

Cyclotrimeratrylene Dendrimers with a Fullerene C₆₀ in the Dendritic Branches

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Authors' contributions

This work was carried out in collaboration between all authors. Authors KESM and MEMK made the synthesis. Author TK made the analysis of spectroscopy data, and revised the first draft of the manuscript. Author MMG wrote the paper. All authors read and approved the final manuscript.

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ABSTRACT

Dendrons with dodecyl terminal groups joined to benzyloxy moieties were attached to a cyclotrimeratrylene core. The dendrimers were used in Bingel cyclopropanation reaction with the fullerene C₆₀. The structure of the synthesized dendrimers was confirmed by ¹H- and ¹³C-NMR, MALDI-TOF mass spectrometry and elemental analysis.

Keywords: Cyclotrimeratrylene; fullerene C60; cyclopropanation reaction; dendrimers.

1. INTRODUCTION

The cup-shaped cyclotrimeratrylene derivatives (CTV) are among the key structures that have been exploited for many years for the design of molecular hosts [1-7]. They are interesting starting compounds for the construction of new macromolecular architectures such as solid inclusion complexes [8], biosensors, bis-cryptophanes to study the guest

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exchange between closely bonded molecular cavities [9], chiral scaffolds for triple helix formation [10], organo- or metallo-gels [11], H₂ storage targets [12] or more recently, coordination polymer networks [13], self- assembled monolayers on gold surface [14] and dendrimers [15-19]. The three or six *p*-hydroxybenzyl substituents present on the wider rim of cyclotrimeratrylenes are able to undergo modification to obtain dendrimers without steric restrictions. Dendrimers with polyamidoamine (PAMAM), Polyarylethyl or polyethers groups have applications in drug delivery [20-23] and dendrimers with polyethers in their structure could be used as biodegradable dendrimers with the appropriate enzyme in the drug delivery systems [24]. Recently, we reported the synthesis of cyclotrimeratrylene-dendrimers and their supramolecular complexes with the fullerene C₆₀ [25]. In the present work we report the synthesis of cyclotrimeratrylene-dendrimers with three and six fullerenes in the dendritic branches.

2. MATERIALS AND METHODS

2.1 General

Solvents and reagents were purchased as reagent grade and used without further purification. Acetone was distilled over calcium chloride. Tetrahydrofuran was distilled from sodium and benzophenone. Column chromatography was performed on Merck silica gel 60Å (70-230 mesh). ¹H- and ¹³C-NMR were recorded on a Varian-Unity-300 MHz with tetramethylsilane (TMS) as an internal reference. Infrared (IR) spectra were measured on a spectrophotometer Nicolet FT-SSX. Elemental analysis was determined by Galbraith Laboratories Inc. (Knoxville, TN, USA). FAB+ mass spectra were taken on a JEOL JMS AX505 HA instrument. Electrospray mass spectra were taken on a Bruker Daltonic, Esquire 6000. MALDI-TOF mass spectra were taken on a Bruker Omni FLEX.

2.2 Synthesis of Core

2.2.1 (4-(Allyloxy)-3-methoxyphenyl) methanol 1

A mixture of vanillyl alcohol 10 g (65 mmol), allyl bromide (6.3 ml, 73 mmol) and potassium carbonate 10 g (65 mmol) in 100 ml of acetone was refluxed for 12 h with magnetic stirring. Then, after most of the solvent was stripped off, water was added and the organic material was extracted with dichloromethane. This product was recrystallized from 100 ml of diethyl ether to yield 14 g (80 %) of a white powder [25].

2.2.2 2,7,12-Trimethoxy-3,8,13-tris (2-propenyloxy)-10,15-dihydro -5 Htribenzo [a,d,g] cyclononene 2

p-Toluensulfonic acid 0.49 g (2.57 mmol) was mixed with the phenol protected vanillyl alcohol 0.5 g (2.57 mmol) in solid state and stirred for 20 min. The resulting purple solid was incubated at room temperature for 48 h. The reaction mixture was redissolved by addition of dichloromethane and the organic phase was thoroughly washed with water until neutral pH. The dichloromethane solution was partially dried over sodium sulphate and evaporated under vacuum, after which, ether was added, affording a crystalline residue, which was purified by digestion in 200 ml of ether overnight and finally isolated by suction filtration, to yield 0.22 g (37 %) of a white powder [25].

2.2.3 2,7,12-Trihydroxy-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo [a,d,g] cyclononene (cyclotrimeratrylene) 3

The tris(allyl ether) 2, 1.0 g (1.8 mmol) was dissolved in 10 ml of hot dioxane, and to this solution 11 ml of ethanol, 0.2 g of 10 % palladium on charcoal and (dropwise) 0.2 ml of 70 % perchloric acid were added. This mixture was stirred under nitrogen at 55 – 60°C for 18 h. The catalyst was filtered off and washed, first with 10 ml of dioxane and then with 10 ml of dichloromethane. The organic filtrate was thoroughly washed with water, dried over sodium sulphate and concentrated to 5 ml. The desired triphenol, which was allowed to crystallize overnight, was finally collected by suction filtration, to yield 0.42 g (55 %) of white needles [25].

2.3 Synthesis of Dendrons

2.3.1 Methyl 3, 5-bis (Dodecyloxy) benzoate 4 was obtained in agreement with reference [25].

2.3.2 (3, 5-bis (Dodecyloxy) phenyl) methanol 5 was obtained in agreement with reference [25].

2.3.3 3-(3,5-bis(Dodecyloxy)benzyloxy)-3-oxopropanoic acid 6 was obtained in agreement with reference [25].

2.3.4 Diethyl 5-(((tert-butyldimethylsilyl)oxy) methyl) isophthalate 8

A mixture of TBSCl (3.0 g, 19.80 mmol), 1H-imidazole (2.7 g, 39.70 mmol), and diethyl 5-(hydroxymethyl)isophthalate 7 (5.0 g, 19.80 mmol) in THF (75 ml) was stirred at 0°C under nitrogen for 12 h. The precipitate was filtered, dissolved in DCM, washed with brine, dried (Na₂SO₄), and evaporated; yielding 8 (6.0 g, 16.40 mmol, 83 %). White solid. UV (CH₂Cl₂, nm): 287, 267, 248, 207. IR (KBr, cm⁻¹): 2956, 2932, 1725, 1606, 1467, 1368, 1236, 1193, 1028, 932, 671. ¹H NMR (CDCl₃, 200 MHz): δ= 0.09 (s, 6H, CH₃-Si), 0.93 (s, 9H, C(CH₃)₃), 1.38 (t, J= 7.0, 6H, CH₃), 4.40 (d, J= 7.0, 4H, OCH₂CH₃), 4.80 (s, 2H, CH₂O), 8.17 (d, J= 2.0, 2H, Ar-H), 8.54 (t, J= 1.6, H, Ar-H). ¹³C NMR (CDCl₃): δ= -5.4 (CH₃-Si), 14.2 (CH₃), 25.8 (C(CH₃)₃), 61.1 (CH₂O), 64.0 (CH₂O-Si), 129.1(Ar), 130.9 (Ar), 142.3 (Ar_{ipso}), 165.7 (C=O). MS (m/z): 366 [M]⁺. Anal. Calcd. for C₁₉H₃₀O₅Si: C 62.26, H 8.25 %. Found: C 62.24, H 8.25 %.

