Pergamon

Tetrahedron Letters 40 (1999) 269–272

TETRAHEDRON
LETTERS

Preparation of Dendrons with Peripheral Fullerene Units

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Received 9 October 1998; accepted 5 November 1998

Abstract: Highly soluble dendritic branches with fullerene subunits at the periphery and a carboxylic acid function at the focal point have been prepared by a convergent approach, using successive DCC-mediated esterifications followed by cleavage of a *t*-butyl ester moiety under acidic conditions.

During the two past decades, two main synthetic strategies have been developed for the preparation of dendrimers: the divergent and convergent approaches.[1] In the divergent strategy, dendrimers are constructed from the central core to the periphery. In each repeat cycle, the n reactive groups on the dendrimer periphery react with n monomer units to add a new generation to the dendrimer. However, due to the increasing number of reactive terminal units, defects in the structures appear rapidly. In the convergent strategy which has been introduced by Hawker and Fréchet,[2] dendritic branches are first built up, then attached to the central core in the final step. In this case, the number of coupling reactions needed to add each new generation, usually 2 or 3, is the same throughout the synthesis making defective products easier to separate. Whereas exactly the same number of steps is required by using a divergent or a convergent approach for the preparation of a given dendrimer, the convergent one appears to be more efficient for the construction of monodisperse dendrimers. Among the development of suitable protocols to produce monodispersed cascade molecules, the design of functional dendrimers is more and more emphasized today and the field expands rapidly in many different directions, including material science and biological applications.[3]

In this paper, we now report an efficient convergent preparation of highly soluble dendritic branches with fullerene subunits at the periphery and a carboxylic acid function at the focal point. In light of the unusual physical and chemical properties of C_{60}, those new dendrons appears as versatile building blocks for the preparation of light harvesting devices. Additionally, it should be noted that all the fullerene-based dendrimers reported to date have been prepared with a C_{60} core[4] but never with fullerene units at their

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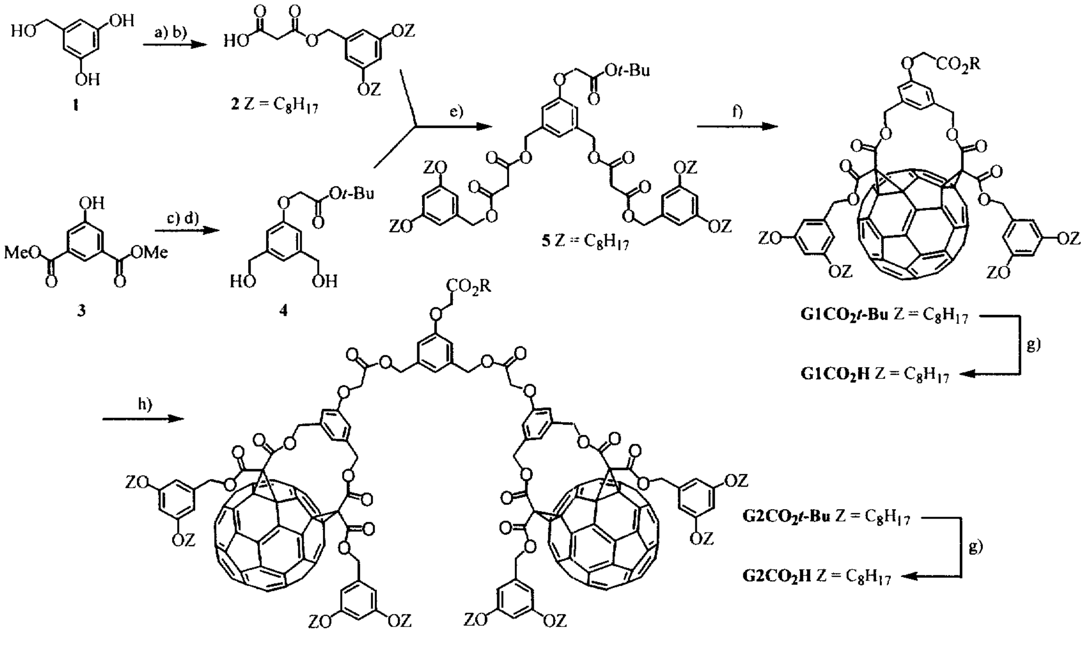
0040-4039/99/$ - see front matter
PII: S0040-4039(98)02378-8

