; 29.61; 31.90; 41.19; 64.57; 67.34; 68.07; 75.55; 101.13; 106.52; 110.39; 137.07; 160.46; 166.02. Anal. calc. for $C_{75}H_{126}O_{14}$ (1251.8): C 71.96, H 10.15; found: C 71.93, H 10.31.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} (7''*S*,11''*S*)-7'',11''-Dihydro-9'',9''-dimethyl-4'',14''-dioxo-3',3''-(methanoxymethano[4,5]-*endo*-[1,3]dioxolomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9:3,15][5,6]fullerene-C$_{60}$-*I*$_h$*-3',3''-dicarboxylate* (**52**) *and Bis{[3,5-bis(dodecyloxy)phenyl]methyl} (7''*S*,11''*S*)-7'',11''-Dihydro-9'',9''-dimethyl-4'',14''-dioxo-3',3''-(methanoxymethano[4,5]-*endo*-[1,3]dioxolomethanoxymethano)-3'*H*,3''*H*-dicyclopropa[1,9:13,14][5,6]fullerene-C$_{60}$-*I*$_h$*-3',3''-dicarboxylate* (**53**). As described for **19**, with (−)-**51** (955 mg, 0.76 mmol), C_{60} (500 mg, 0.69 mmol), I_2 (442 mg, 1.74 mmol), and DBU (0.5 ml, 3.47 mmol) in toluene (800 ml). CC (SiO_2,hexane/CH_2Cl_2 2:1 → 1:1) afforded **52** (186 mg, 12%) and **53** (297 mg, 20%).

Data of **52**: Dark orange glassy product. UV/VIS (CH_2Cl_2): 258 (148300), 317 (45300), 375 (16400), 437 (4400), 466 (sh, 3660). IR (CH_2Cl_2): 1749 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6.5, 12 H); 1.28 (*m*, 72 H); 1.44 (*s*, 6 H); 1.75 (*m*, 8 H); 3.88 (*t*, *J* = 6.5, 4 H); 3.89 (*t*, *J* = 6.5, 4 H); 3.96 – 4.30 (*m*, 3 H); 4.55 – 5.00

(*m*, 3 H); 5.30 (br. *s*, 4 H); 6.40 (*m*, 2 H); 6.47 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.12; 22.70; 26.08; 28.55; 28.64; 29.25; 29.38; 29.44; 29.64; 29.69; 31.93; 42.85; 48.91; 66.90; 67.09; 68.13; 68.78; 70.04; 70.13; 77.19; 78.21; 101.51; 101.57; 106.69; 111.25; 133.82; 136.30; 136.36; 137.39; 137.55; 137.86; 138.06; 138.60; 140.93; 141.21; 141.82; 141.92; 142.39; 143.12; 143.61; 143.87; 144.15; 144.22; 144.28; 144.47; 144.69; 144.76; 145.06; 145.29; 145.62; 145.69; 145.96; 146.16; 147.32; 147.38; 147.47; 149.26; 149.45; 160.48; 162.35; 162.41; 162.71.