2.3.5 (5-(((tert-Butyldimethylsilyl) oxy) methyl)-1,3-phenylene) dimethanol 9

A solution of LiAlH₄ (0.52 g, 14.00 mmol) in dry THF was added dropwise to a stirred solution of 8 (5.00 g, 14.0 mmol) in dry THF (135 ml) at 0°C. The mixture was stirred for 3-4 h at 0°C, and then MeOH/H₂O was carefully added. The mixture was filtered (Celite) and evaporated, yielding 9 (3.6 g, 12.80 mmol, 93 %). Colorless glassy product. UV (CH₂Cl₂, nm): 266. IR (film, cm⁻¹): 3338, 2953, 2931, 2884, 2858, 1608, 1465, 1363, 1255, 1101, 839, 779, 668. ¹H NMR (CDCl₃, 200 MHz): δ= 0.09 (s, 6H CH₃-Si), 0.94 (s, 9H, C(CH₃)₃), 3.13 (br, s, 2H, -OH), 4.56 (s, 2H, CH₂OH), 4.70 (s, 2H, CH₂O-Si), 7.15 (s, 3H, Ar-H). ¹³C NMR (CDCl₃): δ= -5.3 (CH₃-Si), 18.4 (C(CH₃)₃), 25.9(CH₂), 64.8 (CH₂O), 123.8 (Ar), 124.1(Ar), 141.2 (Ar_{ipso}). MS (m/z): 282 [M]⁺. Anal. Calcd. for C₁₅H₂₆O₃Si: C 63.78, H 9.28 %. Found: C 63.79, H 9.26 %.

2.3.6 Bis (3,5-bis (Dodecyloxy)benzyl)O,O'-((5-(((tert-butyl)dimethylsilyl)oxy)methyl)-1,3-phenylene) bis (methylene) dimalonate 10

To a solution of compound 6 (2.40 g, 4.30 mmol) and compound 9 (0.60 g, 2.13 mmol) in 50 ml of CH₂Cl₂, N, N-dicyclohexylcarbodiimide (DCC) 0.56 g (2.70 mmol) and 4-(N, N-dimethylamino) pyridine (DMAP) 0.03 g (0.25 mmol) was added, under nitrogen and constantly stirred for 22 h. The organic phase was evaporated under vacuum and purified by column chromatography (SiO₂, CH₂Cl₂/ ethylacetate 8:2) to yield 10, 2.0 g (1.45 mmol, 70 %), as yellow oil. UV (CHCl₃, nm): 280, 251, 206. IR (film, cm⁻¹): 2925, 2854, 1742, 1598, 1464, 1295, 1168, 684. ¹H NMR (CDCl₃, 300 MHz): δ= 0.10 (s, 6 H CH₃-Si), 0.88 (t, 12H, CH₃, J= 6.4 Hz), 0.94 (s, 9 H, C(CH₃)₃), 1.26 (m, 72H, CH₂), 1.78 (m, 8H, CH₂), 3.50 (s, 4H, O=C-CH₂-C=O), 3.92 (t, 8H, CH₂-O, J= 6.5 Hz), 4.72 (s, 2H, CH₂-OSi), 5.10 (s, 4H, CH₂-O), 5.16 (s, 4H, CH₂-O), 6.40 (t, 2H, Ar, J= 2.1 Hz), 6.50 (d, 4H, Ar, J= 2 Hz), 7.20 (t, 1H, Ar, J= 2 Hz), 7.30 (d, 2H, Ar, J= 2 Hz). ¹³C NMR (CDCl₃): δ= -5.3 (CH₃-Si), 14.1 (CH₃), 22.7 (CH₂), 24.6 (C(CH₃)₃), 26.0 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.6 (CH₂), 32.0 (CH₂), 41.4 (O=C-CH₂-C=O), 67.2 (CH₂-O), 68.0 (CH₂-OH), 101.1 (Ar), 106.3 (Ar), 125.7 (Ar), 126.4.1 (Ar), 135.6 (Ar_{ipso}), 137.2 (Ar_{ipso}), 142.5 (Ar_{ipso}), 160.4 (C=O), 166.2 (C=O). ES MS (m/z): 1370 [M]⁺. Anal. Calcd. for C₈₃H₁₃₈O₁₃Si: C 72.76, H 10.14 %. Found: C 72.78, H 10.12 %.

2.3.7 Bis(3,5-bis(Dodecyloxy)benzyl)O,O'-((5-(hydroxymethyl)-1,3-phenylene)bis (methylene) dimalonate 11

A solution of 1M Bu₄NF (3.30 ml, 3.30 mmol) in THF, was added to a stirred solution of 10 (4.60 g, 3.30 mmol) in THF (50 ml) at 0°C. After 4 hrs, the mixture was evaporated. The residue was taken up with CH₂Cl₂, washed with a saturated aqueous NH₄Cl solution, dried (Na₂SO₄), and evaporated, yielding 11 (4.3 g, 3.4 mmol, 95 %). as yellow oil. UV (CHCl₃, nm): 281, 254, 206. IR (film, cm⁻¹): 3381, 2924, 2853, 1739, 1600, 1461, 1165, 1062. ¹H NMR (CDCl₃, 300 MHz): δ= 0.89 (t, 12H, CH₃, J= 6.4 Hz), 1.27 (m, 72H, CH₂), 1.76 (m, 8H, CH₂), 3.49 (s, 4H, O=C-CH₂-C=O), 3.91 (t, 8H, CH₂-O, J= 6.4 Hz), 4.60 (s, 2H, CH₂-OH), 5.02 (s, 4H, CH₂-O), 5.10 (s, 4H, CH₂-O), 6.33 (t, H, Ar, J= 2.2 Hz), 6.40 (t, 2H, Ar, J= 2.0 Hz), 6.45 (d, 4H, Ar, J= 1.8Hz), 6.51 (d, 2H, Ar, J= 2.0 Hz). ¹³C NMR (CDCl₃): δ= 14.0 (CH₃), 22.5 (CH₂), 26.0 (CH₂), 29.0 (CH₂), 29.5 (CH₂), 31.7 (CH₂), 41.3 (O=C-CH₂-C=O), 67.0 (CH₂-OH), 67.8 (CH₂-O), 100.7 (Ar), 101.0 (Ar), 106.1 (Ar), 106.2 (Ar), 137.0 (Ar_{ipso}), 138.0 (Ar_{ipso}), 144.0 (Ar_{ipso}), 160.3 (C=O), 166.2 (C=O). ES MS (m/z): 1256 [M]⁺. Anal. Calcd. for C₇₇H₁₂₄O₁₃: C 73.53, H 9.94 %. Found: C 73.55; H 9.94 %.

