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TETRAHEDRON
LETTERS

# Methanofullerene-functionalized dendritic branches

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## Abstract

Fullerene-functionalized dendrons containing a $C_{60}$ sphere at each branching unit have been prepared by a convergent approach using successive DCC-mediated esterifications followed by cleavage of a *t*-butyl ester moiety under acidic conditions. © 1999 Elsevier Science Ltd. All rights reserved.

Dendrimers have attracted increasing attention in the past decade because of their unique structures and properties.[1,2] Of the various cores utilized for the synthesis of dendrimers, $C_{60}$ appears to be a versatile tecton for dendrimer chemistry.[3] Effectively, the almost spherical shape of the fullerene leads to globular systems even with low-generation dendrons. Furthermore, variable degrees of addition within the fullerene core, especially from mono- up to hexaadducts, are possible.[3] It has also been shown that the dendritic part of amphiphilic dendrimers with a $C_{60}$ core is able to prevent the aggregation of the fullerene moieties during the preparation of Langmuir films.[4] We have recently reported the efficient preparation of dendritic branches with peripheral fullerene units[5] and their attachment to a functional core yielded monodisperse fullerene-rich macromolecules.[6] We have also shown that the fullerene-rich microenvironment is able to modulate the physical properties of the central core.[7] As part of this research, we now report the synthesis of the first examples of fullerene-functionalized dendrons containing a $C_{60}$ sphere at each branching unit.

The preparation of **1** and **2**, the two key building blocks for the preparation of the fullerene-functionalized dendritic branches, is depicted in Scheme 1. Compound **1** can be considered as the first generation dendron and diol **2** is the branching unit. *N*,*N′*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of **3**[5] with *t*-butyl 2-hydroxyacetate[8] in $CH_2Cl_2$ yielded malonate **4** in 93% yield. The subsequent functionalization of $C_{60}$ with **4** and iodine in the presence of diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature is based on the Bingel reaction[9] and gave methanofullerene **5** in 44% yield. Selective cleavage of the *t*-butyl ester moiety with $CF_3CO_2H$ in $CH_2Cl_2$ then gave **1** in 97% yield. Treatment of 1,6-hexanediol with $Ag_2O$ and *p*-methoxybenzyl chloride (PMBCl) under the conditions developed by A. Bouzide and G. Sauvé[10] afforded the mono-protected derivative **6** in

