

## 25. Methanofullerene Molecular Scaffolding: Towards C<sub>60</sub>-Substituted Poly(triacetylenes) and Expanded Radialenes, Preparation of a C<sub>60</sub>-C<sub>70</sub> Hybrid Derivative, and a Novel Macrocyclization Reaction

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The synthesis of (*E*)-hex-3-ene-1,5-diyne and 3-methylidene-penta-1,4-diyne with pendant methano[60]-fullerene moieties as precursors to C<sub>60</sub>-substituted poly(triacetylenes) (PTAs, *Fig. 1*) and expanded radialenes (*Fig. 2*) is described. The *Bingel* reaction of diethyl (*E*)-2,3-dialkynylbut-2-ene-1,4-diyl bis(2-bromopropanedioates) **5** and **6** with two C<sub>60</sub> molecules (*Scheme 2*) afforded the monomeric, silyl-protected PTA precursors **9** and **10** which, however, could not be effectively desilylated (*Scheme 4*). Also formed during the synthesis of **9** and **10**, as well as during the reaction of C<sub>60</sub> with the desilylated analogue **16** (*Scheme 5*), were the macrocyclic products **11**, **12**, and **17**, respectively, resulting from double *Bingel* addition to one C-sphere. Rigorous analysis revealed that this novel macrocyclization reaction proceeds with complete regio- and diastereoselectivity. The second approach to a suitable PTA monomer attempted *N,N'*-dicyclohexylcarbodiimide (DCC)-mediated esterification of (*E*)-2,3-diethynylbut-2-ene-1,4-diol (**18**, *Scheme 6*) with mono-esterified methanofullerene-dicarboxylic acid **23**; however, this synthesis yielded only the corresponding decarboxylated methanofullerene-carboxylic ester **27** (*Scheme 7*). To prevent decarboxylation, a spacer was inserted between the reacting carboxylic-acid moiety and the methano C-atom in carboxymethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**28**, *Scheme 8*), and DCC-mediated esterification with diol **18** afforded PTA monomer **32** in good yield. The formation of a suitable monomeric precursor **38** to C<sub>60</sub>-substituted expanded radialenes was achieved in 5 steps starting from dihydroxyacetone (*Schemes 9* and *10*), with the final step consisting of the DCC-mediated esterification of **28** with 2-[1-ethynyl(prop-2-ynylidene)]propane-1,3-diol (**33**). The first mixed C<sub>60</sub>-C<sub>70</sub> fullerene derivative **49**, consisting of two methano[60]fullerenes attached to a methano[70]fullerene, was also prepared and fully characterized (*Scheme 13*). The C<sub>s</sub>-symmetrical hybrid compound was obtained by DCC-mediated esterification of bis[2-(2-hydroxyethoxy)ethyl] 1,2-methano[70]fullerene-71,71-dicarboxylate (**46**) with an excess of the C<sub>60</sub>-carboxylic acid **28**. The presence of two different fullerenes in the same molecule was reflected by its UV/VIS spectrum, which displayed the characteristic absorption bands of both the C<sub>70</sub> and C<sub>60</sub> mono-adducts, but at the same time indicated no electronic interaction between the different fullerene moieties. Cyclic voltammetry showed two reversible reduction steps for **49**, and comparison with the corresponding C<sub>70</sub> and C<sub>60</sub> mono-adducts **46** and **30** indicated that the three fullerenes in the composite fullerene compound behave as independent redox centers.

**1. Introduction.** – Conjugated polymers are widely explored as advanced materials for electronic [1], photonic [2], and nonlinear optical applications [3]. For many years, polyacetylenes [4] and poly(diacetylenes) [5] were the only known single-strand conjugated polymers with a non-aromatic all-C-atom backbone; however, recently we succeeded in preparing first oligomers [6] and polymers [7] with a poly(triacetylene) (PTA) back-

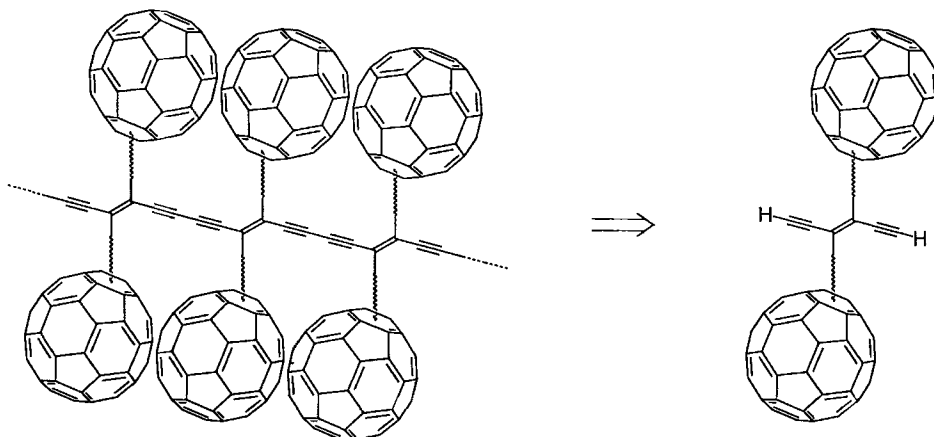


Fig. 1. Proposed synthesis of  $C_{60}$ -substituted poly(triacetylenes) (PTAs) by oxidative acetylenic couplings of (*E*)-hex-3-ene-1,5-diyne precursors with two pendant fullerene spheres

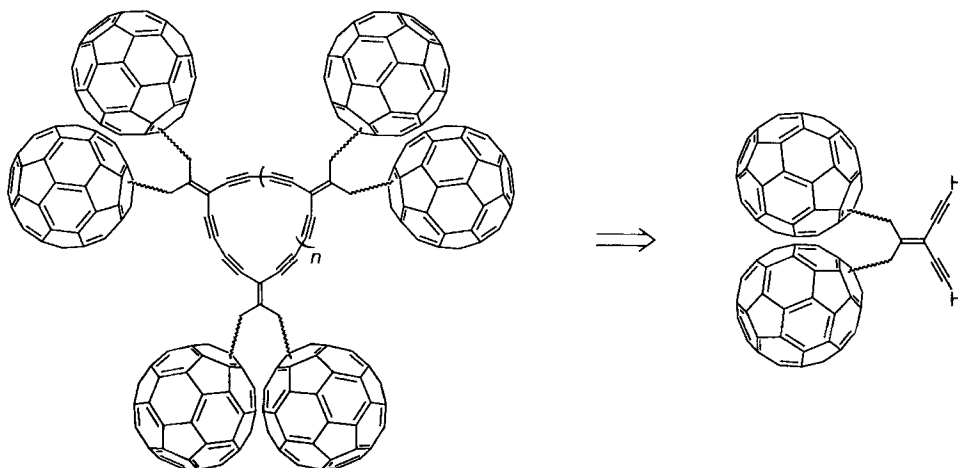


Fig. 2. Proposed synthesis of  $C_{60}$ -substituted expanded radialenes by oxidative cyclization of 3-methylidenepenta-1,4-diyne precursors

bone. As part of our research in C-scaffolding and the construction of C-rich nanomaterials [8], we became interested in the preparation of PTA oligomers and polymers with laterally appended  $C_{60}$  spheres (Fig. 1). In view of the many intriguing properties of  $C_{60}$ , such as large nonlinear optical effects [9], superconductivity of the alkali metal salts  $M_3C_{60}$  [10a–d], and ferromagnetism of charge-transfer complexes with amines [10e,f], conjugated polymers with pendant fullerene spheres were also expected to display a variety of interesting material features [11].

Whereas oxidative coupling of  $C_{60}$ -substituted (*E*)-hex-3-ene-1,5-diyne should yield linearly conjugated molecular rods with the PTA backbone, the corresponding geminally ethynylated 3-methylidenepenta-1,4-diyne should give  $C_{60}$ -substituted macrocycles, namely expanded radialenes (Fig. 2). Recently, first examples of these robust, multi-

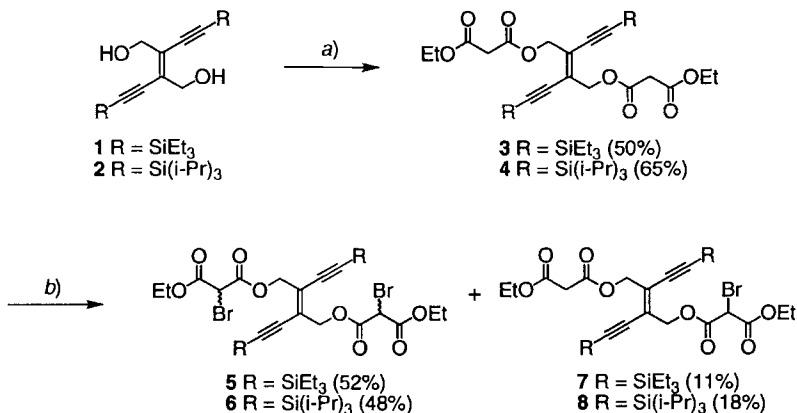
nanometer-sized C-rich cores were described and found to readily undergo multiple reversible one-electron reductions [7b] [12]. Therefore, C<sub>60</sub>-substituted expanded radialenes might have great potential as electron sponges [13], combining the well established electron-accepting ability of lower fullerene adducts [14] with that of the expanded radialene core.

Herein, we report the synthesis of C<sub>60</sub>-substituted monomeric precursors for the construction of fullerene-containing PTAs and expanded radialenes, as depicted in *Figs. 1* and *2*, respectively. We also describe some of the interesting reactivity encountered during the synthesis of these molecules, specifically, a new, direct regio- and diastereoselective bis-functionalization of C<sub>60</sub> and a new synthesis of methanofullerene-carboxylic esters. As part of this research program on oligomeric and polymeric fullerene materials, we also communicate the preparation of a mixed C<sub>60</sub>-C<sub>70</sub> fullerene compound which consists of a C<sub>70</sub> derivative bearing two C<sub>60</sub> substituents. This hybrid is the first member of a new class of mixed fullerene oligomers.

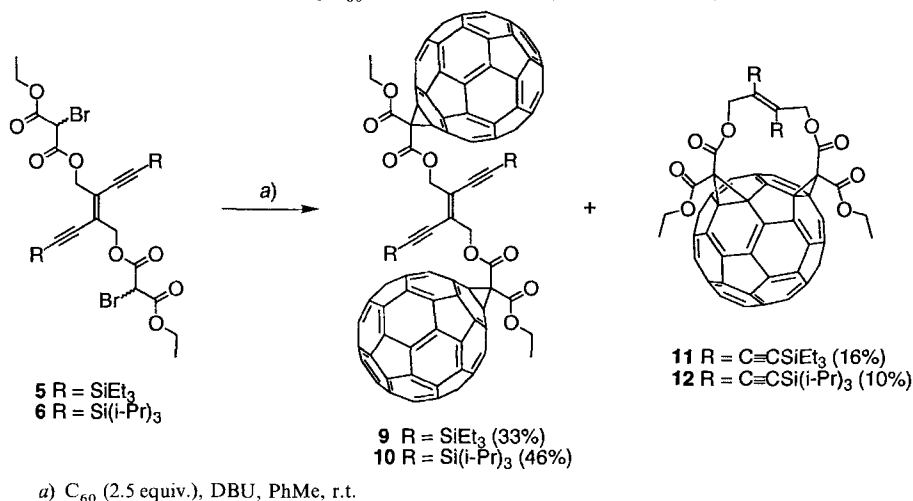
**2. Results and Discussion.** – 2.1. *PTA Monomers by Direct Functionalization of C<sub>60</sub> and a Novel Macrocyclization on the Fullerene Core.* We planned to directly attach two C<sub>60</sub> molecules to an (*E*)-hex-3-ene-1,5-diyne moiety by taking advantage of the versatile *Bingel* reaction [15], *i.e.*, the addition of 2-bromomalonates to 6,6-bonds of the fullerene (bonds common to two six-membered rings) in the presence of base under formation of methanofullerenes [16]. Therefore, we prepared (*E*)-hex-3-ene-1,5-diyne derivatives with two pendant 2-bromomalonate residues starting from diols **1** and **2** [17] (*Scheme 1*). Reaction of **1** and **2** with ethyl 3-chloro-3-oxopropanoate ('ethyl malonyl chloride') in the presence of C<sub>5</sub>H<sub>5</sub>N in CH<sub>2</sub>Cl<sub>2</sub> yielded the dimalonates **3** and **4**, respectively. Subsequent bromination (CBr<sub>4</sub>, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) in THF afforded **5** and **6**, respectively, as mixtures of diastereoisomers, in addition to small amounts of the respective mono-brominated derivatives **7** and **8**.

Dibromides **5** and **6** were added to C<sub>60</sub> by *Bingel* reaction (DBU, PhMe) to form the bis(1,2-methanofullerene) derivatives **9** and **10**, respectively (*Scheme 2*). Their solubility

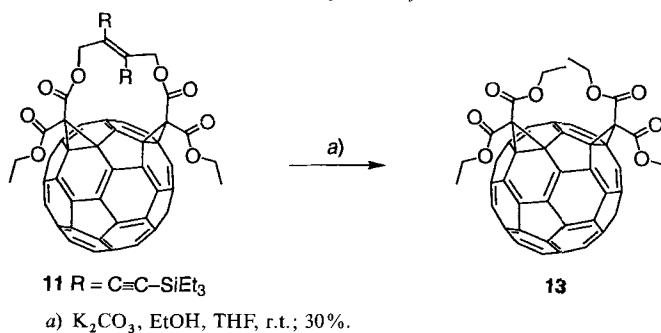
Scheme 1. Synthesis of the Tethered Bis(2-bromomalonates) **5** and **6**



a) EtO<sub>2</sub>CCH<sub>2</sub>COCl, C<sub>5</sub>H<sub>5</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 0° to r.t. b) DBU (2 equiv.), THF, 0° to r.t., then -78°, CBr<sub>4</sub> (2 equiv.).

Scheme 2. Reactions of  $C_{60}$  with the Tethered Bis(2-bromomalonates) **5** and **6**

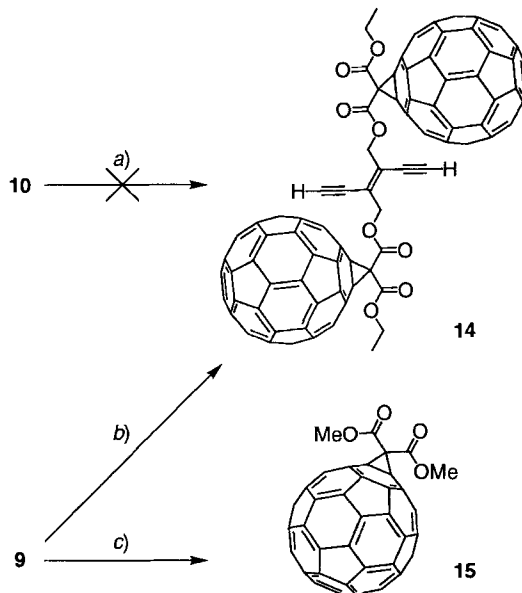
in aromatic and chlorinated organic solvents was sufficient to allow for complete spectroscopic characterization. The UV/VIS spectra of **9** and **10** displayed similar absorption bands and end absorptions ( $\lambda$  690 nm) to those measured for diethyl 1,2-methano[60]-fullerene-61,61-dicarboxylate [**15a**]. As previously reported for other bis-fullerene derivatives [**18**] [**19**], there exists no electronic communication between the two fullerene moieties. Interestingly, the  $C_{60}$  bis-adducts **11** and **12**, resulting from a macrocyclization reaction on the  $C_{60}$  core, were also isolated as major side products. When the reaction between **6** and  $C_{60}$  was performed under high dilution conditions, only a trace amount of **10** was formed, and bis-adduct **12** was isolated in 15% yield. This new, direct bis-functionalization of  $C_{60}$  was highly regioselective. In effect, the linker between the two malonate moieties acted as a directing tether [**20**], and only one out of nine possible, constitutionally isomeric bis-adducts [**21**] [**22**] was formed. The relative position of the two cyclopropane rings on the  $C_{60}$  core was unambiguously determined by transformation of **11**, via transesterification, into the known  $C_s$ -symmetrical *cis*-2 tetraethyl ester **13** [**21**] (Scheme 3). Although there exist a total of four possible  $C_1$ -symmetrical *cis*-2

Scheme 3. Transesterification of Bis-adduct **11**

diastereoisomers [22], compounds **11** and **12** were formed with complete diastereoselectivity. Due to the in/out stereoisomerism [23], the two ethoxycarbonyl residues in **11** and **12** can either adopt an ‘out-out’ (as shown in *Scheme 2*), an ‘in-out’, or an ‘in-in’ orientation with respect to each other. Furthermore, due to the restricted rotation of the *trans*-alkene moiety in the 13-membered ring, two ‘in-out’ diastereoisomers are possible. Steric considerations derived from molecular and computer modeling strongly suggested that the two bis-adducts **11** and **12** should adopt the ‘out-out’-configuration, in analogy to a related macrocyclic *cis*-2 bis-adduct for which an X-ray crystal structure was obtained [22]. Following the isolation of **11** and **12**, the general character of this facile methodology for the selective preparation of C<sub>60</sub> bis-adducts was established and recently reported in a preliminary communication [22].