2.3.8 Bis(3,5-bis(Dodecyloxy)benzyl)O,O'-((5-(chloromethyl)-1,3-phenylene)bis (methylene) dimalonate 12

0.5 g (0.40 mmol) of 11 was added to a mixture of pyridine 0.04 ml (0.52 mmol) and CH₂Cl₂ (25 ml) and cooled at 0°C under nitrogen and vigorously stirred for 20 min. Thionyl chloride 0.041 ml, (0.56 mmol) was added dropwise. The reaction was continued for 20 h at room temperature and the resulting mixture was washed with hexane, filtered and evaporated, to give 12 0.46 g (0.40 mmol, 90 %), as yellow oil. UV (CHCl₃, nm); 281, 254, 206. IR (Film, cm⁻¹): 2925, 2854, 1740, 1600, 1461, 1167, 1064, 833. ¹H NMR (CDCl₃, 300 MHz): δ= 0.88 (t, 12H, CH₃, J= 6.3 Hz), 1.26 (m, 72H, CH₂), 1.74 (m, 8H, CH₂), 3.48 (s, 4H, O=C-CH₂-C=O), 3.90 (t, 8H, CH₂-O, J= 6.4 Hz), 4.49 (s, 2H, CH₂-Cl), 5.01 (s, 4H, CH₂-O), 5.10 (s, 4H, CH₂-O), 6.38 (t, H, Ar, J= 2.1 Hz), 6.40 (t, 2H, Ar, J= 2.1 Hz), 6.45 (d, 4H, Ar, J= 2.4 Hz), 6.41 (d, 2H, Ar, J= 2.1 Hz). ¹³C NMR (CDCl₃): δ= 14.0 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 32.0 (CH₂), 41.5 (O=C-CH₂-C=O), 67.2 (CH₂-Cl), 68.1 (CH₂-O),

101.2 (Ar), 106.3 (Ar), 106.9 (Ar), 137.2 (Ar_{ipso}), 141.0 (Ar_{ipso}), 160.5 (C=O). ES MS (m/z): 1274[M]⁺. Anal. Calcd. for C₇₇H₁₂₃ClO₁₂: C 72.46; H 9.71 %; Found: C 72.45, H, 9.72 %.

2.3.9 Tetrakis(3,5-bis(dodecyloxy)benzyl)O,O',O'',O'''-((((5-(hydroxymethyl)-1,3-phenylene)bis(oxy))bis(methylene))bis(benzene-5,3,1-triyl))tetrakis(methylene)) tetramalonate 13

A mixture of 12 1.50 g (1.20 mmol), cesium carbonate 0.30 g (4.10 mmol) and 3,5-dihydroxybenzyl alcohol 0.33 g (1.2 mmol) in dry acetone (80 ml) was heated to reflux and stirred vigorously under nitrogen for 4 days. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. To yield 13 1.40 g (0.53 mmol, 45 %); as yellow oil. UV (CHCl₃, nm): 283, 245, 263. IR (film, cm⁻¹): 3431, 2924, 2854, 1737, 1598, 1461, 1381, 1166, 1062, 833. ¹H NMR (CDCl₃, 300 MHz): δ= 0.88 (t, 24H, CH₃, J= 6.0 Hz), 1.4 (m, 144H, CH₂), 1.75 (m, 16H, CH₂), 3.93 (t, 24H, CH₂-O, J= 6.3 Hz), 4.61 (d, 2H, CH₂-OH, J= 3.6 Hz), 5.01 (s, 20H, CH₂-O), 6.37 (t, 4H, Ar-H, J= 2.6 Hz), 6.39 (t, 3H, Ar-H, J= 3.0 Hz), 6.47 (d, 6H, Ar-H J= 2.1 Hz), 6.49 (d, 8H, Ar, J= 2.4 Hz). ¹³C NMR (CDCl₃): δ= 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 41.5 (O=C-CH₂-C=O), 67.2 (CH₂-OH), 68.0 (CH₂-O), 100.1 (Ar), 101.0 (Ar), 106.3 (Ar), 106.8 (Ar), 137.2 (Ar_{ipso}), 143.2 (Ar_{ipso}), 160.5 (C=O). MALDI-TOF MS (m/z): 2617 [M]⁺. Anal. Calcd. for C₁₆₁H₂₅₂O₂₇: C 73.81, H 9.70 %. Found: C 73.83; H 9.70 %.

2.3.10 Tetrakis(3,5-bis(dodecyloxy)benzyl)O,O',O'',O'''-((((5-(chloromethyl)-1,3-phenylene)bis(oxy))bis(methylene))bis(benzene-5,3,1-triyl))tetrakis(methylene)) tetramalonate 14

0.90 g (0.34 mmol) of 13 was added to a mixture of pyridine 0.04 ml (0.48 mmol) and CH₂Cl₂ (25 ml) and cooled at 0°C under nitrogen and vigorously stirred for 20 min. Thionyl chloride 0.037 ml, (0.51 mmol) was added dropwise. The reaction was continued for 46 h at room temperature and the resulting mixture was washed with hexane, filtered and evaporated, to give 14 0.87 g (0.33 mmol, 96%), as dark yellow oil. UV (CHCl₃, nm): 283, 244, 271, 208. IR (KBr, cm⁻¹): 2925, 2854, 1739, 1599, 1461, 1380, 1168, 1061, 834, 682. ¹H NMR (CDCl₃, 300 MHz): δ= 0.88 (t, 24H, CH₃, J= 6.3 Hz), 1.41 (m, 144H, CH₂), 1.78 (m, 16H, CH₂), 3.93 (t, 24H, CH₂-O, J= 6.4 Hz), 4.49 (s, 2H, CH₂-Cl), 5.02 (s, 20H, CH₂-O), 6.37 (t, 3H, Ar-H, J= 2.1 Hz), 6.39 (d, 6H, Ar-H, J= 1.8 Hz), 6.46 (d, 8H, Ar-H J= 2.1 Hz), 6.51 (t, 4H, Ar, J= 2.4 Hz). ¹³C NMR (CDCl₃): δ= 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.8 (CH₂), 41.5 (O=C-CH₂-C=O), 66.3 (CH₂-Cl), 68.1 (CH₂-O), 100.6 (Ar), 101.0 (Ar), 101.3 (Ar), 105.1 (Ar), 106.4 (Ar), 106.9 (Ar), 137.9 (Ar_{ipso}), 139.3 (Ar_{ipso}), 139.9 (Ar_{ipso}), 141.9 (Ar_{ipso}), 143.2 (Ar_{ipso}), 145.7 (Ar_{ipso}), 160.4 (C=O). MALDI-TOF MS (m/z): 2635 [M]⁺. Anal. Calcd. for C₁₆₁H₂₅₁ClO₂₆: C 73.30, H 9.59 %. Found: C 73.32, H 9.57 %.

2.4 Synthesis of Dendrimers

A mixture of 12 or 14 (0.36 mmol), cesium carbonate (0.36 mmol) in N,N-dimethylformamide anhydrous (8 ml) was heated to reflux and stirred vigorously under nitrogen after 20 min. The cyclotrimeratrylene 3 (0.07 mmol) dissolved in N,N-dimethylformamide anhydrous (10 ml) was added dropwise and the reaction was continued for 31 h at reflux. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure and the residue was chromatographed on silica gel with ethyl hexane as the eluent to afford the cyclotrimeratrylene-dendrimer.

