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LETTERS

Fullerodendrimers with peripheral triethyleneglycol chains

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Abstract

Triethylene glycol terminated poly(aryl ether) dendritic branches with an aldehyde function at the focal point have been prepared and attached to C_{60} by a 1,3-dipolar cycloaddition. © 2000 Elsevier Science Ltd. All rights reserved.

The synthesis and the study of fullerene-functionalised dendrimers (fullerodendrimers) have attracted increasing attention in the past decade.[1–4] Dendrimers with a C_{60} core,[2] peripheral C_{60} subunits[3] or a C_{60} sphere at each branching unit[4] have been described. As far as fullerodendrimers with a C_{60} core are concerned, it should be noted that the functionalisation of the fullerene sphere with dendrons dramatically improves the solubility of the C_{60}. Furthermore, the encapsulation of the fullerene in the middle of a dendritic structure provides a compact insulating layer around the carbon sphere. This latest peculiarity has been exploited in the design of amphiphilic fullerene derivatives for efficient incorporation in Langmuir films[5] or for the preparation of fullerene-containing liquid crystals.[6] In both cases, the surrounding dendritic branches prevent unfavourable effects of the C_{60} sphere such as aggregation or steric hindrance. As part of this research, we now report the synthesis of new fullerodendrimers by direct functionalisation of C_{60} with water soluble poly(aryl ether) dendritic branches for future applications in materials science.

The preparation of the triethylene glycol terminated poly(aryl ether) dendritic branches is depicted in Scheme 1. They have been obtained by a convergent synthesis using a modified Fréchet type methodology.[7] Indeed, due to the water solubility of the dendrons, aqueous work-up procedures have been avoided all along the synthesis. Treatment of triethylene glycol monomethyl ether (**1**) with toluene-*p*-sulfonyl chloride (TsCl) and pyridine, followed by reaction