All efforts to efficiently deprotect the bis-fullerene derivatives **9** or **10** toward formation of the desired PTA monomer **14** were disappointing (*Scheme 4*). Reaction of **10** with Bu<sub>4</sub>NF under various conditions led to polymerization and/or decomposition, as had been previously reported for the attempted F<sup>-</sup>-mediated deprotection of (i-Pr)<sub>3</sub>Si–C≡C-substituted methanofullerenes [24]. Removal of the more labile Et<sub>3</sub>Si-protecting groups in **9** by protodesilylation (K<sub>2</sub>CO<sub>3</sub>/MeOH/THF) did not give **14** but rather dimethyl ester **15** (65% yield), resulting from remarkably facile transesterification. On a very small, preparatively impractical scale (0.003 mM runs), Et<sub>3</sub>Si-protected **9** could be transformed with a catalytic amount of Bu<sub>4</sub>NF on SiO<sub>2</sub> in wet THF into the free *trans*-enediynes **14** in 94% yield. All attempts, however, to scale up this reaction failed, and only decomposition products were observed.

Scheme 4. Attempted Desilylation of Bis-fullerene Derivatives **9** and **10**

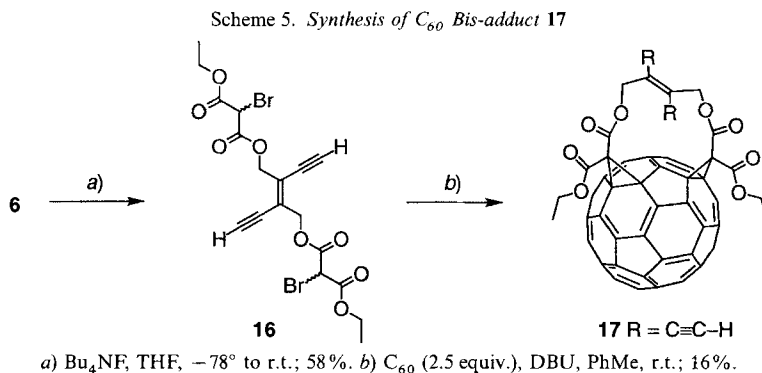


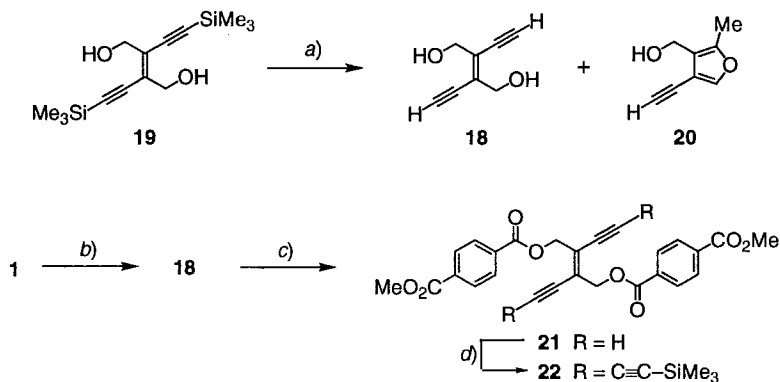
a) Bu<sub>4</sub>NF, THF, –78° or r.t.; or Bu<sub>4</sub>NF on SiO<sub>2</sub>, THF, –78° or r.t. b) 0.0034 mM **9**, Bu<sub>4</sub>NF on SiO<sub>2</sub>, THF, r.t.; 94%. c) K<sub>2</sub>CO<sub>3</sub>, MeOH, THF, r.t.; 65%.

To avoid the problematic removal of the  $R_3Si$ -protecting groups in **9** and **10**, deprotection of the *trans*-enediynes was performed before the coupling reaction with  $C_{60}$ . Actually, protection of terminal alkynes in substrates for the *Bingel* addition to  $C_{60}$  is *a priori* not necessary, since DBU ( $pK_a$  24.3 in MeCN) [25] is not sufficiently basic to deprotonate a terminal ethynyl group. Also, previous experience [7a] suggested that unprotected *trans*-enediynes **16** would have sufficient stability for isolation and further reaction. Deprotection of **6** with  $Bu_4NF$  in THF indeed afforded **16** in 58% yield; the subsequent *Bingel* addition, however, gave none of the desired bis-fullerene derivative **14** but rather, as the only isolable product, the macrocyclic bis-adduct **17** (16%, *Scheme 5*). The product distribution in the *Bingel* reaction of **5**, **6**, and **16** with  $C_{60}$  (*Schemes 2* and *5*) is clearly dependent upon the nature of the alkyne substituents (R), with bulky groups apparently retarding the macrocyclization due to unfavorable steric demands. Thus, the bis-adduct/bis-fullerene product ratio increases from 1:5 (R = (i-Pr) $_3$ Si), to 1:2 (R = Et $_3$ Si), to bis-adduct formation only (R = H).

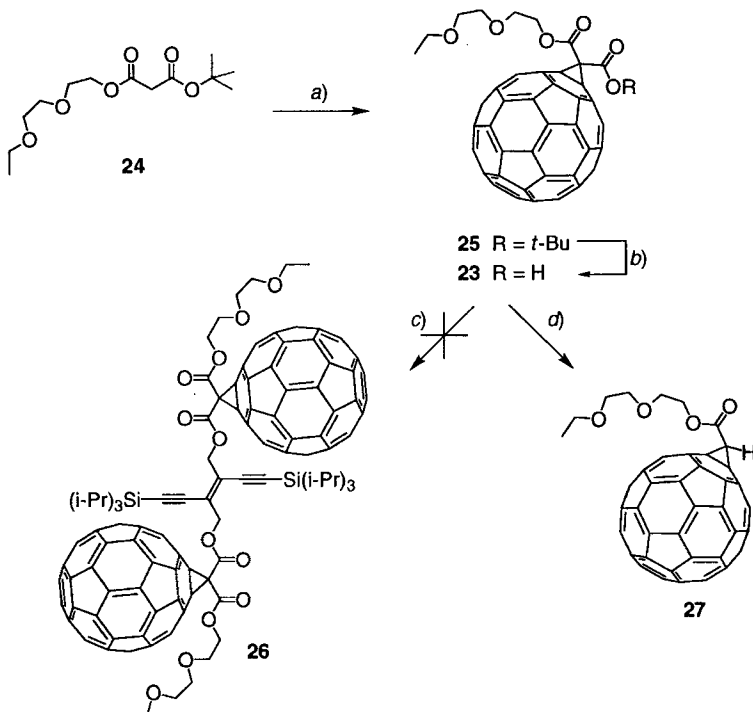
2.2. A PTA Monomer by Esterification of 1,2-Methano[60]fullerene-carboxylic Acids. To avoid the problems of alkyne deprotection and competing macrocyclization encountered in the synthesis of **14** (*Sect. 2.1*), an alternative route to PTA monomers was pursued by esterification of 1,2-methano[60]fullerene carboxylic-acid derivatives with (*E*)-2,3-diethynylbut-2-ene-1,4-diol (**18**). This diol was obtained in low yield (6%) by protodesilylation ( $K_2CO_3/MeOH/THF$ ) of **19** [7a] [26], with the major product formed being furan **20** resulting from *exo-dig* cyclization of **19** under the basic conditions [18b] [27] (*Scheme 6*). Fortunately, the undesired furan formation could be avoided by preparing **18** *via* deprotection of **1** with  $Bu_4NF$  in THF. In model reactions to support the feasibility of the new route towards PTA monomers and polymers, diol **18** was transformed in 61% yield into diester **21** by *N,N'*-dicyclohexylcarbodiimide(DCC)-mediated esterification [28] with terephthalic acid. Subsequently, the potential of *trans*-enediynes diesters in oxidative coupling reactions was successfully demonstrated by reacting **21** under *Hay* conditions [29] with  $Me_3Si-C\equiv C-H$  giving **22** in 72% yield.

As the second component in the 'esterification route' towards a PTA monomer, methanofullerene-carboxylic acid **23** was prepared starting from the mixed malonate ester **24** (*Scheme 7*). Reaction of malonyl dichloride with *t*-BuOH and diethyleneglycol monoethyl ether in  $CH_2Cl_2$  in the presence of  $C_5H_5N$  afforded **24**, which was treated with  $C_{60}$  in PhMe in the presence of DBU and  $I_2$  [15b] to give highly soluble **25**, of which



Scheme 6. Synthesis of Diol **18**, Model Esterification, and Oxidative Coupling Reactions


a) K<sub>2</sub>CO<sub>3</sub>, MeOH, THF, r.t.; 6% (**18**) and 60% (**20**). b) Bu<sub>4</sub>NF, THF, r.t. c) Methyl hydrogen terephthalate, DCC, 4-(dimethylamino)pyridine (DMAP), CH<sub>2</sub>Cl<sub>2</sub>, r.t.; 61% (from **1**). d) Me<sub>3</sub>Si–C≡C–H (100 equiv.), CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, r.t.; 72%.

 Scheme 7. Synthesis of Methanofullerene-carboxylic Acid **23** and Decarboxylation to **27**


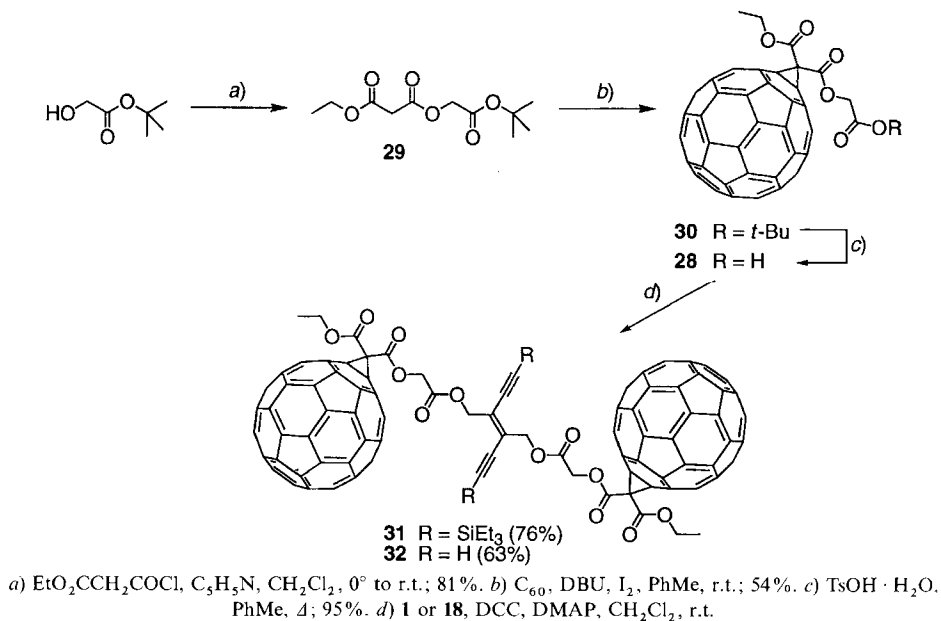
a) C<sub>60</sub>, DBU, I<sub>2</sub>, PhMe, r.t.; 51%. b) TsOH · H<sub>2</sub>O, PhMe, Δ; 95%. c) **2**, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, r.t. d) DMAP, CH<sub>2</sub>Cl<sub>2</sub>, r.t.; 85%.

350 mg could be dissolved in *ca.* 1 ml of  $\text{CDCl}_3$ . Selective hydrolysis of the *t*-Bu ester moiety with toluene-4-sulfonic acid (TsOH) in refluxing PhMe [30] gave **23** which also was readily soluble in chlorinated organic solvents. DCC-Mediated esterification of **23** with diol **2** in  $\text{CH}_2\text{Cl}_2$ , however, was not successful and afforded methanofullerene **27** by rapid decarboxylation rather than desired **26**. It was subsequently determined that decarboxylation of **23** readily occurs in the presence of a catalytic amount of DMAP in  $\text{CH}_2\text{Cl}_2$  at r.t., affording **27** in high yield (85%).

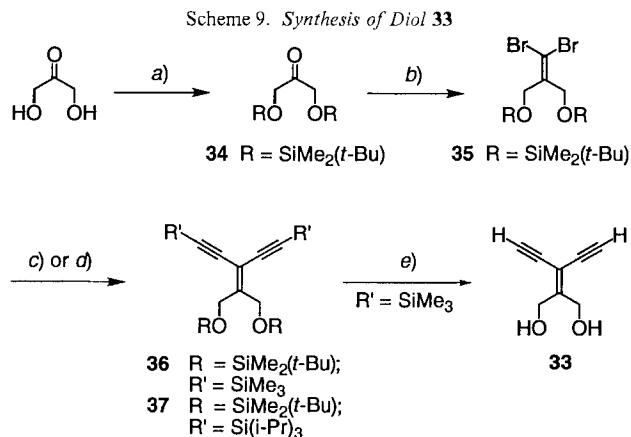
Methanofullerene-monocarboxylic esters such as **27** were previously prepared in generally modest yields by 1,3-dipolar cycloaddition of the corresponding diazo esters to  $\text{C}_{60}$ , followed by elimination of  $\text{N}_2$  [16a] [31]. In addition, these reactions led to mixtures of 6,6-closed and 6,5-open (addition to bonds shared by a 5- and a 6-membered ring) isomers which had to be subsequently equilibrated to the thermodynamically more stable 6,6-closed product. The *Bingel* addition of mixed malonate esters such as **24** to  $\text{C}_{60}$ , followed by hydrolysis of the *t*-Bu ester moiety and decarboxylation appears to be a mild, efficient alternative for the preparation of methanofullerene-monocarboxylic esters.