2.4.1 Dendrimer 15

Yield (0.25 g, 0.13 mmol, 42 %), dark-red glassy. UV (CHCl₃, nm): 284, 247. IR (Film, cm⁻¹): 2925, 2854, 1741, 1600, 1461, 1253, 1166, 1064, 834, 721. ¹H NMR (CDCl₃, 400 MHz): δ = 0.88 (t, 36H, CH₃, *J* = 6.1 Hz), 1.26 (m, 216H, CH₂), 1.70 (m, 24H, CH₂), 3.45 (s, 12H, O=C-CH₂-C=O), 3.50 (d, 3H, CH₂, *J* = 13.0 Hz), 3.80 (t, 24H, CH₂-O, *J* = 5.3 Hz), 3.84 (s, 9H, CH₃-O), 4.61 (s, 6H, CH₂-O), 4.60 (d, 3H, CH₂, *J* = 12.0 Hz), 5.04 (s, 12H, Ar-CH₂-O), 5.08 (s, 12H, Ar-CH₂-O), 6.35-6.60 (m, 27H, Ar-H), 7.54 (s, 3H, Ar-H), 7.70 (s, 3H, Ar-H). ¹³C NMR (CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂), 26.1 (CH₂), 29.4 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 36.3 (CH₂), 44.8 (O=C-CH₂-C=O), 56.1 (CH₃-O), 68.0 (CH₂-O), 70.2 (CH₂-O), 71.6 (ArCH₂-OCTV), 100.6 (Ar), 101.1 (Ar), 104.9 (Ar), 106.2 (Ar), 113.6 (Ar-HCTV), 115.5 (Ar-HCTV), 131.2 (ArCTV-CH₂), 132.4 (ArCTV-CH₂), 137.2 (Ar_{ipso}), 141.3 (Ar_{ipso}), 143.8 (Ar-O), 144.2 (Ar_{ipso}), 145.2 (Ar-O), 160.4 (C=O), 162.0 (C=O); MALDI-TOF-MS: *m/z* 4124 [M]⁺. Anal. Calcd. for C₂₅₅H₃₉₀O₄₂: C, 74.20, H, 9.52 %. Found: C 74.18, H 9.52

2.4.2 Dendrimer 16

Yield (0.33 g, 0.10 mmol, 31 %), dark-brown glassy. UV (CHCl₃, nm): 283, 243. IR (Film, cm⁻¹): 3422, 2925, 2854, 1740, 1599, 1461, 1244, 1166, 1063, 833. ¹H NMR (CDCl₃, 300 MHz): δ = 0.89 (t, 72H, CH₃, *J* = 6.3 Hz), 1.27 (m, 432H, CH₂), 1.74 (m, 48H, CH₂), 3.48 (s, 24H, O=C-CH₂-C=O), 3.51 (d, 3H, CH₂, *J* = 12.6 Hz), 3.91 (s, 9H, CH₃-O), 3.94 (t, 48H, CH₂-O, *J* = 6.3 Hz), 4.62 (s, 6H, CH₂), 4.84 (d, 3H, CH₂, *J* = 11.2 Hz), 5.02 (s, 36H, ArCH₂-O), 5.05 (s, 24H, ArCH₂-O), 5.10 (s, 6H, ArCH₂-O), 6.41 (t, 12H, Ar-H, *J* = 2.1 Hz), 6.46 (d, 18H, Ar-H, *J* = 2.4 Hz), 6.48 (d, 24H, Ar-H, *J* = 2.1 Hz), 6.51 (t, 9H, Ar-H, *J* = 3.0 Hz), 7.60 (s, 3H, Ar-H), 7.61 (s, 3H, Ar-H). ¹³C NMR (CDCl₃): δ = 14.1 (CH₃), 23.0 (CH₂), 26.1 (CH₂), 29.4 (CH₂), 29.6 (CH₂), 32.0 (CH₂), 36.5 (CH), 46.4 (O=C-CH₂-C=O), 56.1 (CH₃-O), 66.3 (CH₂-O), 68.1 (CH₂-O), 100.6 (Ar), 101.0 (Ar), 101.4 (Ar), 105.1 (Ar), 106.5 (Ar), 107.0 (Ar), 112.3 (Ar-H-CTV), 115.6 (Ar-CTV), 132.7 (ArCVT-CH₂), 133.8 (ArCTV-CH₂), 137.2 (Ar_{ipso}), 137.9 (Ar_{ipso}), 139.3 (Ar_{ipso}), 143.2 (Ar_{ipso}), 145.2 (Ar-O), 160.5 (C=O), 170.8 (C=O). MALDI-TOF-MS: *m/z* 8213 [M]⁺. Anal. Calcd. for C₅₀₇H₇₇₄O₈₄: C, 74.14, H, 9.50 %. Found: C 74.16, H 9.51 %.

2.5 Synthesis of Fullerene Derivatives

DBU (0.43 mmol) and I₂ (0.020 mmol) were added at room temperature to a solution of C₆₀ (0.17 mmol) and 15 or 16 (0.17 mmol) in 17 ml of toluene anhydrous. The mixture was stirred for 3 days, filtered, evaporated under vacuum and purified by column chromatography (SiO₂, CH₂Cl₂/methanol, 8:2).

2.5.1 Fullerene derivative 17

Yield (0.06 g, 0.01 mmol, 26 %), dark-brown solid. UV (CHCl₃, nm): 248. IR (Film, cm⁻¹): 3258, 2925, 2854, 1733, 1648, 1600, 1459, 1292, 1164, 1067, 835, 751. ¹H NMR (CDCl₃, 300 MHz): δ = 0.85 (t, 36H, CH₃, *J* = 6.1 Hz), 1.23 (m, 216H, CH₂), 1.70 (m, 24H, CH₂), 3.50 (d, 3H, CH₂, *J* = 13.0 Hz), 3.80 (t, 24H, CH₂-O, *J* = 5.3 Hz), 3.84 (s, 9H, CH₃-O), 4.61 (s, 6H, CH₂), 4.60 (d, 3H, CH₂, *J* = 12.0 Hz), 5.04 (s, 12H, Ar-CH₂-O), 5.08 (s, 12H, Ar-CH₂-O), 6.35-6.60 (m, 27H, Ar-H), 7.54 (s, 3H, Ar-H), 7.70 (s, 3H, Ar-H). ¹³C NMR (CDCl₃): δ = 14.2 (CH₃), 22.8 (CH₂), 26.1 (CH₂), 26.2 (CH₂), 29.4 (CH₂), 29.8 (CH₂), 32.0 (CH₂), 37.3 (CH₂), 56.3 (CH₃-O), 66.8 (C₆₀), 67.0 (C₆₀), 68.1 (CH₂-O), 69.5 (C₆₀), 100.6 (Ar), 101.0 (Ar), 101.1 (Ar), 101.5 (Ar), 105.1 (Ar), 106.3 (Ar), 106.5 (Ar), 125.1 (C₆₀), 126.7 (C₆₀), 126.7 (C₆₀), 128.9 (C₆₀), 130.9 (Ar-CH₂), 132.4 (Ar-CH₂), 133.8 (C₆₀), 135.3 (C₆₀), 136.7 (Ar_{ipso}),