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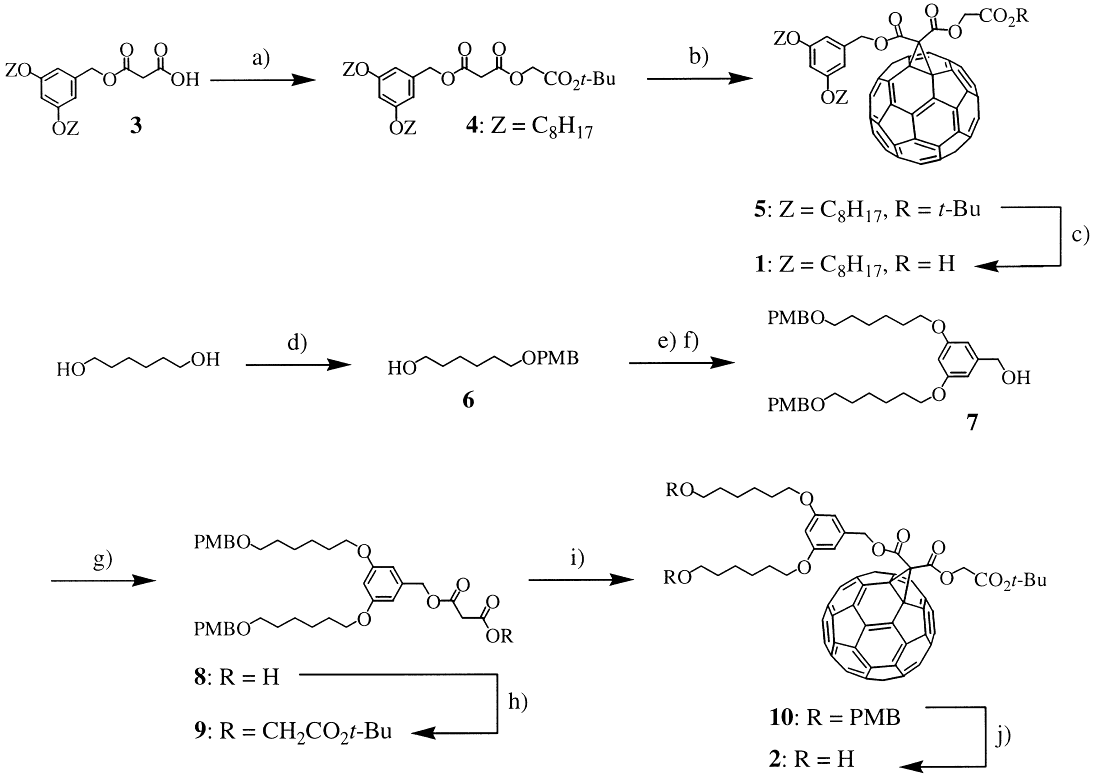
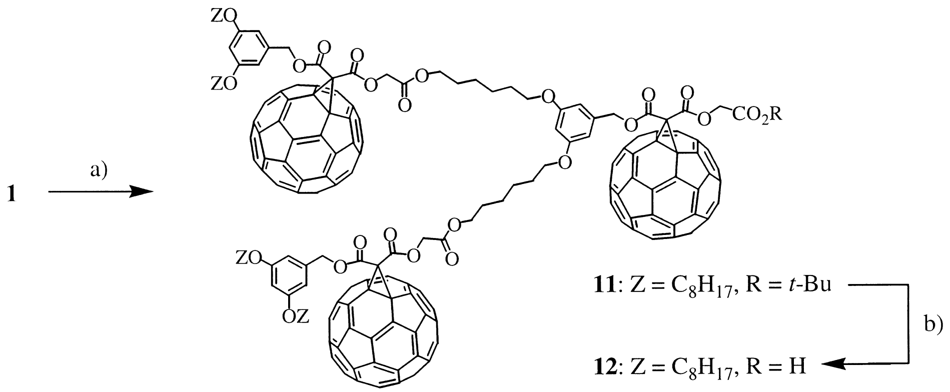
58% yield. Treatment with $CBr_4/PPh_3$ in THF at room temperature followed by the reaction of the resulting bromide with 3,5-dihydroxybenzyl alcohol in DMF at 70°C in the presence of $K_2CO_3$ yielded **7**. Subsequent reaction with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)[5] at 120°C gave the mono-ester **8** of malonic acid in a quantitative yield. DCC-mediated esterification of **8** with *t*-butyl 2-hydroxyacetate in $CH_2Cl_2$ then yielded malonate **9**, which after treatment with $C_{60}$, $I_2$ and DBU in toluene at room temperature gave **10** in 30% yield.



Scheme 1. Synthesis of **1** and **2**. Reagents and conditions: (a) *t*-butyl 2-hydroxyacetate, DCC, DMAP, $CH_2Cl_2$, 0°C to rt, 24 h (93%); (b) $C_{60}$, $I_2$, DBU, toluene, rt, 6 h (44%); (c) $CF_3CO_2H$, $CH_2Cl_2$, rt, 1 h (97%); (d) PMBCl, $Ag_2O$, $CH_2Cl_2$, rt, 4 h (58%); (e) $CBr_4$, $PPh_3$, THF, rt, 30 min (79%); (f) 3,5-dihydroxybenzyl alcohol, DMF, $K_2CO_3$, 70°C, 20 h (52%); (g) Meldrum's acid, 120°C, 3 h (99%); (h) *t*-butyl 2-hydroxyacetate, DCC, DMAP, $CH_2Cl_2$, 0°C to rt, 48 h (91%); (i) $C_{60}$, $I_2$, DBU, toluene, rt, 6 h (30%); (j) DDQ, $CH_2Cl_2$, $H_2O$, rt, 1 h (84%)