To prevent decarboxylation reactions under the conditions of DCC/DMAP-mediated esterifications, a spacer was introduced between the bridging C-atom of the methanofullerene and the reacting carboxylic-acid group. The synthesis of the targeted acid **28** started with the reaction of *tert*-butyl 2-hydroxyacetate [32] with ethyl 3-chloro-3-oxopropanoate to give the mixed malonate ester **29** (Scheme 8). Methanofullerene **30** was obtained by *Bingel* reaction of  $\text{C}_{60}$  with **29** in the presence of DBU and  $\text{I}_2$  in PhMe, and selective cleavage of the *tert*-butyl ester (TsOH, PhMe) yielded the desired carboxylic acid **28**. DCC-Mediated esterification of **28** with diols **1** and **18** subsequently afforded the

Scheme 8. Synthesis of *trans*-Eneidyne **32**, a Direct Precursor for the Oxidative Cyclization to  $\text{C}_{60}$ -Appended Poly(triacetylenes)







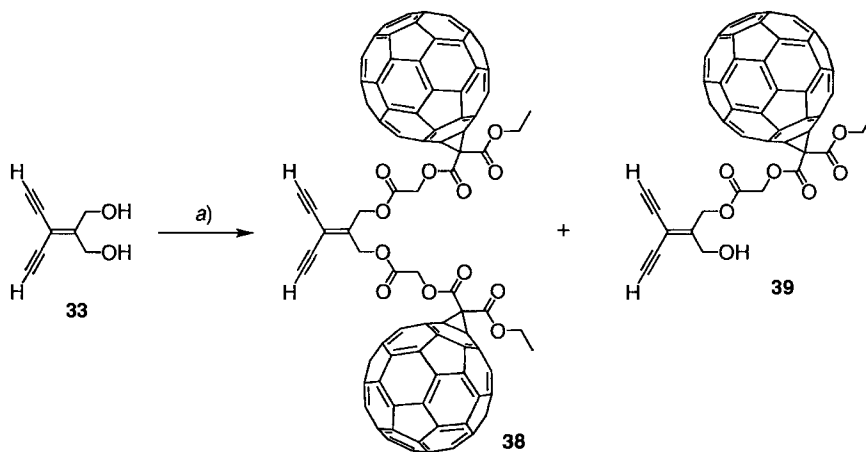
a) 1*H*-Imidazol, Me<sub>2</sub>(*t*-Bu)SiCl, DMF, r.t. b) CBr<sub>4</sub>, PPh<sub>3</sub>, PhH, r.t.; 38%. c) Me<sub>3</sub>Si-C≡CH, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, Et<sub>3</sub>N, r.t.; 73%. d) (i-Pr)<sub>3</sub>Si-C≡CH, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, Et<sub>3</sub>N, r.t.; 86%. e) Bu<sub>4</sub>NF (5 equiv.), wet THF, 0°; 66%.

protected and deprotected PTA monomers **31** and **32**, respectively, in good yields. It should be noted that the described route readily provides access to multigram quantities of **32** that are required for the exploration of the oxidative coupling to C<sub>60</sub>-appended PTA oligomers and polymers. Compound **32** displays low solubility in common organic solvents but is remarkably stable and does not melt or decompose below 280°.

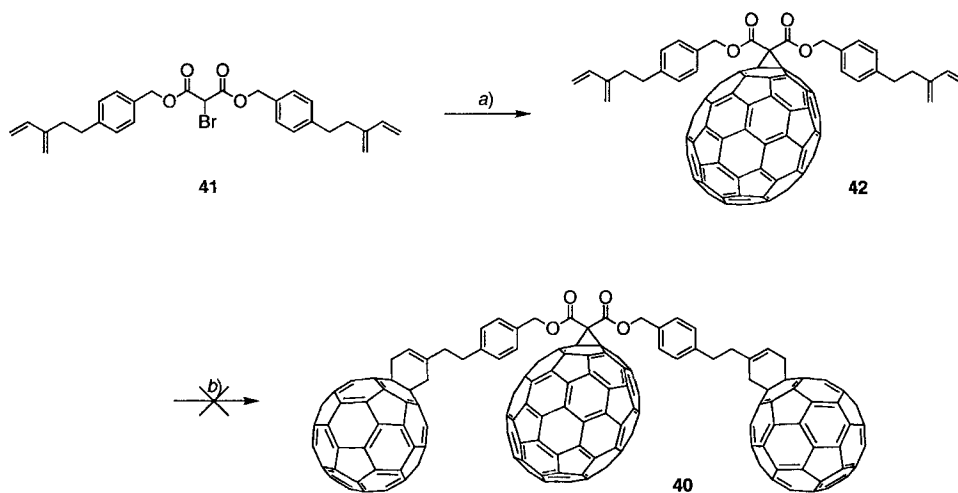
**2.3. Synthesis of a Monomer for the Preparation of C<sub>60</sub>-Substituted Expanded Radialenes.** The synthesis of a direct monomer for the oxidative cyclization to expanded radialenes with pendant methano[60]fullerene residues followed the 'esterification route' employed for the preparation of PTA monomer **32** (Sect. 2.2). To obtain diol **33** required for this route (Scheme 9), protected dihydroxyacetone **34** was synthesized as reported by Tamm and coworkers [33], and subsequent Corey-Fuchs dibromoolefination (CBr<sub>4</sub>/PPh<sub>3</sub>) [34] afforded **35** as a stable oil. Pd-Catalyzed coupling of **35** with either Me<sub>3</sub>Si- or (i-Pr)<sub>3</sub>Si-protected acetylene gave the geminal diynes **36** and **37** in high yields, respectively [35]. Deprotection of **36** with Bu<sub>4</sub>NF in THF at 0° led to diol **33** as an unstable oily solid. Under these conditions, **33** did not react further under undesirable furan formation.

Because of its instability, diol **33** was quickly carried on to the next step without further purification. Under the DCC-mediated esterification conditions, methano[60]fullerene-carboxylic acid **28** reacted with **33** to yield the bis- and mono-adducts **38** and **39** in 25 and 23% yields, respectively (Scheme 10). The solubility of both products was sufficient to allow full spectroscopic characterization. Similar to the isomeric PTA monomer **32**, the direct precursor **38** to the expanded radialenes is highly stable under normal laboratory conditions.

**2.4. Synthesis of a Mixed C<sub>60</sub>-C<sub>70</sub> Fullerene Derivative: a Member of a New Class of Fullerene-Based Oligomers.** The first target in our attempts to prepare mixed fullerene oligomers was compound **40** with two C<sub>60</sub> Diels-Alder adducts attached to a central methano[70]fullerene (Scheme 11). Bingel addition of the anchor-tether-reactive-group conjugate **41** [20a] to C<sub>70</sub> was expected to occur selectively at the most curved bond near

Scheme 10. Synthesis of the Direct Precursor **38** to  $C_{60}$ -Substituted Expanded Radialenes

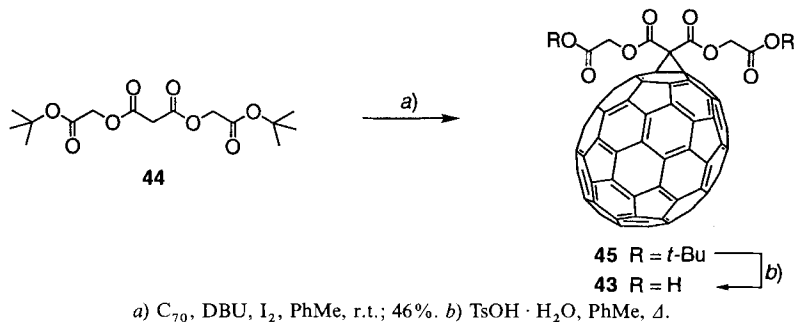
a) **28**, DCC, DMAP,  $CH_2Cl_2$ , r.t.; 25% (**38**) and 23% (**39**).

Scheme 11. Attempted Synthesis of Mixed Fullerene Compound **40**

a)  $C_{70}$ , DBU, PhMe, r.t. b)  $C_{60}$ , PhMe,  $\Delta$ .

the pole, yielding **42**. In contrast to the previous findings with  $C_{60}$  [20a], however, regioselective double intramolecular *Diels-Alder* addition of **42** should be disfavored, because the tether directs the two reactive 1,3-diene groups to 6,6-bonds of low reactivity [36] in the flatter equator region of the  $C_{70}$  sphere. Hence, intermolecular additions of **42** to  $C_{60}$  molecules present in solution should preferentially occur under formation of the mixed fullerene compound **40**.

Cyclopropanation of  $C_{70}$  with **41** [20a] in PhMe with DBU as base yielded mono-adduct **42** which is stable in dilute solution but polymerizes rapidly in the neat state. The

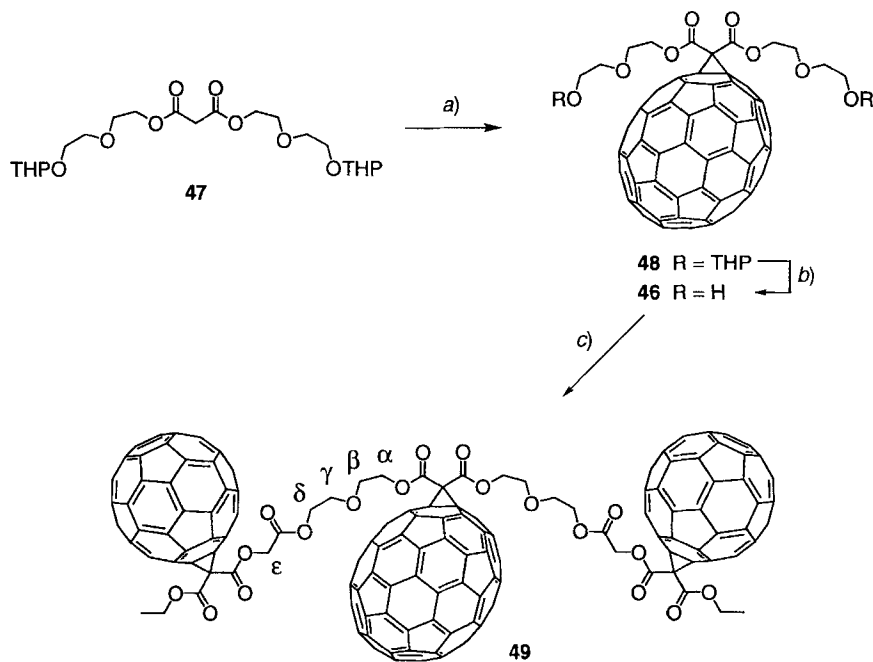
Scheme 12. Synthesis of 1,2-Methano[70]fullerene Dicarboxylic Acid **43**

subsequently attempted intermolecular *Diels-Alder* addition between the two buta-1,3-diene moieties of **42** and two C<sub>60</sub> molecules [37], however, did not produce isolable amounts of hybrid compound **40**.

We subsequently intended to prepare a mixed fullerene compound by DCC-mediated esterification of methano[70]fullerene-dicarboxylic acid **43** (Scheme 12) with two equiv. of a suitable methano[60]fullerenol derivative. For the synthesis of **43**, malonate **44** was prepared by reacting *tert*-butyl 2-hydroxyacetate [32] with malonyl dichloride and subsequently added by *Bingel* reaction regioselectively [15a] [38] to the 1,2-bond at the pole of C<sub>70</sub> under formation of **45**. The <sup>13</sup>C-NMR spectrum confirmed the C<sub>s</sub> symmetry, displaying the 36 out of the 37 expected fullerene resonances (34 between 130 and 150 ppm, two of which showed half intensity, and 2 at 66.03 and 66.55 ppm), as well as 6 non-fullerenic signals (162.49 and 165.35 (C=O), 63.29 (CH<sub>2</sub>), 28.10 and 83.00 (CMe<sub>3</sub>), and 36.24 ppm (methano bridge)). Cleavage of the *t*-Bu ester groups in **45** (TsOH, PhMe) afforded diacid **43** as a very insoluble compound. Due to the low solubility, attempted DCC-mediated esterifications with **43** in CH<sub>2</sub>Cl<sub>2</sub> failed and, therefore, the synthesis of a mixed fullerene compound needed to be changed again.

It was now planned to prepare the fullerene hybrid by esterification of methano[70]fullerenediol **46** with 2 equiv. of methano[60]fullerene-carboxylic acid **28**, which was already in hand (Scheme 13). On this, ultimately, successful route, malonate **47** was obtained by reacting 2-[2-(3,4,5,6-tetrahydro-2*H*-pyran-2-yloxy)ethoxy]ethanol [39] with malonyl dichloride and subsequently added to C<sub>70</sub> under formation of 1,2-mono-adduct **48** which was obtained as a mixture of diastereoisomers. Deprotection (TsOH/EtOH/PhMe) afforded the readily soluble diol **46** which was doubly esterified with **28** to give the desired C<sub>60</sub>-C<sub>70</sub> hybrid **49** as a dark brown solid in 23% yield. Due to the low solubility of **28**, the esterification required high dilution and prolonged reaction times, which led to partial decomposition. The low yield of **49** was due to this decomposition as well as due to the difficulties in separating the target compound from the degradation products.

The structure of **49** was confirmed by matrix-assisted laser-desorption time-of-flight (MALDI-TOF) mass spectrometry, which depicted a strong molecular ion peak at *m/z* 2900 (*M*<sup>+</sup>, C<sub>215</sub>H<sub>30</sub>O<sub>18</sub> requires 2900.6). The C<sub>s</sub>-symmetrical compound **49** was poorly soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> but sufficiently soluble in Cl<sub>2</sub>DCCDCl<sub>2</sub> to record both its <sup>1</sup>H- and <sup>13</sup>C-NMR spectra.

Scheme 13. Synthesis of the  $C_{60}$ - $C_{70}$  Hybrid Compound **49**

a)  $C_{70}$ , DBU,  $I_2$ , PhMe, r.t.; 65%. b) TsOH ·  $H_2O$ , PhMe, EtOH, 60°; 60%. c) **28** (3 equiv.), DCC, DMAP,  $CH_2Cl_2$ , r.t.; 23%.

The  $^1H$ -NMR spectrum of **49** displayed seven signals between 1.4 and 5.0 ppm corresponding to the 5 different  $CH_2$  groups  $\alpha$ – $\epsilon$  (Scheme 13) and the  $t$  and  $q$  for the ethyl-ester groups. The  $CH_2(\epsilon)$  protons are diastereotopic; however, they appeared as a sharp  $s$  resulting from a pseudo-plane of symmetry perpendicular to the mirror plane of the  $C_s$ -symmetrical compound. This pseudo-symmetry was also revealed in the  $^{13}C$ -NMR spectrum, and both the  $C_{60}$  and  $C_{70}$  core resonances appeared with the typical pattern of  $C_s$ -symmetrical fullerenes. Of the 37 core resonances expected for a  $C_s$ -symmetrical  $C_{70}$  and the 32 ones for two identical, pseudo- $C_s$ -symmetrical  $C_{60}$  moieties in **49**, a total of 60 were observed. As a result of this pseudo-symmetry, there is a large difference in intensity between the  $C_{70}$  and  $C_{60}$  signals, with the latter having twice the relative intensity of the former, and they are, therefore, easily distinguishable.

The electronic absorption spectra of **30**, **46**, and **49** are shown in Fig. 3. In the range between 430 nm and the end absorption above 700 nm, the spectrum of **49** closely resembles that of the  $C_{70}$  derivative **46**. As a result of the domination of the  $C_{70}$  chromophore in the visible absorption range, solutions of **49** have the classical brown-red color generally observed for  $C_{70}$  mono-adducts [36] [38]. Below 430 nm, the characteristic absorption bands of a methano[60]fullerene at 257, 325, and 425 nm [40], dominate the spectrum of hybrid **49**. Thus, the UV/VIS spectrum of **49** clearly reflects the presence of the two different fullerenes. Since the spectrum of **49** is remarkably similar in shape and intensity to a calculated UV/VIS spectrum resulting from addition of the spectra of **46** and **30** in a 1:2 ratio, there exists no special electronic interaction between the different fullerene sub-units in **49**. This is not surprising since the three fullerene moieties in the hybrid compound are separated by rather long tethers.