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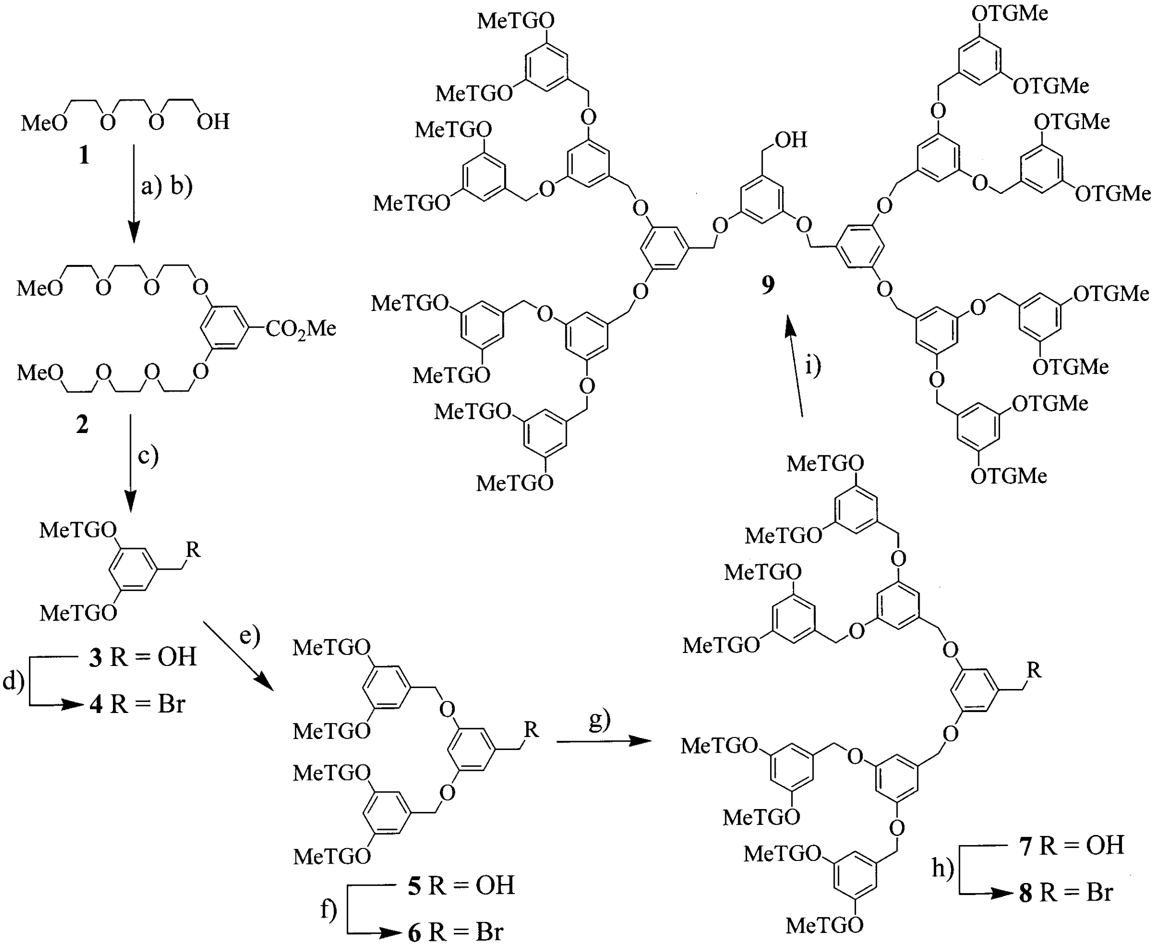
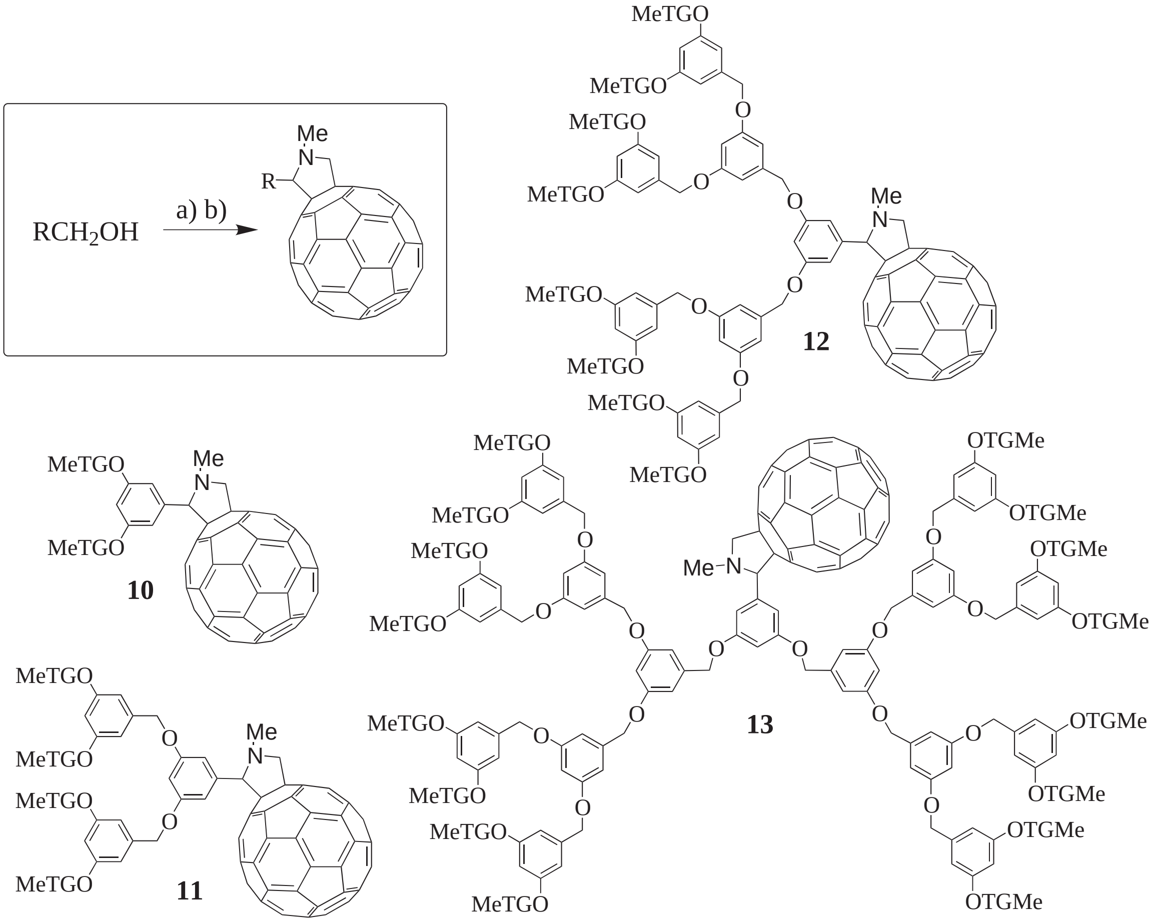