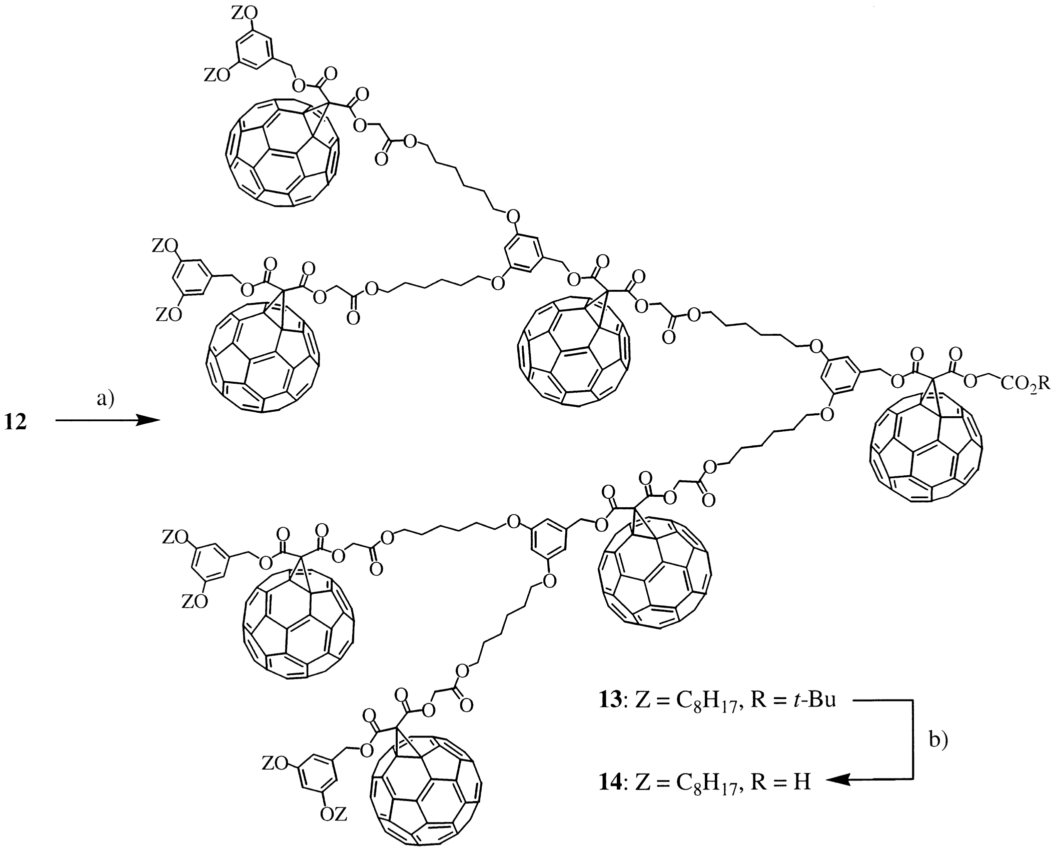
The choice of the appropriate protecting group for the two alcohol groups in **10** was the key to this synthesis. Effectively, the deprotection conditions must not be acidic to preserve the *t*-butyl ester moiety and may not be basic to preserve the other ester functions. Furthermore, the decomposition of fullerene derivatives under reaction conditions using fluoride[11] prevents the use of silyl protecting groups. The PMB protecting groups in **10** could be removed with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in $CH_2Cl_2$ containing a small amount of water at room temperature.[12] Under these neutral conditions, all the ester functions remained unchanged and compound **2** was thus obtained in a good yield (84%).