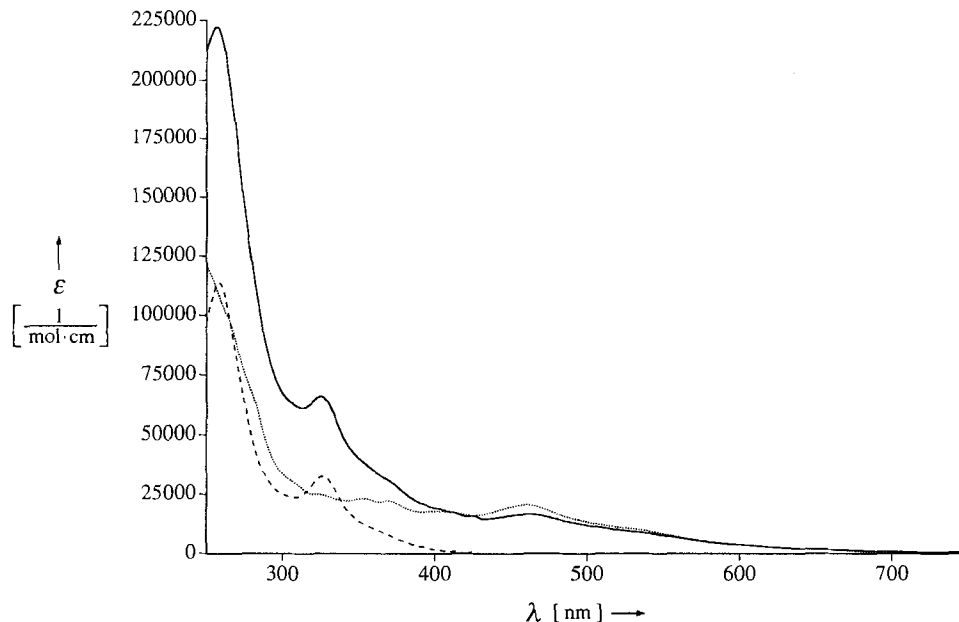


Fig. 3. UV/VIS Spectra of **30** (---), **46** (···), and **49** (—) in  $\text{CH}_2\text{Cl}_2$

2.5. *Electrochemical Studies.* The redox behavior of **30**, **46**, and **49** is summarized in the Table. On the available potential range, **30** and **46** gave in  $\text{CH}_2\text{Cl}_2$  several reduction steps [14a], the first two being reversible on the time scale of the cyclic voltammetry. Indeed, for all sweep rates, the current ratio  $I_{pc}/I_{pa}$  was unity, and the peak potential difference, for sweep rates lower than  $0.2 \text{ Vs}^{-1}$ , was close to 90 mV for **30** and 70 mV for **46**, respectively (uncorrected for ohmic drop). All these features are characteristic of a reversible one-electron charge transfer.

For the mixed fullerene derivative **49**, only two reversible reduction steps were observed in the solvent mixture  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  95:5. The cyclic voltammograms were not well defined for sweep rates higher than  $0.2 \text{ Vs}^{-1}$  due to adsorption phenomena. For sweep rates lower than  $0.2 \text{ Vs}^{-1}$ , the voltammogram showed reversible couples. Rotating disk electrode (RDE) experiments gave rise to two well defined reduction waves, each having the same amplitude. The slopes of these waves, by plotting  $E$  vs.  $\log(I/I_d - I)$  were equal to 70 mV.

Table. Reduction Characteristics of the Fullerene Derivatives **30**, **46**, and **49** Observed by Cyclic Voltammetry on a Glassy Carbon Electrode in  $\text{CH}_2\text{Cl}_2$  (+ 0.1M  $(\text{Bu}_4\text{N})\text{PF}_6$ )

	$E_{\text{red1}}^0$ ([V] vs. $\text{Fc}/\text{Fc}^+$ ) <sup>a)</sup>	$E_{\text{red2}}^0$ ([V] vs. $\text{Fc}/\text{Fc}^+$ ) <sup>a)</sup>
<b>30</b>	-1.00(86)	-1.38(93)
<b>46</b>	-1.02(68)	-1.39(82)
<b>49</b> <sup>b)</sup>	-1.00(66)	-1.40(83)

<sup>a)</sup> In parentheses,  $\Delta E_p$  in mV at  $v=0.1 \text{ V s}^{-1}$ .

<sup>b)</sup>  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  95:5 was used instead of  $\text{CH}_2\text{Cl}_2$  for solubility reasons.

As the number and the reduction potentials are quite identical in the mixed fullerene derivative **49**, as compared to the separate  $C_{60}$  and  $C_{70}$  adducts (*Table*), it is clear that the three fullerenes in **49** behave as independent redox centers. The resulting voltammogram is consistent with the sum of the individual constituents. It can, therefore, be assumed that each of the two reversible reduction steps of **49** involves three electrons, namely one for each independent redox center on each fullerene. The near identity of the potentials at which the first three one-electron reductions occur in  $C_{60}$  and  $C_{70}$  [41] had been established shortly after the discovery of the bulk preparation method for fullerenes in 1990 [42]. The presence of three independent redox centers in **49** was, to some extent, expected as the fullerene sub-units in **49** are separated by rather long, saturated chains. These results are also in agreement with the UV/VIS spectra discussed above.

**3. Conclusions.** – (*E*)-Hex-3-ene-1,5-diyne and 3-methylidenepenta-1,4-diyne with pendant  $C_{60}$  moieties were synthesized as precursors to fullerene-substituted poly(triacetylenes) (PTAs) and expanded radialenes, respectively. The direct precursors to PTAs, *i.e.*, **32**, and to expanded radialenes, *i.e.*, **38**, each contain two terminal free alkyne groups, yet both constitutionally isomeric compounds are remarkably stable. Other attractive features are their relatively good solubility, despite two appended  $C_{60}$  moieties and molecular weights above 1900 D, as well as their potential availability in multigram quantities. Investigations into the formation of the targeted  $C_{60}$ -substituted PTAs and expanded radialenes are now further pursued in our laboratory.

During the development of suitable PTA monomers in this study, a new macrocyclization reaction, consisting of a double *Bingel* addition of a tethered bis-malonate to  $C_{60}$  was discovered. Thus, reactions of bis-bromomalonates **5**, **6**, and **16** yielded the macrocyclic products **11**, **12**, and **17**, respectively, with complete regio- and diastereoselectivity. In the meantime, the versatility of this simple bis-functionalization of  $C_{60}$  was further established, and bis-malonates with optically active tethers were even applied to the enantioselective preparation of optically active  $C_{60}$  bis-adducts [22] whose chirality exclusively results from the chiral addition pattern [43].

Also during the search for suitable monomers for  $C_{60}$ -substituted expanded radialenes, a new synthesis of methano[60]fullerene-monocarboxylic esters was discovered which should hold distinct advantages, such as high yields and versatile access, over the established preparation of these compounds by 1,3-dipolar cycloaddition of diazo esters followed by  $N_2$  elimination. The new synthetic sequence consists of *i*) the *Bingel* addition of mixed *tert*-butyl malonate esters (such as **24**) to  $C_{60}$ , *ii*) selective hydrolysis of the *tert*-butyl ester moiety, and *iii*) decarboxylation of the resulting acid (such as **23**) by stirring with DMAP in  $CH_2Cl_2$  under formation of the desired monoester (such as **27**).

Finally, with **49**, the first mixed  $C_{60}$ - $C_{70}$  fullerene derivative, which is composed of a  $C_{70}$ -mono-adduct bearing two  $C_{60}$  substituents, was prepared and fully characterized. Compound **49** can be viewed as the first representative of a new family of mixed fullerene oligomers, and this work demonstrates that by choosing the right building blocks and coupling conditions, soluble fullerene composites with  $M_w \approx 3000$  D and above can be prepared.

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### Experimental

**General.** Reagents and solvents were purchased reagent grade and used without further purification. Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona (AZ) 85706, USA. THF was distilled from sodium benzophenone ketyl.  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{CaH}_2$  or dried over molecular sieves (4 Å).  $\text{C}_{60}$  [40] and  $\text{C}_{70}$  [38b] were purified as previously reported. *tert*-Butyl 2-hydroxyacetate [32], 2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethanol [39], compounds **1** [17b], **2** [17a], **19** [7a] [26], **34** [33], and **41** [20a] were prepared as previously reported. All reactions were performed in standard glassware under an inert atmosphere of  $\text{N}_2$  or Ar. Evaporation and concentration was done at water-aspirator pressure, and compounds were dried at  $10^{-2}$  Torr. Column chromatography (CC):  $\text{SiO}_2$ -60 (230–400 mesh, 0.040–0.063 mm) from *E. Merck*. Thin-layer chromatography (TLC): glass sheets coated with  $\text{SiO}_2$ -60  $F_{254}$  from *E. Merck*; visualization by UV light. Melting points: *Büchi Smp-20*; uncorrected. UV/VIS Spectra ( $\lambda_{\text{max}}$  in nm ( $\epsilon$ )): *Varian Cary-5*-spectrophotometer. IR spectra ( $\text{cm}^{-1}$ ): *Perkin-Elmer 1600-FTIR*. NMR Spectra: *Bruker AM 500* and *Varian Gemini 300* or *200* at 296 or 300 K, with solvent peaks as reference. EI-MS ( $m/z$  (%)): *VG Tribrid* instrument; 70 eV. FAB-MS: *VG ZAB 2SEQ* instrument; 3-nitrobenzyl alcohol as matrix. MALDI-TOF-MS: measured with reflectron detection in the positive- or negative-ion mode, acceleration voltage 15–20 kV, on a *Bruker-REFLEX* spectrometer; 2,5-dihydroxybenzoic acid (DHB, 0.1M in MeCN/EtOH/ $\text{H}_2\text{O}$  50:45:5),  $\alpha$ -cyano-4-hydroxycinnamic acid (CCA, 0.1M in MeCN/EtOH/ $\text{H}_2\text{O}$  50:45:5) or 1,8,9-anthracenetriol (dithranol; 0.05M in  $\text{CHCl}_3/\text{MeOH}$  1:1) were used as matrices. Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie, ETH-Zürich*.

(*E*)-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Dipropanedioate (**3**). Ethyl 3-chloro-3-oxopropanoate (4.0 ml, 31 mmol) was added to a stirred soln. of **1** (4.55 g, 12.5 mmol) and  $\text{C}_5\text{H}_5\text{N}$  (5 ml, 63 mmol) in  $\text{CH}_2\text{Cl}_2$  (400 ml) at  $0^\circ$ . The mixture was allowed to warm slowly to r.t. (over 1 h) and stirred for 12 h, then washed with  $\text{H}_2\text{O}$  (2  $\times$ ), dried ( $\text{MgSO}_4$ ), and evaporated. CC ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ /hexane 4:3) yielded **3** (3.67 g, 50%). Colorless oil. IR (neat): 2148 ( $\text{C}\equiv\text{C}$ ), 1759 ( $\text{C}=\text{O}$ ), 1741 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 0.59 (*m*, 12H); 0.95 (*t*,  $J = 7.8$ , 18H); 1.23 (*t*,  $J = 7.2$ , 6H); 3.35 (*s*, 4H); 4.16 (*q*,  $J = 7.2$ , 4H); 4.91 (*s*, 4H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz): 3.84; 7.07; 13.69; 40.88; 61.14; 64.29; 100.11; 107.15; 127.25; 165.65; 165.75. FAB-MS: 563 (18,  $[\text{M} - \text{Et}]^+$ ), 461 (65,  $[\text{M} - \text{O}_2\text{CCH}_2\text{CO}_2\text{Et}]^+$ ), 115 (100,  $\text{SiEt}_3^+$ ). Anal. calc. for  $\text{C}_{30}\text{H}_{48}\text{O}_8\text{Si}_2$  (592.88): C 60.78, H 8.17; found: C 60.94, H 8.27.

(*E*)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Dipropanedioate (**4**). Ethyl 3-chloro-3-oxopropanoate (2.0 ml, 15.6 mmol) was added to a stirred soln. of **2** (2.80 g, 6.25 mmol) and  $\text{C}_5\text{H}_5\text{N}$  (2.5 ml, 31 mmol) in  $\text{CH}_2\text{Cl}_2$  (200 ml) at  $0^\circ$ . The mixture was allowed to slowly warm to r.t. (over 1 h) and stirred for 10 h, then washed with  $\text{H}_2\text{O}$  (2  $\times$ ), dried ( $\text{MgSO}_4$ ), and evaporated. CC ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ /hexane 4:3) afforded **4** (2.75 g, 65%). Colorless oil. IR (neat): 2148 ( $\text{C}\equiv\text{C}$ ), 1759 ( $\text{C}=\text{O}$ ), 1742 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 1.05 (*s*, 42H); 1.24 (*t*,  $J = 7.0$ , 6H); 3.36 (*s*, 4H); 4.17 (*q*,  $J = 7.0$ , 4H); 4.96 (*s*, 4H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz): 10.81; 13.72; 18.25; 40.90; 61.17; 64.47; 100.92; 106.30; 127.26; 165.65; 165.76. FAB-MS: 633 (44,  $[\text{M} - \text{i-Pr}]^+$ ), 545 (100,  $[\text{M} - \text{O}_2\text{CCH}_2\text{CO}_2\text{Et}]^+$ ).

(*E*)-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(2-bromopropanedioate) (**5**) and (*E*)-3-[(3-Ethoxy-1,3-dioxopropoxy)methyl]-5-(triethylsilyl)-2-[(triethylsilyl)ethynyl]pent-2-en-4-ynyl Ethyl-2-Bromopropanoate (**7**). DBU (1.05 ml, 7.08 mmol) was added under  $\text{N}_2$  to a stirred soln. of **3** (2.10 g, 3.54 mmol) in dry THF (200 ml) at  $0^\circ$ . The mixture was allowed to warm slowly to r.t. (over 30 min) and then cooled to  $-78^\circ$ .  $\text{CBr}_4$  (2.35 g, 7.08 mmol) was added, and stirring under  $\text{N}_2$  at  $-78^\circ$  was continued for 3 h. After addition of sat. aq.  $\text{NH}_4\text{Cl}$  soln. (40 ml) and hexane, the mixture was extracted with sat. aq.  $\text{NaCl}$  soln. (2  $\times$ ), dried ( $\text{MgSO}_4$ ), and evaporated. CC ( $\text{SiO}_2$ ) eluting with hexane/ $\text{CH}_2\text{Cl}_2$  5:4 gave **5** (1.39 g, 52%) and eluting with hexane/ $\text{CH}_2\text{Cl}_2$  1:1 yielded **7** (263 mg, 11%).

**5**: Colorless oil. IR (neat): 2147 ( $\text{C}\equiv\text{C}$ ), 1771 ( $\text{C}=\text{O}$ ), 1748 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 0.63 (*m*, 12H); 0.98 (*t*,  $J = 7.8$ , 18H); 1.29 (*t*,  $J = 7.1$ , 6H); 4.27 (*q*,  $J = 7.1$ , 4H); 4.84 (*s*, 2H); 5.01 (*AB*,  $J = 12.3$ , 4H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz): 4.31; 7.59; 14.02; 42.05; 63.47; 66.25; 100.29; 108.55; 127.69; 164.47; 164.65. FAB-MS: 723/721/719 (4/6/3,  $[\text{M} - \text{Et}]^+$ ), 541/539 (22/19,  $[\text{M} - \text{O}_2\text{CCHBrCO}_2\text{Et}]^+$ ), 115 (100,  $\text{SiEt}_3^+$ ). Anal. calc. for  $\text{C}_{30}\text{H}_{46}\text{Br}_2\text{O}_8\text{Si}_2$  (750.68): C 48.00, H 6.18; found: C 47.83, H 6.01.