Scheme 1. Preparation of the triethylene glycol terminated poly(aryl ether) dendrons. Reagents and conditions: (a) TsCl, pyridine, CH_2Cl_2, 0°C, 18 h (69%); (b) methyl 3,5-dihydroxybenzoate, K_2CO_3, DMF, 70°C, 48 h (83%); (c) LAH, THF, 0°C, 3 h (91%); (d) TMSBr, $CHCl_3$, rt, 4 h (84%); (e) 3,5-dihydroxybenzyl alcohol, K_2CO_3, acetone, Δ, 72 h (82%); (f) PBr_3, C_6H_6, 0°C, 5 h (76%); (g) 3,5-dihydroxybenzyl alcohol, K_2CO_3, acetone, Δ, 72 h (92%); (h) PBr_3, C_6H_6, 0°C, 5 h (51%); (i) 3,5-dihydroxybenzyl alcohol, K_2CO_3, acetone, Δ, 48 h (83%)

of the resulting tosylate with methyl 3,5-dihydroxybenzoate in the presence of K_2CO_3 in DMF at 70°C afforded ester **2**. Lithium aluminum hydride (LAH) reduction then gave benzylic alcohol **3**. Treatment of **3** with trimethylsilyl bromide (TMSBr) in $CHCl_3$ yielded bromide **4**. It is worth noting that the bromination step could also be achieved with CBr_4/PPh_3, however, the separation of the resulting bromide from the triphenylphosphine oxide by-product was nearly impossible. This was also true for the preparation of the dendritic bromides of higher generation. Reaction of bromide **4** with 3,5-dihydroxybenzyl alcohol in the presence of K_2CO_3 in refluxing acetone afforded the first generation alcohol **5**. Each new generation dendron was then obtained via successive bromination followed by alkylation of 3,5-dihydroxybenzyl alcohol.[8] It should be mentioned that the bromination step was carried out using PBr_3 since partial cleavage of the benzylic ether functions was observed when TMSBr was used.

The attachment of dendrons **3**, **5**, **7** and **9** to the fullerene sphere was achieved in a two-step procedure, as depicted in Scheme 2. MnO_2 oxidation of the benzylic alcohol followed by the



Scheme 2. Preparation of the fullerodendrimers **10**–**13**. Reagents and conditions: (a) MnO_2, CH_2Cl_2, rt, 3 h; (b) C_{60}, *N*-methylglycine, toluene, Δ, 24–70 h (**10**: 37% from **3**; **11**: 35% from **5**; **12**: 36% from **7**; **13**: 40% from **9**)

1,3-dipolar cycloaddition[9] of C_{60} with the azomethine ylide, generated in situ from the resulting benzaldehyde, afforded the corresponding fullerodendrimer. In a typical procedure, a solution of the benzaldehyde resulting from the oxidation of dendron **9** (900 mg), C_{60} (150 mg) and *N*-methylglycine (160 mg) in toluene (150 ml) was refluxed under argon for 70 h. After cooling, the resulting solution was evaporated to dryness and column chromatography (SiO_2, toluene/acetone 3:2) followed by gel permeation chromatography (Biorads, Biobeads SX-1, CH_2Cl_2) yielded fullerodendrimer **13** (472 mg, 44% yield). The ^1H and ^{13}C NMR spectra and the elemental analysis data of **13** were in full agreement with the proposed molecular structure and the UV–vis spectrum shows typical bands of fulleropyrrolidine derivatives.[9] The structure of **13** was also confirmed by MALDI-TOF mass spectrometry with the potassium-molecular ion complex peak at $m/z = 4973$ (calcd for $C_{279}H_{319}NO_{78}K$: 4973.6).

Fullerodendrimers **10**–**13** are quite soluble in a wide range of solvents (CH_2Cl_2, $CHCl_3$, toluene, THF and alcohols). The two highest generation dendrimers are also water soluble. Whereas the solubility has not been quantified, compounds **10**–**13** are soluble to at least 20 mg/ml in the mixture of solvents (THF/H_2O, 1:1) used in the sol-gel process.[10] Therefore, direct inclusion of these compounds in sol-gel glasses can be achieved during the gelation process to afford suitable doped sol-gel glasses for optical limiting applications.[11] The dendritic structure has been designed to encapsulate the C_{60} core in order prevent the fast S_1–S_0 relaxation resulting from the micellar aggregation due to the strong fullerene–fullerene interactions,[10] thus the sol-gel samples should be suitable for optical limitation applications against nanosecond laser pulses.[10] This study is still under way in our laboratories.

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