Reaction of acid **1** with diol **2** under esterification conditions using DCC, 1-hydroxybenzotriazole (BtOH) and 4-dimethylaminopyridine (DMAP) led to the *t*-butyl-protected second generation dendron **11** in 70% yield (Scheme 2). Subsequent hydrolysis of the *t*-butyl ester group under acidic conditions afforded acid **12** in high yield (98%).



Scheme 2. Synthesis of dendron **12**. Reagents and conditions: (a) **2**, DCC, DMAP, BtOH, $CH_2Cl_2$, 0°C to rt, 24 h (70%); (b) $CF_3CO_2H$, $CH_2Cl_2$, rt, 1 h (98%)

Esterification of acid **12** with diol **2** (DCC/DMAP/BtOH) afforded **13** in 37% yield and subsequent hydrolysis of the *t*-butyl ester group with $CF_3CO_2H$ gave the third generation carboxylic acid **14** (Scheme 3). All of the spectroscopic studies were consistent with the proposed molecular structures assigned to the dendrons of each generation.[13]



Scheme 3. Synthesis of dendron **14**. Reagents and conditions: (a) **2**, DCC, DMAP, BtOH, $CH_2Cl_2$, 0°C to rt, 24 h (37%); (b) $CF_3CO_2H$, $CH_2Cl_2$, rt, 3 h (80%)

Whereas the FAB-MS spectra of methanofullerenes **1**, **2** and **5** showed the expected molecular ion peaks, no characteristic peaks could be observed for the dendrons of highest generation. Actually, due to aggregation resulting probably from fullerene–fullerene interactions, high energy is required for dissociation during FAB-MS analysis and therefore fragmentation occurs, especially on the fragile benzylic ester functions. Furthermore, the molecular masses are quite high and no easily protonable sites are present in these dendrons. Nevertheless, the $^{1}H$ and $^{13}C$ NMR, IR, UV–vis and elemental analysis data obtained for the dendrons provide good evidence for the proposed structures.

Following the preparation of dendrimers with a fullerene core or with peripheral $C_{60}$ subunits, we have now succeeded in the preparation of fullerene-functionalized dendrons containing a $C_{60}$ sphere at each branching unit. Those new dendritic branches appear to be versatile building blocks for the preparation of fullerene-rich macromolecules and their attachment on a functional core is now under investigation in our laboratory.

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13. Selected spectroscopic data for **11**: $^{1}H$ NMR ($CDCl_3$, 200 MHz): 0.88 (t, J=6, 12H), 1.20–1.43 (m, 52H), 1.53 (s, 9H), 1.60–1.80 (m, 12H), 3.86 (t, J=6, 4H), 3.90 (t, J=6, 8H), 4.22 (t, J=6, 4H), 4.84 (s, 2H), 4.94 (s, 4H), 5.46 (s, 6H), 6.33 (t, J=2, 1H), 6.40 (t, J=2, 2H), 6.57 (d, J=2, 2H), 6.60 (d, J=2, 4H). Anal. calcd for $C_{264}H_{122}O_{24}$: C 86.22%, H 3.34%. Found: C 86.07%, H 3.36%. For **13**: $^{1}H$ NMR ($CDCl_3$, 400 MHz): 0.88 (t, J=6, 24H), 1.20–1.46 (m, 116H), 1.54 (s, 9H), 1.56–1.79 (m, 28H), 3.85 (t, J=6, 4H), 3.86 (t, J=6, 8H), 3.91 (t, J=6, 16H), 4.23 (t, J=6, 4H), 4.24 (t, J=6, 8H), 4.85 (s, 2H), 4.94 (s, 12H), 5.45 (s, 2H), 5.47 (s, 12H), 6.33 (t, J=2, 1H), 6.35 (t, J=2, 2H), 6.42 (t, J=2, 4H), 6.56 (d, J=2, 4H), 6.58 (d, J=2, 2H), 6.61 (d, J=2, 8H). Anal. calcd for $C_{608}H_{266}O_{56}\cdot 3CHCl_3$: C 83.16%. H 3.07%. Found: C 83.09%, H 3.18%.