**7**: Colorless oil. IR (neat): 2148 ( $\text{C}\equiv\text{C}$ ), 1747 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz): 0.63 (*m*, 12H); 0.98 (*m*, 18H); 1.27 (*t*,  $J = 7.2$ , 3H); 1.29 (*t*,  $J = 7.2$ , 3H); 3.39 (*s*, 2H); 4.19 (*q*,  $J = 7.2$ , 2H); 4.27 (*q*,  $J = 7.2$ , 2H);

4.84 (s, 1 H); 4.95 (s, 2 H); 5.01 (AB,  $J = 12.4$ , 2 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz): 4.16; 7.42; 13.85; 14.04; 41.22; 41.87; 61.53; 63.21; 64.55; 66.11; 100.16; 100.24; 107.88 (2  $\times$ ); 126.51; 128.40; 164.09; 164.28; 166.00; 166.11. FAB-MS: 643/641 (25/24,  $[\text{M}-\text{Et}]^+$ ), 541/539 (66/61,  $[\text{M}-\text{O}_2\text{CCH}_2\text{CO}_2\text{Et}]^+$ ), 461 (100,  $[\text{M}-\text{O}_2\text{CCHBrCO}_2\text{Et}]^+$ ). Anal. calc. for  $\text{C}_{30}\text{H}_{47}\text{BrO}_8\text{Si}_2 \cdot 1.8 \text{CH}_2\text{Cl}_2$  (824.66): C 46.32, H 6.18; found: C 46.46, H 6.15.

(E)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(2-bromopropanedioate) (**6**) and (E)-3-[(3-Ethoxy-1,3-dioxopropoxy)methyl]-5-(triisopropylsilyl)-2[(triisopropylsilyl)ethynyl]pent-2-en-4-ynyl Ethyl 2-Bromopropanoate (**8**). DBU (0.88 ml, 5.9 mmol) was added under  $\text{N}_2$  to a stirred soln. of **4** (2.00 g, 2.95 mmol) in dry THF (200 ml) at  $0^\circ$ . The mixture was warmed slowly to r.t. (over 30 min) and then cooled to  $-78^\circ$ .  $\text{CBr}_4$  (1.96 g, 5.90 mmol) was added, and stirring was continued for 5 h under  $\text{N}_2$  at  $-78^\circ$ . After addition of sat. aq.  $\text{NH}_4\text{Cl}$  soln. (30 ml) and dilution with hexane, the mixture was extracted with sat. aq.  $\text{NaCl}$  soln. (2  $\times$ ), dried ( $\text{MgSO}_4$ ), and evaporated. CC ( $\text{SiO}_2$ ) eluting with  $\text{CH}_2\text{Cl}_2$ /hexane 1:1 yielded **6** (1.18 g, 48%) and eluting with  $\text{CH}_2\text{Cl}_2$ /hexane 2:1 gave **8** (410 mg, 18%).

**6**: Colorless oil. IR (neat): 2149 ( $\text{C}\equiv\text{C}$ ), 1769 ( $\text{C}=\text{O}$ ), 1749 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 1.07 (s, 42 H); 1.28 (t,  $J = 7.1$ , 6 H); 4.26 (q,  $J = 7.1$ , 4 H); 4.82 (s, 2 H); 5.04 (AB,  $J = 12.9$ , 4 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz): 10.84; 13.56; 18.30; 41.50; 62.92; 65.96; 100.58; 106.99; 127.11; 163.76; 163.93. FAB-MS: 793/791/789 (80/100/82  $[\text{M}-\text{i-Pr}]^+$ ). Anal. calc. for  $\text{C}_{36}\text{H}_{58}\text{Br}_2\text{O}_8\text{Si}_2$  (834.84): C 51.79, H 7.00; found: C 51.75, H 6.98.

**8**: Colorless oil. IR (neat): 2144 ( $\text{C}\equiv\text{C}$ ), 1744 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz): 1.07 (s, 42 H); 1.25 (t,  $J = 7.1$ , 3 H); 1.28 (t,  $J = 7.1$ , 3 H); 3.37 (s, 2 H); 4.18 (q,  $J = 7.1$ , 2 H); 4.25 (q,  $J = 7.1$ , 2 H); 4.82 (s, 1 H); 4.98 (s, 2 H); 5.03 (AB,  $J = 12.3$ , 2 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz): 11.11; 13.83; 14.03; 18.56; 41.20; 41.82; 61.51; 63.18; 64.68; 66.36; 101.04 (2  $\times$ ); 106.92; 106.98; 126.41; 128.56; 164.07; 164.24; 165.96; 166.07. FAB-MS: 713/711 (100/87,  $[\text{M}-\text{i-Pr}]^+$ ). Anal. calc. for  $\text{C}_{36}\text{H}_{59}\text{BrO}_8\text{Si}_2$  (755.94): C 57.20, H 7.87; found: C 57.33, H 7.84.

(E)-2,3-bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**9**) and ( $\pm$ )-(E)-endo,endo-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl 1,2:7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate (**11**). DBU (0.2 ml, 1.4 mmol) was added under  $\text{N}_2$  at r.t. to  $\text{C}_{60}$  (500 mg, 0.694 mmol) and **5** (209 mg, 0.278 mmol) in PhMe (600 ml), and the mixture was stirred under  $\text{N}_2$  at r.t. for 4 h, then filtered over a short plug of  $\text{SiO}_2$  (PhMe), and evaporated. CC ( $\text{SiO}_2$ ) eluting with hexane/PhMe 2:1 yielded unreacted  $\text{C}_{60}$  (108 mg), with hexane/ $\text{CH}_2\text{Cl}_2$  2:1 **11** (59 mg, 16%), and with hexane/ $\text{CH}_2\text{Cl}_2$  5:3 to 5:4 **9** which was recrystallized from pentane/ $\text{CH}_2\text{Cl}_2$  (184 mg, 33%).

**9**: Dark-red solid. M.p.  $> 280^\circ$ . UV/VIS ( $\text{CH}_2\text{Cl}_2$ ): 258 (250400), 303 (sh, 79800), 327 (76000), 426 (4810), 488 (2890), 688 (390). IR (KBr): 2146 ( $\text{C}\equiv\text{C}$ ), 1749 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 0.69 (m, 12 H); 1.04 (t,  $J = 7.5$ , 18 H); 1.51 (t,  $J = 7.1$ , 6 H); 4.58 (q,  $J = 7.1$ , 4 H); 5.35 (s, 4 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz): 4.33; 7.70; 14.31; 51.82; 63.41; 66.37; 71.47; 100.75; 108.54; 128.17; 138.75; 139.59; 140.85; 140.92; 141.82; 142.19; 142.91; 142.99; 143.00; 143.08; 143.86; 143.89; 144.59; 144.60; 144.63; 144.66; 144.68; 144.89; 145.08; 145.16; 145.18; 145.19; 145.26; 145.31; 145.49; 163.18; 163.20. FAB-MS: 2028 (1,  $\text{M}^+$ ), 1308 (7,  $[\text{M}-\text{C}_{60}]^+$ ), 720 (100,  $\text{C}_{60}^+$ ). Anal. calc. for  $\text{C}_{150}\text{H}_{44}\text{O}_8\text{Si}_2 \cdot \text{CH}_2\text{Cl}_2$  (2115.12): C 85.75, H 2.19; found: C 85.68, H 2.36.

**11**: Dark red solid. M.p.  $> 280^\circ$ . UV/VIS ( $\text{CH}_2\text{Cl}_2$ ): 260 (118700), 290 (sh, 62900), 308 (sh, 54100), 374 (sh, 10100), 409 (sh, 3270), 437 (2530), 469 (2300). IR (KBr): 2152 ( $\text{C}\equiv\text{C}$ ), 1752 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 0.68 (m, 6 H); 0.76 (m, 6 H); 1.03 (t,  $J = 7.5$ , 9 H); 1.11 (t,  $J = 7.5$ , 9 H); 1.34 (t,  $J = 7.1$ , 3 H); 1.35 (t,  $J = 7.1$ , 3 H); 4.25–4.55 (m, 4 H); 4.52 (d,  $J = 10.3$ , 1 H); 5.09 (d,  $J = 10.7$ , 1 H); 5.29 (d,  $J = 10.7$ , 1 H); 6.11 (d,  $J = 10.3$ , 1 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz): 4.21; 4.37; 7.64; 14.08; 48.73; 49.38; 62.88; 62.92; 65.73; 65.89; 67.29; 67.45; 70.22; 70.42; 102.46; 102.63; 107.83; 107.94; 129.53; 130.75; 135.59; 135.86; 136.42; 136.70; 137.24; 137.43; 139.89; 140.52; 141.03; 141.11; 141.20; 141.22; 142.21; 142.31; 142.96; 143.08; 143.16; 143.30; 143.58; 143.59; 143.62; 143.91; 143.93; 144.22; 144.52; 144.53; 144.59; 144.61; 144.67; 145.14; 145.18; 145.19; 145.20; 145.22; 145.39; 145.46; 145.56; 145.59; 145.70; 145.73; 145.87; 145.99; 146.00; 146.08; 146.10; 147.27; 147.46; 147.53; 161.56; 161.86; 162.42; 162.46. FAB-MS: 1309 (20,  $\text{MH}^+$ ), 720 (100,  $\text{C}_{60}^+$ ). Anal. calc. for  $\text{C}_{90}\text{H}_{44}\text{O}_8\text{Si}_2$  (1309.52): C 82.55, H 3.39; found: C 82.50, H 3.49.

(E)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**10**) and ( $\pm$ )-(E)-endo,endo-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl 1,2:7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate (**12**). DBU (0.2 ml, 1.4 mmol) was added under  $\text{N}_2$  at r.t. to  $\text{C}_{60}$  (500 mg, 0.694 mmol) and **6** (232 mg, 0.278 mmol) in PhMe (600 ml), and the soln. was stirred under  $\text{N}_2$  at r.t. for 4 h, then filtered over a short plug of  $\text{SiO}_2$  (PhMe) and evaporated. CC ( $\text{SiO}_2$ ) eluting with hexane/PhMe 4:1 yielded unreacted  $\text{C}_{60}$  (110 mg), with hexane/ $\text{CH}_2\text{Cl}_2$  3:1 **12** (39 mg, 10%), and with hexane/ $\text{CH}_2\text{Cl}_2$  2:1 to 4:3 **10** which was recrystallized from hexane/ $\text{CH}_2\text{Cl}_2$  (272 mg, 46%).

**10**: Dark-red solid. M.p.  $> 280^\circ$ . UV/VIS ( $\text{CH}_2\text{Cl}_2$ ): 258 (249300), 304 (sh, 68800), 327 (67700), 426 (4130), 488 (2520), 688 (290). IR ( $\text{CHCl}_3$ ): 2144 ( $\text{C}\equiv\text{C}$ ), 1745 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 1.13 (s, 42 H); 1.49 (t,  $J = 7.1$ , 6 H); 4.56 (q,  $J = 7.1$ , 4 H); 5.37 (s, 4 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz): 11.38; 14.31; 18.79; 51.93;



63.36; 66.59; 71.56; 101.65; 107.73; 128.28; 138.88; 139.51; 140.85; 140.92; 141.87; 141.96; 142.24; 142.95; 143.01; 143.04; 143.11; 143.12; 143.91; 143.93; 144.62; 144.64; 144.70; 144.71; 144.93; 145.03; 145.14; 145.20; 145.21; 145.26; 145.30; 145.53; 163.15; 163.18. FAB-MS: 2114 (2,  $MH^+$ ), 1393 (6,  $[M-C_{60}]^+$ ), 720 (100,  $C_{60}^+$ ). Anal. calc. for  $C_{156}H_{56}O_8Si_2$  (2114.35): C 88.62, H 2.67; found: C 88.50, H 2.95.

**12**: Dark-red solid. M.p. > 280°. UV/VIS ( $CH_2Cl_2$ ): 260 (113700), 292 (61300), 309 (53800), 374 (sh, 10600), 409 (sh, 3300), 437 (2650), 469 (2380). IR ( $CHCl_3$ ): 2144 ( $C\equiv C$ ), 1748 ( $C=O$ ).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.13 (s, 21 H); 1.19 (s, 21 H); 1.32 (t,  $J = 7.1$ , 3 H); 1.33 (t,  $J = 7.1$ , 3 H); 4.25–4.55 (m, 4 H); 4.46 (d,  $J = 10.5$ , 1 H); 5.01 (d,  $J = 10.9$ , 1 H); 5.35 (d,  $J = 10.9$ , 1 H); 6.21 (d,  $J = 10.5$ , 1 H).  $^{13}C$ -NMR ( $CDCl_3$ , 125 MHz): 11.11; 11.37; 14.07; 14.08; 18.68; 18.74; 18.77; 18.79; 48.30; 48.89; 62.80; 62.86; 66.00; 66.12; 67.25; 67.42; 70.12; 70.29; 103.18; 103.27; 106.58; 106.72; 129.41; 130.48; 135.60; 136.03; 136.61; 137.05; 137.35; 137.65; 137.93; 139.80; 140.62; 141.02; 141.10; 141.16; 141.19; 142.19; 142.34; 142.84; 143.00; 143.10; 143.26; 143.59; 143.61; 143.86; 144.19; 144.20; 144.22; 144.24; 144.50; 144.62; 144.69; 145.16; 145.21; 145.31; 145.39; 145.46; 145.52; 145.56; 145.70; 145.72; 145.74; 145.89; 145.96; 146.07; 146.08; 147.25; 147.45; 147.53; 148.19; 148.68; 161.35; 161.66; 162.24; 162.27. FAB-MS: 1393 (21,  $MH^+$ ), 720 (100,  $C_{60}^+$ ). Anal. calc. for  $C_{96}H_{56}O_8Si_2 \cdot 1/3 CH_2Cl_2$  (1421.99): C 81.37, H 4.02; found: C 81.06, H 4.41.

*Preparation of 12 under High Dilution Conditions.* A mixture of  $C_{60}$  (258.7 mg, 0.359 mmol) and **6** (300 mg, 0.359 mmol) in PhMe (500 ml) was added dropwise over 36 h under vigorous stirring to a  $N_2$ -flushed soln. of DBU (1 ml, 7.2 mmol) in PhMe (250 ml), and the soln. turned orange-yellow, then orange-red. Filtration over a short plug of  $SiO_2$  (PhMe), evaporation, and CC ( $SiO_2$ ) yielded unreacted  $C_{60}$  (19 mg; with hexane/toluene 4:1) and **12** (with hexane/ $CH_2Cl_2$  3:1). Recrystallization from hexane/ $CHCl_3$ /PhH gave **12** (76 mg, 15%).

*Tetraethyl 1,2:7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate (13).*  $K_2CO_3$  (17.9 mg, 0.130 mmol) was added to **11** (17 mg, 0.013 mmol) in THF/EtOH 1:1 (100 ml), and the mixture was stirred at r.t. for 4 h, then evaporated. The residue was filtered through a pad of  $SiO_2$  ( $CH_2Cl_2$ ), and CC ( $SiO_2$ ,  $CH_2Cl_2$ /hexane 2:1) yielded **13** (4 mg, 30%). Dark-red solid. M.p. > 280°. IR, UV/VIS,  $^1H$ - and  $^{13}C$ -NMR, and FAB-MS: identical to those reported previously [21].

*(E)-2,3-Diethynylbut-2-ene-1,4-diyl Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (14).*  $Bu_4NF$  on  $SiO_2$  (0.2 mg, 0.0017 mmol) was added to **9** (7 mg, 0.0034 mmol) in wet THF (15 ml), and the soln. was stirred for 48 h at r.t. Sat. aq.  $NH_4Cl$  soln. (20 ml) was added, and the mixture was diluted with  $CH_2Cl_2$ , extracted with sat. aq. NaCl soln. (2 ×), dried ( $MgSO_4$ ), and evaporated. CC ( $SiO_2$ ,  $CH_2Cl_2$ /hexane 3:2) afforded **14** (5.8 mg, 94%) which was not fully characterized due to its insolubility. Dark-red solid. M.p. > 280°. IR (KBr): 3289 ( $\equiv C-H$ ), 2194 ( $C\equiv C$ ), 1743 ( $C=O$ ).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.51 (t,  $J = 7.2$ , 6 H); 3.74 (s, 2 H); 4.58 (q,  $J = 7.2$ , 4 H); 5.35 (s, 4 H). FAB-MS: 1800 (3,  $M^+$ ), 720 (100,  $C_{60}^+$ ).

*Dimethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (15).*  $K_2CO_3$  (102 mg, 0.738 mmol) was added to **9** (250 mg, 0.123 mmol) in THF/PhMe/MeOH 25:10:8 (430 ml), and the mixture was stirred at r.t. for 2 h. After addition of AcOH (0.2 ml) and evaporation, the dark-red solid was dissolved in PhMe, filtered through a pad of  $SiO_2$  (PhMe), and purified by CC ( $SiO_2$ , hexane/ $CH_2Cl_2$  5:4): **15** (135 mg, 65%). Dark-red solid. M.p. > 280°. UV/VIS ( $CH_2Cl_2$ ): 258 (147000), 326 (41200), 426 (2410), 487 (1440), 686 (160). IR ( $CHCl_3$ ): 1745 ( $C=O$ ).  $^1H$ -NMR ( $CDCl_3$ , 300 MHz): 4.11 (s, 6 H).  $^{13}C$ -NMR ( $CDCl_3$ , 125 MHz): 51.95; 54.07; 71.42; 139.01; 140.96; 141.92; 142.19; 142.98; 143.01; 143.06; 143.87; 144.62; 144.63; 144.68; 144.90; 145.11; 145.15; 145.18; 145.26; 164.05. FAB-MS: 850 (14,  $M^+$ ), 720 (100,  $C_{60}^+$ ).

*(E)-2,3-Diethynylbut-2-ene-1,4-diyl Diethyl Bis(2-bromopropanedioate) (16).*  $Bu_4NF$  (1M) in THF (0.75 ml, 0.75 mmol) was added to **6** (152 mg, 0.182 mmol) in THF (50 ml) at  $-78^\circ$ ; then the mixture was warmed slowly to r.t. (over 1 h). After evaporation to 10 ml,  $CH_2Cl_2$  was added and the soln. was filtered through a pad of  $SiO_2$  ( $CH_2Cl_2$ ) and evaporated. CC ( $SiO_2$ ,  $CH_2Cl_2$ ) gave **16** (55 mg, 58%) as a colorless glassy product which was used without further purification. IR (neat): 3277 ( $\equiv C-H$ ), 2101 ( $C\equiv C$ ), 1741 ( $C=O$ ).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.31 (t,  $J = 7.3$ , 6 H); 3.67 (s, 2 H); 4.29 (q,  $J = 7.3$ , 4 H); 4.89 (s, 2 H); 5.04 (s, 4 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz): 14.07; 42.10; 63.83; 65.83; 91.75; 101.42; 127.93; 164.59 (2 ×).

*(±)-(E)-endo,endo-2,3-Diethynylbut-2-ene-1,4-diyl Diethyl 1,2:7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate (17).* DBU (0.06 ml, 0.42 mmol) was added under  $N_2$  at r.t. to  $C_{60}$  (189 mg, 0.262 mmol) and **16** (55 mg, 0.105 mmol) in PhMe (200 ml), and the soln. was stirred under  $N_2$  at r.t. for 5 h. Filtration over a short plug of  $SiO_2$  (PhMe) and CC ( $SiO_2$ ) yielded unreacted  $C_{60}$  (141 mg, with hexane/PhMe 4:1) and **17** (with  $CH_2Cl_2$ ) which was recrystallized from hexane/ $CH_2Cl_2$  (18 mg, 16%). Dark-red solid. M.p. > 280°. IR (KBr): 3285 ( $\equiv C-H$ ), 2098 ( $C\equiv C$ ), 1744 ( $C=O$ ).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.35 (t,  $J = 7.2$ , 3 H); 1.36 (t,  $J = 7.2$ , 3 H); 3.85 (s, 1 H); 3.97 (s, 1 H); 4.42 (m, 4 H); 4.58 (d,  $J = 10.9$ , 1 H); 5.19 (AB,  $J = 11.4$ , 2 H); 6.02 (d,  $J = 10.9$ , 1 H).  $^{13}C$ -NMR ( $CDCl_3$ , 125 MHz): 15.09; 64.11; 66.31; 66.50; 68.21; 68.22; 71.32; 71.34; 80.52; 81.07; 92.57; 93.11; 129.79; 130.66; 135.09; 136.02; 136.19; 136.59; 137.73; 139.99; 140.23; 141.04; 141.08; 141.24; 142.35; 143.04;

143.14; 143.26; 143.30; 143.60; 143.73; 143.76; 144.14; 144.24; 144.52; 144.55; 144.64; 145.19; 145.26; 145.46; 145.64; 145.75; 145.83; 145.95; 146.17; 147.32; 147.49; 147.54; 148.50; 148.73; 162.05; 162.33; 162.54; 162.69. FAB-MS: 1081 (100,  $MH^+$ ), 720 (78,  $C_{60}^+$ ).

(E)-2,3-Diethynylbut-2-ene-1,4-diol (**18**) and 4-Ethynyl-2-methylfuran-3-methanal (**20**).  $K_2CO_3$  (2.46 g, 17.8 mmol) was added to **19** (1.00 g, 3.57 mmol) in THF/MeOH 7:3 (100 ml), and the mixture was stirred at r.t. for 75 min. Evaporation to 10 ml, dilution with  $CH_2Cl_2$ , and extraction with sat. aq. NaCl soln. ( $2 \times$ ) afforded an org. layer which was dried ( $MgSO_4$ ) and evaporated. Recrystallization from hexane/ $CH_2Cl_2$  1:1 yielded colorless crystals of **18** (31 mg, 6%) which were collected by filtration and used without further purification.  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.89 (m, 2 H); 3.66 (s, 2 H); 4.44 (d,  $J = 4.6$ , 4 H).

The filtrate was evaporated, and recrystallization from hexane/ $CH_2Cl_2$  10:1 provided **20** (291 mg, 60%). Colorless crystals. M.p.  $71^\circ$ . IR (KBr): 3293 (O–H), 3254 ( $\equiv C-H$ ), 2115 ( $C\equiv C$ ).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.90 (br. s, 1 H); 2.27 (s, 3 H); 3.15 (s, 1 H); 4.50 (d,  $J = 4.3$ , 2 H); 7.48 (s, 1 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz): 11.37; 54.79; 80.97; 88.57; 107.06; 119.88; 144.25; 149.90. EI-MS: 136 (100,  $M^+$ ), 121 (4,  $[M-Me]^+$ ), 118 (52,  $[M-H_2O]^+$ ), 105 (6,  $[M-CH_2OH]^+$ ). Anal. calc. for  $C_8H_8O_2$  (136.15): C 70.58, H 5.92; found: C 70.60, H 5.90.

Dimethyl (E)-2,3-Diethynylbut-2-ene-1,4-diyl Bis(benzene-1,4-dicarboxylate) (**21**).  $Bu_4NF$  (1M) in THF (14.7 ml, 14.7 mmol) was added to **1** (1.34 g, 3.68 mmol) in THF/ $H_2O$  10:1 (110 ml) at r.t., and the mixture was stirred for 1 h. After addition of sat. aq.  $NH_4Cl$  soln. (100 ml), the mixture was diluted with  $CH_2Cl_2$ , extracted with sat. aq. NaCl ( $2 \times$ ), dried ( $MgSO_4$ ), and evaporated to yield crude **18** as a pale yellow solid which was directly used in the next step. DCC (1.67 g, 8.10 mmol) and DMAP (150 mg, 1.23 mmol) were added to crude **18** followed by methyl hydrogen benzene-1,4-dicarboxylate (1.46 g, 8.10 mmol) in  $CH_2Cl_2$  (150 ml) at r.t., and the mixture was stirred for 5 h, then filtered through a pad of  $SiO_2$  ( $CH_2Cl_2$ ). After cooling to  $0^\circ$ , the colorless crystals of dicyclohexylurea (DCU) were removed by filtration and evaporation afforded a pale-yellow solid which was dissolved in a minimum amount of  $CH_2Cl_2$  and cooled at  $-20^\circ$  overnight. After filtration of residual DCU and evaporation, recrystallization from hexane/ $CH_2Cl_2$  yielded **21** (1.03 g, 61%). Colorless crystals. M.p.  $171^\circ$  (dec.). IR (KBr): 3238 ( $\equiv C-H$ ), 2097 ( $C\equiv C$ ), 1714 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 3.66 (s, 2 H); 3.95 (s, 6 H); 5.24 (s, 4 H); 8.14 (AB,  $J = 8.5$ , 8 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz): 52.19; 64.15; 78.05; 90.63; 127.77; 129.31; 129.50; 133.17; 133.89; 165.00; 165.95. FAB-MS: 460 (100,  $M^+$ ), 445 (13,  $[M-Me]^+$ ). Anal. calc. for  $C_{26}H_{20}O_8 \cdot 0.5 H_2O$  (468.45): C 66.52, H 4.51; found: C 66.61, H 4.66.

(E)-2,3-Bis[4-(trimethylsilyl)buta-1,3-diyne]but-2-ene-1,4-diyl Dimethyl Bis(benzene-1,4-dicarboxylate) (**22**).  $CuCl$  (1.4 g, 14.1 mmol) and TMEDA (2.1 ml, 14 mmol) were added to  $Me_3SiC\equiv CH$  (4.0 ml, 28 mmol) and **21** (130 mg, 0.282 mmol) in  $CH_2Cl_2$  (100 ml), and the soln. was vigorously stirred for 5 h in the presence of dry air. After evaporation to 10 ml and addition of hexane, the mixture was filtered over a short plug of  $SiO_2$ , first with hexane to remove bis(trimethylsilyl)butadiyne, then with  $CH_2Cl_2$ . Recrystallization from  $CH_2Cl_2$ /hexane gave **22** (132 mg, 72%). Pale-yellow crystals. M.p.  $96^\circ$  (dec.). IR (KBr): 2093 ( $C\equiv C$ ), 1727 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 0.19 (s, 18 H); 3.95 (s, 6 H); 5.15 (s, 4 H); 8.14 (AB,  $J = 8.5$ , 8 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz):  $-0.47$ ; 52.68; 64.76; 71.48; 86.97; 89.33; 98.30; 129.94 ( $2 \times$ ); 130.23; 133.71; 134.55; 165.60; 166.64. FAB-MS: 653 ( $MH^+$ ). Anal. calc. for  $C_{36}H_{36}O_8Si_2$  (652.85): C 66.23, H 5.56; found: C 66.52, H 5.51.

tert-Butyl 2-(2-Ethoxyethoxy)ethyl Propanedioate (**24**). Malonyl dichloride (6 ml, 62 mmol) was added to *t*-BuOH (5.9 ml, 62 mmol), 2-(2-ethoxyethoxy)ethanol (8.4 ml, 62 mmol), and  $C_3H_5N$  (10.9 ml, 136 mmol) in  $CH_2Cl_2$  (400 ml) at  $0^\circ$  and, after warming slowly to r.t. (over 1 h), the soln. was stirred for 5 h. Washing with sat. aq.  $NH_4Cl$  soln. ( $4 \times$ ) and drying ( $MgSO_4$ ), followed by distillation afforded as the first fraction di(*tert*-butyl) malonate (2.86 g, 21%). Colorless oil. B.p.  $60^\circ/0.2$  Torr.  $^1H$ - and  $^{13}C$ -NMR: identical to those of the commercial product.

The second fraction contained **24** (7.30 g, 43%). Colorless oil. B.p.  $135^\circ/0.2$  Torr. IR (neat): 1749, 1730 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.09 (t,  $J = 7.0$ , 3 H); 1.36 (s, 9 H); 3.20 (s, 2 H); 3.41 (q,  $J = 7.0$ , 2 H); 3.50 (m, 4 H); 3.63 (t,  $J = 4.9$ , 2 H); 4.18 (t,  $J = 4.9$ , 2 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz): 15.22; 27.99; 42.86; 64.51; 66.78; 69.06; 69.95; 70.81; 82.10; 165.90; 167.23. FAB-MS: 277 (100,  $MH^+$ ), 219 (59,  $[M-t-Bu]^+$ ). Anal. calc. for  $C_{13}H_{24}O_6$  (276.33): C 56.51, H 8.75; found: C 56.47, H 8.58.

tert-Butyl 2-(2-Ethoxyethoxy)ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**25**). DBU (0.2 ml, 1.4 mmol) was added under  $N_2$  at r.t. to  $C_{60}$  (500 mg, 0.694 mmol),  $I_2$  (176 mg, 0.694 mmol), and **24** (192 mg, 0.694 mmol) in PhMe (600 ml), and the soln. was stirred for 4 h. Filtration over a short plug of  $SiO_2$ , first with PhMe to remove unreacted  $C_{60}$  (48 mg), then with  $CH_2Cl_2$  followed by CC ( $SiO_2$ ,  $CH_2Cl_2$ ) and recrystallization from pentane/ $CH_2Cl_2$  provided **25** (351 mg, 51%). Dark-red solid. M.p.  $> 280^\circ$ . UV/VIS ( $CH_2Cl_2$ ): 258 (125000), 326 (38000), 393 (sh, 4370), 401 (sh, 3170), 413 (sh, 2240), 426 (2340), 493 (1390), 688 (180). IR (KBr): 1742 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.20 (t,  $J = 7.0$ , 3 H); 1.67 (s, 9 H); 3.52 (q,  $J = 7.0$ , 2 H); 3.60 (m, 2 H); 3.68 (m, 2 H); 3.88 (t,  $J = 4.8$ , 2 H); 4.63 (t,  $J = 4.8$ , 2 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz): 15.00; 27.80; 52.76;

65.80; 66.49; 68.59; 69.58; 70.50; 71.55; 84.85; 138.60; 138.82; 140.58; 140.63; 141.59; 141.91; 142.70; 142.77; 143.58; 144.26; 144.37; 144.54; 144.85; 144.93; 145.09; 145.31; 161.84; 163.64. FAB-MS: 995 (100,  $MH^+$ ), 720 (72,  $C_{60}^+$ ). Anal. calc. for  $C_{73}H_{22}O_6$  (994.99): C 88.12, H 2.23; found: C 88.11, H 2.02.

2-(2-Ethoxyethoxy)ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**23**). A soln. of **25** (320 mg, 0.322 mmol) and TsOH · H<sub>2</sub>O (306 mg, 1.61 mmol) in PhMe (150 ml) was heated to reflux for 4 h, then cooled to r.t., washed with H<sub>2</sub>O (5 ×), dried (MgSO<sub>4</sub>), and evaporated. The residue was washed with acetone and hexane, then dried under high vacuum and recrystallized from CHCl<sub>3</sub>/hexane to give **23** (282 mg, 95%). Dark-red solid. M.p. > 280°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 258 (74900), 327 (22700), 393 (sh, 3420), 402 (sh, 2460), 413 (sh, 1830), 426 (1810), 488 (1060), 686 (140). IR (KBr): 3384 (O–H), 1740 (C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz): 1.34 (t, *J* = 7.0, 3 H); 3.65–3.80 (m, 6 H); 3.92 (m, 2 H); 4.68 (m, 2 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): 14.90; 52.41; 65.85; 67.34; 68.57; 70.21; 70.36; 71.71; 138.99; 139.03; 140.97; 141.97; 142.08; 142.23; 143.00; 143.05; 143.87; 144.58; 144.70; 144.82; 145.16; 145.23; 145.24; 145.46; 163.77; 164.14. FAB-MS: 939 (75,  $MH^+$ ), 720 (100,  $C_{60}^+$ ). Anal. calc. for  $C_{69}H_{14}O_6 \cdot CHCl_3$  (1058.26): C 79.45, H 1.43; found: C 79.32, H 1.63.