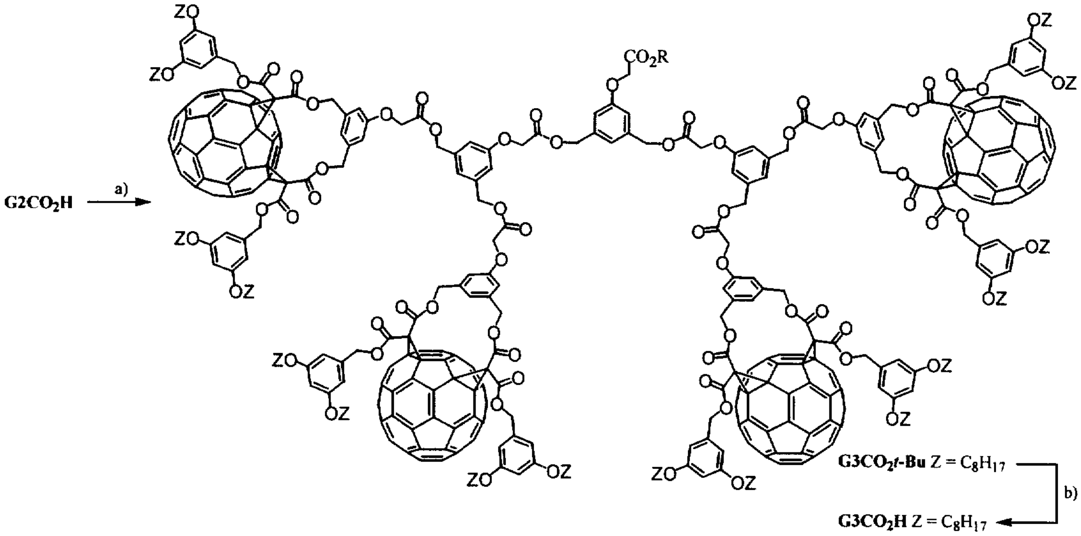
surface. A few examples of multi-fullerene derivatives can be, however, considered as dendrimers of first generation with peripherical C_{60} units.[5]

The fullerene-functionalized dentritic branches **G1CO$_2$H** and **G2CO$_2$H** were prepared as depicted in Scheme 1. Alkylation of 3,5-dihydroxybenzyl alcohol (**1**) with 1-bromooctane in *N*,*N*-dimethylformamide (DMF) at 60°C with K_2CO_3 as base followed by reaction of the resulting 3,5-dioctyloxybenzyl alcohol with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)[6] at 110-120°C yielded the mono-ester **2** of malonic acid in an overall yield of 70%. Diisobutylaluminium hydride (DIBAL-H) reduction of diester **3** and subsequent alkylation of the resulting 3,5-dihydroxymethylphenol with *t*-butyl 2-bromoacetate in DMF at 60°C in the presence of K_2CO_3 afforded diol **4** (54% overall yield). *N*,*N'*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of **2** with diol **4** in CH_2Cl_2 gave bis-malonate **5** in 83% yield. The functionalization of C_{60} is based on the highly regioselective macrocyclisation reaction of the carbon sphere with bis-malonate derivatives developed by Diederich and co-workers.[4d,7] Reaction of bis-malonate **5** with C_{60}, I_2, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature gave the C_s-symmetric *cis*-2 bis-adduct **G1CO$_2$*t*-Bu** in 59% yield.



Scheme 1. Synthesis of dendrons **G1CO$_2$H** and **G2CO$_2$H**. Reagents and conditions: a) 1-Bromooctane, K_2CO_3, DMF, 60°C (70%); b) 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid), 110-120°C (quantitative); c) DIBAL-H, THF, 0°C (77%); d) *t*-Butyl 2-bromoacetate, K_2CO_3, DMF, 60°C (70%); e) DCC, DMAP, CH_2Cl_2, 0°C to r.t. (83%); f) C_{60}, DBU, I_2, toluene, r.t. (59%); g) CF_3CO_2H, CH_2Cl_2, r.t. (99%); h) 4, DCC, DMAP, BtOH, CH_2Cl_2, 0°C to r.t. (90%).