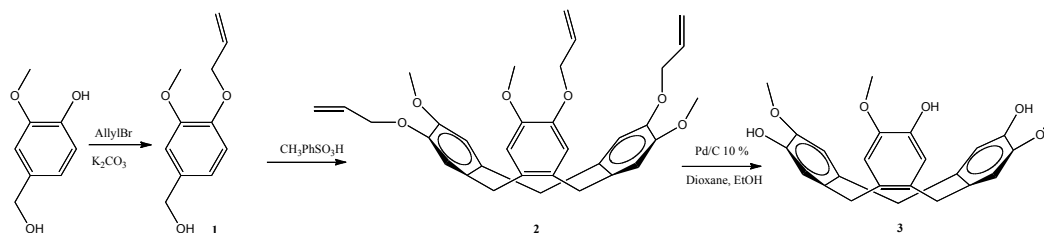
137.5(C₆₀), 137.6 (C₆₀), 138.1 (C₆₀), 138.2 (C₆₀), 138.4 (C₆₀), 139.0 (C₆₀), 139.3 (C₆₀), 140.7 (C₆₀), 141.3 (C₆₀), 142.2 (C₆₀), 142.6 (C₆₀), 143.4 (Ar_{ipso}), 143.5 (C₆₀), 143.9 (C₆₀), 144.2 (Ar-O, C₆₀), 144.6 (C₆₀), 144.7 (C₆₀), 144.8 (C₆₀), 145.4 (Ar-O, C₆₀), 145.6 (C₆₀), 145.7 (C₆₀), 145.8 (C₆₀), 145.9 (C₆₀), 146.3 (C₆₀), 146.4 (C₆₀), 146.6 (C₆₀), 147.0 (C₆₀), 147.3 (C₆₀), 147.8 (C₆₀), 148.1 (C₆₀), 155.2 (Ar_{ipso}), 160.4 (C=O), 165.5 (C=O). MALDI-TOF-MS: m/z 6295 [M+Na]⁺. Anal. Calcd. for C₄₃₅H₃₇₈O₄₂: C, 83.23, H, 6.07 %. Found: C 83.25, H 6.09 %

2.5.2 Fullerene derivative 18

Yield (0.06 g, 0.01 mmol, 26 %), red-brown solid. UV (CHCl₃, nm): 247. IR (Film, cm⁻¹): 3422, 2925, 2854, 1740, 1599, 1461, 1244, 1166, 1063, 833, 721. ¹H NMR (CDCl₃, 300 MHz): δ = 0.89 (t, 72H, CH₃, J = 6.3 Hz), 1.27 (m, 432H, CH₂), 1.74 (m, 48H, CH₂), 3.49 (d, 3H, CH₂, J = 14.0 Hz), 3.85 (s, 9H, CH₃-O), 3.94 (t, 48H, CH₂-O, J = 6.3 Hz), 4.62 (s, 6H, CH₂), 4.70 (d, 3H, CH₂, J = 13.2 Hz), 5.02 (s, 36H, ArCH₂-O), 5.05 (s, 24H, ArCH₂-O), 5.10 (s, 6H, ArCH₂-O), 6.41 (t, 12H, Ar-H, J = 2.1 Hz), 6.46 (d, 18H, Ar-H, J = 2.4 Hz), 6.48 (d, 24H, Ar-H, J = 2.1 Hz), 6.51 (t, 9H, Ar-H, J = 3.0 Hz), 7.60 (s, 3H, Ar-H), 7.61 (s, 3H, Ar-H). ¹³C NMR (CDCl₃): δ = 14.0 (CH₃), 22.7 (CH₂), 26.1 (CH₂), 26.2 (CH₂), 29.4 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 38.0 (CH₂), 56.1(CH₃-O), 66.1 (C₆₀), 66.5 (C₆₀), 68.3 (CH₂-O), 69.5 (C₆₀), 100.6 (Ar), 100.7 (Ar), 101.0 (Ar), 101.1 (Ar), 101.5 (Ar), 105.5 (Ar), 105.8 (Ar), 106.1 (Ar), 106.3 (Ar), 113.2 (Ar-H-CTV), 114.0 (ArH-CTV), 125.3 (C₆₀), 126.5 (C₆₀), 127.0 (C₆₀), 128.8 (C₆₀), 131.4 (Ar-CH₂), 132.3 (ArCTV-CH₂), 133.4 (C₆₀), 135.2 (C₆₀), 136.6 (Ar_{ipso}), 137.0(C₆₀), 137.3 (C₆₀), 138.3 (C₆₀), 138.5 (C₆₀), 139.6 (C₆₀), 139.7 (C₆₀), 140.4 (C₆₀), 141.7 (C₆₀), 142.2 (C₆₀), 143.1 (C₆₀), 143.6 (C₆₀), 143.7 (Ar_{ipso}), 143.8 (C₆₀), 143.9 (C₆₀), 144.2 (Ar-O, C₆₀), 145.3 (C₆₀), 145.4 (C₆₀), 145.5 (Ar-O, C₆₀), 145.6 (C₆₀), 145.7 (C₆₀), 145.8 (C₆₀), 145.9 (C₆₀), 146.0 (C₆₀), 146.5 (C₆₀), 147.2 (C₆₀), 147.3 (C₆₀), 147.8 (C₆₀), 148.1 (C₆₀), 155.2 (Ar_{ipso}), 158.2 (C=O), 158.4 (C=O). MALDI-TOF-MS: m/z 12513 [M]⁺. Anal. Calcd. for C₈₆₇H₇₅₀O₈₄: C, 82.20, H, 6.04 %. Found: C 83.30, H 6.06 %.

3. RESULTS AND DISCUSSION

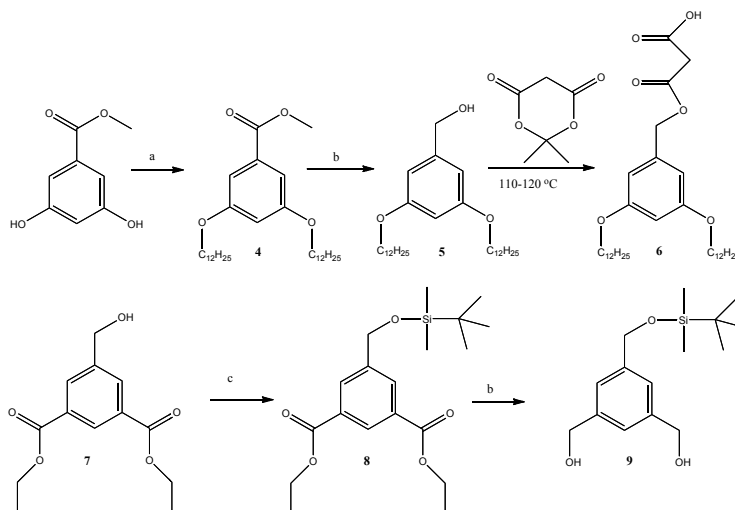
The synthesis of the cyclotrimeratrylene derivatives is depicted in Scheme 1. Precursor CTV (OH)₃ was obtained in three steps from commercially available vanillyl alcohol, according to the subsequent multistep transformations. The (4-(allyloxy)-3-methoxyphenyl) methanol **1** undergoes smooth trimerisation in the presence of *p*-toluenesulfonic acid in solid state, affording the C3-cyclotrimeratrylene derivative **2** in 24 % yield. The allyl ethers of **2** can then be cleaved back to phenols under mild condition, giving **3** in ca. 47 % [25].