2-(2-Ethoxyethoxy)ethyl 1,2-Methano[60]fullerene-61-carboxylate (**27**). A soln. of DMAP (0.6 mg, 0.005 mmol) and **25** (10 mg, 0.011 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was stirred for 5 h at r.t., then filtered over a short plug (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>), and recrystallization from pentane/CH<sub>2</sub>Cl<sub>2</sub> gave **27** (8.2 mg, 85%). Dark-red solid. M.p. > 280°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 259 (107800), 327 (31600), 394 (sh, 3990), 402 (sh, 2910), 414 (sh, 2000), 427 (2220), 491 (1230), 690 (140). IR (KBr): 1741 (C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz): 1.24 (t, *J* = 7.0, 3 H); 3.57 (q, *J* = 7.0, 2 H); 3.68 (m, 2 H); 3.76 (m, 2 H); 3.94 (t, *J* = 4.7, 2 H); 4.62 (t, *J* = 4.7, 2 H); 4.84 (s, 1 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz): 15.45; 39.09; 65.62; 67.08; 69.31; 70.15; 70.82; 71.12; 136.78; 141.02; 141.30; 141.53; 142.46; 142.59; 142.81; 143.20; 143.36; 143.47; 143.66; 144.12; 144.36; 144.81; 144.99; 145.07; 145.47; 145.60; 145.98; 146.05; 148.63; 166.80. FAB-MS: 895 (72,  $MH^+$ ), 720 (100,  $C_{60}^+$ ). Anal. calc. for  $C_{68}H_{14}O_4 \cdot 0.4 CH_2Cl_2$  (928.84): C 88.45, H 1.61; found: C 88.32, H 1.72.

2-(tert-Butoxy)-2-oxoethyl Ethyl Propanedioate (**29**). Ethyl 3-chloro-3-oxopropanoate (4.0 g, 26.6 mmol) was added to tert-butyl 2-hydroxyacetate (3.50 g, 26.6 mmol) and C<sub>5</sub>H<sub>5</sub>N (2.6 ml, 32 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (200 ml) at 0°, then the soln. was allowed to warm slowly to r.t. (over 1 h) and stirred for an additional 6 h. Washing with sat. aq. NH<sub>4</sub>Cl soln. (4 ×), drying (MgSO<sub>4</sub>), and distillation under reduced pressure afforded **29** (5.27 g, 81%). Colorless oil. B.p. 115–120°/0.2 Torr. IR (neat): 1747 (C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz): 1.18 (t, *J* = 7.1, 3 H); 1.37 (s, 9 H); 3.36 (s, 2 H); 4.10 (q, *J* = 7.1, 2 H); 4.44 (s, 2 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz): 13.62; 27.56; 40.66; 61.16; 61.41; 82.13; 165.55; 165.62; 165.78. FAB-MS: 247 (37,  $MH^+$ ), 191 (100,  $[M-t-Bu]^+$ ). Anal. calc. for C<sub>11</sub>H<sub>18</sub>O<sub>6</sub> (246.26): C 53.65, H 7.37; found: C 53.48, H 7.16.

2-(tert-Butoxy)-2-oxoethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**30**). DBU (0.2 ml, 1.4 mmol) was added under N<sub>2</sub> at r.t. to C<sub>60</sub> (500 mg, 0.694 mmol), I<sub>2</sub> (176 mg, 0.694 mmol), and **29** (171 mg, 0.694 mmol) in PhMe (600 ml), and the soln. was stirred under N<sub>2</sub> at r.t. for 7 h. Filtration over a plug of SiO<sub>2</sub> (PhMe) yielded first unreacted C<sub>60</sub> (48 mg), then the crude product which was recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub> to give **30** (361 mg, 54%). Dark-red solid. M.p. > 280°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 258 (113800), 327 (32600), 393 (sh, 4300), 402 (sh, 2970), 413 (sh, 2150), 426 (2150), 490 (1310), 686 (130). IR (KBr): 1747 (C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz): 1.50 (t, *J* = 7.1, 3 H); 1.54 (s, 9 H); 4.60 (q, *J* = 7.1, 2 H); 4.86 (s, 2 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz): 14.39; 28.33; 52.04; 63.40; 63.94; 71.68; 83.35; 139.13; 139.76; 141.34; 142.28; 142.29; 142.60; 143.35; 143.41; 144.27; 145.03; 145.04; 145.28; 145.57; 145.66; 145.79; 163.47; 163.53; 165.79. FAB-MS: 964 (55,  $M^+$ ), 720 (100,  $C_{60}^+$ ). Anal. calc. for C<sub>71</sub>H<sub>16</sub>O<sub>6</sub> (964.92): C 88.38, H 1.67; found: C 88.12, H 1.69.

Carboxymethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**28**). A soln. of **30** (300 mg, 0.311 mmol) and TsOH · H<sub>2</sub>O (296 mg, 1.56 mmol) in PhMe (300 ml) was refluxed for 5 h, then cooled to r.t., washed with H<sub>2</sub>O (4 ×), dried (MgSO<sub>4</sub>), and evaporated. The residue was washed with Et<sub>2</sub>O and hexane, then dried at 10<sup>−5</sup> Torr to yield **28** (268 mg, 95%) as a dark-red solid which was used without further purification. M.p. > 280°. IR (KBr): 3355 (O–H), 1734 (C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz): 1.50 (t, *J* = 7.2, 3 H); 4.59 (q, *J* = 7.2, 2 H); 5.05 (s, 2 H). FAB-MS: 909 (55,  $MH^+$ ), 720 (100,  $C_{60}^+$ ).

2,2'-(E)-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyloxy}bis[2-oxoethan-2,1-yl] Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**31**). DCC (97 mg, 0.472 mmol) and DMAP (10 mg, 0.082 mmol) were added to **28** (268 mg, 0.295 mmol) and **1** (43 mg, 0.118 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (150 ml) at r.t., and the mixture was stirred for 24 h. After addition of SiO<sub>2</sub> (10 g) and evaporation, CC (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane 6:5) followed by recrystallization from hexane/CHCl<sub>3</sub> yielded **31** (192 mg, 76%). Dark-red solid. M.p. > 280°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 258 (248500), 299 (sh, 78100), 327 (70700), 393 (sh, 9460), 402 (sh, 6770), 413 (sh, 5020), 426 (4820), 487 (2790), 687 (250). IR (CHCl<sub>3</sub>): 2117 (C≡C), 1750 (C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 0.66 (m, 12 H); 1.02 (t, *J* = 7.7, 18 H); 1.50 (t, *J* = 7.1, 6 H); 4.59 (q, *J* = 7.1, 4 H); 5.03 (s, 4 H); 5.07 (s, 4 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): 4.26; 7.61; 14.21; 51.56; 62.23; 63.68; 64.44; 71.27; 100.05; 108.43; 127.38; 139.08; 139.20; 140.92; 140.95; 141.88;

142.21; 142.97; 143.00; 143.06; 143.87; 144.63; 144.65; 144.68; 144.89; 145.12; 145.14; 145.18; 145.27; 162.90; 162.99; 165.84. FAB-MS: 2145 (100,  $M^+$ ), 720 (20,  $C_{60}^+$ ). Anal. calc. for  $C_{154}H_{48}O_{12}Si_2$  (2146.26): C 86.18, H 2.25; found: C 86.02, H 2.51.

2,2'-[(E)-2,3-Diethynylbut-2-ene-1,4-diyloxy]bis[2-oxoethan-2,1-yl] Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**32**). DCC (188 mg, 0.912 mmol) and DMAP (10 mg, 0.082 mmol) were added to **28** (659 mg, 0.725 mmol) and **18** (31 mg, 0.228 mmol) in  $CH_2Cl_2$  (250 ml), and the soln. was stirred at r.t. for 24 h. After addition of  $SiO_2$  (15 g) and evaporation, CC ( $SiO_2$ , PhMe/ $CH_2Cl_2$  5:2) followed by recrystallization from pentane/ $CHCl_3$  afforded **32** (276 mg, 63%) which was not fully characterized due to its limited solubility. Dark-red solid. M.p. > 280°. IR (KBr): 3288 ( $\equiv C-H$ ), 2101 ( $C\equiv C$ ), 1746 ( $C=O$ ).  $^1H-NMR$  ( $CDCl_3$ , 200 MHz): 1.50 (*t*,  $J = 7.2$ , 6 H); 3.73 (*s*, 2 H); 4.59 (*q*,  $J = 7.2$ , 2 H); 5.06 (*s*, 4 H); 5.07 (*s*, 4 H). FAB-MS: 1917 (100,  $M^+$ ), 720 (52,  $C_{60}^+$ ). Anal. calc. for  $C_{142}H_{20}O_{12} \cdot 2.5 CHCl_3$  (2216.18): C 78.32, H 1.02; found: C 78.34, H 1.37.

1,1-Dibromo-3-[(tert-butyl)dimethylsilyloxy]-2-[(tert-butyl)dimethylsilyloxymethyl]propane (**35**). To **34** (3.0 g, 9.4 mmol) and  $CBr_4$  (4.11 g, 12.4 mmol) in PhH (150 ml) was added  $PPh_3$  (6.48 g, 24.7 mmol), and the soln. was stirred at 20° for 48 h. After addition of hexane (100 ml) and filtration through a large pad of Celite, CC ( $SiO_2$ , hexanes/ $CH_2Cl_2$  2:1) yielded **34** (1.85 g, 38%). Light-yellow oil. IR (neat): 2930, 1472, 1253, 1078, 837.  $^1H-NMR$  (200 MHz,  $CDCl_3$ ): 0.11 (*s*, 12 H); 0.92 (*s*, 18 H); 4.38 (*s*, 4 H).  $^{13}C-NMR$  (50 MHz,  $CDCl_3$ ): -5.25; 18.37; 25.92; 62.57; 90.29; 143.71. FAB-MS: 473/475/471 (65/100/50,  $M^+$ ). Anal. calc. for  $C_{16}H_{34}Br_2O_2Si_2$  (474.42): C 40.51, H 7.22; found: C 40.33, H 7.07.

5-[(tert-Butyl)dimethylsilyloxy]-4-[(tert-butyl)dimethylsilyloxymethyl]-1-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-3-en-1-yne (**36**). A mixture of **35** (0.829 g, 1.75 mmol),  $Me_3SiC\equiv CH$  (0.514 g, 5.24 mmol),  $[PdCl_2(PPh_3)_2]$  (80 mg, 0.11 mmol), and CuI (40 mg, 0.21 mmol) in degassed  $Et_3N$  (30 ml) was stirred at r.t. for 16 h. Additional  $Me_3SiC\equiv CH$  (0.20 g, 2.0 mmol) and  $[PdCl_2(PPh_3)_2]$  (25 mg, 0.036 mmol) were added, and the mixture was stirred for 12 more h. Evaporation and CC ( $SiO_2$ , hexanes/ $CH_2Cl_2$  10:1) provided **36** (0.647 g, 73%). Light-yellow oil. IR (neat): 2956, 2153 ( $C\equiv C$ ), 1250.  $^1H-NMR$  (200 MHz,  $CDCl_3$ ): 0.01 (*s*, 18 H); 0.12 (*s*, 12 H); 0.82 (*s*, 18 H); 4.42 (*s*, 4 H).  $^{13}C-NMR$  (50.3 MHz,  $CDCl_3$ ): -5.25; -0.15; 18.42; 25.98; 60.24; 98.14; 99.89; 103.23; 157.90. EI-MS: 508 (4,  $M^+$ ), 73 (100,  $SiMe_3^+$ ). Anal. calc. for  $C_{26}H_{52}O_2Si_4$  (509.04): C 61.35, H 10.30; found: C 61.24, H 10.38.

5-[(tert-Butyl)dimethylsilyloxy]-4-[(tert-butyl)dimethylsilyloxymethyl]-1-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]pent-3-en-1-yne (**37**). A mixture of **35** (2.00 g, 4.22 mmol), (*i*-Pr) $_3SiC\equiv CH$  (1.75 g, 9.62 mmol),  $[PdCl_2(Ph_3P)_2]$  (150 mg, 0.21 mmol), and CuI (75 mg, 0.39 mmol) in degassed  $Et_3N$  (35 ml) was stirred at r.t. for 24 h. After evaporation, the residue was dissolved in  $Et_2O$ , washed with sat. aq.  $NH_4Cl$  soln., dried ( $MgSO_4$ ), and chromatographed ( $SiO_2$ , hexanes/ $CH_2Cl_2$  10:1): **37** (2.46 g, 86%). Light-yellow oil. IR ( $CCl_4$ ): 2944, 2151 ( $C\equiv C$ ), 1464, 1256, 1066, 838.  $^1H-NMR$  (200 MHz,  $CDCl_3$ ): 0.06 (*s*, 12 H); 0.88 (*s*, 18 H); 1.06 (*s*, 42 H); 4.53 (*s*, 4 H).  $^{13}C-NMR$  (50.3 MHz,  $CDCl_3$ ): -5.31; 11.27; 18.43; 18.63; 25.94; 60.35; 94.93; 102.21; 103.97; 155.75. EI-MS: 676 (4,  $M^+$ ), 619 (20,  $[M-(t-Bu)]^+$ ), 532 (100,  $[M-(t-Bu)Me_2Si]^+$ ). HR-MS: 676.4931 ( $M^+$ ,  $C_{38}H_{76}O_2Si_4^+$ ; calc. 676.4922).

2-(1-Ethynylprop-2-ynylidene)propane-1,3-diol (**33**).  $Bu_4NF$  (1M) in THF (2.28 ml, 2.28 mmol) was added to **36** (0.230 g, 0.456 mmol) in wet THF (25 ml) at 0°, and the mixture was stirred for 8 h. Dilution with  $Et_2O$ , washing with sat. aq.  $NH_4Cl$  soln., drying ( $MgSO_4$ ), and evaporation gave **33** (41 mg, 66%) as an unstable oily solid that was used without further purification. IR (neat): 3364 (O-H), 3289 ( $\equiv C-H$ ), 2925, 2100 ( $C\equiv C$ ), 1436.

2,2'-[2-(1-Ethynylprop-2-ynylidene)propane-1,3-diyloxy]bis[2-oxoethan-2,1-diyloxy] Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**38**) and Ethyl 2-[3-Ethynyl-2-(hydroxymethyl)pent-2-en-4-ynyl]-2-oxoethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**39**). A mixture of **28** (0.450 g, 0.500 mmol), **33** (30 mg, 0.221 mmol), DCC (0.188 g, 0.912 mmol), and DMAP (10 mg, 0.082 mmol) in  $CH_2Cl_2$  was stirred at r.t. for 24 h. After addition of  $SiO_2$  (10 g) and evaporation, CC (2 ×;  $SiO_2$ , PhMe, → PhMe/ $CH_2Cl_2$  1:1 →  $CH_2Cl_2$ ; then  $SiO_2$ ,  $CH_2Cl_2$ ) afforded **38** (0.106 g, 25%) and **39** (0.052 g, 23%).

**38**: Dark-brown solid. M.p. > 250°. UV/VIS ( $CHCl_3$ ): 258 (241700), 326 (70600), 412 (5800), 426 (5300), 479 (2800). IR ( $CCl_4$ ): 3292 ( $\equiv C-H$ ), 2933, 2108 ( $C\equiv C$ ), 1746 ( $C=O$ ), 1233.  $^1H-NMR$  (500 MHz,  $CDCl_3$ ): 1.50 (*t*,  $J = 7.1$ , 6 H); 3.39 (*s*, 2 H); 4.59 (*q*,  $J = 7.1$ , 4 H); 5.05 (*s*, 4 H); 5.20 (*s*, 4 H).  $^{13}C-NMR$  (125 MHz,  $CDCl_3$ ): 14.23; 51.46; 62.41; 62.80; 63.74; 71.22; 84.74; 108.59; 135.98; 139.03; 139.23; 140.94; 140.96; 141.87; 142.20; 142.96; 143.00; 143.05; 143.87; 144.62; 144.65; 144.67; 144.79; 144.89; 145.08; 145.13; 145.17; 145.27; 146.85; 162.98; 163.13; 166.11. FAB-MS: 1917 (100,  $M^+$ ), 720 (32,  $C_{60}^+$ ). Anal. calc. for  $C_{142}H_{20}O_{12}$  (1917.74): C 88.94, H 1.05; found: C 88.80, H 1.35.