Data of **53**: Dark brown glassy product. UV/VIS (CH_2Cl_2): 256 (149800), 313 (51300), 406 (6960), 459 (3230), 628 (680), 693 (320). IR (CH_2Cl_2): 1746 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, $J = 6.5$, 12 H); 1.27 (*m*, 78 H); 1.78 (*m*, 8 H); 3.91 (*t*, $J = 6.5$, 8 H); 3.95 (*m*, 2 H); 4.33 (br. *s*, 2 H); 4.65 (*m*, 2 H); 5.31 (*d*, $J = 12.5$, 2 H); 5.42 (*d*, $J = 12.5$, 2 H); 6.42 (*d*, $J = 2$, 2 H); 6.54 (*t*, $J = 4$ H, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.65; 26.06; 27.87; 29.22; 29.32; 29.41; 29.60; 31.89; 48.85; 64.84; 68.11; 68.83; 68.99; 71.67; 75.57; 101.67; 106.94; 109.91; 129.95; 136.30; 136.49; 138.76; 139.05; 140.84; 140.95; 141.57; 141.67; 141.76; 142.11; 142.30; 143.53; 144.20; 144.38; 144.60; 144.76; 144.94; 145.21; 145.39; 146.26; 146.58; 160.46; 163.05.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} (7″*S*,8″*S*)-7″,8″-Dihydroxy-4″,11″-dioxo-3′,3″-(methanoxybutanoxymethano)-3′*H*,3″*H*-dicyclopropa[1,9 :3,15][5,6]fullerene-*C_{60}-I_h*-3′,3″-dicarboxylate* (**54**). A mixture of **52** (95 mg, 0.048 mmol) and CF_3COOH (4 ml) in CH_2Cl_2/H_2O 2 : 1 (6 ml) was stirred at r.t. for 48 h. The org. layer was then washed with H_2O, dried ($MgSO_4$), and evaporated. CC (SiO_2, CH_2Cl_2) yielded **54** (83 mg, 89%). Dark orange glassy product. UV/VIS (CH_2Cl_2): 258 (149670), 318 (45810), 376 (16620), 436 (4370), 467 (3590). IR (CH_2Cl_2): 3610 (O–H), 1746 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*m*, 12 H); 1.28 (*m*, 72 H); 1.75 (*m*, 8 H); 2.83 (*d*, $J = 6$, 1 H); 3.29 (*d*, $J = 7.5$, 1 H); 3.80 (*m*, 1 H); 3.89 (*t*, $J = 6.5$, 4 H); 3.90 (*t*, $J = 6.5$, 4 H); 4.04 (*m*, 1 H); 4.14 (*m*, 1 H); 4.71 (*m*, 1 H); 5.22 (*d*, $J = 12$, 2 H); 5.39 (*d*, $J = 12$, 2 H); 6.40 (*t*, $J = 2$, 1 H); 6.41 (*t*, $J = 2$, 1 H); 6.50 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.12; 22.70; 26.06; 29.22; 29.38; 29.44; 29.64; 29.69; 31.93; 45.82; 49.11; 66.29; 67.36; 68.21; 68.29; 68.61; 68.70; 69.91; 70.23; 70.33; 101.47; 106.74; 106.97; 134.45; 136.40; 136.61; 137.01; 137.58; 137.73; 138.16; 138.31; 138.67; 139.08; 140.90; 141.05; 141.20; 141.76; 142.08; 142.30; 143.13; 143.58; 143.64; 143.80; 143.93; 144.09; 144.24; 144.35; 144.61; 144.73; 145.05; 145.14; 145.28; 145.46; 145.69; 145.89; 145.94; 146.10; 146.16; 147.31; 147.40; 147.47; 148.85; 149.90; 160.37; 162.16; 162.55; 162.70. Anal. calc. for $C_{132}H_{118}O_{14}$ (1928.4): C 82.22, H 6.17; found: C 81.94, H 6.16.

*Bis{[3,5-bis(dodecyloxy)phenyl]methyl} (7″*S*,8″*S*)-7″,8″-Dihydroxy-4″,11″-dioxo-3′,3″-(methanoxybutanoxymethano)-3′*H*,3″*H*-dicyclopropa[1,9 :13,14][5,6]fullerene-*C_{60}-I_h*-3′,3″-dicarboxylate* (**55**). As described for **54**, with **53** (259 mg, 0.132 mmol) and CF_3COOH (10 ml) in CH_2Cl_2/H_2O 2 : 1 (15 ml). CC (SiO_2, CH_2Cl_2) yielded **55** (169 mg, 67%). UV/VIS (CH_2Cl_2): 255 (117050), 316 (39610), 406 (5090), 451 (2420), 628 (570), 695 (290). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, $J = 6$, 12 H); 1.27 (*m*, 72 H); 1.76 (*m*, 8 H); 2.43 (*d*, $J = 7$, 2 H); 3.91 (*t*, $J = 6.5$, 8 H); 4.02 (*m*, 2 H); 4.25 (*t*, $J = 10.5$, 2 H); 4.71 (*dd*, $J = 10.5$, 5, 2 H); 5.33 (*d*, $J = 12$, 2 H); 5.42 (*d*, $J = 12$, 2 H); 6.42 (*t*, $J = 2$, 2 H); 6.54 (*d*, $J = 2$, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.12; 22.68; 26.09, 29.25; 29.35; 29.44; 29.63; 31.91; 49.55; 64.50; 66.17; 68.16; 68.99; 71.61; 101.61; 106.94; 129.76; 136.05; 136.39; 138.47; 138.91; 140.64; 140.93; 141.07; 141.44; 141.73; 142.17; 142.38; 143.52; 143.61; 144.22; 144.28; 144.41; 144.64; 144.72; 144.95; 145.24; 145.34; 145.43; 145.62; 146.30; 146.61; 160.49; 162.63; 162.96. Anal. calc. for $C_{132}H_{118}O_{14}$ (1928.4): C 82.22, H 6.17; found: C 82.15, H 6.37.

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