Scheme 1. Synthesis of cyclotrimeratrylene

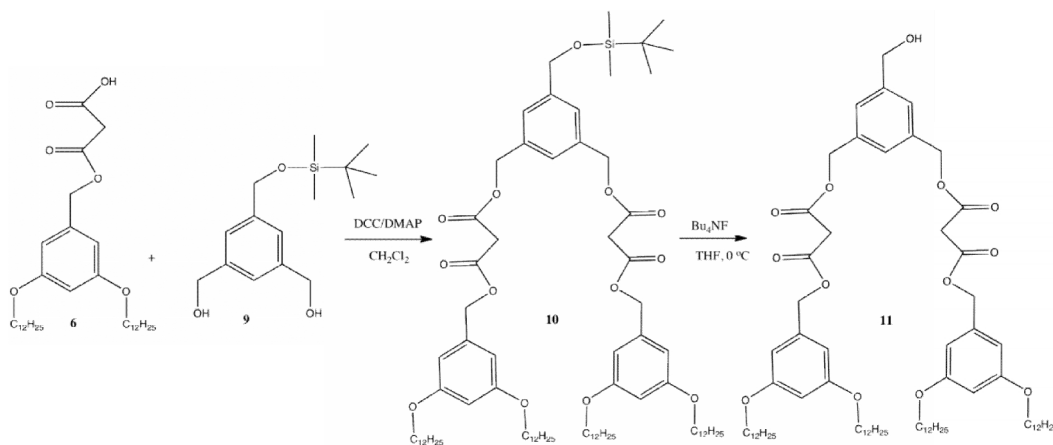
Dendrons containing polybenzyl ether groups were prepared starting from the O-alkylation reaction of the commercially available methyl 3,5-dihydroxybenzoate **1** with 1-bromododecane in acetone using potassium carbonate as a catalyst (Scheme 2) in

agreement with the literature data [21-25]. The compound 9 was obtained from the diethyl 5-(hydroxymethyl) isophthalate 7, which first was protected with *tert*-butylchlorodimethylsilane to obtain the compound 8, followed by the reduction with LiAlH_4 in THF to give the compound 9 (Scheme 2).



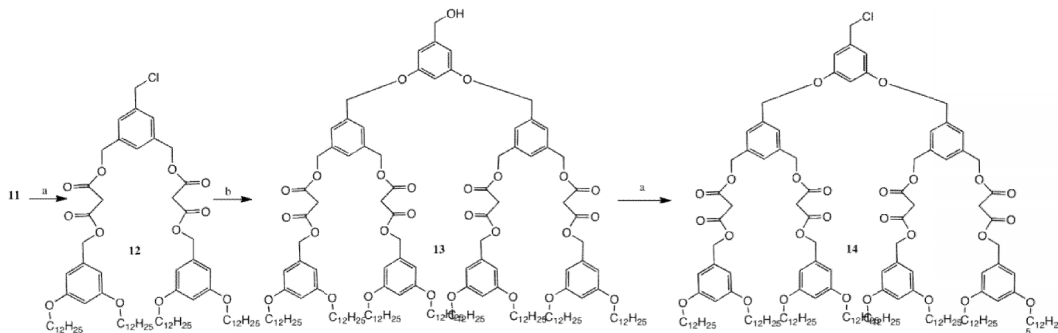
Scheme 2. Synthesis of compounds 6 and 9. a) $\text{C}_{12}\text{H}_{25}\text{Br}$, K_2CO_3 , KI , acetone; b) THF, LiAlH_4 , 0°C ; c) TBSCl, imidazole, THF, 0°C

Compound 6 was attached to compound 9 to obtain the bismalonate 10 in CH_2Cl_2 with DCC and DMAP. Bismalonate 10 was treated with 1.0 M tetrabutylammonium fluoride to obtain Bismalonate 11 (Scheme 3).



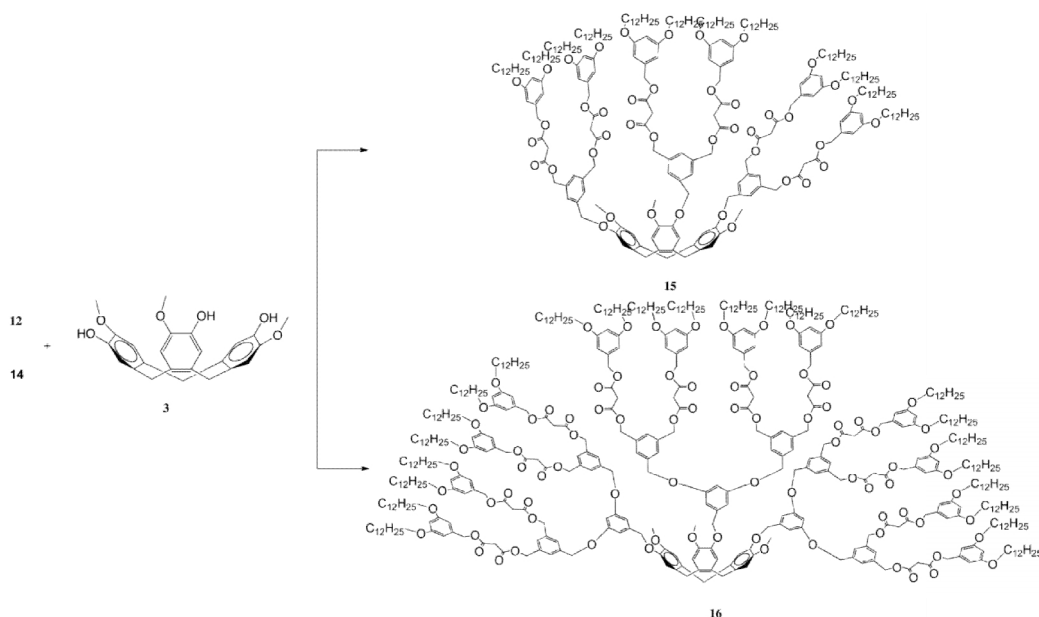
Scheme 3. Synthesis of bismalonate 11

Bismalonate 11 was used to obtain the first generation activated dendron 12 upon treatment with SOCl_2 , which when coupled to the 3,5-dihydroxybenzyl alcohol was used to obtain the second generation activated dendron 14 (Scheme 4).