**39**: Dark-brown solid. M.p. > 250°. UV/VIS ( $CHCl_3$ ): 258 (210700), 326 (57000), 413 (11900), 425 (3800), 485 (2400). IR ( $CCl_4$ ): 3427 (O-H), 3294 ( $\equiv C-H$ ), 3000, 2933, 2105 ( $C\equiv C$ ), 1749 ( $C=O$ ), 1235, 906.  $^1H-NMR$  (500 MHz,  $CDCl_3$ ): 1.50 (*t*,  $J = 7.2$ , 3 H); 2.31 (*s*, 1 H); 3.31 (*s*, 2 H); 4.56 (*s*, 2 H); 4.59 (*q*,  $J = 7.2$ , 2 H); 5.04

(s, 2 H); 5.22 (s, 2 H).  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ): 14.20; 51.46; 60.91; 61.58; 62.49; 63.81; 71.91; 77.78; 77.94; 82.93; 83.27; 105.76; 138.93; 139.23; 140.97; 140.99; 141.86; 142.20; 142.97; 143.02; 143.05; 143.07; 143.87; 144.60; 144.65; 144.69; 144.92; 145.09; 145.11; 145.18; 145.20; 145.29; 152.75 163.13; 163.25; 166.60. FAB-MS: 1027 (36,  $M^+$ ), 720 (100,  $C_{60}^+$ ). HR-MS: 1027.0785 ( $MH^+$ ,  $C_{75}H_{15}O_7^+$ , calc. 1027.0818).

*Bis[2-(tert-butoxy-2-oxoethyl)] Propanedioate (44)*. A soln. of *tert*-butyl 2-hydroxyacetate (1.029 g, 7.8 mmol) and  $C_5H_5N$  (0.63 ml, 7.8 mmol) in dry  $CH_2Cl_2$  (15 ml) was purged with Ar and cooled with an ice bath. Malonyl dichloride (0.38 ml, 3.9 mmol) was added dropwise within 5 min ( $\rightarrow$  yellow, then dark-violet). After 2.5 h, the ice bath was removed, and stirring was continued for 14 h at r.t. Extraction with  $H_2O$ , filtration, and evaporation, followed by CC ( $SiO_2$ ,  $CH_2Cl_2$ ) gave **44** (0.827 g, 64%). Yellow oil. IR (neat): 1749 (C=O).  $^1H$ -NMR (200 MHz,  $CDCl_3$ ): 1.27 (s, 18 H); 3.38 (s, 2 H); 4.35 (s, 4 H).  $^{13}C$ -NMR (50 MHz,  $CDCl_3$ ): 27.43; 39.94; 61.36; 81.91; 164.93; 165.62. FAB-MS: 333 ( $MH^+$ ). Anal. calc. for  $C_{15}H_{24}O_8$  (332.35): C 54.21, H 7.28, O 38.51; found: C 54.10, H 7.38, O 38.59.

*Bis[2-(tert-butoxy-2-oxoethyl)] 1,2-Methano[70]fullerene-71,71-dicarboxylate (45)*. A soln. of  $C_{70}$  (60 mg, 0.071 mmol) in dry PhMe (70 ml) was sonicated and purged with Ar, after which **44** (0.026 g, 0.079 mmol),  $I_2$  (0.020 g, 0.079 mmol), and DBU (0.027 g, 0.178 mmol), each dissolved in PhMe, were added. After 1 h, more  $I_2$  (0.005 g, 0.020 mmol) in PhMe was added, and stirring was continued for 14 h at r.t. Evaporation and CC ( $SiO_2$ ,  $CH_2Cl_2$ /hexane 2:1) gave **45** (39 mg, 46%). Black solid. M.p.  $> 280^\circ$ . UV/VIS ( $CH_2Cl_2$ ): 265 (sh, 96700), 323 (24700), 353 (23100), 369 (21800), 402 (17700), 460 (20300), 540 (sh, 9400), 661 (sh, 1000). IR (KBr): 1749 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 500 MHz): 1.53 (s, 18 H); 4.85 (s, 4 H).  $^{13}C$ -NMR ( $CDCl_3$ , 125 MHz): 28.10; 36.24; 63.29; 66.03; 66.55; 83.00; 130.79; 130.93; 132.79; 133.53; 136.65; 140.94; 141.59; 142.38; 142.56; 142.84; 143.53; 143.82; 143.93; 144.91; 145.88; 145.93; 146.45; 146.98; 147.27; 147.49; 147.57; 148.45; 148.47; 148.56; 148.75; 149.08; 149.23; 149.31; 150.55; 150.68; 151.14; 151.31; 151.33; 155.07; 162.49; 165.30. MALDI-TOF-MS (CCA): 1170.9 ( $M^-$ ), 1115.3, 840.7 ( $C_{70}^-$ ).

*Bis(carboxymethyl) 1,2-Methano[70]fullerene-71,71-dicarboxylate (43)*. A soln. of **45** (33 mg, 0.029 mmol) and  $TsOH \cdot H_2O$  (43 mg, 0.228 mmol) in PhMe (50 ml) was heated to reflux for 5 h. Additional  $TsOH \cdot H_2O$  (44 mg) was added and, after refluxing for 14 h, the soln. was evaporated and the solid washed with  $H_2O$ . Dissolution in THF, drying ( $MgSO_4$ ), followed by evaporation yielded crude **43** which was dried at  $10^{-2}$  Torr and used without further purification. Dark-red solid. M.p.  $> 280^\circ$ .  $^1H$ -NMR ( $(D_8)THF$ , 200 MHz): 4.06 (s, 4 H).

*Bis[2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethyl] Propanedioate (47)*. Malonyl dichloride (0.5 ml, 5.11 mmol) was added to 2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethanol [39] (1.94 g, 10.22 mmol) and  $C_5H_5N$  (0.9 ml, 11.15 mmol) in  $CH_2Cl_2$  (200 ml) at  $0^\circ$ , and the soln. was allowed to warm slowly to r.t. (over 1 h) and stirred for 3 h at this temperature. After washing with sat. aq.  $NH_4Cl$  soln. (2  $\times$ ) and drying ( $MgSO_4$ ), CC ( $SiO_2$ ,  $CH_2Cl_2$ /MeOH 97:3) afforded **47** as a mixture of diastereoisomers (1.42 g, 62%). Colorless oil. IR (neat): 1739 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.40–1.80 (m, 12 H); 3.36 (s, 2 H); 3.40–3.85 (m, 16 H); 4.19–4.25 (m, 4 H); 4.55 (br. s, 2 H).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz): 19.10; 25.07; 30.19; 40.91; 61.82; 64.27; 66.26; 68.45; 70.19; 98.56; 166.10. FAB-MS: 449 ( $MH^+$ ). Anal. calc. for  $C_{21}H_{36}O_{10}$  (448.52): C 56.24, H 8.09; found: C 56.08, H 8.00.

*Bis[2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate (48)*. A soln. of  $C_{70}$  (61.1 mg, 0.073 mmol) in dry PhMe (70 ml) was sonicated and purged with Ar, after which **47** (0.036 g, 0.080 mmol),  $I_2$  (0.021 g, 0.080 mmol), and DBU (0.028 g, 0.182 mmol), each dissolved in PhMe, were added. After stirring for 14 h at r.t., CC ( $SiO_2$ ) eluting with  $CH_2Cl_2$  gave unreacted  $C_{70}$  and with  $CH_2Cl_2$ /MeOH 99.5:0.5 **48** (61 mg, 65%) as a mixture of diastereoisomers. Black solid. M.p.  $> 280^\circ$ .  $^1H$ -NMR ( $CDCl_3$ , 200 MHz): 1.20–1.90 (m, 12 H); 3.46–3.93 (m, 16 H); 4.57–4.64 (m, 6 H). MALDI-TOF-MS (DHB): 1287.0 ( $M^-$ ).

*Bis[2-(2-hydroxyethoxy)ethyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate (46)*. A soln. of **48** (0.061 g, 0.047 mmol) in PhMe/EtOH 1:3 (80 ml) was purged with Ar and, after addition of  $TsOH \cdot H_2O$  (0.091 g, 0.472 mmol) was stirred at  $60^\circ$  for 2 h. Evaporation and CC ( $SiO_2$ ,  $CH_2Cl_2 \rightarrow CH_2Cl_2$ /MeOH 98:2) gave **46** (32 mg, 60%). Black solid. M.p.  $> 280^\circ$ . UV/VIS ( $CH_2Cl_2$ ): 265 (sh, 97400), 324 (24900), 353 (23300), 369 (22100), 403 (17900), 461 (20700), 538 (sh, 9900), 654 (sh, 1600). IR (KBr): 2920 (O–H), 1744 (C=O).  $^1H$ -NMR ( $CDCl_3$ , 500 MHz): 2.78 (br. s, 2 H); 3.68–3.70 (m, 4 H); 3.77–3.81 (m, 4 H); 3.89–3.92 (m, 4 H); 4.61–4.64 (m, 4 H).  $^{13}C$ -NMR ( $CDCl_3$ , 125 MHz): 36.81; 61.76; 66.17; 66.22; 66.79; 68.68; 72.68; 130.80; 130.91; 130.93; 132.81; 133.54; 136.80; 140.86; 141.61; 142.28; 142.74; 142.85; 143.55; 143.84; 143.94; 144.85; 145.89; 145.96; 146.45; 147.00; 147.29; 147.50; 147.59; 148.47; 148.49; 148.58; 148.75; 149.12; 149.26; 149.34; 150.57; 150.70; 151.15; 151.33 (2  $\times$ ); 155.01; 163.49. MALDI-TOF-MS (DHB): 1118.8 ( $M^-$ ).

*Bis[2-{2-[2-(61-(Ethoxycarbonyloxy)-1,2-methano[60]fullerene-61-ylcarbonyloxy]-1-oxoethoxy}ethoxy]ethyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate (49)*. DCC (13.2 mg, 0.064 mmol) and DMAP (2.6 mg,

0.0214 mmol) were added at r.t. to a stirred soln. of **46** (24 mg, 0.0214 mmol) and **28** (58.3 mg, 0.0642 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 ml). The mixture was stirred for 36 h, and an additional portion of **28** (39 mg, 0.0428 mmol) was added each 12 h. Evaporation followed by CC ( $2 \times$ ;  $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  99.5:0.5  $\rightarrow$  99:1) and recrystallization from  $\text{CHCl}_3/\text{MeOH}$  provided **49** (14 mg, 23%). Dark-brown solid. M.p.  $> 280^\circ$ . UV/VIS ( $\text{CH}_2\text{Cl}_2$ ): 257 (222200), 325 (66000), 408 (sh, 18000), 425 (16000), 462 (16600), 551 (sh, 7700), 598 (sh, 3900). IR (KBr): 1748 ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz): 1.41 (t,  $J = 7.1$ , 6 H); 3.70 (t,  $J = 4.5$ , 4 H); 3.80 (t,  $J = 4.5$ , 4 H); 4.32 (t,  $J = 4.5$ , 4 H); 4.50 (q,  $J = 7.1$ , 4 H); 4.54 (m, 4 H); 4.97 (s, 4 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz): 14.63 (Me); 39.43 (methano bridge); 39.47 (methano bridge); 62.92; 64.22; 64.88; 65.67; 66.45; 68.96; 69.09; 71.52; 75.18; 130.97 ( $\text{C}_{70}$ ); 131.07 ( $\text{C}_{70}$ ); 131.12 ( $\text{C}_{70}$ ); 133.02 ( $\text{C}_{70}$ ); 133.71 ( $\text{C}_{70}$ ); 137.03 ( $\text{C}_{70}$ ); 139.12 ( $\text{C}_{60}$ ); 139.50 ( $\text{C}_{60}$ ); 141.04 ( $\text{C}_{70}$ ); 141.14 ( $\text{C}_{60}$ ); 141.17 ( $\text{C}_{60}$ ); 141.78 ( $\text{C}_{70}$ ); 142.08 ( $\text{C}_{60}$ ); 142.10 ( $\text{C}_{60}$ ); 142.41 ( $\text{C}_{60}$ ); 142.49 ( $\text{C}_{60}$ ); 142.96 ( $\text{C}_{70}$ ); 143.03 ( $\text{C}_{70}$ ); 143.18 ( $\text{C}_{60}$ ); 143.21 ( $\text{C}_{60}$ ); 143.23 ( $\text{C}_{60}$ ); 143.30 ( $\text{C}_{60}$ ); 143.73 ( $\text{C}_{70}$ ); 144.03 ( $\text{C}_{70}$ ); 144.08 ( $\text{C}_{60}$ ); 144.13 ( $\text{C}_{70}$ ); 144.81 ( $\text{C}_{60}$ ); 144.86 ( $\text{C}_{60}$ ); 144.88 ( $\text{C}_{60}$ ); 144.90 ( $\text{C}_{60}$ ); 145.01 ( $\text{C}_{60}$ ); 145.03 ( $\text{C}_{70}$ ); 145.11 ( $\text{C}_{60}$ ); 145.31 ( $\text{C}_{60}$ ); 145.37 ( $\text{C}_{60}$ ); 145.39 ( $\text{C}_{60}$ ); 145.49 ( $\text{C}_{60}$ ); 146.11 ( $\text{C}_{70}$ ); 146.17 ( $\text{C}_{70}$ ); 146.63 ( $\text{C}_{70}$ ); 147.21 ( $\text{C}_{70}$ ); 147.49 ( $\text{C}_{70}$ ); 147.69 ( $\text{C}_{70}$ ); 147.77 ( $\text{C}_{70}$ ); 148.65 ( $\text{C}_{70}$ ); 148.68 ( $\text{C}_{70}$ ); 148.74 ( $\text{C}_{70}$ ); 148.96 ( $\text{C}_{70}$ ); 149.35 ( $\text{C}_{70}$ ); 149.44 ( $\text{C}_{70}$ ); 149.52 ( $\text{C}_{70}$ ); 150.76 ( $\text{C}_{70}$ ); 150.91 ( $\text{C}_{70}$ ); 151.34 ( $\text{C}_{70}$ ); 151.52 ( $\text{C}_{70}$ ); 151.54 ( $\text{C}_{70}$ ); 155.22 ( $\text{C}_{70}$ ); 163.31 ( $\text{C}=\text{O}$ ); 163.36 ( $\text{C}=\text{O}$ ); 163.66 ( $\text{C}=\text{O}$ ); 166.76 ( $\text{C}=\text{O}$ ). MALDI-TOF-MS (dithranol): 2900 ( $M^+$ ).

**Electrochemistry.** The electrochemical experiments were carried out in a classical three-electrode cell in  $\text{CH}_2\text{Cl}_2$  or in  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  95:5 containing 0.1M ( $\text{Bu}_4\text{N}$ )PF<sub>6</sub>. The working electrode was a glassy carbon disk electrode ( $\varnothing$  2 mm, EDI-type, SOLEA-Tacussel, Villeurbanne, France) used either motionless (for cyclic voltammetry from 0.01 to 10 V/s) or as a rotating disk electrode (RDE). The auxiliary electrode was a Pt wire, and a Ag wire was used as a pseudo-reference electrode. The electrochemical cell was connected to a computerized multipurpose electrochemical device DACFAMOV (Microtec-CNRS, Toulouse, France) interfaced with an Apple II microcomputer. The accessible range of potentials was +1.2 to  $-2.2$  V vs  $\text{Fc}/\text{Fc}^+$  in  $\text{CH}_2\text{Cl}_2$  and +1.2 to  $-1.9$  V vs  $\text{Fc}/\text{Fc}^+$  in  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  95:5. All the potentials given are referred to the ferrocene/ferricinium ( $\text{Fc}/\text{Fc}^+$ ) couple used as internal standard.

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