Selective cleavage of the *t*-butyl ester moiety[8] with CF_3CO_2H in CH_2Cl_2 gave **G1CO$_2$H** in a quantitative yield. The preparation is thus easily carried out on a multi-gram scale. Reaction of **G1CO$_2$H** with diol **4** under esterification conditions using DCC, 1-hydroxybenzotriazole (BtOH) and 4-dimethylaminopyridine (DMAP) led to the *t*-butyl-protected dendron **G2CO$_2$*t*-Bu** of second generation in 90% yield. Subsequent treatment with CF_3CO_2H in CH_2Cl_2 afforded **G2CO$_2$H** in high yield (99%). Esterification of **G2CO$_2$H** with diol **4** (DCC/DMAP/BtOH) gave **G3CO$_2$*t*-Bu** in 84% yield (Scheme 2) and subsequent hydrolysis of the *t*-butyl ester group under acidic conditions afforded the third generation carboxylic acid **G3CO$_2$H**. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures assigned to the dendrons of each generation.[9]



Scheme 2. Synthesis of dendron **G3CO$_2$H**. Reagents and conditions: a) 4, DCC, DMAP, BtOH, CH_2Cl_2, 0°C to r.t. (84%); b) CF_3CO_2H, CH_2Cl_2, r.t. (83%).

The dendrons **G1-3CO$_2$H** reported herein are highly soluble in common organic solvents and appear to be interesting building blocks for the preparation of monodisperse fullerene-rich macromolecules. This is shown in the following communication which describes their attachment to a phenanthroline diol derivative and the preparation of the corresponding copper(I) complexes. By attachment of several of those C_{60} dendrons on a functional group like a chromophore, ionophore, receptor or electron donor, the fullerene-rich microenvironment should modulate the physical properties at the central core. Furthermore, intramolecular processes between the fullerene groups and the core such as photoinduced energy or electron transfer should become more efficient due to the high number of surrounding C_{60} subunits. Finally, those new dendrons are amphiphilic compounds and their incorporation in Langmuir-Blodgett films is now under investigation in our laboratory.

Acknowledgements: We thank L. Oswald for technical help and Hoechst AG for samples of C_{60}.

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9) All new compounds were characterized by ^{1}H- and ^{13}C-NMR, IR, UV/Vis and gave satisfactory elemental analysis. Selected spectroscopic data: **G1CO$_2$H**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.89 (t, J = 7, 12 H), 1.28 (m, 40 H), 1.73 (m, 8 H); 3.84 (t, J = 6.5, 8 H), 4.68 (s, 2 H), 5.08 (d, J = 13, 2 H), 5.29 (s, 4 H), 5.76 (d, J = 13, 2 H), 6.36 (t, J = 2, 2 H), 6.49 (d, J = 2, 4 H), 6.80 (br s, 2 H), 7.14 (br s, 1 H); Anal. calc. for $C_{122}H_{88}O_{15}.H_2O$: C 80.87, H 5.01; found: C 80.78, H 5.15 ; **G2CO$_2$H**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.85 (t, J = 7, 24 H), 1.28 (m, 80 H), 1.71 (m, 16 H); 3.84 (t, J = 6, 16 H), 4.61 (s, 2 H), 4.73 (s, 4 H), 5.06 (d, J = 13, 4 H), 5.23 (s, 4 H), 5.29 (s, 8 H), 5.69 (d, J = 13, 4 H), 6.35 (t, J = 2, 4 H), 6.46 (d, J = 2, 8 H), 6.76 (br s, 4 H), 6.85 (br s, 2 H), 6.97 (br s, 1 H), 7.12 (br s, 2 H); Anal. calc. for $C_{254}H_{184}O_{33}.2H_2O$: C 80.28, H 4.99; found: C 80.11, H 5.09; **G3CO$_2$H**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.89 (t, J = 7, 48 H), 1.33 (m, 160 H), 1.77 (m, 32 H); 3.85 (t, J = 7, 32 H), 4.52 (s, 2 H), 4.70 (s, 12 H), 5.05 (d, J = 13, 8 H), 5.15 (s, 4 H), 5.17 (s, 8 H), 5.30 (s, 16 H), 5.72 (d, J = 13, 8 H), 6.35 (t, J = 2, 8 H), 6.47 (d, J = 2, 16 H), 6.77 (br s, 8 H), 6.85 (br s, 2 H), 6.88 (br s, 4 H), 6.99 (br s, 3 H), 7.13 (br s, 4 H); Anal. calc. for $C_{518}H_{376}O_{69}.5H_2O$: C 79.82, H 4.99; found: C 79.59, H 4.95.