Scheme 4. Synthesis of activated dendrons 12 and 14; a) SOCl₂, pyridine, CH₂Cl₂ b) 3,5-dihydroxybenzyl alcohol, Cs₂CO₃, DMF

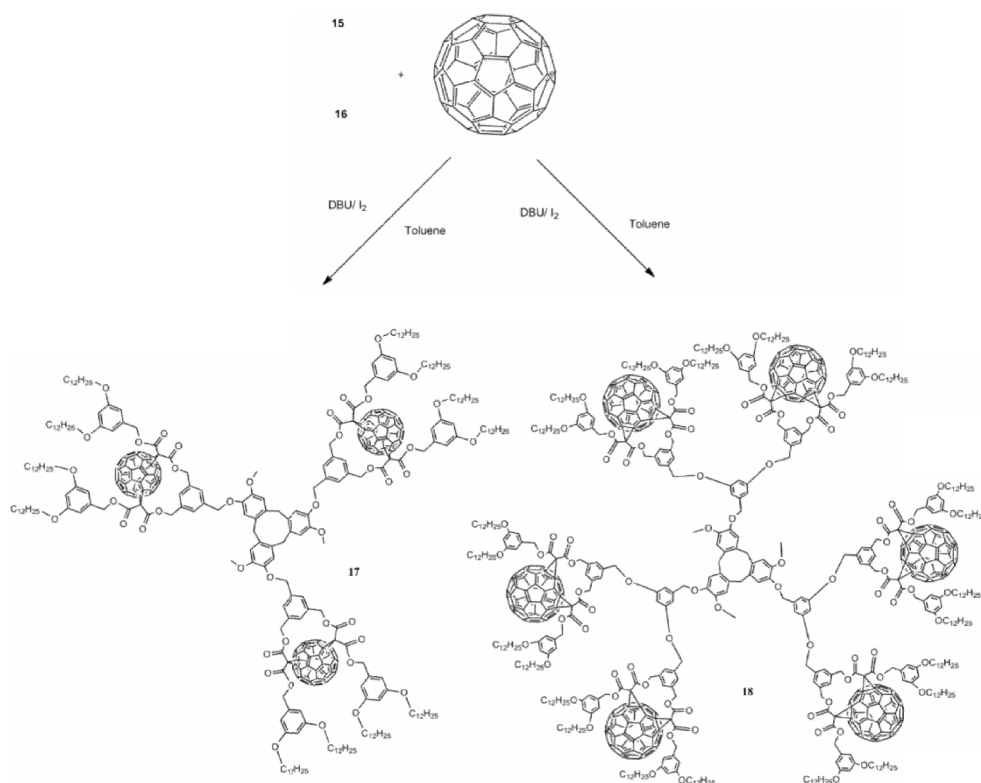
The dendrons of first and second generation 12 and 14, respectively, were attached to the cyclotrimeratrylene 3 to obtain the dendrimers 15 and 16 (Scheme 5). The reaction was carried out in DMF and Cs₂CO₃ at reflux for 2 days, and the dendrimers 15 and 16 were obtained in good yields.



Scheme 5. Synthesis of dendrimers 15 and 16

The ¹H NMR spectra of dendrimers 15 and 16 showed one broad signal at δ_H 0.87, 1.26, 1.71 and at d_n 3.80, due to the aliphatic chain, at δ_H 3.45 due to the CO-CH₂-CO. The signal at δ_H 3.84 is assigned to the O-CH₃ and signals at δ_H 4.61, 5.04 and 5.08 are ascribed to the -CH₂-O protons. For dendrimers 15 and 16, the aromatic protons give singlets and multiplets at δ_H 6.46, 7.50, and at 7.70. In both cases, two doublets were observed at δ_H 3.63, and at δ_H 4.70 due to the protons at the CH₂ groups of the cyclotrimeratrylene with a coupling constant *J* = 15.00 Hz.

The functionalization of C_{60} was made using the double Bingel cyclopropanation [26-31]. Treatment of C_{60} with dendrimers 15 or 16, I_2 , and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature gave the fullerene derivatives 17 and 18 in 21 and 18 % yield, respectively (Scheme 6). All the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures assigned to the fullerene derivatives. All the compounds were characterized by 1H and ^{13}C NMR, IR, and mass spectrometry (Electrospray and MALDI-TOF).



Scheme 6. Synthesis of fullerene derivatives 17 and 18

In the 1H NMR spectra of compounds 17a and 18b (Fig. 1a and 1b respectively) are observed at δ_H 0.85-1.70 and 3.80 signals due to the aliphatic chain. Two doublets at δ_H 3.50 and 4.60 assigned to the $-CH_2-$ groups of the cyclotrimeratrylene. Signals at δ_H 4.61, 5.04, and at δ_H 5.08 were ascribed to the $-CH_2-O$ protons. For dendrimers 17 and 18, signals are also observed from the aromatic protons at the macrocycle and of the benzyloxy chains. In the ^{13}C NMR spectra of the cyclotrimeratrylene-fullerene-dendrimers, 35 signals were ascribed to the fullerene.

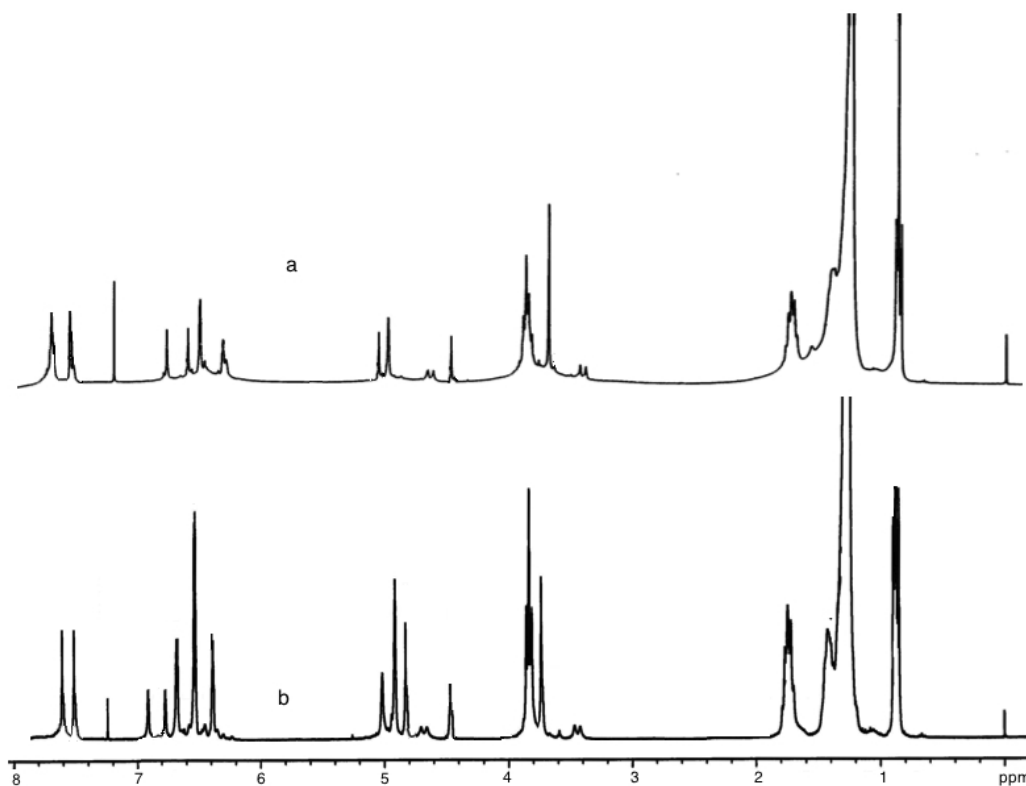
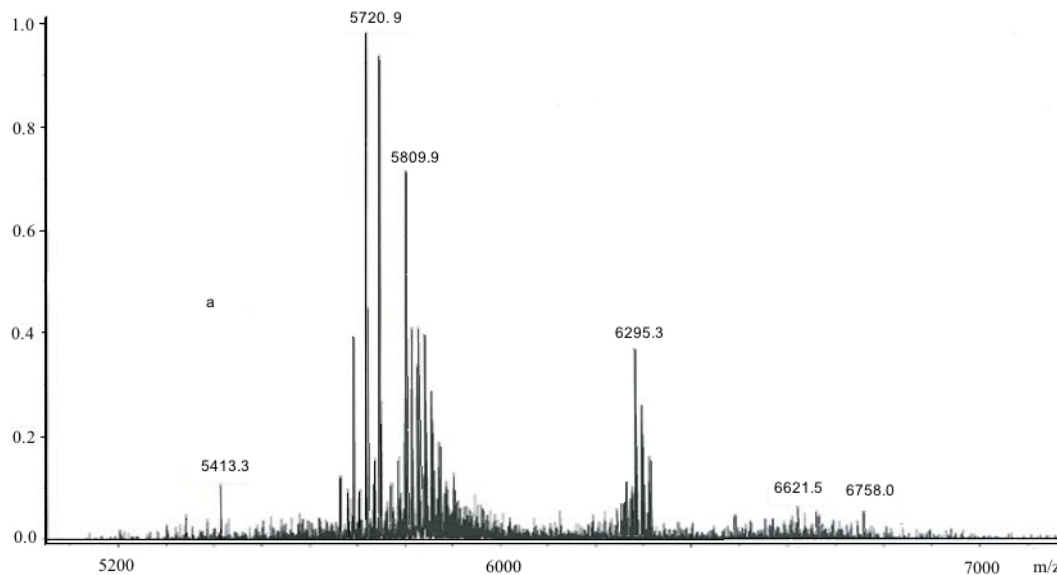


Fig. 1. ¹H NMR spectra of dendrimers a) 17 and b) 18 in CDCl₃

In the Fig. 2 the MALDI-TOF mass spectra for dendrimers 17 and 18 contain a peak at $m/z=6295$ ($M+Na$) and 12513 respectively.



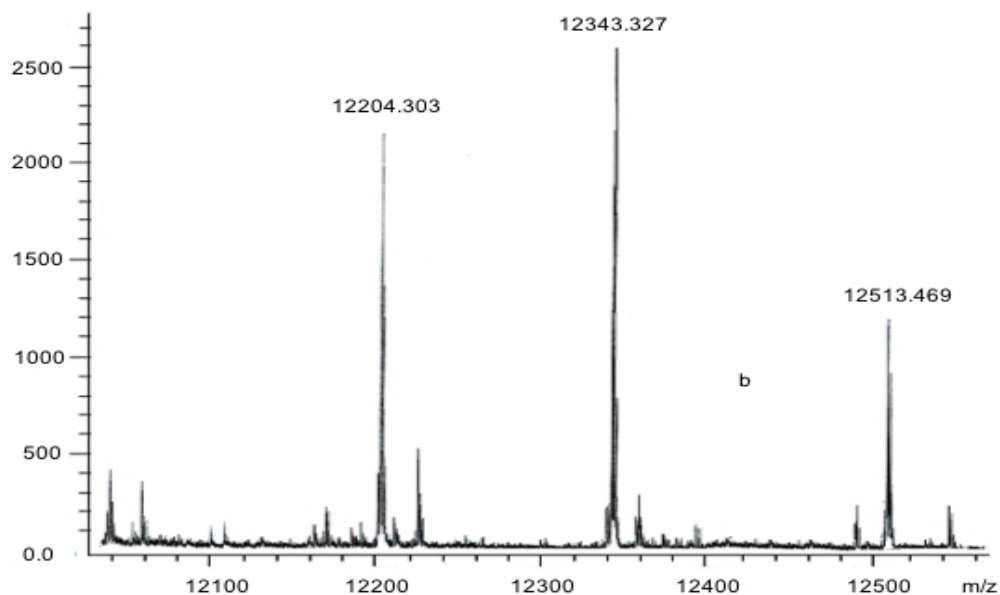


Fig. 2. MALDI-TOF MS spectra of dendrimers a) 17 and b) 18

4. CONCLUSION

The cyclotrimeratrylene dendrimers were obtained from dendrons 12 and 14, and then the fullerene C_{60} was introduced in the dendritic branches by a cyclization reaction. Adding the fullerene C_{60} in the last step of the synthesis gave good yields. The cycloadditions could occur in different places as show in Fig. 3. The *cis* cycloadditions gives 30 to 35 signals in the ^{13}C NMR spectrum. The *trans* cycloadditions gives in the ^{13}C NMR spectrum more than 35 signals. In our case the 1H , ^{13}C NMR and UV-vis studies showed that the double Bingel cyclopropanation reaction afforded only *cis*-2 adducts, in agreement with the literature data [32,33].

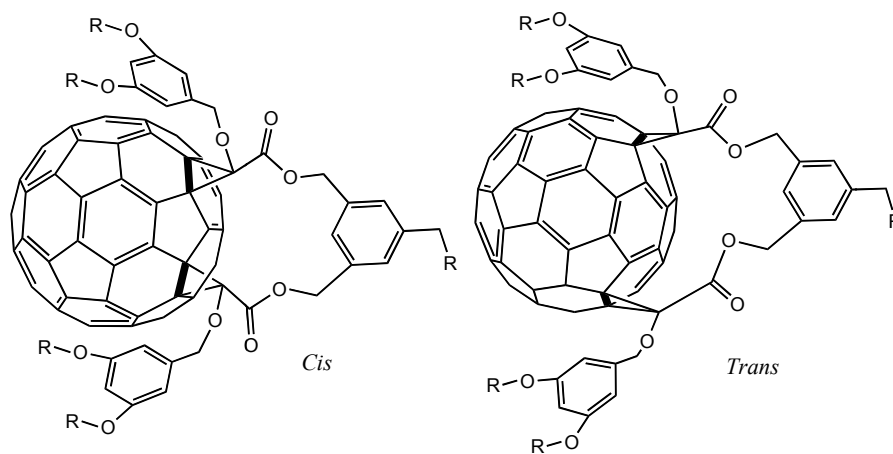


Fig. 3. Cycloadducts *cis* and *trans*

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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